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# Air Quality Criteria for Particulate Matter and Sulfur Oxides

## Volume II
## Air Quality

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## Preface to Volume II

This volume discusses the chemical and physical characteristics of sulfur oxides and particulate matter, the methods used to measure them, their sources, emission rates, atmospheric concentrations and exposure, transport, transformation and removal. Thus, this volume provides background information for discussion of welfare effects in Volume III (Chapters 7, 8, 9, 10) and health effects in Volume IV (Chapters 11, 12, 13, 14).

The link between human activities and air pollution was recognized at least as far back as the 13th century, when King Edward I of England banned the burning of "sea coal," under penalty of death, in an attempt to clear the smoky sky of London. In today's industrial world, the problem is much more profound, and a quantitative link between emissions and overall air quality is often difficult to determine. Key factors include measurement methods, source, emissions, mixing and dilution in the atmosphere, chemical transformations that occur during transport, the efficiency of removal processes for pollutant gases and particles, and the actual concentrations to which people are exposed.

An indirect approach to evaluating the impact of man-made sulfur emissions on atmospheric composition is to compare measurements with other continental areas similar geographically to the United States but affected to a much lesser degree by industrial activity. Measurements in the South American continent show fine particulate sulfur concentrations frequently in the range 0.05 to 0.1 $\mu g/m^3$ of air. These concentrations are 10 to 100 times lower than those often observed in the United States, which are 1 to 10 $\mu g/m^3$. This difference suggests that the atmosphere of the United States is 10 to 100

times above natural levels. It is reasonable to believe that man-made emissions of $SO_2$ and its conversion to sulfates are principally responsible.

The assessment of man-made emissions on air quality is complex because of the varied nature of particulate matter. Some effects are associated with the mass of particulate matter, while other effects are related to particle size. In addition, certain elemental constituents of particulate matter may be toxic to humans, animals, and plants. Thus, the chemical composition of particulate matter, especially in different particle size ranges, is of considerable importance in evaluating the impact of particulate matter on air quality.

Some particles are emitted to the atmosphere from local pollution sources, while others are generated by the action of wind on soils, the movement of vehicular traffic, and other processes. Particulate matter may be reentrained in the atmosphere by primary processes such as dispersion of dusts and oceanic aerosol formation. Particulate matter may also be formed in the atmosphere by secondary processes, such as the condensation of vapors or the chemical reaction of atmospheric trace gases to form compounds stable in liquid or solid form.

The particle size characteristics and chemical composition of particulate emissions may vary considerably with pollution control technology and the types of fuels used in combustion sources. As an example, particle collectors may greatly reduce the emissions of coarse particles but may be less effective in reducing emissions of fine particulate matter. The combustion of unleaded gasoline in automobiles will reduce ambient lead concentrations. The control of combustion and exhaust gas temperatures in stationary sources may affect the content of certain heavy metals in fly ash emissions. Many methods have been used to measure sulfur oxides and particulate matter. Early methods were not as accurate or as precise as current methods. By evaluating these methods,

more accurate assessments of historical ambient air data can be made. For example, information of this type is useful in reevaluating concentrations and exposures reported is epidemiological studies.

Monitoring data provide information on total mass concentrations of particulate matter but, for the most part, do not adequately reflect particle size and chemical composition.

The fossil fuels used in energy production include fuel oil, coal, and natural gas. In 1975 almost two-thirds of the total sulfur oxide emissions in the United States were attributed to coal-fired power plants, almost entirely in the form of sulfur dioxide. Because some of the gaseous sulfur dioxide may be oxidized to sulfate in the ambient air before removal at the surface, the ambient air sulfate concentrations stem mainly from $SO_2$ emissions.

Nationwide, man-made emissions of sulfur oxides during the 1970's have declined somewhat, even though the amount of fossil fuels burned has remained almost the same. This result is attributed to the use of low-sulfur oil, controls on the combustion process, and the use of pollution-control techniques.

In order to determine the impact of particulate matter and sulfur oxide emissions on health and welfare, the concentrations actually delivered to man and his environment must be determined. For both sulfur oxides and particulate matter this determination is complex, because exposure to these pollutants is influenced by many variables, such as geographic location, occupation, and individual activity patterns.

In summary, the readers of this volume will find that Volume II presents an analysis of ambient air concentrations on a wide variety of time and geographical scales to provide a broad background for later assessments of effects. In many cases the adverse effects on visibility and climate, vegetation, acid rain, and other materials covered in Volume III involve wide area, long-term

analysis while human health effects covered in Volume IV may involve either short-term high-level or long-term low-level exposures. In reading the effects chapters in these later volumes, the reader is cautioned to be aware of the exposure variables and to refer to the appropriate sections of Volume II for background data.

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Mr. John Acquavella
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Roy E. Albert
Institute of Environmental Medicine
New York University Medical Center
New York, New York 10016

Dr. Martin Alexander
Department of Agronomy
Cornell University
Ithaca, New York 14850

Dr. A. P. Altshuller
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. David S. Anthony
Department of Botany
University of Florida
Gainesville, Florida 32611

Mr. John D. Bachmann
Strategies and Air Standards Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Allen C. Basala
Strategies and Air Standards Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Neil Berg
Monitoring and Data Analysis Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Michael A. Berry
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Francis M. Black
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Joseph Blair
Environmental Division
U. S. Department of Energy
Washington, D.C. 20545

Dr. Edward Bobalek
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Ms. F. Vandiver P. Bradow
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Ronald L. Bradow
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Robert Bruce
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Angelo Capparella
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Robert Chapman
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Robert J. Charlson
Department of Environmental Medicine
University of Washington
Seattle, Washington 98195

Dr. Peter Coffey
New York State Department of Environmental Conservation
Division of Air Resources
Albany, New York 12233

Mr. Chatten Cowherd
Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

Dr. Ellis B. Cowling
School of Forest Resources
North Carolina State University
Raleigh, North Carolina 27650

Mr. William M. Cox
Monitoring and Data Analysis Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. T. Timothy Crocker
Department of Community and Environmental Medicine
Irvine, California 92664

Mr. Stanley T. Cuffe
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Thomas C. Curran
Monitoring and Data Analysis Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Michael Davis
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Gerrold A. Demarrais
National Oceanic and Atmospheric Administration
U. S. Department Of Commerce

Dr. Jerrold L. Dodd
Natural Resources Ecology Laboratory
Colorado State University
Fort Collins, Colorado 80523

Dr. Thomas G. Dzubay
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Thomas G. Ellestad
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. John Evans
School of Public Health
Harvard University
Boston, Massachusetts 02115

Dr. Lance Evans
Department of Energy and Environment
Brookhaven National Laboratory
Upton, New York 11973

Mr. Douglas Fennell
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Benjamin G. Ferris, Jr.
School of Public Health
Harvard University
Boston, Massachusetts 02115

Mr. Patrick Festa
New York Department of Environmental Conservation
Division of Fish and Wildlife
Albany, New York 12233

Mr. Terrence Fitz-Simmons
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Christopher R. Fortune
Northrop Services, Inc.-Environmental Sciences
P. O. Box 12313
Research Triangle Park, North Carolina 27709

Dr. Robert Frank
Department of Environmental Health
University of Washington
Seattle, Washington 98195

Dr. Warren Galke
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Phil Galvin
New York Department of Environmental Conservation
Division of Air Resources
Albany, New York 12233

Dr. Donald Gardner
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. J.H.B. Garner
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Donald Gillette
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Judy Graham
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Lester D. Grant
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Armin Gropp
Department of Chemistry
University of Miami
Miami, Florida 33124

Dr. Jack Hackney
Rancho Los Amigos Hospital
Downey, California 90242

Mr. Bertil Hagerhall
Ministry of Agriculture
Fack
S-163 20 Stockholm
Sweden

Dr. Douglas Hammer
2910 Wycliff Road
Raleigh, North Carolina 27607

Mr. R. P. Hangebrauck
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Thomas A. Hartlage
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Victor Hasselblad
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Thomas R. Hauser
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Carl Hayes
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Fred H. Haynie
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Walter Heck
Department of Botany
North Carolina State University
Raleigh, North Carolina 27650

Dr. Howard Heggestad
USDA-SAE
The Plant Stress Laboratory
Plant Physiology Institute
Beltsville, Maryland 20705

Dr. George R. Hendrey
Department of Energy and Environment
Brookhaven National Laboratory
Upton, New York 11973

Dr. Ian Higgins
Department of Epidemiology
School of Public Health
University of Michigan
Ann Arbor, Michigan 48109

Mrs. Patricia Hodgson
Editorial Associates
Chapel Hill, North Carolina 27514

Mr. George C. Holzworth
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Robert Horton
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Steven M. Horvath
Institute of Environmental Stress
University of California
Santa Barbara, California 93106

Dr. F. Gordon Hueter
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Janja Husar
CAPITA
Washington University
St. Louis, Missouri 63130

Dr. Rudolf Husar
Department of Mechanical Engineering
Washington University
St. Louis, Missouri 63130

Dr. William T. Ingram
Consulting Engineer
7 North Drive
Whitestone, New York 11357

Dr. Patricia M. Irving
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Dr. Jay Jacobson
Boyce Thompson Institute
Cornell University
Ithaca, New York 14850

Mr. James Kawecki
Biospherics, Inc.
4928 Wyaconda Road
Rockville, Maryland 20852

Dr. Sagar V. Krupa
Department of Plant Pathology
University of Minnesota
St. Paul, Minnesota 55108

Dr. Edmund J. LaVoie
Section of Metabolic Biochemistry
American Health Foundation
Dana Road
Valhalla, New York 10592

Dr. Michael D. Lebowitz
Arizona Health Sciences Center
1501 North Campbell
Tucson, Arizona 85724

Dr. Robert E. Lee
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Allan H. Legge
Environmental Science Center
University of Calgary
Calgary, Alberta, Canada T2N 1N4

Ms. Peggy Le Sueur
Atmospheric Environment Service
Downsview, Ontario, Canada M3H5T4

Dr. Morton Lippmann
Institute of Environmental Medicine
New York University
New York, New York 10016

Dr. James P. Lodge
385 Broadway
Boulder, Colorado 80903

Dr. Gory J. Love
Institute of Environmental Studies
University of North Carolina
Chapel Hill, North Carolina 27514

Dr. David T. Mage
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Delbert McCune
Boyce Thompson Institute
Cornell University
Ithaca, New York 14850

Mr. Frank F. McElroy
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. David J. McKee
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Thomas McMullen
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Daniel B. Menzel
Department of Pharmacology
Duke University Medical Center
Durham, North Carolina 27710

Dr. Edwin L. Meyer
Monitoring and Data Analysis Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Fred Miller
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. John O. Milliken
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Jarvis Moyers
Department of Chemistry
University of Arizona
Tucson, Arizona 85721

Dr. Thaddeus J. Murawski
New York State Department of Health
Empire State Plaza
Albany New York 12337

Dr. David S. Natusch
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

Dr. Stephen A. Nielsen
Environmental Affairs
Joyce Environmental Consultants
414 Live Oak Boulevard
Casselberry, Florida 32707

Dr. Kenneth Noll
Department of Environmental Engineering
Illinois Institute of Technology
Chicago, Illinois 60616

Mr. John R. O'Connor
Strategies and Air Standards Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Thompson G. Pace
Monitoring and Data Analysis Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Jean Parker
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Nancy Pate
Strategies and Air Standards Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Thomas W. Peterson
Department of Chemical Engineering
University of Arizona
Tucson, Arizona 85721

Mr. Martin Pfeiffer
New York State Department of Environmental Conservation
Bureau of Fisheries
Raybrook, New York 12977

Dr. Marlene Phillips
Atmospheric Chemistry Division
Environment Canada
Downsview, Ontario, Canada M3H5T4

Dr. Charles Powers
Environmental Research Laboratory
U.S. Environmental Protection Agency
Corvallis, Oregon 97330

Mr. Larry J. Purdue
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. John C. Puzak
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Otto Raabe
Radiobiology Laboratory
University of California
Davis, California 95616

Mr. Danny Rambo
Environmental Research Laboratory
U.S. Environmental Protection Agency
Corvallis, Oregon 97330

Mr. Kenneth A. Rehme
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Elmer Robinson
Department of Chemical Engineering
Washington State University
Pullman, Washington 99163

Mr. Charles E. Rodes
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Douglas R. Roeck
GCA Corporation
Technology Division
Burlington Road
Bedford, Massachusetts 01730

Mr. J. C. Romanovsky
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. August Rossano
University of Washington
Seattle, Washington 98195

Mr. Joseph D. Sableski
Control Programs Development Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Dallas Safriet
Monitoring and Data Analysis Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Victor S. Salvin
University of North Carolina at Greensboro
Greensboro, North Carolina 27408

Dr. Shahbeg Sandhu
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. Joseph P. Santodonato
Life and Material Sciences Division
Syracuse Research Corporation
Merrill Lane
Syracuse, New York 13210

Dr. Herbert Schimmel
Neurology Department
Albert Einstein Medical College
26 Usonia Road
Pleasantville, New York 10570

Dr. Carl L. Schofield
Department of Natural Resources
Cornell University
Ithaca, New York 14850

Dr. David Shriner
Environmental Sciences Division
Oak Ridge National Laboratory

Ms. Donna Sivulka
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. John M. Skelly
Department of Plant Pathology and Physiology
Virginia Polytechnic Institute
Blacksburg, Virginia 24061

Mr. Scott Smith
Biospherics, Inc.
4928 Wyaconda Road
Rockviell, Maryland 20852

Ms. Elaine Smolko
Department of Pharmacology
Duke University Medical Center
Durham, North Carolina

Dr. Frank Speizer
School of Public Health
Harvard University
Boston, Massachusetts 02115

Dr. John D. Spengler
School of Public Health
Harvard University
Boston, Massachusetts 02115

Mr. Robert K. Stevens
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. George E. Taylor, Jr.
Environmental Sciences Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

Dr. Larry Thibodeau
School of Public Health
Harvard University
Boston, Massachusetts 02115

Dr. W. Gene Tucker
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. D. Bruce Turner
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. James B. Upham
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. Robert Waller
Toxicology Unit
St. Bartholomew's Hospital
London, England

Mr. Stanley Wallin
Warren Spring Laboratory
Department of Industry
Stevenage, Hertfordshire SGI 2BX
England

Dr. Joseph F. Walling
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. James Ware
School of Public Health
Harvard University
Boston, Massachusetts 02115

Dr. David Weber
Office of Air, Land, and Water Use
U.S. Environmental Protection Agency
Washington, D. C. 20460

Dr. Jean Weister
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Mr. R. Murray Wells
Radian Corporation
8500 Shaol Creek Boulevard
Austin, Texas 78766

Dr. Kenneth T. Whitby
Mechanical Engineering Department
University of Minnesota
Minneapolis, Minnesota 55455

Dr. Warren White
CAPITA
Washington, University
St. Louis, Missouri 63130

Dr. Raymond Wilhour
Environmental Research Laboratory
U.S. Environmental Protection Agency
Corvallis, Oregon 97330

Dr. William E. Wilson
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. John W. Winchester
Department of Oceanography
Florida State University
Tallahassee, Florida 32306

Mr. Larry Zaragoza
Strategies and Air Standards Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dr. William H. Zoller
Chemistry Department
University of Maryland
College Park, Maryland 20742

We wish to thank everyone who contributed their efforts to the preparation of this document, including the following staff members of the Environmental Criteria and Assessment Office, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina:

Mrs. Dela Bates
Ms. Hope Brown
Ms. Diane Chappell
Ms. Deborah Doerr
Ms. Mary Eling
Ms. Bettie Haley
Mr. Allen Hoyt
Ms. Susan Nobs
Ms. Evelynne Rash
Ms. Connie van Oosten
Ms. Donna Wicker

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# CHAPTER 2. PHYSICAL AND CHEMICAL PROPERTIES OF SULFUR OXIDES AND PARTICULATE MATTER AND ANALYTICAL TECHNIQUES FOR THEIR MEASUREMENT

## 2.1 INTRODUCTION

The 1970 Air Quality Criteria documents for Sulfur Oxides and Particulate Matter provided a reasonably thorough review of measurement techniques at the date of their publication. Since that time, considerable new information and advancements in the measurement technology for these pollutants has resulted in a substantial amount of new information. This chapter provides a review of both the earlier techniques, which are still important in evaluating earlier monitoring and effects data, as well as newer methods and technology.

Present measurements of ambient sulfur oxides and particulate matter are oriented toward a variety of objectives, the most salient of which are:

- Trend Monitoring to Support Epidemilogical Studies,
- Compliance monitoring to determine conformance to air quality standards,
- Long-term trend monitoring to determine effectiveness of control strategies, and
- Various research-related studies.

Research activities include such diverse subjects as studies of sources of emissions; methodology development; transport and transformation; influence on visibility and local or regional climate; effects on human health and vegetation damage, soiling and corrosion of materials.

Compliance and long-term trend monitoring requires well defined and

characterized methods for mass concentrations having sensitivities and averaging times compatible with the form and level of existing regulatory standards.

Monitoring for research purposes involves broader areas of concern and entails more complex, less well defined requirements. In addition to mass concentration, particulate measurement techniques frequently must include fractionation of the particulate matter into particle size ranges and the particles subjected to chemical analysis to determine their composition.

Measurement technology for sulfur oxides and particulate matter is complex and highly technical. Descriptions of the various methods in this chapter are necessarily very brief, leaving the bulk of technical detail to the numerous references cited. Emphasis is given primarily to those methods that are pertinent to the discussions in Chapter 14 and to the most commonly used methodology that figures prominently in current or imminent monitoring for compliance and research measurement purposes.

## 2.2 PHYSICAL AND CHEMICAL PROPERTIES OF SULFUR OXIDES AND PARTICULATE MATTER

### 2.2.1 Sulfur Oxides

Sulfur dioxide ($SO_2$) is a colorless gas that can be detected by taste at concentrations of 1000 to 3000 $\mu g/m^3$ (0.38 to 1.15 ppm). At higher concentrations (above about 10,000 $\mu g/m^3$ or 3.8 ppm), it has a pungent, irritating odor. It has an absorption maximum in the ultraviolet region of the spectrum at around 254 nanometers (nm). The physical properties of $SO_2$ are summarized in Table 2-1.

Chemically, $SO_2$ acts both as an oxidizing agent and as a reducing agent. The reducing properties are more important, particularly those involving aqueous solutions of $SO_2$. The gas dissolves readily in water or alkaline

TABLE 2-1. PHYSICAL PROPERTIES OF SULFUR DIOXIDE

| | |
|---|---|
| Molecular weight | 64.06 |
| Density (gas), g/liter | 2.927 at 0°C; 1 atm |
| Specific gravity (liquid) | 1.434 at -10°C |
| Molecular volume (liquid), ml | 44.7 |
| Melting point, °C | -75.46 |
| Boiling point, °C | -10.02 |
| Critical temperature, °C | 157.2 |
| Critical pressure, atm | 77.7 |
| Heat of fusion, Kcal/mole | 1.769 |
| Heat of vaporization, Kcal/mole | 5.96 |
| Dielectric constant (practical units) | 13.8 at 14.5°C |
| Viscosity, dyne sec/$cm^2$ | 0.0039 at 0°C |
| Molecular boiling point constant, °C/1000 g | 1.45 |
| Dipole moment, Debye units | 1.61 |

solution to form sulfurous acid ($H_2SO_3$). In solution there is a series of equilibria between $SO_2$ and $H_2O$, $H_2SO_3$ and its ions:

$$SO_2 + H_2O \rightleftarrows H_2SO_3$$

$$H_2SO_3 \rightleftarrows H^+ + HSO_3^-$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^=$$

An aqueous solution of $SO_2$ has the properties of a weak acid and is slowly oxidized to sulfuric acid ($H_2SO_4$) by dissolved oxygen ($O_2$). Oxidation to $H_2SO_4$ is more rapid in the presence of catalyzing impurities such as manganese and iron ions. Sulfur dioxide also reacts in the gas phase with oxygen or other air pollutants to form sulfur trioxide ($SO_3$), $H_2SO_4$, and metal and organic sulfates.

Sulfur trioxide ($SO_3$) is a highly reactive gas derived either directly from combustion sources or from oxidation of atmospheric $SO_2$. In the presence of moisture in the air, it rapidly hydrates to $H_2SO_4$ aerosol. In the atmosphere, therefore, it occurs as $H_2SO_4$ aerosol rather than as $SO_3$.

Sulfuric acid ($H_2SO_4$) is a strong, corrosive acid with a high boiling point. When heated, it initially dissociates into $SO_3$ and $H_2O$. Further heating produces a constant boiling acid consisting of 98 percent $H_2SO_4$. It is commonly formed in the atmosphere from hydration of $SO_3$ and oxidation of hydrogen sulfide ($H_2S$).

Sulfuric acid readily reacts with many metals and metal oxides to form metal sulfates. Common sulfate species in the atmosphere include solid particulate metal salts and liquid droplets containing either dissolved metal sulfates or

$H_2SO_4$. Because $H_2SO_4$ and many of its salts are strongly hygroscopic, droplets of this type can readily take up moisture from the air until reaching equilibrium. If ammonia is present, it will react with $H_2SO_4$ to form ammonium sulfate [$(NH_4)_2SO_4$] or ammonium bisulfate ($NH_4HSO_4$) which will continue to exist as aerosols (in droplet or crystalline form, depending on the relative humidity).

### 2.2.2 Particulate Matter

Atmospheric particulate matter is often very complex. Individual particles can be composed of different chemical species, can be homogeneous or heterogeneous in structure, and may vary in size and shape. Particles dispersed in a gas can be characterized by many different physical and chemical properties. The single most important characteristic of airborne particulate matter is particle size.

The basic definitions of particle size are related to the velocity at which particles fall as a result of their aerodynamic behavior in the earth's gravitational field. The aerodynamic equivalent diameter of a particle does not refer to an actual measurement of the particle but is the size of a spherical particle of unit density (1 $g/cm^3$) which falls at the same speed. The Stokes equivalent diameter, in a similar fashion, refers to the physical diameter of a spherical particle of the same average density and the same falling velocity. The aerodynamic diameter is the most useful definition relative to particle sampling and deposition.

Recent studies of atmospheric particles have been conducted which have led to important advances in the understanding of their size distribution (Whitby, 1975; Wilson et al., 1976; Willeke and Whitby, 1975). A schematic

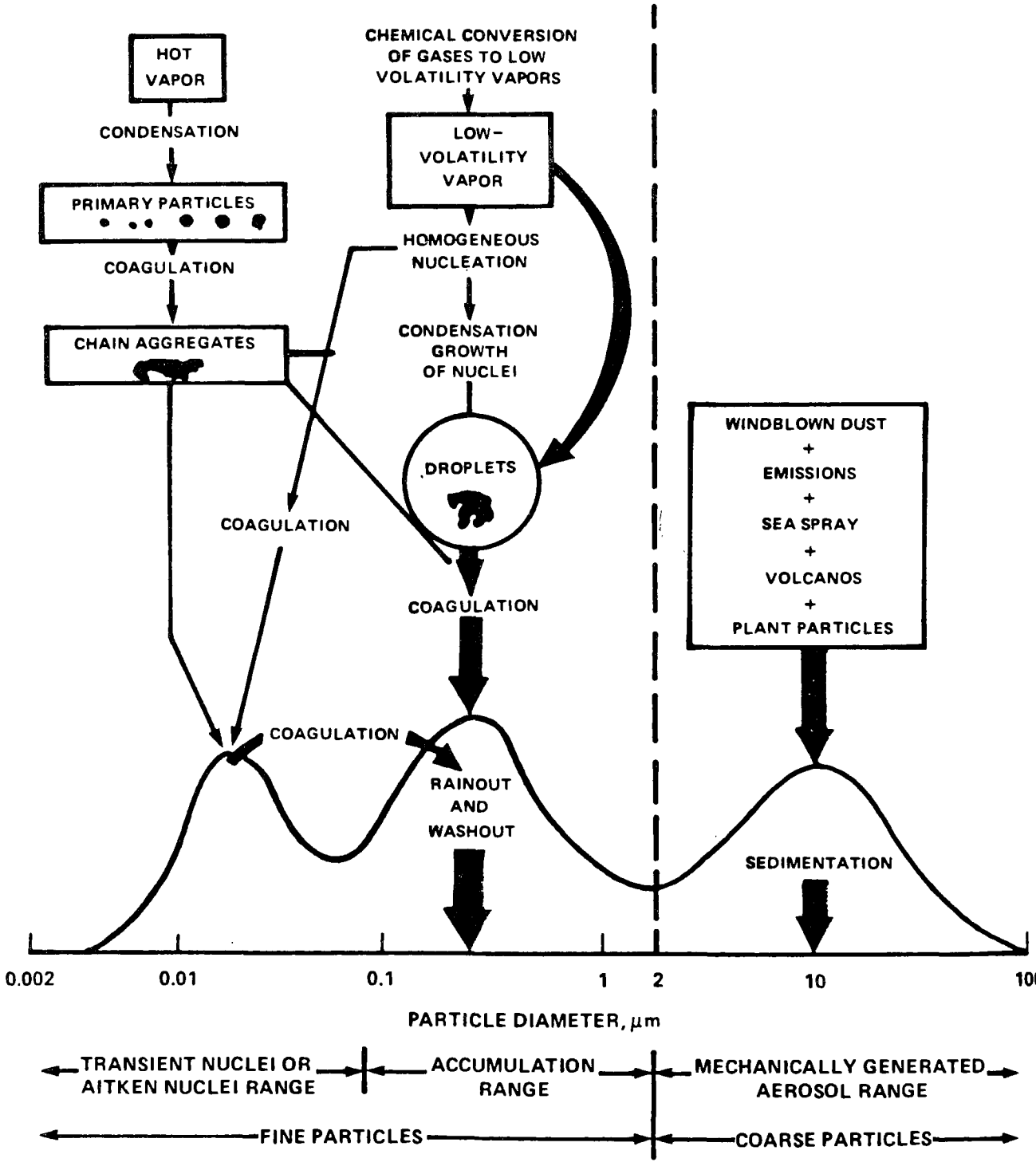



Figure 2-1. Schematic shows an atmospheric aerosol surface area distribution showing the three modes, main source of mass for each mode, the principal processes involved in inserting mass into each mode, and the principal removal mechanisms.

Source: K.T. Whitby (1977)

diagram of the size distribution of a typical atmospheric particles as described by Whitby (1977) is shown in Figure 2-1. The distribution is trimodal in that three distinct peaks are apparent. The figure shows the three principal modes, the main source of mass within each mode, and the principal processes involved in inserting and removing mass from each mode. Particles in the Aitken or nuclei mode,from 0.005 to 0.05 μm diameter, are formed by condensation of vapors produced by processes such as fossil fuel combustion. Particles in the accumulation mode, from 0.05 to 2 μm, are formed by coagulation or agglomeration of nuclei mode particles and by growth of particles in the nuclei mode through vapor condensation. Accumulation mode particles normally do not continue to grow into the coarse mode. Typically, 80 percent or more of the atmospheric sulfate particulate matter is found in the accumulation mode. The upper size limit of fine particles is in the range of 1 to 3 μm and is commonly stated as being 2.0 μm. Coarse particles, those in the > 2.0 μm aerosol range, include reintrained surface dust and particles formed by processes such as grinding and by the evaporation of liquid droplets.

Fine particles often serve as condensation nuclei, are associated mechanically with liquid particles of rain, mist, or snow, and are often classified into two major sources. Primary particles are a direct result of the discharge of fine particles from industrial and other man-made or natural sources; secondary particles are formed by chemical and physical reactions in the atmosphere. Most of the reactants that form secondary particles are emitted to the atmosphere as gaseous pollutants.

The actual density of ambient aerosols is difficult to determine precisely. The use of the density reported for bulk chemicals can cause significant problems in the interpretation of data. The density derived from chemical

composition cannot be used in the relations between aerodynamic diameter and volume or between aerodynamic diameter and area without challenge. Many fine particles are flocculi and agglomerates having densities well below the "true density" based on bulk chemical composition. Often the density of flocculent aerosols is 10 to 30 times lower than the density of the substances of origin (Hesketh, 1974).

Water is often exempted from the definition of particulate matter although moisture can be combined with a particle chemically, physicochemically and mechanically (Falkowski, 1951). From the aerodynamic point of view, the manner in which water is combined with a particle is not important. However, the effect of water vapor on the properties of fine particulate matter is an important factor. Hygroscopic particles can grow in size when exposed to relative humidity above 70 percent, and in humid weather appreciably contribute to visibility degradation.

Morphology relates to particle shape and surface features. The concept of the aerodynamic diameter does not accommodate particle shape or morphological features such as porosity and roughness. Some examples of fine particles and their shapes are shown in Table 2-2. Particles larger than 0.5 μm can be examined with a conventional light microscope; particles in the size range 0.001 to 0.5 μm must be examined with an electron microscope. The shape of a particle will determine the ratio between its surface area and its volume. The absorption surface comprises the total particle surface, including the surface of pores to which there is an external access. The area of the absorption surface determines the ability of the particle to adsorb gases or electric charges.

The electric charge of a particle depends on the state of its surface and

TABLE 2-2. SOME EXAMPLES OF SHAPES OF FINE PARTICLES

| Shape | Nature of aerosols (fine particles) |
|---|---|
| Spherical | carbon black, iron oxide, plastics, glass, pollen |
| Rectangular (irregular polyhedral) | iron, quartz, mineral ash |
| Celliform | epidermal minerals |
| Fiber | textiles, asbestos, plants (cellulose) |
| Splinter | cement, organic dyes |
| Flocculent | coal fumes |
| Platelet | mica, graphite, bronze |
| Rodlet | talc, fluorine |

on the value of its dielectric constant and/or its size (Andrezejewski, 1968). The electrical properties of atmospheric particles can affect the collection capability of ambient samples. In principle, large particles greater than 3 μm carry a negative charge and fine particles less than 0.01 μm carry a positive charge. The electric charges of particles can also affect the coagulation rate and the speed of the dry deposition of particles (Brock and Marlow, 1975).

Another aspect of the physical properties of fine particles is their ability to scatter or absorb light. The absorption of light will generally increase with particle size. However, the ability of a particle to scatter light will vary in a complex way with particle size. Particle scattering will usually show a maximum when the particle diameter is approximately equal to the wavelength of light. The scattering and absorption by individual particles and the number of such particles per unit of gas volume can be related to bulk optical properties, i.e., the bulk extinction coefficient and the scattering cross-section.

Additional information concerning the physical and chemical properties of particulate matter can be found in Aerosol Measurement (Lundgren et al., ed. 1979), Aerosol Science (Davies, ed., 1966), Smoke, Dust, and Haze (Friedlander, 1977), Fine Particles, Aerosol Generation, Measurement and Analysis (Liu, 1976), Handbook on Aerosols (Dennis, ed. 1976), and Airborne Particles (National Academy of Sciences, 1979).

## 2.3 MEASUREMENT TECHNIQUES FOR SULFUR DIOXIDE

### 2.3.1 Introduction

This section discusses the methods used to measure atmospheric concentrations of sulfur dioxide. Each method is either integrated or continuous.

The measurement of $SO_2$ by an integrated method represents the concentration averaged over a specified time period. With a continuous method, the measurement represents the instantaneous (or very nearly instantaneous) concentration of $SO_2$ in the air sample. Most integrated methods consist of separate procedures for sample collection and analytical measurement. In continuous methods, sample collection and analysis are performed constantly and automatically, and such methods are generally referred to as continuous analyzers.

This section will focus on a brief description of each method with emphasis on measurement principle and method characteristics such as range, sensitivity, and interferences. Sample collection and method calibration will be discussed for integrated and for continuous methods. Among the integrated methods, those that have experienced the most widespread use are discussed first. The sulfation methods are presented last only because they measure "sulfation rate" rather than $SO_2$ concentration per se. Among the continuous methods, the discussion tends to follow a more or less chronological order with the earlier analyzers described first.

Included in this section is a discussion of various continuous analyzers designated by EPA as equivalent methods for the measurement of $SO_2$ in the atmosphere to determine compliance with the National Ambient Air Quality Standards (NAAQS). Information from various comparison studies is also presented.

### 2.3.2 Integrated Methods

2.3.2.1 Sample Collection--Early research focused on methods to estimate sulfur dioxide after it had been collected from a given volume of air. The following critique of existing methods for the collection of sulfur dioxide addresses their efficiency, selectivity, and ability to stabilize the collected material.

2.3.2.1.1 Direct Sampling. Several of the integrated methods use direct sampling, and determination of the amount of gas present in a flowing stream of ambient air that passes through or around the sampling device. In general, such methods suffer from a lack of sensitivity, an inability to discriminate between different sulfur-containing species, or insufficient ruggedness for long-term use in the field. Such shortcomings are of little consequence for industrial emissions sampling when concentrations are high and the sulfur species are known.

A variation of direct sampling involves collection of a small volume of air in a gas-tight syringe or other suitable container for later analysis. The reactivity of sulfur dioxide is a major problem, however. Natusch and Bauer (1978) have reported extensive adsorption losses of $SO_2$ on thick-walled mylar laminates, tygon, Teflon®, and stainless steel container walls.

2.3.2.1.2 Absorption. A number of integrated methods use aqueous solutions for collection of sulfur dioxide. The efficiency of mass transfer of sulfur dioxide from air to the solution phase depends on the gas-liquid contact time, the diffusion coefficients of sulfur dioxide in the gas and liquid phases, the bubble size, the concentration of sulfur dioxide, and the solubility of sulfur dioxide in solution. Calvert and Workman (1960) have produced a method to predict the efficiency of various bubbler designs in collecting sulfur dioxide. Their method is predominantly qualitative, but it can serve as a useful guide. The more efficient designs include that of Wartburg et al. (1969); the Petticoat bubbler the Greenberg-Smith impinger (Smith et al., 1961); midget impingers (Jacobs et al., 1957); Dreschel bottles (Wartburg et al., 1969); and packed columns (Bostrom, 1966), which are useful where low flow rates (2 to 4 liters/minute) are involved. In using such devices, care must be taken to

prevent carryover of solution at high flow rates and to compensate for solvent losses by evaporation.

Collection efficiency depends in part on the solution in which sulfur dioxide is actively dissolved and stabilized. One current method involves stabilization of the sulfite anion in a solution of potassium tetrachloromercurate, with which the sulfite anion complexes. A second approach involves collection in aqueous solution and direct oxidation to the sulfate anion, which is then determined analytically. In the latter case, a number of oxidizing agents such as hydrogen peroxide are used.

Although stabilization of sulfur dioxide as the sulfate anion can be effective, any soluble sulfate in the atmospheric aerosol will be collected (unless removed by a particle filter) and added to the sample; thus, discrimination between sulfur dioxide and sulfate may be impossible. Stabilization of the sulfite anion with potassium tetra-chloromercurate is currently the basis of the EPA reference method to determine sulfur dioxide in ambient air. To prevent conversion of sulfite to sulfate, the temperature of the collecting solution must be maintained below 20°C. Failure to maintain temperature control of samples during collection, shipment, and storage will lead to underestimation of the amount of sulfur dioxide present in the atmosphere, particularly during summer months.

Several analytical procedures employ alkaline solutions for the absorption of sulfur dioxide and their collection efficiency is quite high (Hochheiser, 1964). However, alkaline solutions rapidly oxidize the collected sulfite anion to sulfate unless some means are available for the direct complexation and stabilization of the sulfite anion.

2.3.2.1.3 Adsorption. There are several methods to collect sulfur dioxide by adsorption. The Stratmann method (Katz, 1968; Stratman, 1954) utilizes a quartz

tube packed with silica gel which removes sulfur dioxide from the air that passes through the tube. The exact form of the collected sulfur dioxide has not been determined, but it seems probable that stabilization as either a sulfite or a sulfate occurs. Since the subsequent analytical procedure involves desorption at elevated temperatures with a stream of hydrogen, any sulfate species collected from the atmospheric aerosol may also be desorbed, resulting in poor discrimination between sulfur dioxide and sulfate species. Comparative tests show that this method yields highly erratic results (Organization for European Economic Cooperation, European Productivity Agency, 1961).

The second adsorption procedure involves the use of filter papers or tapes impregnated with an alkaline reagent such as potassium hydroxide, triethanolamine, or potassium carbonate, together with small amounts of glycerine as an humectant. The adsorbed sulfur dioxide is supposed to be maintained as a sulfite, but it may become oxidized to sulfate. Although laboratory tests have shown that such oxidation can be negligible, field tests have produced very erratic results. Particulate matter collected from air passing through the filter contains traces of transition metal ions, which promote rapid oxidation of sulfite to sulfate.

The third adsorption method involves the reaction of sulfur dioxide with lead peroxide to form lead sulfate (Katz, 1968; Hochheiser, 1964). The sulfur dioxide is stabilized in the form of a sulfate, eliminating the problem of oxidative conversion. However, any particulate material containing sulfate species which come in contact with the collection surface will lead to errors.

2.3.2.2 Calibration--The relationship between true pollutant concentration and its measurement by any method is determined by calibration. For those

integrated methods that measure relative exposure to sulfur species (e.g., sulfation methods), no calibration is usually attempted. The use of uniform reagents, equipment, and procedures is recommended with these methods in order to compare exposure data over time and space.

Those integrated methods that involve collection of an air sample for later analysis or collection of the $SO_2$ in an air sample by absorption or adsorption require calibration of both the sample volume measurement and the analytical measurement.

Devices used for sample volume measurement are generally calibrated against reliable volume standards. The analytical measurement is often calibrated statically using a known amount of the sulfite or sulfate anion in solution. Static calibration is a rapid and simple method for checking the analytical procedure, but does not subject the overall measurement method to scrutiny since the process of $SO_2$ collection is circumvented.

Dynamic calibration of integrated methods has an advantage over the static approach by subjecting the total measurement to scrutiny, but it is time consuming and therefore is not used routinely. This approach, described in more detail in a later section on continuous methods, uses synthetic atmospheres containing the pollutant in known concentrations to define the response of the method.

2.3.2.3 Analytical Methods--The principal methods of determining sulfur dioxide in the air are discussed in this section.

2.3.2.3.1 Colorimetric Method: Pararosaniline. The West-Gaeke method is probably the most widely used colorimetric procedure for $SO_2$ determination in ambient air (West and Gaeke, 1956). It is also the basis of the EPA reference method for manual measurement of $SO_2$ in the atmosphere (U.S. Environmental Protection Agency, 1979).

In the West-Gaeke method, air is bubbled into fritted bubblers containing 0.1 M sodium tetrachloromercurate (TCM) solution, which forms the stable dichlorosulfitomercurate ion with $SO_2$. The TCM complex is reacted with bleached pararosaniline and formaldehyde to form red-purple pararosaniline methylsulfonic acid. The optical absorbance of the solution is measured spectrophotometrically at 560 nm and is, within limits, linearly proportional to the concentration of sulfur dioxide. The method is capable of measuring $SO_2$ concentrations from 13 to 13,000 $\mu g/m^3$ (0.005 to 5 ppm). Ozone, nitrogen dioxide, and heavy metals were negative interferences in early versions of this method.

An improved version of the West-Gaeke method was adopted by EPA in 1971 as the reference method for the determination of $SO_2$ in the atmosphere. Several important parameters were optimized, resulting in greater sensitivity and reproducibility, as well as adherence to Beer's Law throughout a greaterworking range.

In the EPA method, $SO_2$ is collected in impingers containing 0.04 M potassium tetrachloromercurate. A 20-minute wait before analysis allows ozone, a potential interferent, to decompose. Sulfamic acid is then added, followed by a 10-minute wait to remove interference from nitrogen oxides. Interference by heavy metals is eliminated by the use of phosphoric acid in the dye reagent and the disodium salt of ethylenediaminetetraacetic acid (EDTA) in the TCM absorbing solution. The complex is then reacted with a purified pararosaniline dye reagent and formaldehyde to form the colored pararosaniline methylsulfonic acid. Absorbance is measured at 548 nm.

Accuracy depends on rigid control of many critical variables: pH, temperature, reagent purity, color development time, age of solutions, and

concentrations of some atmospheric interferents (Scaringelli et al., 1967). The final color can be stabilized with phosphoric acid. Because temperature affects the rate of color formation and color fading, a constant-temperature bath is recommended for maximum precision. Highly purified reagents, especially the pararosaniline dye, are vital for acceptable reproducibility.

The precision of the analytical procedure in the EPA reference method was estimated using standard sulfite samples (Scaringelli et al., 1967) and was reported as 4.6 percent at the 95 percent confidence level. The lower limit of detection of $SO_2$ in 10 ml of TCM absorbing solution was 0.75 μg, representing a concentration of 25 μg $SO_2/m^3$ (0.01 ppm) in an air sample of 30 liters. A collaborative study (McCoy et al., 1973) of the 24-hour EPA reference method procedure indicated the following: method repeatability (day-to-day variability within an individual laboratory) varies linearly with $SO_2$ concentration from ± 18 μg/m$^3$ (0.007 ppm) at concentration levels of 100 μg/m$^3$ (0.04 ppm) to ± 51 μg/m$^3$ (0.019 ppm) at concentration levels of 400 μg/m$^3$ (0.15 ppm); method reproducibility (day-to-day variability between two or more laboratories) varies linearly with $SO_2$ concentration from ± 37 μg/m$^3$ (0.014 ppm) at 100 μg/m$^3$ to ± 104 μg/m$^3$ (0.040 ppm) at 400 μg/m$^3$.

A recent investigation (Fuerst et al., 1976) showed that collected $SO_2$ TCM samples decay at a temperature dependent rate. Significant decay can occur during collection of ambient samples and during shipment and storage of collected samples when the TCM solutions are exposed to temperatures above 20°C. The effect of this decay is to underestimate the concentration of $SO_2$ in the air sample. Measures to minimize these effects have been investigated by Martin (1977), who recommends the use of thermostatted shelters to house the

sampling equipment during sample collection. The temperature of samples during shipment can be controlled with cold-pack shipping containers. When samples are stored before being analyzed, refrigeration at 5°C minimizes further decay. Temperature control procedures are currently being incorporated in the EPA reference method.

2.3.2.3.2 Titrimetric Method: Hydrogen Peroxide. In this British Standard Method, atmospheric $SO_2$ is absorbed in 0.03 N (1-Vol)hydrogen peroxide and adjusted to pH 4.5 (British Standard 1747, Part 3, 1963). It is oxidized to sulfuric acid by the absorbing solution and titrated with standard alkali. Only simple equipment is required, and samples may be stored for long periods before titration. With an 850-liter air sample, 25 μg $SO_2/m^3$ (0.01 ppm) may be detected (Katz, 1968).

This method has several weaknesses; its sensitivity is insufficient for instantaneous analysis, long sampling times (24-hr) are needed and accuracy is reduced at low concentrations. Since it measures total acidity rather than $SO_2$, any atmospheric acid will produce positive errors. Similarly, ammonia will neutralize absorbed $SO_2$ to give low results. If a particle filter is in line before the bubbler, $SO_2$ may be absorbed; this would also give a low result.

2.3.2.3.3 Titrimetric Method: Barium Perchlorate-Thorin. Atmospheric $SO_2$ is absorbed in 1 percent hydrogen peroxide adjusted to pH 9 with ammonia. Interfering aerosol sulfate is removed by first passing the air through phosphoric acid. The sulfate formed from $SO_2$ is titrated in isopropanol with barium perchlorate, using thorin as the indicator. A color change from yellow to pink when excess barium ions are present indicates the end point. The titration is followed spectrophotometrically at 550 nm (Fritz and Yamamura, 1955). The limit of detection with an air sample of 1000-liters is 50 μg $SO_2/m^3$ (0.02 ppm). Heavy metals, which complex with thorin, may be removed initially with a particulate filter.

2.3.2.3.4 Turbidimetric Method: Hydrogen Peroxide. Hydrogen peroxide (0.03 N) is the absorbent solution for removing $SO_2$ from air. Dilute HCl and a glycerol-alcohol solution is added to an aliquot of the resultant sulfate solution. The optical absorbance of this solution is measured against a water blank at 500 nm. Solid barium chloride crystals are added, and the solution is shaken and permitted to stand for 40 minutes. The absorbance of the turbid mixture is measured against water and corrected for the previous reading. Factors that must be controlled in this method are pH, sulfate concentration, stability of the colloidal barium sulfate suspension, barium ion concentration, and aging of the barium chloride solution (Volmer and Frohlich, 1944).

2.3.2.3.5 Colorimetric Method: Barium Chloranilate. This method is based upon the reaction of solid barium chloranilate with sulfate ions to form barium sulfate and colored acid chloranilate ion (Bertolacini and Barney, 1957). $SO_2$ is scrubbed by a 0.5 percent hydrogen peroxide solution. The solution is buffered at pH 4 with potassium acid phthalate; solid barium chloranilate and 95 percent ethyl alcohol are then added. Excess barium chloranilate and precipitated barium sulfate are removed by filtration or centrifugation, and the optical absorbance of the liberated red-purple acid chloranilate ion is measured at 530 nm. A limit of detection of 130 μg $SO_2/m^3$ (0.05 ppm) with a 1-$m^3$ sample has been noted. Phosphate, fluoride, and chloride interfere and require preliminary separation.

2.3.2.3.6 Colorimetric Method: Iodine. An absorbing solution containing soluble starch, potassium iodide, dilute sulfuric acid, and standard 0.01 N iodine solution is prepared (Katz, 1950). $SO_2$ in the air sample reacts with

this 8 x $10^{-5}$ N iodine solution to decolorize the blue iodine-starch complex. The reduction in color intensity is measured spectrophotometrically. The range of applicability is 25 to 2600 μg $SO_2/m^3$ (0.01 to 1 ppm), depending upon the volume and concentration of absorbent solution and the volume of air sampled.

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

2.3.2.3.7 Titrimetric Method: Iodine. Air is bubbled through a sodium hydroxide solution which absorbs $SO_2$ (Jacobs, 1960). After acidification of the solution, the liberated sulfurous acid is titrated with standard iodine solution, using starch as an indicator. Because sulfite oxidizes to sulfate in the alkaline absorbent solution, samples cannot be stored. Oxidizing agents, nitrogen dioxide, and ozone interfere by underestimating the analysis. Hydrogen sulfide and reducing agents overestimate the analysis. For an 850-liter air sample collected at 30 liters/min, sensitivity is 25 μg $SO_2/m^3$ (0.01 ppm) (Terraglio and Manganelli, 1962).

2.3.2.3.8 Titrimetric Method: Iodine-Thiosulfate. In this method, $SO_2$ is absorbed in a solution of iodine, potassium iodide, starch, and sulfuric acid. Some of the iodine is reduced by the $SO_2$; the excess iodine is titrated with a standard thiosulfate solution (Katz, 1969). Interferences are the same as in the previously described iodimetric methods.

2.3.2.3.9 Colorimetric Method: Ammonium Molybdate. Stratmann (Katz, 1968) developed a method that uses silica gel in a quartz tube to adsorb $SO_2$ from air that is passed through the tube. The collected sample in the tube is placed in a 500°C furnace, and a stream of hydrogen is passed through. Sulfur dioxide is desorbed and then reduced to hydrogen sulfide by passing it over a platinum wire mesh catalyst heated to 600°C. The hydrogen sulfide is absorbed in a solution containing ammonium molybdate, sulfuric acid, and urea. Absorbance of the resulting molybdenum blue complex is measured at 570 nm. A limit of detection of 25 μg $SO_2/m^3$ (0.01 ppm) can be obtained with a 40-liter air sample (Katz, 1968).

Sulfuric acid, sulfur trioxide, and hydrogen sulfide interfere. $H_2SO_4$ and $SO_3$ may be eliminated by prior passage through phosphoric acid. Samples containing more than 300 mg of water must be dried by preliminary passage through phosphorous pentoxide, although some $SO_2$ is lost in the process. In a series of comparative tests, this method has yielded erratic results (Organization for European Economic Cooperation, European Productivity Agency, 1961).

2.3.2.3.10 Ion-Exchange Chromatographic Method. Ion-exchange resins can be used to provide excellent separation of ions. However, the continuous determination of ionic species as they are eluted from an ion-exchange column has been difficult, due principally to the electrolyte solution used as a eluant. Recently, Small and co-workers (1975) devised a novel combination of resins which effectively neutralize the eluant and suppress its conductivity without affecting the analyte, permitting the use of a conductivity cell as a monitor for even ppm levels of either cationic or anionic species.

A method for collection and ion chromatographic analysis of atmospheric $SO_2$ has recently been developed by EPA (Mulik et al., 1978). The method uses

dilute (0.6 percent) hydrogen peroxide to collect the ambient $SO_2$. The resultant sulfate ion is analyzed by ion-exchange chromatography. When a prefilter is used in the sampling train to remove aerosol sulfates, there are no apparent interferences. Collection efficiency is approximately 100 percent over the range of the method, 25 to 1300 μg $SO_2/m^3$ (0.01 to 0.5 ppm).

2.3.2.3.11 Sulfation Method: Lead Peroxide. Sulfation methods are based on the reaction of gaseous $SO_2$ in air with lead peroxide ($PbO_2$) paste to form lead sulfate ($PbSO_4$). They are cumulative methods for estimating average concentrations over extended time periods.

In the lead candle method (Wilsdon and McConnell, 1934), the paste is prepared by mixing $PbO_2$, gum tragacanth, alcohol, and water. The paste is applied to a piece of cotton gauze wrapped around a cylinder 10 cm round and 10 cm high. After drying, the cylinder is exposed to the atmosphere in a sheltered location. After exposure, the sulfated lead candle is treated with sodium carbonate solution to dissolve the lead sulfate. Sulfate is then determined gravimetrically or turbidimetrically. Measurements with the method are reported as sulfation rates (mg $SO_3$/100 $cm^2$/day).

In the sulfation plate method (Huey, 1968), a similar paste containing glass fiber filters is poured into a petri dish and, after drying, is exposed to the atmosphere. Sulfation methods have the advantage of being inexpensive, but their accuracy is subject to many physical and chemical variables and interferents.

The rate of sulfate formation is proportional to atmospheric $SO_2$ concentration up to 15 percent conversion of the lead peroxide (Wilsdon and McConnell, 1934). Reaction rate increases with temperature and with humidity. Other

factors affecting rate of sulfation are wind velocity, purity of lead peroxide, and shape of the shelter (Bowden, 1964). The consistency of lead peroxide, both within batch and between batches, is difficult to control. Consequently, the area of any sulfation surface could vary, giving different rates. Factors affecting surface area are particle size of lead peroxide and the density and thickness of the layer. Positive errors are contributed by hydrogen sulfide and sulfate aerosols. Methyl mercaptan is a potential negative interferent.

The relationship between sulfation rates (mg $SO_3$/100 $cm^2$/day) and $SO_2$ concentration (ppm) is discussed in detail in section 2.3.5.1.

2.3.3 Continuous Methods

2.3.3.1 Sample Collection--In continuous sulfur dioxide analyzers sample collection is an integral part of the total automated measurement process. The sample line leading from the sample manifold to the inlet of the analyzer should be constructed of an inert material such as Teflon®. The sample line should be as short as is practically possible and its internal diameter should assure short residence times and insignificant pressure drops between the sample manifold and the analyzer inlet. The use of a particle filter at the inlet of the analyzer should depend on the analyzer's susceptibility to interference, malfunction, or damage due to particulate matter. Heavy loading of particulate matter on the filter may lead to erroneous $SO_2$ measurements; therefore, it may be necessary to change the filter frequently.

2.3.3.2 Calibration--The relationship between true pollutant concentration and the response of a continuous analyzer is best determined by dynamic calibration. In dynamic calibration, standard atmospheres containing $SO_2$ in known concentrations are introduced into the analyzer. The analyzer is adjusted accordingly to produce the proper response. Dynamic calibration provides evidence that all components of the instrument are functioning properly.

Standard gas for calibration purposes may be obtained from permeation tubes (O'Keeffe and Ortman, 1966), which are sealed Teflon® tubes containing liquified gas. Gas diffuses through the walls at a low, known constant rate at constant temperature. By diluting the emitted gas with varying flows of clean air in a mixing chamber, a wide range of concentrations may be generated. Permeation tubes with certified permeation rates are available from the National Bureau of Standards (NBS) as Standard Reference Materials (SRMs). Tubes with certified rates traceable to NBS are also available from commercial suppliers.

When enclosed in an inert plastic tube, a liquefiable gas such as $SO_2$ escapes at a constant temperature-dependent rate that can be determined by measuring the weight loss of the tube over a long period of time. The concentration of $SO_2$ in air flowing over the permeation tube at a given flow rate is given by

$$C = \frac{R \times K}{F}$$

where

$C$ = $SO_2$ concentration, ppm

$R$ = rate of weight loss of permeation tube at constant temperature, μg/min

$K$ = 0.382 μl $SO_2$/μg $SO_2$ (at 25°C and 760 mm Hg)

$F$ = air flowrate (corrected to 25°C and 760 mm Hg), liter/min

A variation of this procedure allows pure $SO_2$ from a gas cylinder to diffuse at a constant rate through a ceramic frit into the airstream. Permeation tubes provide a simple and accurate method for preparing known $SO_2$ concentrations in air. However, adsorption losses restrict the lower limits at which $SO_2$ concentrations can be considered reliable. To achieve precise

calibrations, the temperature of the permeation tube must be carefully controlled. Permeation tubes presently provide the simplest and most reliable method of calibration.

Dynamic calibration may also be carried out using known mixtures of $SO_2$ gas in high pressure cylinders. For stability purposes they are usually prepared in high concentrations and dynamically diluted to the desired level. Traceability of such standards to NBS SRMs may be established by the gas standard manufacturer or by the user.

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

2.3.3.3 Analytical Methods

2.3.3.3.1 Conductimetric analyzers. Conductimetric analyzers were the first commercially available instruments for continuously monitoring $SO_2$ in the atmosphere and are still used today. In their operation, air is brought into contact with an absorbing solution, which dissolves $SO_2$. The ions formed by $SO_2$ dissolution increase the conductivity, which is proportional to the concentration. The absorbent may be either deionized water or acidified hydrogen peroxide solution. When water is used, conductance is increased by formation and dissociation of sulfurous acid:

$$SO_2 + H_2O \rightarrow H_2SO_3$$

Hydrogen peroxide solution oxidizes $SO_2$ to form sulfuric acid:

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$

Conductance is measured by a pair of inert (platinum) electrodes within the cell. To increase accuracy, comparison is made to a reference cell, which measures conductance of unused absorbent. Typical features of conductimetric analyzers are detection limits of 25 μg $SO_2/m^3$ to about 5000 μg/$m^3$ (0.01 to 2 ppm), lag time (time interval from change in input concentration to change in output signal) of about 20 seconds, and response time (time interval from change in input concentration to 90 percent of maximum output signal) of 2 minutes.

The major disadvantage of conductimetric analyzers stems from their operation; i.e., any species that either forms or removes ions from solution and changes conductivity can interfere. The degree of interference depends on humidity, temperature, $SO_2$ concentration, and the particular instrument. The worst interferents are chlorine, hydrochloric acid, and ammonia; nitrogen dioxide and carbon dioxide interfere to a lesser extent (Roberts and Friedlander, 1976). Airborne particles, especially ocean-borne salt aerosols, are potentially damaging. Several methods have been used to minimize these problems (Intertech Corp., undated). Chemical scrubbers which selectively remove gaseous interferents have been incorporated into some conductimetric analyzers. Particulate filters have also been employed.

2.3.3.3.2 <u>Colorimetric analyzers</u>. Colorimetric analyzers are based upon the reaction of $SO_2$ with solutions of organic dyes to form colored species. Optical absorbance of the ensuing solution, measured spectrophotometrically, is within limits linearly proportional to the concentration of the colored species in accordance with Beer's Law.

Most instruments utilize improved versions of the manual pararosaniline method developed by West and Gaeke. Automation of the West-Gaeke method per se does not ensure a practical continuous monitoring instrument since some solutions require daily preparation.

Typical features for some commercially available instruments are detection limits of ~13 to 5000 μg $SO_2/m^3$ (0.005 to 2 ppm), lag time of 2 minutes, and response time of 8 minutes (~~Instrumentation for Environmental Monitoring, Air, 1972~~ Lawrence Berkeley Laboratory, 1972). Advantages of these instruments include simplicity, high sensitivity, and, with proper control, good specificity. Interferences by nitrogen oxides may be controlled by using a sulfamic acid reagent. Heavy metals may be complexed with EDTA in the scrubbing solution or with phosphoric acid in the dye solution. Ozone interference may be controlled by the use of a delay coil downstream from the absorber to allow time for ozone to decay, but this results in longer lag and response times. Major disadvantages of these instruments are the need for reagent and pump tubing replacement and frequent recalibration.

2.3.3.3.3 Flame photometric analyzers. The flame photometric detector (FPD) is based on the measurement of the band emission of excited $S_2^*$ molecules during passage of sulfur-containing compounds through a hydrogen-hyperventilated (reducing) flame. The emitted light passes through a narrow-pass optical filter, which isolates the 394 nm $S_2^*$ band, and is detected by a photomultiplier tube (PMT). Application of the FPD to the detection of $SO_2$ was first made by Crider (1965) and analyzers using FPD have been widely accepted for ambient $SO_2$ monitoring.

Typical operational features of continuous flame photometric $SO_2$ analyzers are a sensitivity of 0.005 to 1 ppm, lag time of 3 seconds, and response time of 10 seconds (~~Instrumentation for Environmental Monitoring, Air~~, 1972). Lawrence Berkeley Laboratory

Although the FPD is insensitive to nonsulfur species, it will detect sulfur compounds other than $SO_2$. Since the concentration of $H_2S$, mercaptans, and other organic sulfur compounds in the atmosphere is usually less than 10 percent of the $SO_2$ level, their potential interference is normally minimal. Particulate filters will remove troublesome aerosol sulfates along with other particulates to eliminate clogging and light scattering. Selective filters may be used to reduce interference from other gaseous sulfur compounds; e.g., an $H_2S$ filter is used on most commercial instruments. Interference by carbon dioxide can be minimized by maintaining identical $CO_2$ concentrations in the calibration and sample matrices.

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

Disadvantages of FPD systems include the need for a compressed hydrogen source and sensitivity to all sulfur compounds. Photomultiplier tube output is proportional to the square of $SO_2$ concentration; hence, an electronic system to "linearize" output is a desirable feature. Advantages of FPD systems include low maintenance, high sensitivity, very fast response, and good selectivity for sulfur compounds. No reagents are necessary other than compressed hydrogen.

2.3.3.3.4 <u>Coulometric (amperometric) analyzers</u>. Coulometric analyzers are based on the reaction of $SO_2$ with a halogen, formed directly by electrolysis of a halide solution:

$$SO_2 + 2H_2O + \underset{(I_2)}{Br_2} \rightarrow H_2SO_4 + \underset{(2HI)}{2HBr}$$

The current necessary to replace the depleted halogen is proportional to the amount of $SO_2$ absorbed in the solution, and hence to the $SO_2$ concentration in the air.

In one common coulometric system, an inner chamber, into which air is introduced, is contiguous with an outer chamber (Treon and Crutchfield, 1942). Both contain a solution of potassium bromide and bromine in dilute sulfuric acid. Potential difference between both chambers, relative to a reference potential, is measured by the reference electrodes. As absorbed $SO_2$ reduces the $Br_2$ concentration in the inner chamber, the amplifier produces a current to restore the $Br_2$ content in the inner chamber until the potential difference is again zero.

In a second system, the change in halogen concentration is detected as a current change rather than a potential difference. The cell is filled with a potassium iodide solution, buffered to pH 7. At the platinum anode, a constant current source continuously generates iodine, which is subsequently reduced at the cathode. An equilibrium concentration of iodine is established, and no current is generated at an activated-carbon bipolar reference electrode, connected in parallel. Reaction with $SO_2$ decreases the equilibrium concentration of iodine, which cannot transport the charge generated by the constant-current source. Part of the current is diverted through the reference electrode; this flow is proportional to the $SO_2$ in the air sample.

Interferent species are those able to oxidize halides, reduce halogens, or complex with either. They consist primarily of sulfur compounds (hydrogen sulfide, mercaptans, and organic sulfides and disulfides) with sensitivities comparable to that of $SO_2$. Other potential interferents, at lower sensitivities, are ozone, nitrogen oxides, chlorine, ethylene, aldehydes, benzene, chloroform,

α-pyrene, other nitrogen or halogen-containing compounds, and other hydrocarbons (DeVeer et al., 1969; Thoen et al., 1968). Interferences can be minimized by selective filters, which are sometimes built into the instrument or offered as optional features. For example, a heated silver gauze filter is reported to remove hydrogen sulfide, ozone, chlorine, nitrogen oxides, carbon disulfide, ethylene, aldehydes, benzene, and chloroform, but will not remove mercaptans (Philips Electronic Instruments). updated

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

2.3.3.3.5 Fluorescence analyzers. Fluorescence analyzers are based on detection of the characteristic fluorescence released by the sulfur dioxide molecule when it is irradiated by ultraviolet light (Okabe et al., 1973). This fluorescent light is also in the ultraviolet region of the spectrum, but at a different wavelength than the incident radiation. The fluorescent wavelengths usually monitored are between 190 and 230 nm. In this region of the spectrum, there is relatively little quenching of the fluorescence by other molecules occurring in ambient air. The light is detected by a PMT that, through the use of electronics, produces a voltage proportional to the light intensity and $SO_2$ concentration.

The fluorescent light reaching the PMT is usually modulated to facilitate the high degree of amplification necessary. Some analyzers mechanically "chop" the incident irradiation before it enters the reaction chamber. This process is accomplished by a fan-blade-like chopper rotating at a constant

speed, which alternately blocks and passes the light to the chamber. Other instruments electronically pulse the incident light source at a constant rate.

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

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

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

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

Sensitivity is greatly enhanced over ordinary spectrometers because the output is an AC signal of known wavelength and phase, adaptable to high-gain electronic amplification. Uniqueness of the curvature of a given molecular band enables this type of instrument to be highly specific. Measurements are independent of sample flow rate, but relatively high flow rates (4 liters/min) are necessary to achieve reasonable response time.

2.3.3.3.7 Other Methods. Electrochemical transducer (ECT) analyzers measure the current generated by electrochemical oxidation of $SO_2$ at a sensing electrode. All the chemical reactions take place within a sealed transducer module, eliminating the wet chemistry of conductimetric, colorimetric, and coulometric analyzers.

Correlation spectrometry is based upon absorption spectrometry of molecular $SO_2$ in a longpath sample of air. Either natural or artificial light may be used. Light is collected by a telescope, collimated, and dispersed by a grating or prism. The spectrum is then focused on the plane of an exit mask, which is a replica of the absorption spectrum of $SO_2$. The difference in light intensity reaching the detector is related to the $SO_2$ concentration in the

path between the light source and the instrument (Barringer Research, Ltd, 1969; Moffat et al., 1971).

Condensation nuclei formation instruments consist of two units: a converter for changing $SO_2$ molecules into condensation nuclei, and a monitor for detecting the nuclei. Sample air is drawn through a glass fiber filter, which removes existing condensation nuclei. $SO_2$ molecules, in the presence of water vapor and UV radiation, are converted into $H_2SO_4$ aerosol. The aerosol, consisting of condensation nuclei, is introduced into the monitor. Constant volume expansion in the presence of water vapor produces a cloud; transmission of this cloud is directly related to the initial $SO_2$ concentration.

Differential lidar is a remote sensing system which provides range-resolved measurements of concentration by reflecting pulses of laser light at two wavelengths with different absorption coefficients from particles along the line of sight. The amount of light that is scattered and received at the detector determines the detection limits. Thus, a high-energy laserpulse operating under conditions of good visibility provides the bes sensitivity.

### 2.3.4 EPA Reference and Equivalent Methods

Under the provisions of EPA's "Ambient Air Monitoring Reference and Equivalent Methods" regulations codified as 40 CFR Part 53 (U.S. Environmental Protection Agency, 1979), several commercial analyzers have been designated as equivalent methods for determining compliance with the NAAQS for sulfur dioxide. These analyzers have been subjected to the required testing and have met EPA's performance specifications for automated methods. These specifications are given in Table 2-3, and a list of the $SO_2$ analyzers, which have been designated as of March 1, 1980, is given in Table 2-4. Information about the designation of these analyzers as equivalent methods may be obtained by writing the Environmental Monitoring Systems Laboratory, Methods Standardization Branch (MD-77),

United States Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

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

Two manual methods have also been designated as equivalent methods (Federal Register, 1975). These methods are identified as:

EQS-0-115-001
~~EQS0775001~~, "Pararosaniline Method for the Determination of Sulfur Dioxide in the Atmosphere Technicon I Automated Analysis System."

EQS-0-115-002
~~EQS0775002~~, "Pararosaniline Method for the Determination of Sulfur Dioxide in the Atmosphere Technicon II Automated Analysis System."

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

TABLE 2-3. PERFORMANCE SPECIFICATIONS FOR AUTOMATED METHODS

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

Source: Federal Register (1975)
U.S. EPA (1979c)

TABLE 2-4. LIST OF DESIGNATED EQUIVALENT METHODS (AUTOMATED ANALYZERS)

| Designation number | Identification and source | Federal vol. | Register page | Notices date |
|---|---|---|---|---|
| EQSA-1275-005 | Lear Siegler Model SM1000 $SO_2$ Ambient Monitor[a] | 41 | 3893 | 1/27/76 |
| | | 41 | 32946 | 8/06/76 |
| | | 42 | 13044 | 3/08/77 |
| | | 45 | 1147 | 1/04/80 |
| | Lear Siegler, Inc.<br>74 Inverness Drive East<br>Englewood, Colorado 80112 | | | |
| EQSA-1275-006 | Meloy Model SA185-2A Sulfur Dioxide Analyzer[b] | 41 | 3893 | 1/27/76 |
| | | 43 | 38088 | 8/25/78 |
| | Meloy Laboratories, Inc.<br>6715 Electronic Drive<br>Springfield, Virginia 22151 | | | |
| EQSA-0276-009 | Thermo Electron Model 43 Pulsed Fluorescent $SO_2$ Analyzer[c] | 41 | 8531 | 2/27/76 |
| | | 41 | 15363 | 4/12/76 |
| | | 42 | 20490 | 4/20/77 |
| | Thermo Electron Corp.<br>108 South Street<br>Hopkinton, Massachusetts 01748 | 44 | 21861 | 4/12/79 |
| | | 45 | 2700 | 1/14/80 |
| EQSA-0676-010 | Philips PW9755 $SO_2$ Analyzer[d] | 41 | 26252 | 6/25/76 |
| | | 41 | 46019 | 10/19/76 |
| | | 42 | 28571 | 6/03/77 |
| | Philips Electronic Instruments, Inc.<br>85 McKee Drive<br>Mahwah, New Jersey 07430 | | | |
| EQSA-0876-011 | Philips PW9700 $SO_2$ Analyzer[d] | 41 | 34105 | 8/12/76 |
| | Philips Electronic Instruments, Inc.<br>85 McKee Drive<br>Mahwah, New Jersey 07430 | | | |
| EQSA-0876-013 | Monitor Labs Model 8450 Sulfur Monitor[b] | 41 | 36245 | 8/27/76 |
| | | 44 | 33476 | 6/11/79 |
| | Monitor Labs, Inc.<br>10180 Scripps Ranch Blvd.<br>San Diego, California 92131 | | | |

TABLE 2-4. LIST OF DESIGNATED EQUIVALENT METHODS (AUTOMATED ANALYZERS) (Contd)

| Designation number | Identification and source | Federal vol. | Register page | Notices date |
|---|---|---|---|---|
| EQSA-0877-024 | ASARCO Model 500 and Model 600 | 42 | 44264 | 9/02/77 |
| | Sulfur Dioxide Monitors[e,*]<br>ASARCO Incorporated<br>3422 South 700 West<br>Salt Lake City, Utah 84119 | 44 | 67522 | 11/26/79 |
| EQSA-0678-029 | Beckman Model 953 Fluorescent | 43 | 35995 | 8/14/78 |
| | Ambient $SO_2$ Analyzer[c]<br>Beckman Instruments, Inc.<br>2500 Harbor Boulevard<br>Fullerton, California 92634 | | | |
| EQSA-1078-030 | Bendix Model 8303 | 43 | 50733 | 10/31/78 |
| | Sulfur Analyzer[b]<br>The Bendix Corporation<br>P. O. Box 831<br>Lewisburg, West Virginia 24901 | | | |
| EQSA-1078-032 | Meloy Model SA285E | 43 | 50733 | 10/31/78 |
| | Sulfur Dioxide Analyzer[b]<br>Meloy Laboratories, Inc.<br>6715 Electronic Drive<br>Springfield, Virginia 22151 | | | |
| EQSA-0779-039 | Monitor Labs Model 8850 | 44 | 44616 | 7/30/79 |
| | Fluorescent $SO_2$ Analyzer[c]<br>Monitor Labs, Inc.<br>10180 Scripps Ranch Blvd.<br>San Diego, California 92131 | | | |

[a] Second derivative spectrometric measurement principle

[b] Flame photometric measurement principle

[c] Fluorescence measurement principle

[d] Coulometric measurement principle

[e] Conductimetric measurement principle

*These analyzers are not offered for sale

2.3.5 Method Comparison Studies

2.3.5.1 Comparisons Involving Sulfation Methods and Relationship Between Sulfation and $SO_2$ Concentration--Stalker et al., (1963) compared the lead candle method and the pararosaniline method to measure sulfur dioxide at 123 stations in Nashville, Tennessee. The lead candle method used to collect monthly sulfation samples was a modified version of the method developed by Wilsdon and McConnell (1934). After exposure, the rate of sulfation was determined by the gravimetric procedure in which barium chloride precipitates the sulfate as barium sulfate. The results of 2800 samples were reported in milligrams of sulfur trioxide per 100 $cm^2$ of exposed gauze per day. Sulfur dioxide concentration was determined by a modified version of the pararosaniline method described by West and Gaeke. The dye concentration was changed from the recommended 0.04 percent pararosaniline hydrochloride-6 percent hydrochloric acid mixture to a 0.005 percent-5 percent mixture in order to use an automated analytical system. The sensitivity of the revised method was 0.006 ppm by volume for a 120-liter air sample scrubbed through 15 ml of collecting solution. Colorimetric results were based on 13,000 24-hr samples and 30,000 2-hr samples (Welch and Terry, 1960).

The lead candle method was considered good for estimating mean $SO_2$ levels in communities during months with arithmetic mean concentrations of at least 0.025 ppm. The reliability of these mean estimates was estimated to be within ±25 percent. The authors concluded that the relationships between results obtained with the two different methods of measuring $SO_2$ were best during the fall and winter, when atmospheric concentrations were highest. During the winter season of high $SO_2$ levels, 1 mg of $SO_3$/100 $cm^2$/day (sulfation rate) measured by the lead candle method was equivalent to 0.042 ppm $SO_2$ measured by the pararosaniline method. During the fall season of moderate $SO_2$ levels,

the 1-mg equivalent was 0.035 ppm $SO_2$. During the spring season, the 1-mg equivalent decreased to only 0.015 ppm $SO_2$. Using an average conversion factor of 0.031, the lead candle measurements of $SO_2$ during the spring season of low $SO_2$ levels would thus be about twice as high as simultaneous 24-hr colorimetric measurements of $SO_2$.

Huey et al., (1969) compared the sulfation plate method with the lead candle method to determine $SO_2$ concentrations at some 250 sampling sites nationwide. Both sulfation plates and lead candles were used at each sampling site. Twenty-five thousand paired samples were analyzed by linear regression. The correlation coefficient was found to be 0.95; the regression equation obtained was $X = 0.03 + 1.1Y$, where Y = sulfation plate result in mg of $SO_3$/100 $cm^2$/day and X = predicted lead candle result in mg of $SO_3$/100 $cm^2$/day.

Obtaining a correlation coefficient of 0.95 confirmed that both methods are measuring the same species. Because no values of less than 0.1 mg of $SO_3$/100 $cm^2$/day were measured, the constant 0.03 in the regression equation can be considered to be zero. The authors concluded from the coefficient of Y that sulfation plates are 10 percent less reactive than lead candles.

Huey and coworkers also compared $SO_2$ conductivity monitors with sulfation results. They concluded that sulfation data could be converted to $SO_2$ concentrations by multiplying by 0.03, and that 95 percent of the time this approximation from a single value will lie within a factor of about 3 of any single instrument measurement.

Turner and Sholtes (1971) investigated atmospheric $SO_2$ levels by exposing a series of lead peroxide cylinders and sulfation plates in parallel to several known concentrations of $SO_2$ for specific times in a 10,000-liter stainless-steel tank (test chamber). Lead peroxide cylinders and sulfation plates were

contained within two different types of shelters. For each experimental run, most sulfation plates were analyzed photometrically, while several were analyzed gravimetrically. Most lead peroxide cylinders were analyzed gravimetrically, while a few were analyzed photometrically. In several experimental runs, the same lead peroxide cylinder was analyzed both by gravimetric and photometric methods.

The authors concluded that gravimetric analysis of lead peroxide cylinders was a long and laborious procedure subject to many errors. A typical problem was the care required to analyze only the lead included in the 100 $cm^2$ area, excluding any that might be outside this zone. The photometric analysis was conparatively quick and simple but less consistent and less reproducible than the gravimetric procedure.

The sulfation plates were easier to prepare and analyze (photometrically) than cylinders (gravimetrically), requiring only about half as much time for preparation and analysis.

The following observations and conclusions were also noted: (1) Lead peroxide cylinders are more sensitive to the effects of $SO_2$ than sulfation plates. This may be due in part to the difference in the geometry of the two devices, since the cylinder presents a more exposed surface than the plate.

(2) The shape, or absence, of the shelter appears to affect the sulfation rate of the plates and cylinders. Samples in round shelters give sulfation results that are closer to open samples than do samples in square shelters.

(3) The factor 0.03 proposed by Huey (1969), which gives a prediction of $SO_2$ concentration in ppm when multiplied by cylinder sulfation in mg of $SO_3$/100 $cm^2$/day, appears to be low. The results of this study indicate the factor would be 0.06-0.09 for cylinders in round shelters and 0.09-0.12 for cylinders in square shelters.

(4) Exposure of cylinders and plates to varying concentrations of $SO_2$ produced curved lines, showing a nonlinear relationship between sulfation rates and $SO_2$ concentration.

(5) Prediction of atmospheric $SO_2$ concentrations in ppm from open sulfation plate analyses can be made by multiplying the sulfation value of the plate in mg of $SO_3$/100 $cm^2$/day by a factor of 0.11.

Rider et al., (1977) studied the performance of Huey sulfation plates and the effects of humidity at high $SO_2$ concentrations. Tests were conducted in a 6.25-liter desiccator for various $SO_2$ concentrations (800 to 3200 ppm) at different relative humidities (0 percent, 50 percent, and 100 percent) and exposure times (1 to 12 days).

Taking the data for 0 percent relative humidity, all concentrations except the highest (3200 ppm) showed a linear increase in plate sulfation with time over a period of several days. For the highest concentration the sulfation rate decreased after a few days, indicating that the plates were saturated on their surfaces and the process became nonlinear in time.

The sulfation rate did not appear to be appreciably affected by changes in humidity, although one concentration (2400 ppm) appeared to exhibit an effect. Rider et al. attribute this result to experimental error, since there was no reason to suspect that such an effect would occur only for this concentration. At 3200 ppm the rate did not change with humidity but the capacity of the plate appeared to increase, and the effects of saturation occurred later.

The authors' analysis of the relationship between sulfation and $SO_2$ concentration using the model

$$[\text{Sulfation } (\mu g\ SO_3/cm^2/day) \times \text{constant} = SO_2\ (ppm)^n]$$

yielded a value for n = 3/2 and a value for the constant = 309 for the high $SO_2$ concentrations tested. A true linear relationship would yield an n value of 1.

Rider et al.'s studies using the 6.25-liter desiccator suggest that ambient $SO_2$ concentration (ppm) could be estimated using a linear correlation factor by multiplying sulfation rate (mg $SO_3$/100 $cm^2$/day) by a value of approximately 800. Preliminary studies by the authors using a 20.7-liter carboy suggested a factor of 260. From these results, those of Huey (1969), and those of Turner and Sholtes (1971) using a 10,000-liter chamber, the authors concluded that (1) the factor depends upon the volume of the container used in the studies, and (2) the factor decreases as the volume of the container increases. Calculations by Rider et al. indicate that the amount of sulfation was roughly proportional to the number of moles of $SO_2$ present in the container. Considering the atmosphere to be approaching an infinite volume, the Huey factor of 0.03 might represent a limiting value that is appropriate for very large volumes.

For low ambient concentrations, the assumption of a linear relationship (n = 1 instead of n = 3/2) appears to be reasonable and the Huey factor appears to be appropriate for converting sulfation rate to $SO_2$ concentration.

2.3.5.2 Comparison of Pararosaniline and Barium Perchlorate-Thorin Methods--The Rijksinstituut voor de Volksgezondheid in the Netherlands made a comparison in 1972-73 of the pararosaniline method and the barium perchlorate-thorin method for determining sulfur dioxide in air (Thrane, 1978). The sampling devices for the two methods were placed side by side at three monitoring stations. The results of a correlation analysis of the data are presented in Table 2-5

TABLE 2-5. RESULTS FROM A CORRELATION ANALYSIS OF THE THORIN METHOD VERSUS THE PARAROSANILINE METHOD

| Station | No. of Samples | Mean $SO_2$ concentration, $\mu g/m^3$ | | Correlation Coefficient | Regression equation |
|---|---|---|---|---|---|
| | | Thorin | Pararosaniline | | |
| Den Helder | 252 | 19.7 | 18.2 | 0.937 | $SO_2(Th) = 0.937\ SO_2\ (Para) - 0.187$ |
| Wageningen | 239 | 32.3 | 27.0 | 0.888 | $SO_2(Th) = 0.897\ SO_2\ (Para) - 0.200$ |
| Witteveen | 223 | 19.1 | 23.7 | 0.912 | $SO_2(Th) = 0.946\ SO_2\ (Para) + 0.511$ |

SOURCE: Thrane (1978)

and show reasonably good agreement between the two methods even at these low $SO_2$ concentrations.

2.3.5.3 Comparisons of Continuous Methods--Palmer et al. (1969) evaluated the field performance of eleven commercially available sulfur dioxide monitors over a 3-month period in New York City. Among the characteristics investigated were calibration drift, maintenance requirements, and comparability of data for each analyzer. The study was conducted during the winter when $SO_2$ concentrations were relatively high. The mean concentration, calculated from the means of the eleven analyzers (8 conductimetric, 2 colorimetric, 1 coulometric) over the course of the study, was 0.206 ppm.

A statistical analysis of the data by the authors revealed the following:

(1) There were significant differences at the 0.001 probability level among instrument means. However, at the 0.01 level, the only significant differences were between one of the colorimetric analyzers and two of the conductimetric analyzers.

(2) There were significant differences between instrument variances (variability from day-to-day as compared with the means of all instruments for each hour of that day). The highest variability was observed with one of the colorimetric analyzers and two of the conductimetric analyzers.

(3) The correlation coefficients for all eleven instruments paired with each other ranged from a minimum of 0.40 (colorimetric vs conductimetric) to a maximum of 0.96 (conductimetric vs conductimetric).

A re-evaluation of the Palmer study reveals that, with the exception of the one colorimetric analyzer and the two conductimetric analyzers, the correlation between monitors was reasonably good (0.80-0.96).

Concern over whether the reasonable agreement found in the Palmer study would hold at lower mean concentrations than those observed in New York City led to a study by Stevens et al. (1972). Ambient $SO_2$ concentrations were measured over an 83-day period by five continuous monitors in Los Angeles. The measurement principles of the five analyzers were: (1) colorimetric (West-Gaeke), (2) conductimetric, (3) coulometric, (4) flame photometric, and (5) gas chromatographic-flame photometric.

A correlation matrix of 24-hourly averages selected over the monitoring period is presented in Table 2-6. Mean values, along with correlation coefficients, can be used to compare measurements on an absolute basis. The authors concluded that the conductimetric and coulometric analyzers (1) exhibited poor correlations with the colorimetric, FPD, and GC-FPD analyzers, and (2) recorded $SO_2$ concentrations as much as twice the values measured with the other analyzers.

Measurements obtained in downtown Los Angeles on a day when the $SO_2$ concentration exceeded 0.100 ppm are shown in Figure 2-2. The corresponding correlation coefficients and mean concentrations for the analyzers operational on that day are given in Table 2-7. The $SO_2$ concentrations recorded by the conductimetric and coulometric analyzers were consistently higher than those observed with the FPD analyzers.

The authors suggest that substances such as fine particulate matter, ozone, oxides of nitrogen, and certain organics, which are generated during the daytime hours by industrial and automotive activity, can produce positive interference in the conductimetric and coulometric analyzers.

The conductimetric analyzer in the Stevens study was not equipped with a chemical scrubber to remove potential interferences. Instead, it relied on

TABLE 2-6. SULFUR DIOXIDE CORRELATION COEFFICIENTS AND MEAN CONCENTRATIONS FOR MEASUREMENTS MADE BETWEEN SEPTEMBER 11 AND NOVEMBER 24, 1970 (1)

| Instrument | Technicon Colorimetric | Meloy FPD | Philips Coulo-metric | Leeds & Northrop Conductimetric | Tracor GC-FPD |
|---|---|---|---|---|---|
| Technicon Colorimetric West-Gaeke | 1 | | | | |
| Meloy FPD | 0.805 | 1 | | | |
| Philips Coulometric | 0.721 | 0.810 | 1 | | |
| Leeds & Northrup Conductimetric | 0.140 | 0.663 | 0.572 | 1 | |
| Tracor GC-FPD | 0.870 | 0.743 | 0.432 | 0.139 | 1 |
| Mean Concentration, ppm | 0.036 | 0.033 | 0.050 | 0.063 | 0.040 |

(1) Data selected for this correlation matrix were restricted to hourly average $SO_2$ concentrations exceeding 0.02 ppm.

SOURCE: Stevens et al. (1972)

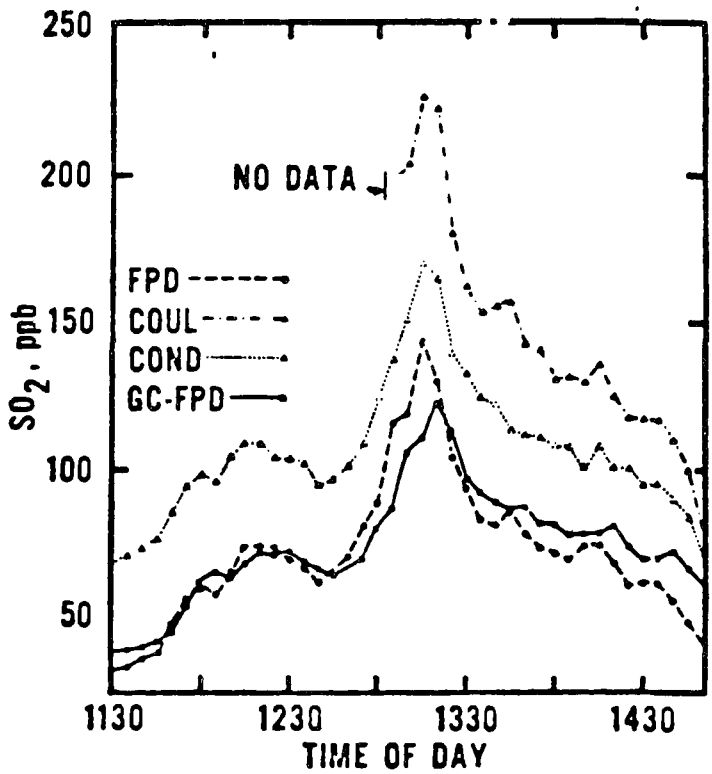



FIGURE 2-2. Sulfur Dioxide Concentrations Between 1200 and 1500 Hours on November 24, 1970.

SOURCE: Stevens et al. (1972)

TABLE 2-7. SULFUR DIOXIDE CORRELATION COEFFICIENTS AND MEAN CONCENTRATIONS FOR MEASUREMENTS MADE NOVEMBER 24, 1970, 1200 to 1355 HOURS[1]

| Instrument | Technicon[2] Colorimetric | Meloy FPD | Philips Coulometric | Leeds & Northrop Conductimetric | Tracor GC-FPD |
|---|---|---|---|---|---|
| Technicon Colorimetric West-Gaeke | --- | | | | |
| Meloy FPD | --- | 1 | | | |
| Philips Coulometric | --- | 0.967 | 1 | | |
| Leeds & Northrup Conductimetric | --- | 0.978 | 0.962 | 1 | |
| Tracor GC-FPD | --- | 0.887 | 0.809 | 0.927 | 1 |
| Mean Concentration, ppm | --- | 0.084 | 0.177 | 0.118 | 0.082 |

(1) 5-Minute Intervals

(2) Colorimetric data not available.

SOURCE: Stevens et al. (1972)

control of absorbing solution pH to derive specificity for $SO_2$. The coulometric analyzer was equipped with a scrubber to remove only $H_2S$. Current analyzers based on these principles are generally equipped with complex chemical and physical scrubbers to minimize interference problems.

2.3.5.4 Comparison of EPA Reference and Equivalent Methods--As part of the required equivalency testing by the manufacturer, all of the continuous $SO_2$ analyzers designated by EPA as equivalent methods have demonstrated a consistent relationship with the reference method. A consistent relationship is demonstrated when the differences between (1) measurements made by the test analyzer and (2) measurements made by the reference method are less than or equal to the maximum discrepancy specification in the last column of Table 2-8, when both methods simultaneously measure $SO_2$ concentrations in a real atmosphere. All of the equivalent methods listed in Table 2-4 have demonstrated this consistent relationship with the reference method. The differences between simultaneous measurements were generally well within the specifications listed in Table 2-8.

A comparison study using EPA designated equivalent methods for $SO_2$ was recently conducted by EPA in an urban-industrial-commercial area of Durham, North Carolina (Environmental Monitoring Systems Laboratory, 1979). Eight continuous $SO_2$ analyzers were compared over a period of 150 days under more or less typical air monitoring conditions. During the study, the analyzers simultaneously measured ambient air sampled from a common manifold. The ambient sample was occasionally augmented with artifically generated pollutant to allow for analyzer comparisons at higher concentrations. Concentration levels at which "spiked" testing occurred were 75, 125, and 250 ppb. A frequency distribution of the 1-hour average $SO_2$ concentrations measured (ambient and ambient + spike) is shown in Table 2-9.

TABLE 2-8. TEST CONCENTRATION RANGES, NUMBER OF MEASUREMENTS REQUIRED, AND MAXIMUM DISCREPANCY SPECIFICATION

| $SO_2$ concentration range, ppm | Simultaneous measurements required | | Maximum discrepancy specification, ppm |
|---|---|---|---|
| | 1-hr | 24-hr | |
| low (0.02-0.05) | - | 3 | 0.02 |
| med (0.10-0.15) | - | 2 | 0.03 |
| high (0.30-0.50) | 7 | 2 | 0.04 |

SOURCE: Federal Register (1975)
U.S. EPA (1979c)

TABLE 2-9. FREQUENCY DISTRIBUTION OF SULFUR DIOXIDE MEASUREMENTS[1]

| Concentration ppm | Percent of Measurements in Concentration Range |
|---|---|
| <0.020 | 44.6 |
| 0.020 - 0.039 | 7.8 |
| 0.040 - 0.059 | 9.5 |
| 0.060 - 0.079 | 2.7 |
| 0.080 - 0.099 | 1.1 |
| 0.100 - 0.119 | 7.8 |
| 0.120 - 0.139 | 12.7 |
| 0.140 - 0.159 | 2.7 |
| 0.160 - 0.179 | 0.2 |
| 0.180 - 0.199 | 2.7 |
| 0.200 - 0.219 | 0.3 |
| 0.220 - 0.239 | 2.0 |
| 0.240 - 0.259 | 3.0 |
| 0.260 - 0.279 | 0.8 |
| 0.280 - 0.299 | 0.3 |
| 0.300 - 0.319 | 0.6 |
| 0.320 - 0.339 | 0.5 |
| 0.340 - 0.359 | 0.5 |
| 0.360 - 0.379 | 0.1 |

(1) Ambient and Ambient + Spike Measurements.

SOURCE: Environmental Monitoring Systems Laboratory, 1979.

A statistical comparison of the hourly averages from each test analyzer with the average of the hourly averages (for corresponding hours) from the other test analyzers is presented in Table 2-10. Each test analyzer is identified in the table by manufacturer, model number, and measurement principle. The data clearly indicate that these continuous $SO_2$ analyzers are capable of excellent performance (high correlation with one another, small mean differences). Two scatter diagrams (for Philips coulometric and Meloy flame photometric analyzers) are shown in Figures 2-3 and 2-4. although only every tenth point is plotted, the statistical analysis pertains to the entire data set. The figures also indicate the absolute relationship of the subject analyzers to the average of the other test analyzers and are fairly typical of all the analyzers tested.

2.3.6 Summary

Methods for the measurement of sulfur dioxide can be classified as integrated methods, which involve collection of the sample over a specified time period and subsequent analysis by a variety of analytical techniques, or continuous methods, in which sample collection and analysis are performed constantly and automatically.

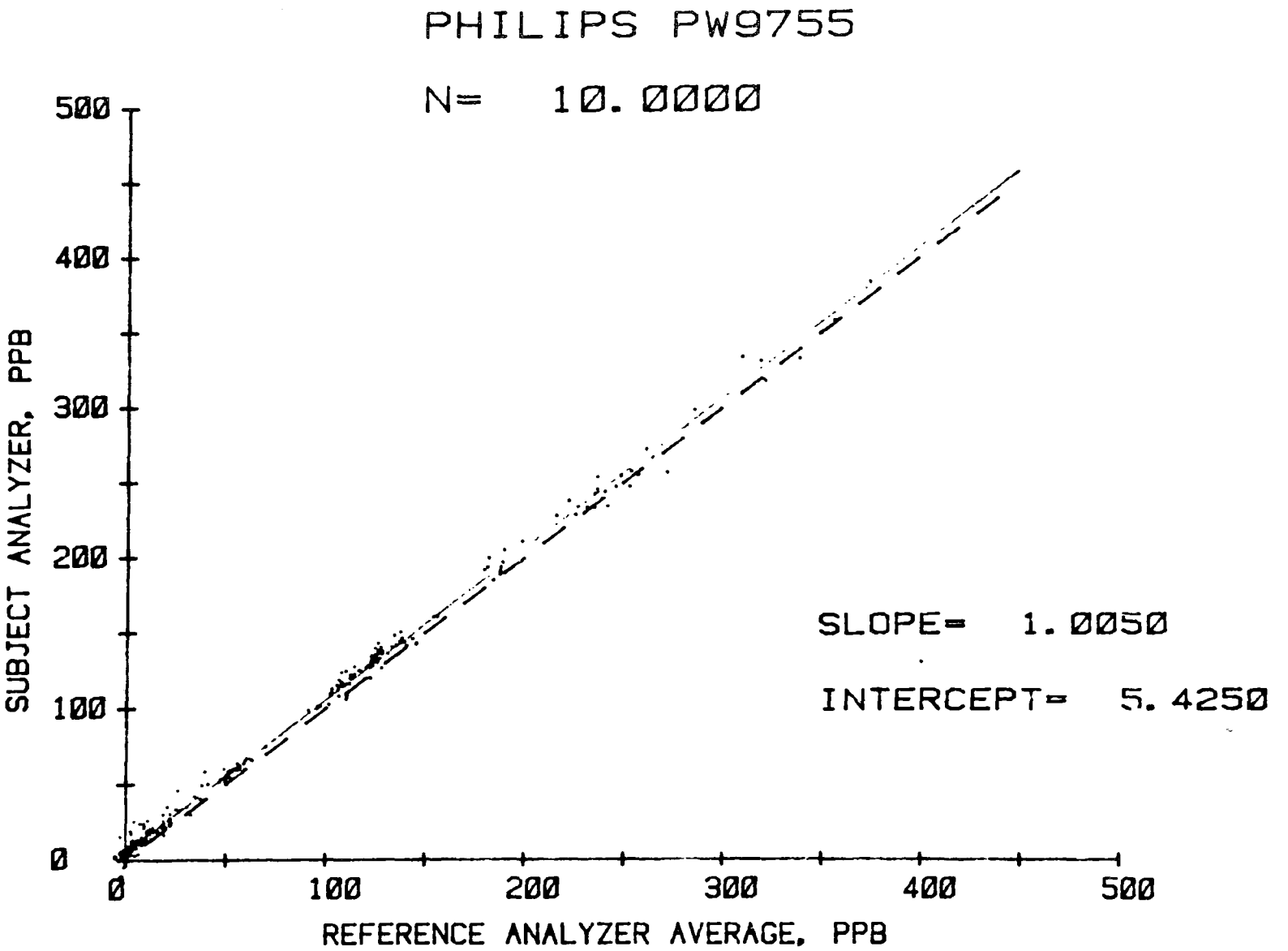
The sampling procedures used in integrated methods can be direct (e.g., collection in an inert container) or based on techniques involving absorption and stabilization in aqueous solution (e.g., collection in dilute hydrogen peroxide) or adsorption and stabilization on a solid substrate (e.g., collection on silica gel). Techniques used for the analysis of the collected sample are commonly based on colorimetric, titrimetric, turbidimetric, gravimetric, and ion-chromatographic measurement principles.

The most widely used integrated method for the determination of atmospheric sulfur dioxide is the pararosaniline method developed by West and Gaeke. An improved version of this colorimetric method, adopted as the EPA reference

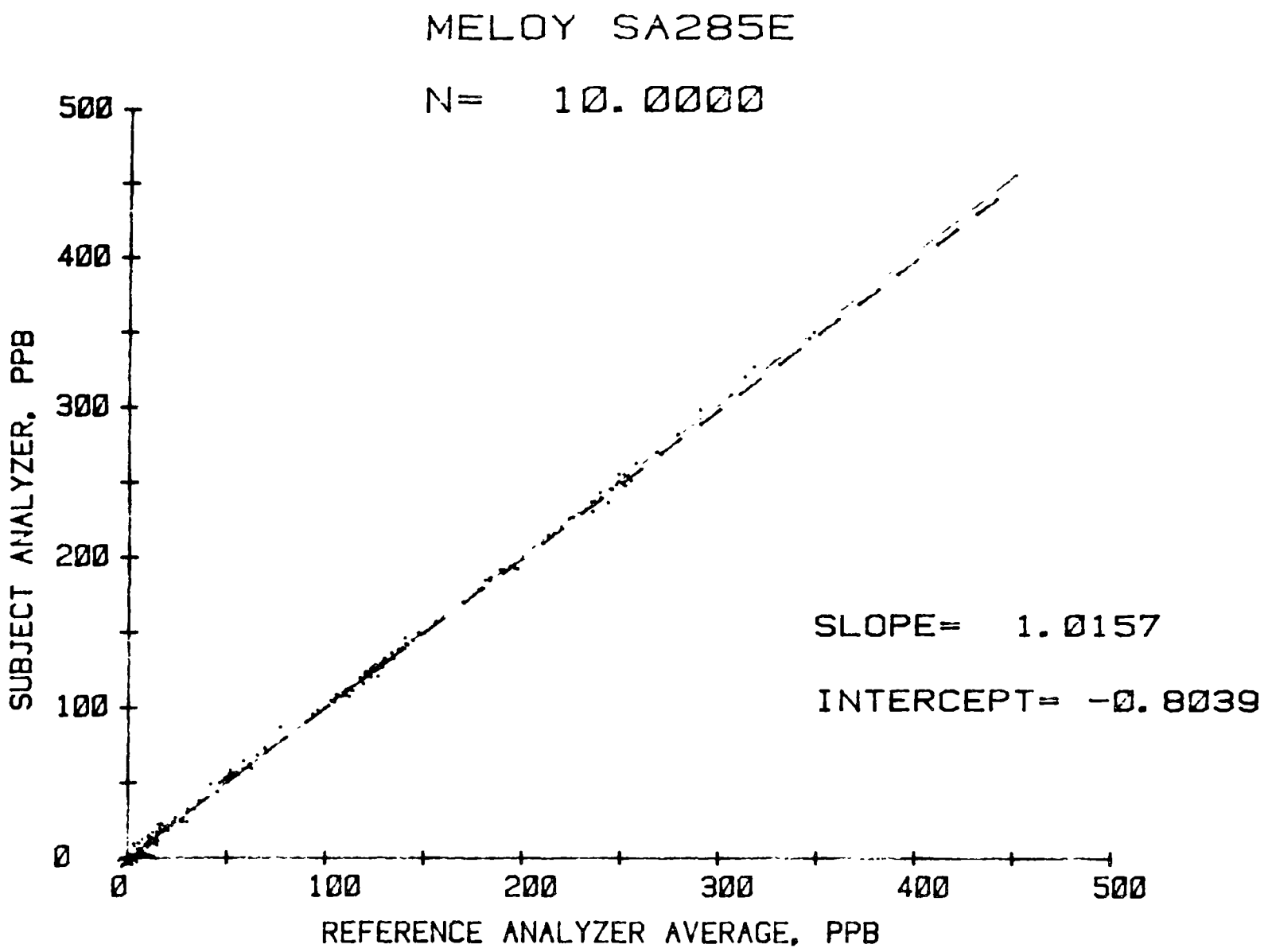
TABLE 2-10. COMPARISON OF EPA DESIGNATED EQUIVALENT METHODS FOR $SO_2$ (CONTINUOUS ANALYZERS)

| | Meloy SA185-2A | Monitor Labs 8450 | Meloy SA285E | Thermo Electron 43 | Beckman 953 | Lear Siegler SM 1000 | Philips PW 9755 | Bendix 8303 |
|---|---|---|---|---|---|---|---|---|
| Measurement principle | Flame photometry | Flame photometry | Flame photometry | Fluorescence | Fluorescence | Second Derivative spectrometry | Coulometry | Flame photometry |
| Correlation coefficient | 0.999 | 0.999 | 0.999 | 0.997 | 0.998 | 0.936 | 0.998 | 0.998 |
| Mean difference ppb | -3.695 | -0.006 | -0.251 | -0.177 | 5.108 | 4.924 | 5.775 | -3.278 |
| Std. dev. of diff. ppb | 3.925 | 4.555 | 3.243 | 8.300 | 6.901 | 20.712 | 4.631 | 4.392 |
| Max. abs. diff. ppb | 19.3 | 19.2 | 15.5 | 29.9 | 25.4 | 100.9 | 25.6 | 21.0 |
| No. of abs. diff. >20 ppb | 0 | 0 | 0 | 49 | 21 | 427 | 13 | 1 |
| No of data pairs | 3302 | 3186 | 3306 | 2170 | 1594 | 1820 | 3070 | 1984 |

SOURCE: Environmental Monitoring Systems Laboratory, 1979.




2-3. Relationship Between Phillips Coulometric Analyzer and Average of reference method analyzers.




2-4. Relationship between Meloy flame photometric analyzer and average of reference method analyzers.

method in 1971, is capable of measuring ambient $SO_2$ concentrations as low as 25 $\mu g/m^3$ (0.01 ppm) with sampling times ranging from 30 minutes to 24 hours. The method has acceptable specificity for $SO_2$, but collected samples are subject to a temperature-dependent decay which can result in an underestimation of the ambient $SO_2$ concentration. Temperature control during sample collection, shipment, and storage effectively minimizes this decay problem.

A titrimetric method based on collection of $SO_2$ in dilute hydrogen peroxide followed by titration of the resultant $H_2SO_4$ with standard alkali is the standard method used extensively in Great Britain. Although simple to perform, the method requires long sampling times (24-hours) and is subject to interference from atmospheric acids and bases.

One of the most sensitive methods now available is a promising new technique that uses ion chromatography to determine ambient levels of $SO_2$ which have been absorbed into dilute hydrogen peroxide and oxidized to sulfate. This method does not distinguish between sulfur dioxide and sulfate actually present in the ambient air unless sampling is conducted in such a way as to separate these two sulfur species. The course of research suggests that ion chromatography will probably become one of the most useful analytical evaluation methods for the sequential determination of both sulfur dioxide and sulfate.

Sulfation methods, based on the reaction of $SO_2$ with lead peroxide paste to form lead sulfate, have commonly been used to estimate ambient $SO_2$ concentration over extended time periods. After exposure, the collection device (lead candle or sulfation plate) is treated with sodium carbonate solution to dissolve the lead sulfate, which is then determined gravimetrically or turbidimetrically. The accuracy of sulfation methods is subject to many physical and chemical variables and interferents. Sulfation rate (mg $SO_3$/100

$cm^2$/day) is commonly converted to $SO_2$ concentration (ppm) by multiplying the rate by the Huey factor (0.03).

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

Continuous sulfur dioxide analyzers using the techniques of flame photometric detection, fluorescence, and second derivative spectrometry have been developed over the past ten years and are commercially available from a number of air monitoring instrumentation companies.

The flame photometric detection of ambient $SO_2$ is based on the measurement of the band emission of excited $S_2^*$ molecules formed from sulfur species in a hydrogen-rich flame. The FPD analyzers exhibit high sensitivity and fast response, but must be used with selective scrubbers or coupled with gas chromatographs when high specificity is desired.

Fluorescence analyzers are based on detection of the characteristic fluorescence of the $SO_2$ molecule when it is irradiated by UV light. These analyzers have acceptable sensitivity and response times, are insensitive to sample flowrate, and require no support gases. They are subject to interference

by water vapor (due to quenching effects) and certain aromatic hydrocarbons, and therefore must incorporate a means to eliminate or minimize these species or their effects.

Second derivative spectrometry is a highly specific technique for the measurement of $SO_2$ in the atmosphere and a continuous analyzer based on this principle is commercially available. The analyzer is insensitive to sample flowrate and requires no support gases. Sample flowrates of 4 liters/min are required to achieve reasonable response times, and frequent realignment of the optics is necessary when the analyzer is used under typical field conditions.

Analyzers based on many of the above measurement principles (conductivity, coulometry, flame photometry, fluorescence, and second derivative spectrometry) have been designated by EPA as equivalent methods for the measurement of $SO_2$ in the atmosphere. Testing of these analyzers by the manufacturers prior to designation have demonstrated adequate performance for use when an EPA reference or equivalent method is desired or required. Testing of these methods by EPA has verified their performance and has also demonstrated excellent comparability between these designated methods under typical monitoring conditions.

## 2.4 MEASUREMENT TECHNIQUES FOR SULFATES

### 2.4.1 Introduction

This section discusses methods for determining sulfates in airborne particulates. The methodology involves collecting particulate matter by various filtration techniques and subsequently analyzing for soluble sulfates, total sulfur or specific sulfate species such as sulfuric acid. The methods are discussed with primary emphasis on their applicability and limitations. Specific details of each method can be obtained from the referenced articles; techniques for the collection of particulates are covered in section 2.5.

### 2.4.2 Total Soluble Sulfate

Although the gravimetric determination of sulfate has been a laboratory experiment in elementary quantitative analysis courses for over 50 years, the determination of sulfate in aqueous solution at concentrations of 1 μg/ml or below remains a tedious and nontrivial task. A comprehensive and up-to-date review of wet chemical methods has recently been compiled by Hoffer and Kothny (1974). The principal methods for determination of trace sulfate that are applicable to aqueous leachates of airborne particle samples are reviewed here.

2.4.2.1 Direct Methods Via Sulfate Precipitation--Accurate analyses for sulfate in aqueous solution are still performed by preconcentration and barium sulfate gravimetry (~~Methods of Air Sampling and Analysis,~~ Intersociety 1972). Simplified procedures for small amounts of sulfate samples at lower concentrations have accrued from measurement of light-scattering properties of colloidal precipitates of barium sulfate. Both nephelometric (90-degree scattering) and turbidimetric (180-degree source attenuation) measurement techniques for sulfate have been developed (Kolthoff et al., 1969). Other advances include automation of the turbidimetric procedure and its extension to organic sulfates. A generally accepted lower detection limit for an automated turbidimetric sulfate determination is 3 μg/ml aqueous extract. Any source of turbidity other than colloidal sulfate (e.g., other anions forming insoluble barium salts) will positively interfere with the determination (Technicon Corp., 1959).

Precipitation of radioactively labeled $BaSO_4$ with addition of a surfactant allowing complete removal of $BaCl_2$ has been reported (Dimitt and Graham, 1976). This procedure appears to be useful for sulfate concentrations as low

as 1 μg/ml. A related technique for sulfate analysis by $BaSO_4$ determination has been reported by Bogen and Welford (1977). This technique uses standard addition of high specific activity $^{35}S$-sulfate to monitor the degree of precipitation, and exceptionally low concentrations of sulfate (to 0.01 μg/ml) may be determined, apparently with no significant interferents except lead (II).

A popular direct titrimetric method for sulfate is titration with millimolar barium ion with thorin indicator and visual or spectrophotometric endpoint detection. Optimization of the thorin method has been reported, and a recommendation of dimethysulfonazo III indicator as best for visual endpoint detection has been made by Scroggins (1974). Recently, Stevens et al ~~Brosset and Ferm~~ (1978) have described a modification of the thorin method that permits rapid determination of sulfate in aqueous leachates with a limit of detection of <0.2 μg/m$^3$.

2.4.2.2 Indirect Methods Via Sulfate Precipitation--Several indirect analytical methods based on the exchange of a more easily determined anion bound to barium with sulfate ion have been devised. Mixtures of barium ion and chloranilate or iodate ion are added to the aqueous sulfate solution with the exchanged chloranilate ion determined spectrophotometrically or the exchanged iodate ion determined by redox conversion to iodine (Bertolacini and Barney, 1957; Klockow and Ronicke, 1973). The precision of the more sensitive and widely used chloranilate method has been improved, and the method has been adapted for automated analysis (Gales et al., 1968).

Hoffer and Kothny (1974) have reported a dye-exchange method illustrated by the following equation:

$$Ba(dye) + SO_4^{2-} \rightarrow BaSO_4 + dye$$

in which the reduction of absorbance of the barium-nitrochromazo dye complex is measured spectrophotometrically in acetonitrile solvent. As little as 3.5 μg of sulfate may be determined by this method. A more sensitive and widely used application of dye-exchange reactions to sulfate analysis was reported by Lazarus et al. (1966) and uses the metallochromic indicator methylthymol blue (MTB). In the refinement of the MTB method reported by Adamski and Villard (1975), equimolar $Ba^{2+}$ and MTB in aqueous ethanol are mixed with sulfate solution at about pH 3 to precipitate $BaSO_4$; then, after adjustment of pH to about 12.5, released MTB is measured colorimetrically. An intercomparison study sponsored by EPA demonstrated that the MTB method is superior in range and the most reliable of the methods tested for long-term, low-volume sampling (Appel et al., 1976). A related technique has been reported in which sulfate is precipitated with 2-aminopyrimidine and the excess reagent is determined colorimetrically. Conversion of the amino reagent to a stronger absorbing derivative by treatment with nitrate/base has reduced the lower detection limit of this method to about 1 μg/ml sulfate based on 0.03 absorbance change (Archer, 1975).

2.4.2.3 Direct Enthalpimetric Methods--Thermometric methods are potentially applicable to the determination of several oxyanions of environmental interest, including sulfate as shown by Ross and Frant (~~1974~~ 1969). Improvements in technique have been reported, and the thermometric titration approach has been partially automated, but its reported application was at sulfate levels about 1 mg/ml. Using the direct enthalpimetric injection approach first employed by Sajo and Sipas (1967), Hansen and coworkers (1976) have extensively modified the method for determination of microgram quantities of sulfate in environmental samples.

The direct addition of concentrated $BaCl_2$ results in a temperature rise of about 0.0032°C/μmol, from which, by reference to a standard curve, the amount of sulfate in solution may be determined.

2.4.2.4 Ion-exchange Chromatography Methods--Ion-exchange resins can be used to provide excellent separation of ions but, until recently, the continuous determination of ionic species as they are eluted from the ion-exchange column has been difficult, due principally to the presence of the electrolyte solution used as eluant. Recently, Small and co-workers (1975) have devised a novel combination of resins which effectively neutralize the eluant and suppress its conductivity without affecting the analyte, thus permitting the use of a conductivity cell as a monitor for microgram levels of either cationic or anionic species. A commercial instrument based on this system is now available for use in trace anion analysis including sulfate (Dionex Corp., 1975). In this system, a strong-base anion exchanger of low capacity, agglomerated onto a surface-sulfonated DVB resin, is used as the analytical column. This is followed by a high-capacity, strong acid exchange column which converts the eluant, typically 0.003 M $Na_2CO_3$ + 0.024 M $NaHCO_3$, into a non-conducting high-sensitivity, multirange conductivity meter.

Stevens et al. (1978) have described the application of ion exchange chromatography to analysis of sulfate, sulfite and nitrate from aerosols collected on teflon filters with dichotomous samplers at several urban areas in the United States. Because the ion chromatograph method is unambiguous, exceptionally accurate, sensitive (<1 μg/ml), and applicable to determination of several anions in the same sample, it may become the preferred method for sulfate in airborne particulate samples. The only significant disadvantages

are the relatively high initial capital cost of the equipment and the relatively high level of operator technique required to fully realize the method's advantages

2.4.2.5 Flash volatilization-FPD Methods--The continuing need for more sensitive determination of sulfate in large numbers of aerosol samples has led to the development of an analytical technique based on flash pyrolysis and flame photometric determination (FPD). This technique was first devised by Roberts and Friedlander (~~1974~~, 1976), who collected samples on stainless-steel impactor slides, then passed a capacitative discharge through the slide heating it to >1000°C and converting aerosol sulfate to $SO_2$ for subsequent detection by FPD. Filter samples and evaporated extracts transferred to the slides were also analyzed, but the short lifetimes of the slides limited the utility of the method. Modifications were subsequently made by Husar et al. (1975, 1976), who substituted a tungsten boat for the stainless-steel slide and obtained precise recoveries exceeding 90 percent for sample concentrations of 1 to 10 μg/ml S with boat lifetimes <100 discharges. Refractory sulfate compounds not volatile at about 1100°C are not determined.

Other modifications of the method have been reported, including using sustained heating of evaporated samples at 500°C instead of an instantaneous discharge (Tanner et al., 1977). This approach avoids problems of recovery from boats, but in effect analyzes only those compounds, $H_2SO_4$, $(NH_4)_2SO_4$, $CuSO_4$, and a few mixed ammonium salts, which decompose at the chamber temperature used. Another modification has been reported by Tanner et al., (1977 ~~1977~~a), who introduced the use of platinum sample containers and, with use of reduced chamber and transfer line volumes and a modified FPD, have achieved reliable determinations of <0.5 μg/ml sulfur. However, since the method does

not distinguish between sulfate and other water-soluble sulfur compounds, does not determine refractories such as $K_2SO_4$, and is subject to irreproducible recoveries when certain constituents are present in the extract, applications of the method may be limited to relatively clean matrices where very low extract volumes are feasible or required.

2.4.3 Total Aerosol Sulfur

Several techniques for determination of total sulfur in airborne particle samples will be discussed in this section. It is generally found that nearly 100 percent of aerosol sulfur mass is present in the form of sulfate, and most of the data on airborne sulfur concentrations can be accurately described as total sulfur calculated as sulfate or total soluble sulfate.

2.4.3.1 X-Ray Fluorescence--One of the most promising techniques under development in recent years for analyzing elements including sulfur in airborne particles is X-ray flourescence (Goulding and Jaklevic, 1973). The sample, collected on an appropriate filter, is irradiated with X-rays, gamma rays, protons, or other charged particles, and the intensity of X-ray fluorescence induced is measured as a function of wavelength or energy to determine the amounts of the constituent elements present. Qualitative and quantitative analysis can be obtained when the system is properly calibrated for each element. This calibration step is difficult, since few standards of known elemental composition are available in disks of known thickness in an appropriate matrix (Adams and Van Grieken, 1975).

The most extensive set of aerosol sulfur data were reported by Stevens et al. (1978) and Loo et al. (1978) using a nondispersive x-ray fluorescence spectrometer designed by Goulding and Jaklevic (1973). Stevens et al. (1978)

reported sulfur and 18 other elements from dichotomous samplers operated in New York City, New York, Philadelphia, Pennsylvania, Charleston, West Virginia, St. Louis, Missouri, Portland, Oregon and Glendora, California. Loo et al. (1978) reported sulfur concentrations collected over a 2-year period from a network of 10 automated dichotomous samplers operated in St. Louis, Missouri during the Regional Air Pollution Study (RAPS). They reported a detection limit of 0.034 $\mu g/cm^2$ of filter, which corresponds to a concentration value of <0.1 $\mu g/m^3$ sulfur for a 2-hr sample collected at 50 liters/minute on a 37-mm filter and is adequately sensitive for a 1-hr time discrimination at ambient S levels. The advantages of proton-induced XRF--lower bremsstrahlung background and higher secondary X-ray cross-sections--may lead to its preferential use when short-time resolution of ambient S levels is desired (Johansson et al., 1975; Lochmuller et al., 1974). A related approach to nondestructive aerosol sulfur analysis based on cyclotron in-beam approach gamma-ray spectroscopy has been reported by Macias (1977). Gamma rays induced by proton or $\alpha$-irradiation are detected by a Li drifted, Ge detector and used to determine S and other light elements such as Mg and C in aerosol samples. It is clear that induced X-ray fluorescence methods will continue to be important tools in determining total sulfur in large numbers of ambient aerosol samples.

2.4.3.2 Electron Spectroscopy for Chemical Analysis (ESCA)--The ESCA method utilizes measurement of the kinetic energy of photoelectrons ejected from a sample irradiated with monochromatic X-rays. The kinetic energy, KE, of an ejected photoelectron is given by the equation:

$$KE = h\nu + E_i$$

where $h\nu$ is the X-ray photon energy and $E_i$ is the binding energy of electrons in the orbital subshell of the bombarded atom. Since these binding energies

are characteristic of atoms of a particular element, the kinetic energy spectrum can be used to identify kinds and amounts of elements present. Novakov (1973) and Novakov et al. (1974) have pioneered in the use of this technique for analysis of sulfur in airborne particle samples.

The most common X-ray photon sources used in ESCA, i.e., Mg or Al kα X-rays, have relatively low energies and resultant sample penetration depths of only 25 A. Thus, this method is particularly sensitive to the surface composition of samples, which is an advantage for surface-oriented studies but a handicap if bulk analysis is desired for samples whose elemental composition is likely to be nonhomogeneous.

2.4.3.3 Direct Flame Photometric Detection--The flame photometric detector (FPD) is based on the measurement of the band emission of excited $S_2$ molecules (sulfur mode) or HPO molecules (phosphorus mode) during passage of S- or P-containing compounds through a hydrogen-hyperventilated (reducing) flame. It has been widely used an an S,P-specific detector in gas chromatography and in the ambient monitoring of gaseous sulfur compounds (Lucero and Paljug, 1974 ~~1973~~; Newman et al., 1975 a and b). Using filtered ambient air as the flame oxidant, commercially available instruments can routinely monitor as little as 2 ppb (v/v) of gaseous $SO_2$.

Application of the FPD to the detection of aerosol sulfur (as sulfate) was first made by Crider et al. (1969), but its use in ambient aerosol sulfur monitoring has been limited by three considerations: sensitivity, selectivity, and specie-variable response. Ambient levels of sulfur range from 1 to 50 $\mu g/m^3$ as sulfate (equivalent to 0.2 to 10 ppb $SO_2$); hence the conventional FPD has not been sensitive enough for the lower range of sulfur concentrations. However, the use of digital signal-averaging techniques can reduce the

signal-to-noise ratio by a factor of 10 and, used with recently introduced commercial instrumentation in which noise reduction through hydrogen flow regulation is substantial, a lower limit of detection for $H_2SO_4$ of 0.25 ppb (1.1 μg/m$^3$) is now obtainable.

Since the flame photometric detector responds to all sulfur compounds, it is necessary to remove gaseous sulfur compounds (principally $SO_2$) in order to monitor only particulate sulfur. Several groups have shown that laminar flow of sample air through a tube whose inside walls are an efficient sink for $SO_2$ will reduce the $SO_2$ concentration (by "diffusion denuding" the air) to less than 1 percent of ambient levels without significant loss of 0.1 μm-diameter particles (Tanner et al., 1978). Further investigation of appropriate wall coatings and sample flows for diffusion-denuding of $SO_2$ and concomitant continuous particulate sulfur monitoring is in progress.

An alternate approach to ambient particulate sulfur monitoring using an FPD has been reported by Kittelson et al. (1977). This system combines the FPD with a pulsed electrostatic precipitator and a lock-in amplifier tuned to the pulse frequency of 0.2 Hz. Since it is reported that particulate sulfur in the size range 0.03 to 1.0 μm is removed with essentially 100 percent efficiency, the signal output from the FPD contains a DC component resulting from the sulfur gases (not affected by the precipitator) and an AC component dependent on the particulate sulfur concentration which can be selectively amplified by the lock-in amplifier. Aerosol sulfur concentrations at ambient levels may be measured in the presence of relatively steady $SO_2$ concentrations by this method, although the accuracy and specificity are not well established.

Since the response of the FPD varies depending on the chemical form of aerosol sulfate (or reduced forms of sulfur), a calibration based on auxiliary

speciation of the sulfate or thermal pretreatment of the aerosol may be necessary for accurate determinations (Huntzicker et al., 1976, 1977).

2.4.4 Specific Sulfate Species

2.4.4.1 Speciation by Thermal Volatilization Techniques--The determination of sulfuric acid by its selective thermal volatilization from filters was first reported by Scaringelli and Rehme (1969). Particulate samples collected on glass fiber filters were heated to 400°C, and the volatilized $H_2SO_4$ (determined by three different techniques) was calculated as percent of total sulfate, which varied from 20 to 100 percent in samples from several urban areas. In this procedure $NH_4HSO_4$, $(NH_4)_2SO_4$, and probably $CuSO_4$ were also volatilized. Thus, the reported $H_2SO_4$ fractions more accurately indicate $H_2SO_4$ and its ammonia neutralization products as percent of total sulfate. Dubois et al. (1969) concurrently developed a microdiffusion method for $H_2SO_4$ which involved thermal volatilization of $H_2SO_4$ at 200°C from a filter sample in a closed petri dish and its subsequent immobilization on the dish cover, which had been coated with NaOH. The immobilized $H_2SO_4$ chemically present as $Na_2SO_4$, was removed from the cover and determined by the thorin method. Reproducibility of the method was adequate only for standard samples, and a potential interference from ammonium sulfate was reported. Reported values for $H_2SO_4$ as percent of total sulfate were about an order of magnitude lower than values reported by Scaringelli and Rehme (1969).

The microdiffusion method was modified by Maddalone et al. (1975), who used perimidylammonium bromide as the immobilizing agent for $H_2SO_4$ volatilized from filters at 125°C. The perimidylammonium sulfate is decomposed quantitatively at 400°C, and the released $SO_2$ is determined by the FPD or the West-Gaeke method. Low recoveries (based on $H_2SO_4$ samples) were reported for glass fiber filters, but >85 percent for samples containing 10 μg of $H_2SO_4$ was recovered from Teflon® filters (Mitex and Fluoropore). Neither Scaringelli

and Rehme nor Maddalone was consistently successful in removing $H_2SO_4$ from ambient particulate-loaded filters by thermally induced microdiffusion. Benarie and coworkers (1973) have applied the microdiffusion technique of Dubois during an air sampling campaign around Rouen, France, from which it was found that 7 percent of airborne sulfur was in the form of $H_2SO_4$.

The perimidylammonium bromide (PDA-Br) method, without the microdiffusion step, has been suggested by Thomas et al. (1976) for $H_2SO_4$, sulfur trioxide, and total soluble sulfate determinations in the 10-μg sulfur range. Sulfuric acid droplets are stabilized at the time of collection on PDA-Brimpregnated glass fiber filters, preventing topochemical reactions of $H_2SO_4$ with previously collected particles. The resulting perimidylammonium sulfate $(PDA)_2(SO_4)$ is then thermally decomposed at 400°C to produce $SO_2$, which is determined by the West-Gaeke method. The authors report that the impregnated glass fiber filters are approximately 90 percent more efficient for $H_2SO_4$ aerosol than Fluoropore filters and are much easier to work with. Ammonium sulfate (and presumably ammonium bisulfate) interferes with the method by large amounts, a serious disadvantage since these sulfates are frequently present in excess of $H_2SO_4$ in ambient aerosol samples.

A more sophisticated thermal speciation technique is the controlled pyrolysis method reported by Leahy et al. (1975). Sulfuric acid samples (both evaporated solutions and laboratory-generated aerosols) were removed from Teflon® filters or quartz boats at 190°C, ammonium bisulfate samples likewise at 275°C, and sodium bisulfate samples at 325°C by passing premoistened $N_2$ through a heated quartz tube. The volatilized samples were rinsed from the tube after each temperature increase and analyzed for sulfate by turbidimetry. Experiments duplicating these results with mixed aerosols generated in a 90-$m^3$

environmental chamber were less successful: only 60 to 70 percent of 100-μg $H_2SO_4$ samples were recovered, and nonreproducible recovery of $H_2SO_4$ from $NaHSO_4$ decomposition at 325°C was observed. This was due principally to reactions between sulfuric acid and particulate matter and emphasizes the extreme difficulty inherent in transferring sulfuric acid in the presence of airborne particles in any system at elevated temperatures. Although not reported, ammonium sulfate should be decomposed and transferred with ammonium bisulfate. Subsequent work with dry $N_2$ in the volatilization procedure did not improve the collection efficiency (Tanner and Cordova, 1978).

The most successful approach to thermal volatilization of $H_2SO_4$ in ambient aerosol samples was reported by Mudgett et al. (1974). Aerosol samples are collected on Fluoropore filters, the $H_2SO_4$ is subsequently volatilized by passage of heated (ca. 150°C), dry $N_2$ in the reverse direction through the filter, and released $H_2SO_4$ is determined with a flame photometric detector. Laboratory aerosol samples of as little as 0.25 μg $H_2SO_4$ may be determined with reasonable precision (Lamothe and Stevens, 1976). A prototype, semiautomated instrument designed with monitoring applications in mind has been developed under EPA contract (Harris, 1975). Although no results have been published, the prototype instrument has been tested in several field monitoring applications. Based on the experience of other workers in removing $H_2SO_4$ from particulate filters at elevated temperatures, difficulty in quantitatively removing $H_2SO_4$ has been encountered. In fact, serious difficulties are encountered in removing $H_2SO_4$ quantitatively in the presence of ammonium bisulfate: $H_2SO_4$ is totally removed at 180°C, but $NH_4HSO_4$ is also partially volatilized; at 140°C, $NH_4HSO_4$ is not volatilized but $H_2SO_4$ is incompletely volatilized. Finally, the use of Fluoropore filters with attendant low flow

rates (1 $m^3$/hr) will require sampling times of 1 hour or more for most ambient applications.

2.4.4.2 Speciation by Solvent Extraction--A solvent extraction procedure to selectively remove collected $H_2SO_4$ aerosol in the presence of other aerosol sulfates was first reported by Barton and McAdie (1971). They concluded that aerosol collection on Nucleopore filters followed by extraction with isopropanol for subsequent analysis by the chloranilate procedure was selective for airborne $H_2SO_4$. Subsequent work reported reduction of interference by buffer control of the isopropanol extract and development of an automated instrument for the extraction procedure (Barton and McAdie, 1973). Leahy et al. (1975) have shown, however, that isopropanol will also extract ammonium bisulfate quantitatively and partially extract other bisulfates. Since ammonium bisulfate is a documented constituent of ambient aerosol, isopropanol cannot be considered as a selective extractant for $H_2SO_4$. It has been demonstrated that benzaldehyde is a selective extractant for $H_2SO_4$ in the presence of bisulfates and sulfates. Subsequent radiochemical experiments with $H_2SO_4$ have established that $H_2SO_4$ may be reproducibly removed from a variety of filter media (Mitex, Fluoropore, $H_3PO_4$-treated quartz) with recoveries varying from 75 percent for 10-μg $H_2SO_4$ samples to 95 percent for 100-μg samples. This procedure may thereby be used to quantitate the presence of $H_2SO_4$ in ambient particulate samples with time resolution of 1 hour or less.

2.4.4.3 Speciation by Gas-Phase Ammonia Titration--A method has been proposed for determination of strong acid aerosol (assumed by the authors to be $H_2SO_4$) by gas-phase reaction with ammonia in excess from a permeation source (Dzubay et al., 1974). The reduction in ammonia concentration produced by reaction with acid aerosol is determined by conversion to NO over gold wool at 1000°C

and measurement by an $O_3$ chemiluminescent NO monitor. The method as reported has inadequate sensitivity (5 ppb $NH_3$ = 10 μg $m^3$ $H_2SO_4$) for ambient monitoring but with state-of-the-art $NO_x$ monitors, a lower detection limit of 2 μg/$m^3$ $H_2SO_4$ would be possible. The method assumes that other than $H_2SO_4$ strong acids reacting with $NH_3$ are absent from ambient aerosol sample; it also requires complete reaction of $NH_3$ with acid aerosol particles and complete conversion of unreacted $NH_3$ to NO.

A more useful, albeit still qualitative, approach to sulfate speciation in aerosol particles by gas-phase $NH_3$ titration has been developed and widely used by Charlson et al. (1974 a and b). An apparatus called a humidograph measures the dependence of the light-scattering coefficient ($b_{scat}$) of airborne particles as a function of relative humidity (RH). Particles consisting mainly of hygroscopic materials such as $H_2SO_4$ or $NH_4HSO_4$ exhibit a monotonic plot of $b_{scat}$ versus RH (the plot is called a humidogram). The presence of a deliquescent substance as a major constituent is denoted by a rapid rise in $b_{scat}$ to an inflection point in the humidogram after a relatively flat curve at lower RH. For example, $(NH_4)_2SO_4$ in aerosol particles exhibits an inflection point at about 80 percent RH. The humidograph may also add ppm quantities of $NH_3$ before recording the humidogram. Production of $(NH_4)_2SO_4$ from the addition of $NH_3$ to acid sulfate aerosol can be detected by appearance of the inflection point near 80 percent RH if at least 30 to 50 percent of the aerosol mass is present as sulfate.

The humidographic technique has the advantages of <u>in situ</u> measurement with short time resolution (15 min). Particle growth into the optical-scattering region during recording of the humidogram does not appear to be a serious problem. There is a serious interference from aerosol nitrate since most

nitrate salts (including $NH_4NO_3$) are hygroscopic. The original method does not distinguish between $H_2SO_4$ and ammonium bisulfate, and attempts to do so by stoichiometric $NH_3$ gas phase titration have only been marginally successful.

2.4.4.4 Speciation by Cation Measurement--Since atmospheric sulfate can be associated with various cations, the compounds of sulfate can sometimes be characterized by measuring the cation. Brosset and Ferm (1978) and Stevens et al. (1978) describe a Gran titration procedure for $H^+$ and a procedure using an ion selective electrode for $NH_4^+$ in aqueous extracts of aerosols collected on Teflon® filters. Stevens et al. (1978) applied such techniques to aerosols collected at Research Triangle Park, North Carolina during the summers of 1977 and 1978 and found a stoichiometric balance between $SO_4^=$ and the sum of $H^+$ and $NH_4^+$ ion concentrations. The acidity was found to range from none (ammonium sulfate) to that of ammonium bisulfate.

2.4.4.5 Infrared Spectroscopy--The use of infrared (IR) spectroscopy for identification of species such as ammonium and sulfate in airborne particles was first described by Blanco and coworkers (1968, 1972). Anderson samplers were used to obtain size-segregated samples with each fraction analyzed by an IR microspectrophotometric technique after incorporation into a KBr pellet. Bands attributed to ammonium and sulfate dominated the submicrometer fractions in urban samples but were not found in desert samples.

In more recent work by Cunningham and Johnson (1976), data were reported from an "acid sulfate" episode during the fall of 1973 in Chicago. Successive 3-hr samples from Lundgren stage four showed reduced sulfate band intensity and appearance of a series of bands at 1205, 1063, 869, and 600 $cm^{-1}$ (and other weaker bands), which the authors attributed to changes in the acid content of the samples with bands assigned to bisulfate and "sulfate more

acidic than bisulfate." Although mixed-acid sulfate phases are known [e.g., $(NH_4)_3H(SO_4)_2$-lavovicite], such complexities do make more difficult the quantitative assessment of the degree of acidity in submicrometer sulfate-containing particles by IR. Application of IR analysis to quantification of other aerosol constituents, especially polynuclear aromatic hydrocarbons, is an especially fruitful area of investigation (Mamantov et al., 1977).

2.4.4.6 Complexation-Spectrophotometry--Huygen (1975) has described a specific method for $H_2SO_4$ whereby dry diethylamine is passed through the aerosol sample after collection on a teflon filter, immobilizing any $H_2SO_4$ present as the bis(diethylammonium) salt. The latter is reacted with carbon disulfide and cupric ion to form the bis-(diethyldithiocarbamate)-copper(II) complex, which may be colorimetrically determined for sulfuric acid samples from 25 to 100 μg. Major interferences are reported for phosphoric acid and ammonium bisulfate under anhydrous conditions and for most weak acids (including ammonium sulfate) under moist conditions. Tanner and Cordova (1978) have used the Huygen method to produce linear calibration curves for 25 to 100 μg $H_2SO_4$, but even under anhydrous conditions a 70 mol percent interference by ammonium bisulfate was observed. The interference problems make this method of marginal value for specific $H_2SO_4$ analysis, although it might be useful as a method for estimation of "total acidic sulfate" in airborne particles.

Dzubay et al. (1979) recently developed a new approach to this method. Aerosol samples collected on Teflon® membrane filters were analyzed by exposing them to $^{14}C$ labeled trimethylamine. The amount of acidity ($H^+$) in the samples is determined by counting the radioactivity and comparing the result with that of a standard. No interferences were observed due to ammonium sulfate or carbon. For replicate samples collected at Research Triangle Park, North Carolina

during the summer of 1979, the results from the radiochemical method were found to be equivalent to those by Gran titration.

2.4.4.7 Heated Filter Collection/FPD--Benarie et al. (1976) have described a method for determining $H_2SO_4$ by a different technique. A Teflon® filter heated to ca. 70°C was found to pass $H_2SO_4$ reasonably quantitatively to a flame photometric detector (FPD), where it was measured along with $SO_2$ and any other gaseous sulfur compounds, while other aerosol sulfate compounds are collected by the filter. By comparing this FPD output with that for an unheated $FeSO_4$-impregnated glass fiber filter (where $H_2SO_4$ was collected as aerosol sulfate), the $H_2SO_4$ content can be determined. This technique was used for $H_2SO_4$ determinations during the air sampling campaign around Rouen, France. Concentrations varied over the range from zero to 13.3 $\mu g/m^3$ during winter and summer seasons. It was concluded that oxidation rates of $SO_2$ to sulfate varied from 0.9 percent to 7.5 percent/hr depending on the amount and composition of suspended particles. Sulfuric acid, averaging 3 percent of total atmospheric sulfur, was measured with a precision of ± 0.9 $\mu g/m^3$ $H_2SO_4$. This promising technique has not been confirmed by other workers, and it is difficult to explain the observation that $H_2SO_4$ aerosol is not collected on Teflon® at 70°C when other workers report difficulty in removing $H_2SO_4$ from filters containing airborne particles at 150°C (Lamothe and Stevens, 1976). Figure 2-5 shows general effects of spurious sulfate formation on filter, while Figure 2-6 shows the effects of filter temperature on sulfate distribution.

2.4.4.8 Electron Microscopy and Related Techniques--The use of electron microscopy for identification and semi-quantitative determination of submicrometer ammonium sulfate aerosol particles has been demonstrated by Heard and Wiffen (1969). The techniques for preparing samples collected on membrane filters

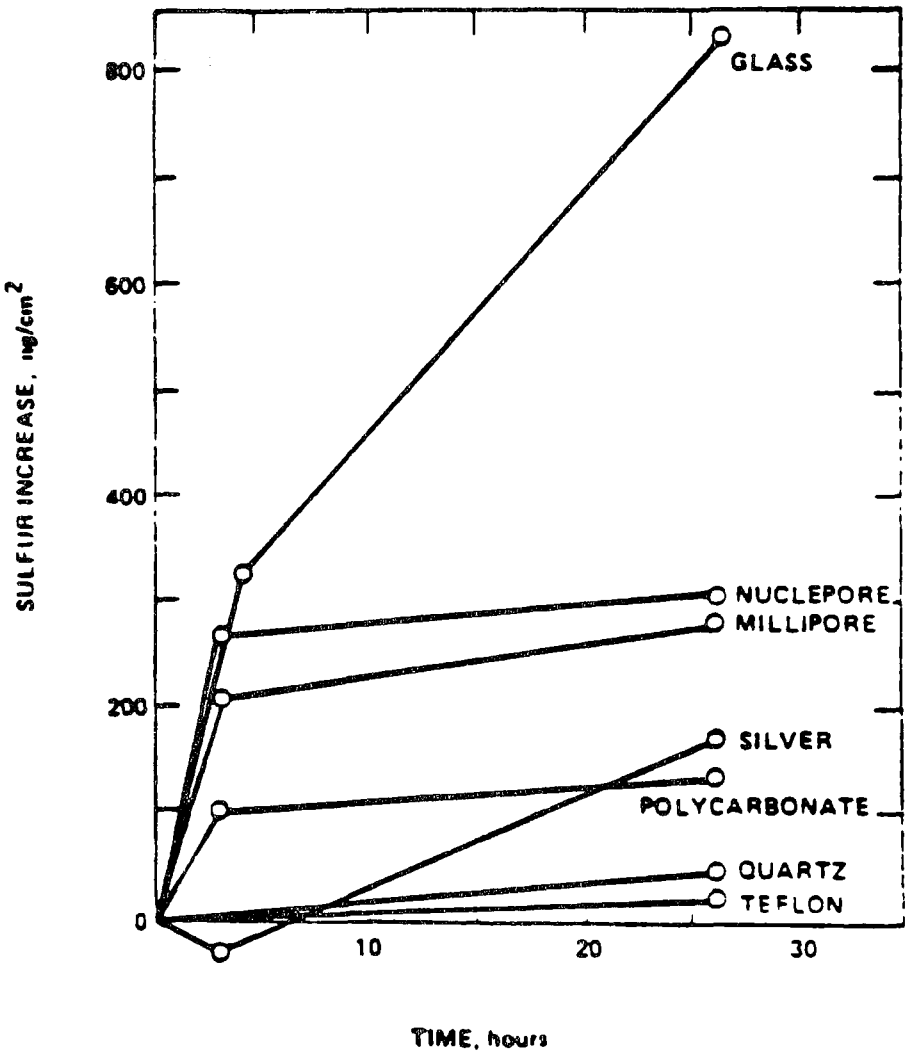



Figure 2-5. The effects of spurious sulfate formation on clean filters is given for extreme exposures (4000 ppm $SO_2$ and 100% r.h.)

Source: Loo et al. (1978).

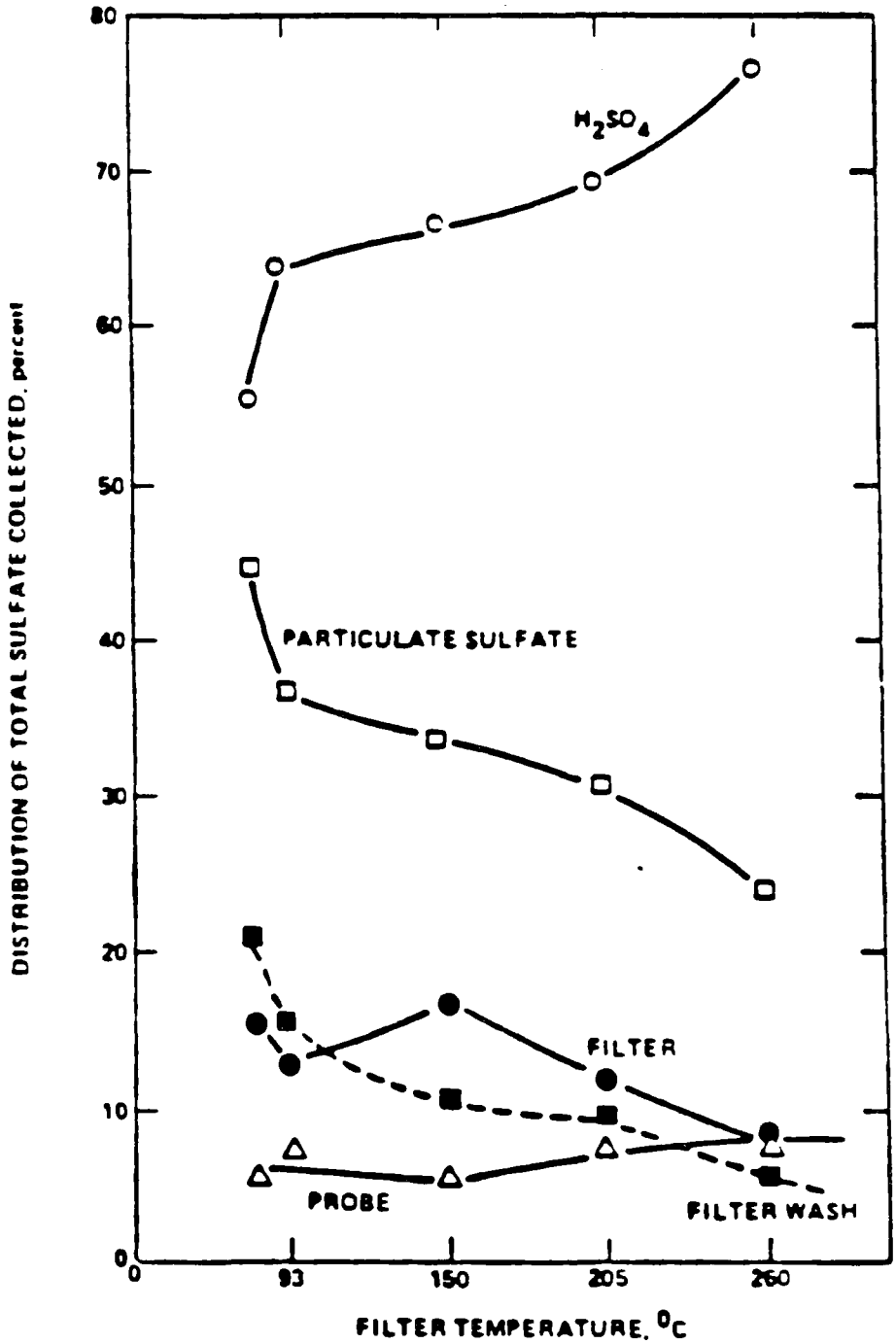



Figure 2-6. Effects of filter temperature on sulfate distribution are shown.

Source: Cheney and Homolya (1979).

and the electron microscopic determination itself are tedious and time consuming, but this method does provide an unambiguous identification of a specific aerosol sulfate species. The collection of acid aerosol particles on various types of films and the counting of number and size of reactive spots with the aid of an electron or optical microscope has been reported by several groups, including Lodge et al. (1960). Differentiation of aerosol particles consisting mainly of $(NH_4)_2SO_4$ or $H_2SO_4$ by electron microscopic examination of the particles collected on BaC-coated carbon grids has been detailed by Mamane and dePena (1978). This procedure is not highly specific for $H_2SO_4/HSO_4$.

2.4.4.9 Acid-Base Indicators--A method has been described for spectrophotometrically determining acidity in airborne particles from the displacement of equilibrium and resultant color change of acid-base indicators (Whittaker Co.). The collected sample is washed from the filter with bromophenol solution, and the change in absorbance at 587 nm is noted. The method determines acidity nonspecifically, and its value of assessing the amount of airborne acid sulfate in the absence of other particulate species is quite limited.

2.4.5 Ammonium and Gaseous Ammonia Determination

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

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

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

There is still a striking need for development of new techniques for real-time and/or short-time-averaged measurement of atmospheric concentrations, especially in view of the important role of $NH_3$ in converting aerosol $H_2SO_4$ to less harmful ammonium salts.

### 2.4.6 Summary

Methods for the determination of soluble sulfates, total sulfates, and specific sulfate species involve the collection of particulate matter and its subsequent analysis by a variety of techniques. Direct methods for water soluble sulfates based on barium sulfate precipitation include gravimetric, nepholometric and turbidimetric, and titrimetric methods. A recent modification of the Thorin method (titrimetric) permits the rapid determination of sulfate in aqueous extracts with a limit of detection of <0.2 $\mu g/m^3$. Indirect methods based on the exchange of barium with a more easily determined anion include chloroanilate, iodate and dye exchange methods. A dye exchange method based on methylthymol blue (MTB) indicator has been demonstrated by EPA to be superior to other frequently used methods in range and reliability for long-term, low-volume sampling. Other anions that form insoluble barium salts will cause positive interference with methods based on barium sulfate precipitation.

A commercial instrument based on ion-exchange chromatography is now availabl for trace soluble sulfate determinations. This method is specific, exceptionally accurate and sensitive (<1 μg/ml). The instrument is relatively expensive and requires a high level of operator technique. A method based on flash volatilization (pyrolysis) of sulfate to $SO_2$ with flame photometric detection of $SO_2$ has been developed. This method offers increased sensitivity (<0.5 μg/ml sulfur) but has several disadvantages including lack of specificity for sulfate (other water soluble sulfur species are detected), irreproducible recoveries, and not determining refractory species such as $K_2SO_4$.

Methods for determining total aerosol sulfur are important because nearly 100 percent of aerosol sulfur mass is present in the form of sulfate. Methods for total sulfur include x-ray flourescence, electron spectroscopy for chemical

analysis (ESCA), and direct flame photometry. Induced X-ray fluorescence methods are non-destructive and applicable to the determination of large numbers of ambient aerosol samples. Although induced X-ray fluorescence methods are difficult to calibrate and the instrumentation is expensive, the method is non-destructive and applicable to a large number of aerosol samples. This method will continue to be an important tool for total sulfur determinations. The detection limit for sulfur for an induced X-ray fluorescence method has been reported as 0.1 $\mu g/cm^2$ of filter which corresponds to a concentration value of <0.1 $\mu g/m^3$ sulfur for a 2-hr sample collected at 50 liters/minute. ESCA methods are sensitive to surface composition of samples, which is an advantage for surface-oriented studies but not for ambient aerosol samples whose elemental composition is likely to be nonhomogeneous. Direct flame photometry has potential as a sensitive total aerosol sulfur analyzer, but is complicated because $SO_2$ must be removed and the FPD response varies with the chemical form of the aerosol sulfates.

Procedures for determining specific sulfate species include thermal volatilization and solvent extraction techniques, gas phase ammonia titration, infrared and visible spectrometry, flame photometry and electron microscopy. The determination of $H_2SO_4$ by its selective thermal volatilization from filters has been reported by several workers. This technique generally suffers from poor $H_2SO_4$ recoveries, poor reproducibility, and interferences from ammonium sulfate salts. A prototype, semiautomated instrument has been developed which collects aerosol samples on Fluoropore filters, passes heated dry $N_2$ in the reverse direction through the filter and detects the volatilized $H_2SO_4$ with a flame photometric detector. Laboratory aerosols containing 0.25 μg sulfur may be determined with reasonable precision with this instrument. However, serious

difficulties are encountered in removing $H_2SO_4$ in the presence of ammonium bisulfate and sampling times of 1-hour or more for most ambient applications are required.

Solvent extraction procedures to remove $H_2SO_4$ selectively in the presence of other aerosol sulfates have been investigated. Isopropanol as an extraction solvent was found to be inadequate because ammonium bisulfate is quantitatively extracted. However, benzaldehyde is a selective extractant for $H_2SO_4$ and can be used to quantify the presence of $H_2SO_4$ in ambient particulate samples.

Several semiquantitative methods for estimating sulfate species have been investigated. These include gas phase ammonia titration techniques methods based on infrared spectroscopy and electron microscopy techniques. Finally, methods for measuring ammonia and gaseous ammonia are reviewed.

## 2.5 MEASUREMENT TECHNIQUES FOR PARTICULATE MATTER

### 2.5.1 Introduction

Measurements of atmospheric particulate matter are complicated by the complex and diverse nature of individual particles. Unlike gaseous pollutants which are typically composed of single compounds, suspended ambient particulate matter includes a wide variety of particle sizes, shapes, and other physical and chemical properties. The collection and examination of particles by their aerodynamic equivalent diameter provides a means of examining mass concentrations that inherently accounts for particle size, shape and other physical properties. Without a detailed understanding of the characteristics of sampling methods for collecting particles, it is impossible to draw conclusions from sampling data and to compare sampling methods. Classical ambient particulate sampling

consists of extracting the suspended particles from a measured volume of ambient air by filtration. This technique is directly applicable for routine monitoring and inherently provides a sample integrated over a specific time interval long enough to collect sufficient mass for subsequent analysis. The particle mass collected is determined by weighing the filter before and after exposure, and mass concentration is obtained by dividing the mass of particulate matter collected by the total air volume sampled to give mass per unit volume. This relatively simple particulate measurement concept is the basis for the high-volume sampling method, which is the current EPA reference method for total suspended particulates (TSP) (U.S. Environmental Protection Agency, 1979 a). This method has been widely used in this country and others, and has provided many of the concentration data used to establish health and other effects. The high-volume sampler also collects sufficient particulate material to allow subsequent chemical analysis.

Alternative filtration techniques, such as the optically-based British Smoke Shade and AISI (American Iron and Steel Institute) tape sampler, have been used for routine monitoring because of their simplicity of analysis. The British Smoke Shade sampler is commonly used in Europe but has been rarely used in the United States. The AISI Tape Sampler is more universally utilized. The dustfall method, an entirely passive collector for settleable particles, is rarely used in current studies but has been used in the past to collect data relative to soiling and material effects. Because such methods do not provide mass concentration directly, many comparison studies in the literature attempt to relate these methods to methods based on direct gravimetric measurement.

A significant problem with the simple filtration methods used in earlier studies is that little or no information was available about the size range of collected particles. The knowledge of the size range of particles reaching the collection surface relative to the true ambient distribution -- as well as the total mass concentration--is very important when utilizing the data to meet specific objectives such as support of epidemiology studies or development of source control strategies.

The particle size range collected by a filtration sampler depends on such parameters such as inlet geometry, internal wall losses, and the efficiency of the filter material. For example, the high-volume sampler defined by EPA in the previous Air Quality Criteria for Particulate Matter (National Air Pollution Control Administration, 1969) and in the reference method for TSP was considered to have captured all sizes up to 100 μm (aerodynamic diameter). However, recent sampler characterization testing by Stevens and Dzubay (1975) and Wedding et al. (1977) has shown that the gable roof used as a weather shield on this sampler produces inefficient collection of particles larger than 50 μm. As shown in Figure 2-7, the sampling efficiency of the high-volume sampler for large particles is also affected by wind speed. Lundgren (1973) has examined the true distribution of large particles up to 200 μm in the atmosphere, and several typical mass distributions are shown in Figure 2-8. After comparing the high-volume sampler collection efficiency data in Figure 2-7 with these particle size distributions it is clear that the high-volume sampler does not

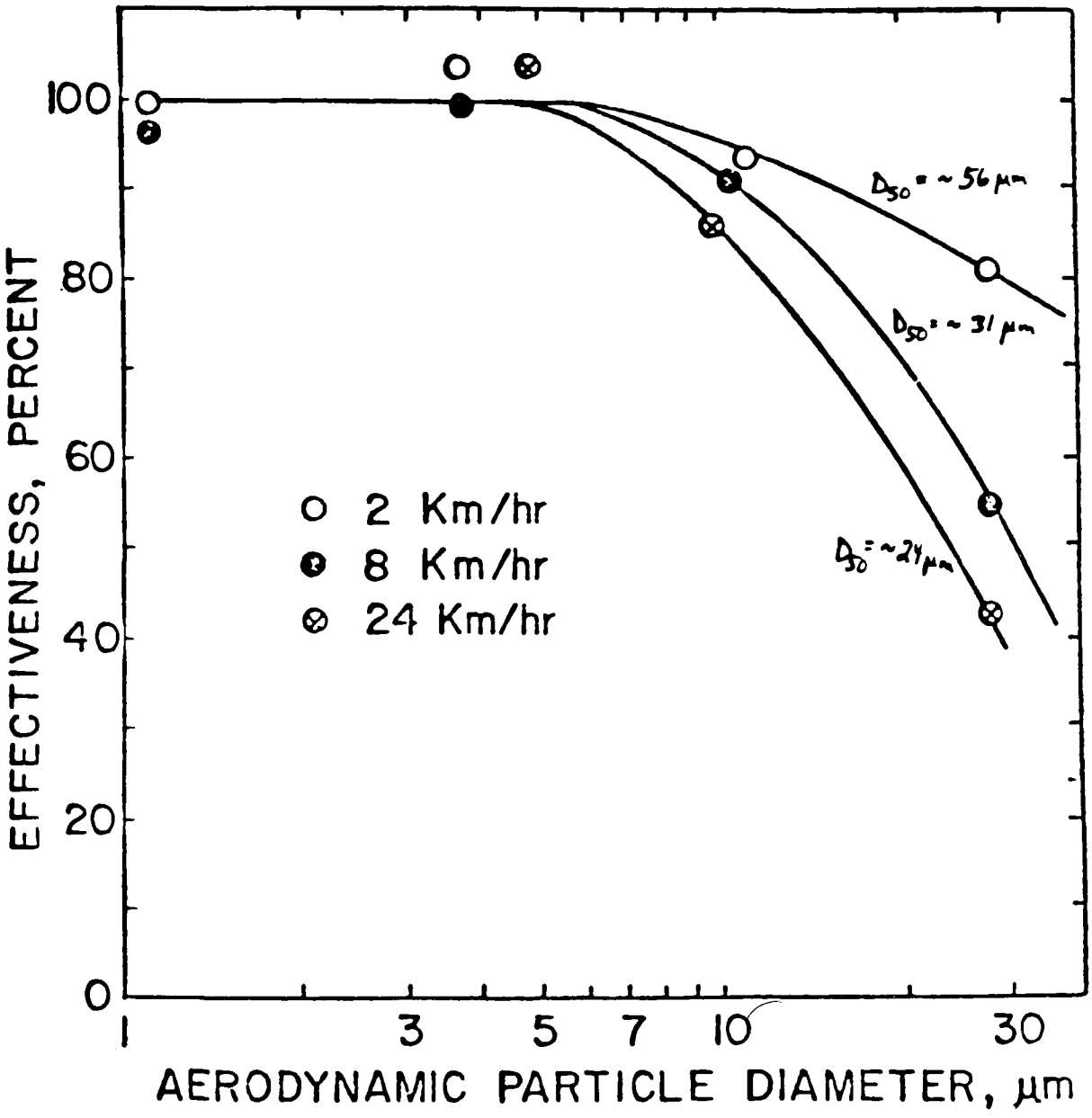



FIGURE 2-7. SAMPLING EFFECTIVENESS OF 11½" x 14" HI-VOL.

Source: McFarland and Rodes (1979)

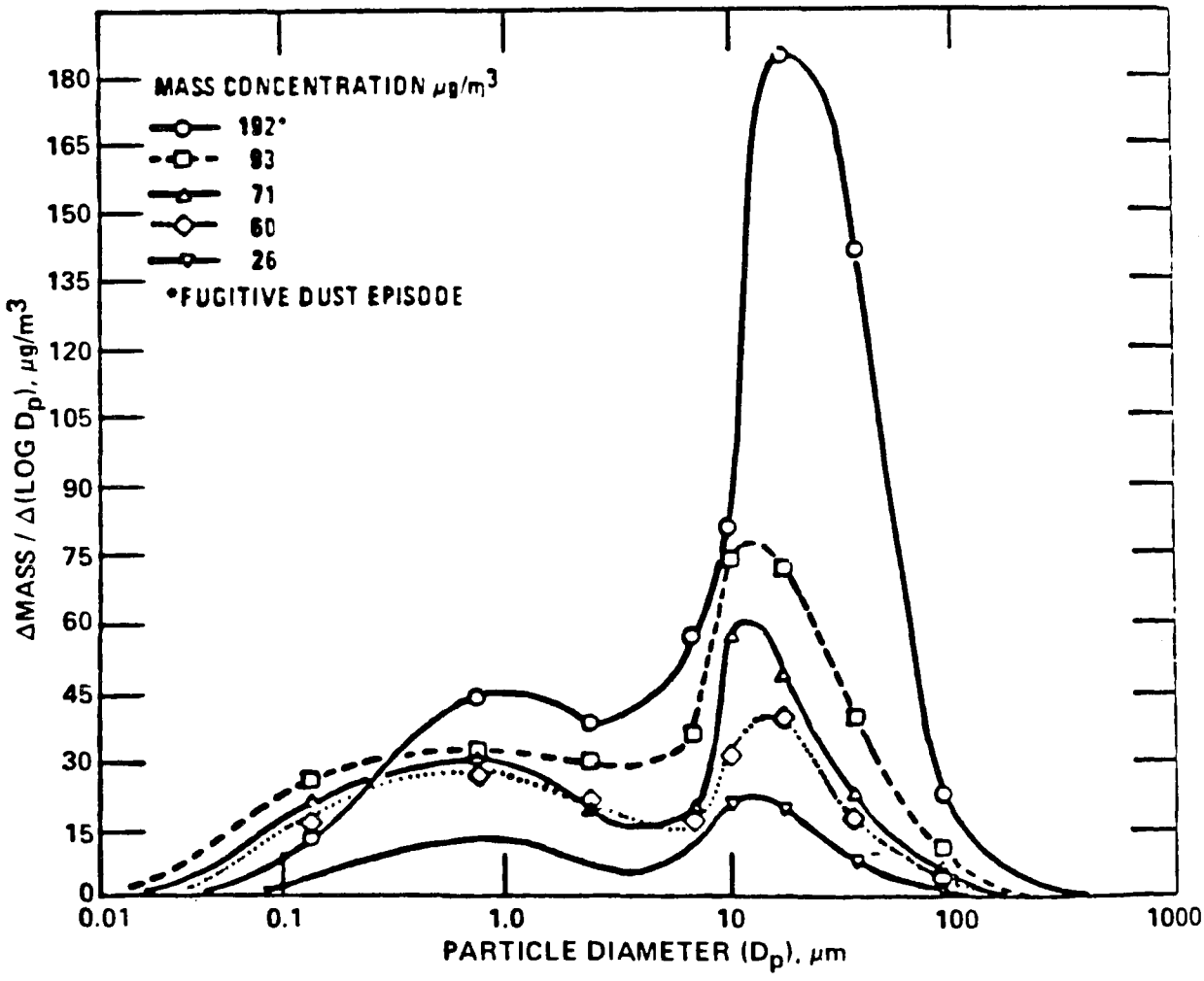



Figure 2-8. Mass distribution data emphasizing large (>10μm) particles.
SOURCE: LUNDGREN, 1973

provide a true measure of the large particles in the atmosphere. Because the mass of a particle increases as a cubic function of the diameter for particles with constant density, the sampling of large particles must be treated carefully when considering a broad size distribution. McFarland (1979) recently determined that the British Smoke Shade sampler collects only a small portion of the particles greater than about 4 μm primarily because of the small diameter of the inlet tubing. Knowledge of such characteristics is essential in making comparisons between two particulate measurement methods.

Size-specific sampler inlets designed to limit the particles collected to a certain size range are a relatively new technology, especially for particles larger than 10 μm. Because these larger particles are difficult to transport quantitatively, a sharp cutoff for large particles is not easily obtained except at high sampler flowrates. The efficiency of a prototype inlet designed to provide a 15 μm cutoff for a low flowrate sampler operating at 1.0 $m^3$/hr is described by Wedding et al. (1977) and is shown in Figure 2-9. The $D_{50}$ or 50% diameter -- the particle size at which 50 percent of the particle mass is passed on to the filter -- for this inlet is approximately 15 μm. The geometric standard deviation of the effective particle distribution (a measure of the sharpness of the size cut-off and denoted as $\sigma_g$) for this inlet is approximately 2.0, as compared to an ideal step-function inlet with a $\sigma_g$ of 1.0. ~~Current~~ An article in Env Science + Technology (, 1978) describes the results for current technology size selective inlets such as the one developed for the high-volume sampler. ~~(ES&T Outlook, 1978)~~ ~~have~~ The $\sigma_g$ values varied from 1.3 to 1.7. The conventional TSP high-volume sampler inlet has a $\sigma_g$ between 2.2 and 2.5, depending on the

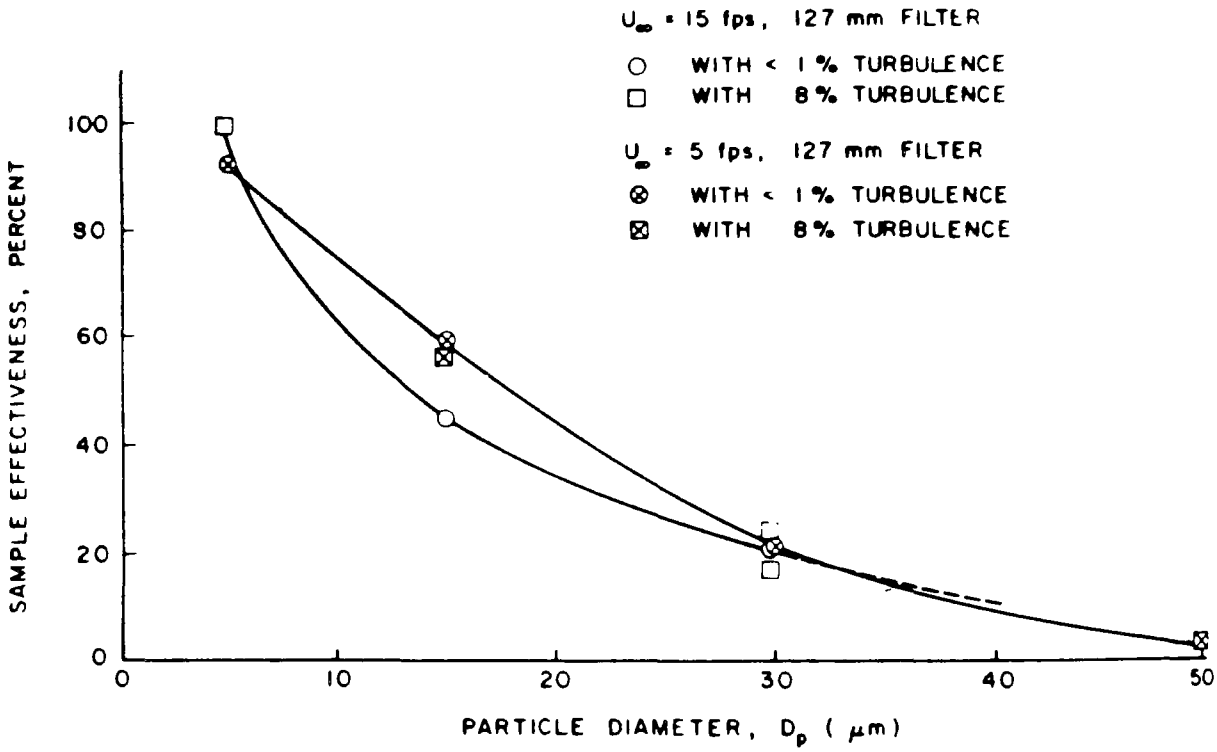



Figure 2-9. Influence of particle size on effectiveness of prototype dichotomous sampler.
SOURCE: WEDDING, et. al. 1977

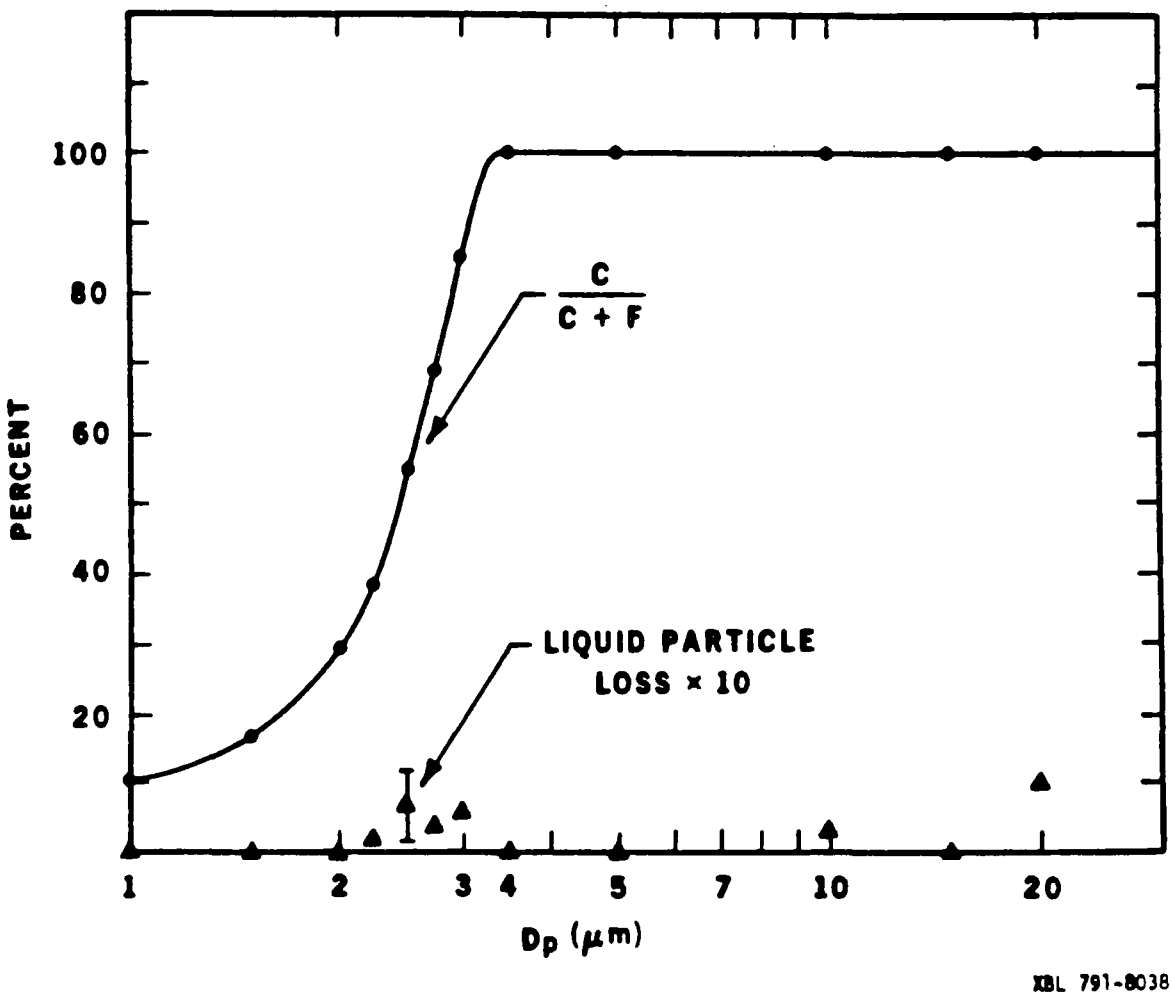



Figure 2-10. The size separation characteristics and wall loss measurement of a 2.5 μm cutpoint virtual impactor as a function of particle size Dp. C and F represent particle collections on the coarse and fine filters respectively.

Source: Loo et al. (1979)

windspeed (McFarland and Rodes, 1979). When used to size-segregate smaller particles (<10 μm), size separation techniques such as cyclones and inertial impactors often have $\sigma_g$ values less than 1.3 (John et al., 1978; Cushing et al., 1978). Figure 2-10 shows an example of the sharpness of a virtual impactor (dichotomous sampler) cutpoint at 2.5 μm as reported by Loo et al. (1979).

After particles pass through the sampler inlet, they can still be lost from the flowstream before collection or measurement by attraction to or impaction on the internal surfaces of the sampler. Minimizing internal loss, especially for larger particles, requires careful design of the sample transport system geometry as well as consideration of factors such as surface charge dissipation. Wedding et al. (1977) reported internal wall losses in a prototype size-specific sampler to exceed 40 percent for particles greater than 15 μm, which can be compared with the minimal losses shown in Figure 2-10.

The efficiency of the filter media used can influence the total mass collected if very small particles are not retained on the filter, or if very large particles bounce off the filter to the sampler walls. The collection efficiencies over a range of particle sizes for a wide variety of filter materials, face velocities, and effective porosities have been determined by Liu et al. (1978). The efficiencies for a majority of the commonly used glass fiber and membrane filters were shown to be nearly 100 percent for particles as small as 0.03 μm. Table 2-11 tabulates selected fractional efficiency data for a commonly used high-volume sampler glass fiber filter, a Teflon® membrane filter, and the cellulose fiber filter material (Whatman No. 1) used in the British Smoke Shade Sampler. Note that the latter filter shows some inefficiency

TABLE 2-11. FRACTIONAL AEROSOL PENETRATION FOR SELECTED SUBSTRATES AS A FUNCTION OF FACE VELOCITY AND PARTICLE SIZE

FILTER: Gelman Type A, glass fiber

| ΔP, cm Hg | 1 | 1.5 | 3 | 10 |
|---|---|---|---|---|
| ∇, cm/sec | 11.2 | 16.9 | 32.7 | 108 |
| $D_p$, μm | PENETRATION | | | |
| 0.035 | <0.0001 | <0.0001 | <0.0001 | 0.0008 |
| 0.10 | <0.0001 | <0.0001 | <0.0001 | 0.00054 |
| 0.30 | <0.0001 | <0.0001 | <0.0001 | <0.00007 |
| 1.0 | <0.0001 | <0.0001 | <0.0001 | <0.00002 |

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

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

FILTER: Whatman No.1, cellulose fiber

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

Source: Liu et al., 1978

at the smallest particle sizes, while the nominal 2 μm porosity Teflon® filter is highly efficient for small particles due to collection mechanisms other than interception.

Non-filtration techniques for size selective particle sampling have been used to determine mass distributions by particle size. The multistage inertial impactors (more commonly called cascade impactors) provide discrete samples associated with selected particle size ranges that can be analyzed for mass or other constituents. Typically, these samplers have had uncharacterized inlets when used for ambient monitoring, which often results in a misinterpretation of the mass median diameter (MMD) with respect to total mass collected. Dzubay et al. (1976) and Cahill (1979) have also noted that allowing entry of particles much larger than the first stage cutpoint can cause particles to bounce to lower stages, shifting the calculated MMD. Cyclone separators have also been used to collect discrete ambient samples primarily for size fractions less than 10 μm, but these devices are more difficult to use in serial operation.

Methods for continuous measurement of ambient particles provide real time measurements, but with current technology do not provide information directly related to mass concentration. Most of these in situ measurements are optically based and provide information such as particle number, surface area, and volume distributions by particle size or parameters related to ambient particles such as light scatter or visible contrast change. These measurements are valuable to researchers and provide input to control strategy assessments, but in general are not currently viable as routine monitoring methods for demonstration of compliance.

2.5.2 Integrated Sampling Methods

2.5.2.1 Introduction--Most particle samplers collect samples integrated over a specified time interval. EPA's National Air Surveillance Network operated high-volume samplers for 24-hour intervals to support the current standard. The British Smoke Shade sampler is also operated over a 24-hour period. Inertial impactors often require operation for shorter periods, depending on the ambient particle concentrations, to eliminate collection stage overloading. Even though some tape samplers can provide a continuous analytical readout, the measurements are reported as an integrated average for a selected time interval, usually 1 to 4 hours per sample.

Sampling methods that were either used to collect aerometry data described in Chapter 14 of this document, or are currently being used extensively in routine monitoring programs are described below.

2.5.2.2 Methodology

2.5.2.2.1 TSP High-Volume Sampler--As noted earlier, the high-volume sampler is the current EPA reference method for total suspended particulates (TSP). It is intended to operate at flowrates from 1.1 to 1.7 $m^3$/min, drawing air through a 200 x 250 mm glass fiber filter. The collected mass of particles on the filter is determined by the difference between gravimetric measurements before and after exposure. The mass concentration is interpreted over the sampling

interval and is normally expressed in μg of mass collected per $m^3$ of air sampled ($\mu g/m^3$). As shown in Figure 2-11, the inlet is formed by the overhang of a gable roof above the filter. The inlet efficiency, as noted in Figure 2-7, does not provide a sharp particle size cutoff and is sensitive to wind speed. Also shown on Figure 2-7 are the estimated particle sizes for 50 percent collection ($D_{50}$) for each of the wind speeds tested. The collection efficiency also is affected by sampler orientation, i.e., it is sensitive to wind direction, as shown in Table 2-12 (Wedding et al. 1977). The sampler flowrate is measured either before and after collection using an external flowmeter or continuously with a flow recorder. The effect of sampler flowrate on particle collection as shown in Figure 2-12 is not substantial. The commonly used filter media for this sampler are nearly 100 percent efficient for 0.3 μm particles (Liu et al., 1978). As noted by Friedlander (1977), this size particle is the most difficult to capture, since the collection of smaller and larger particles is assisted by diffusion and interception, respectively.

The overall accuracy of ambient particulate measurements such as those made by the high volume sampler cannot be quantified with current state-of-the-art technology. Alternatively, estimates of the components of the overall accuracy must be determined, including collection efficiency of the sampler inlet and filter media and accuracy of the flow measurement system. Two commonly used flow measurement devices on high volume samplers are the rotameter (visi float) and the flow recorder. The rotameter is used to measure only the initial and final flowrates from which an average is calculated. The flow

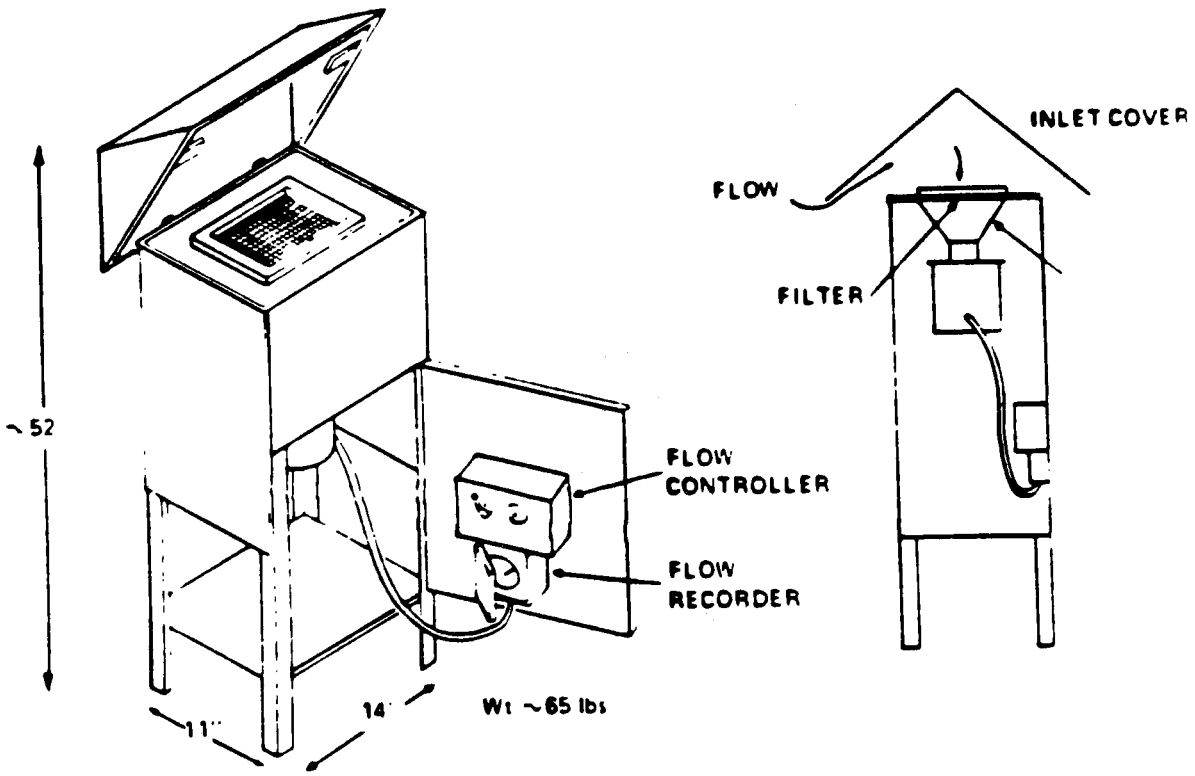



Figure 2-11. TSP Hi-Vol Used in IP Network.

TABLE 2-12. SAMPLING EFFECTIVENESS OF HI-VOLUME SAMPLER AT 15 FT/S

| Particle diameter, μm | | | | | | | |
|---|---|---|---|---|---|---|---|
| 5 | | 15 | | 30 | | 50 | |
| Sampler orientation, ° | | | | | | | |
| 0 | 45 | 0 | 45 | 0 | 45 | 0 | 45 |
| 97% | 100% | 35% | 55% | 18% | 41% | 7% | 34% |

SOURCE: Wedding et al. (1977)

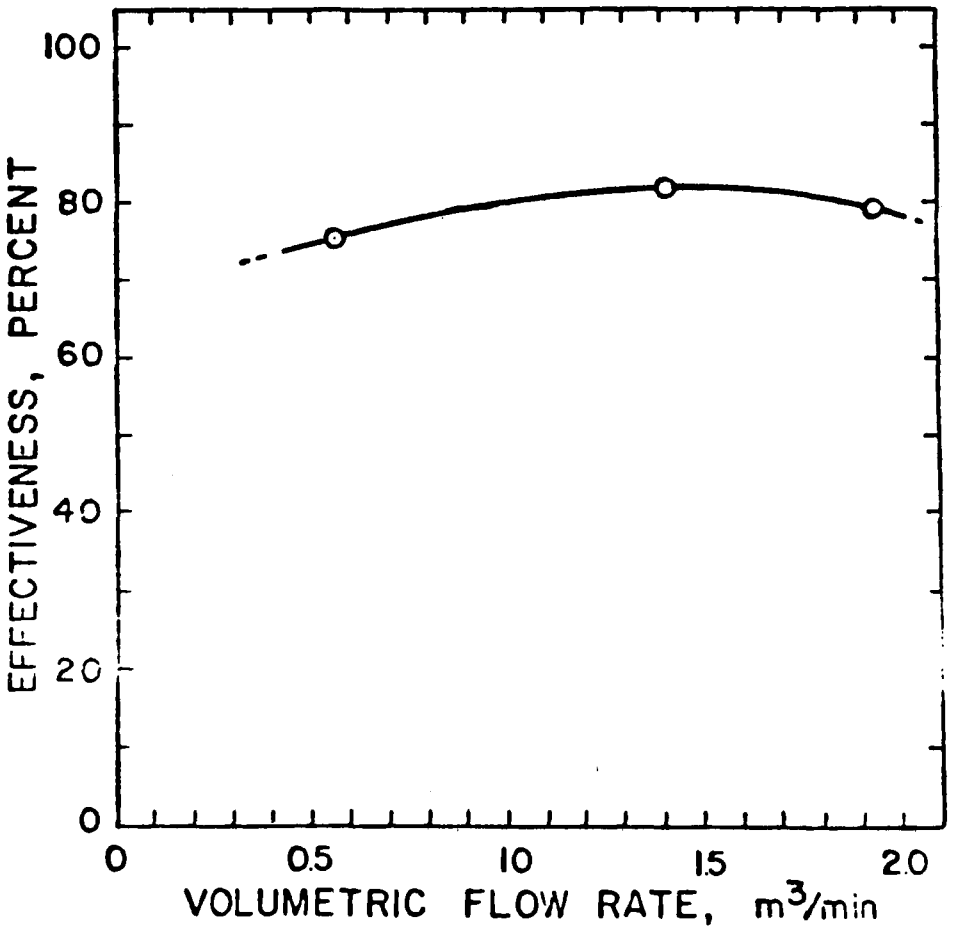



Figure 2-12. EFFECT OF FLOW RATE ON PERFORMANCE OF 11½" x 14" HI-VOL. AERODYNAMIC PARTICLE DIAMETER = 29 μm.

Source: McFarland and Rodes (1979)

recorder provides a continuous trace that can be integrated for a more accurate measurement. Smith et al. (1978) using high volume samplers with both types of devices noted that the flow recorder produced smaller errors (2 to 4 percent) when compared with a reference flow device than the rotameter (6 to 11 percent). The precision of the high volume sampler as determined from collocated sampler measurements under field conditions and expressed by the coefficient of variation (CV) have been reported by several investigators. McKee et al. (1971) determined the CV for a measurement by a single analyst to be 3.0 percent, while the same measure among multiple analysts in a collaborative test was 3.7 percent. The plenum design of the gable roof provides a settling chamber for larger particles blown in during periods when the sampler is not operational. McFarland and Rodes (1979) have quantified this deposition experimentally as shown in Figure 2-13 as a function of particle size and ambient wind speed. Interpreting these relationships requires knowledge of the existing ambient size distribution. For a typical distribution as shown in Figure 2-1, the amount of mass added to a high-volume sampler filter during 5 days of exposure when it was not operational could amount to 6 to 8 percent. This effect has also been measured in a field situation by Sides and Saiger (1976) and Lizarraga-Rocha (1976), who measured weight increases from 3 to 12 percent. Errors from this effect may be reduced by equipping the sampler with one of the commercially available automatic mechanical devices that keeps the filter covered during nonsampling periods.

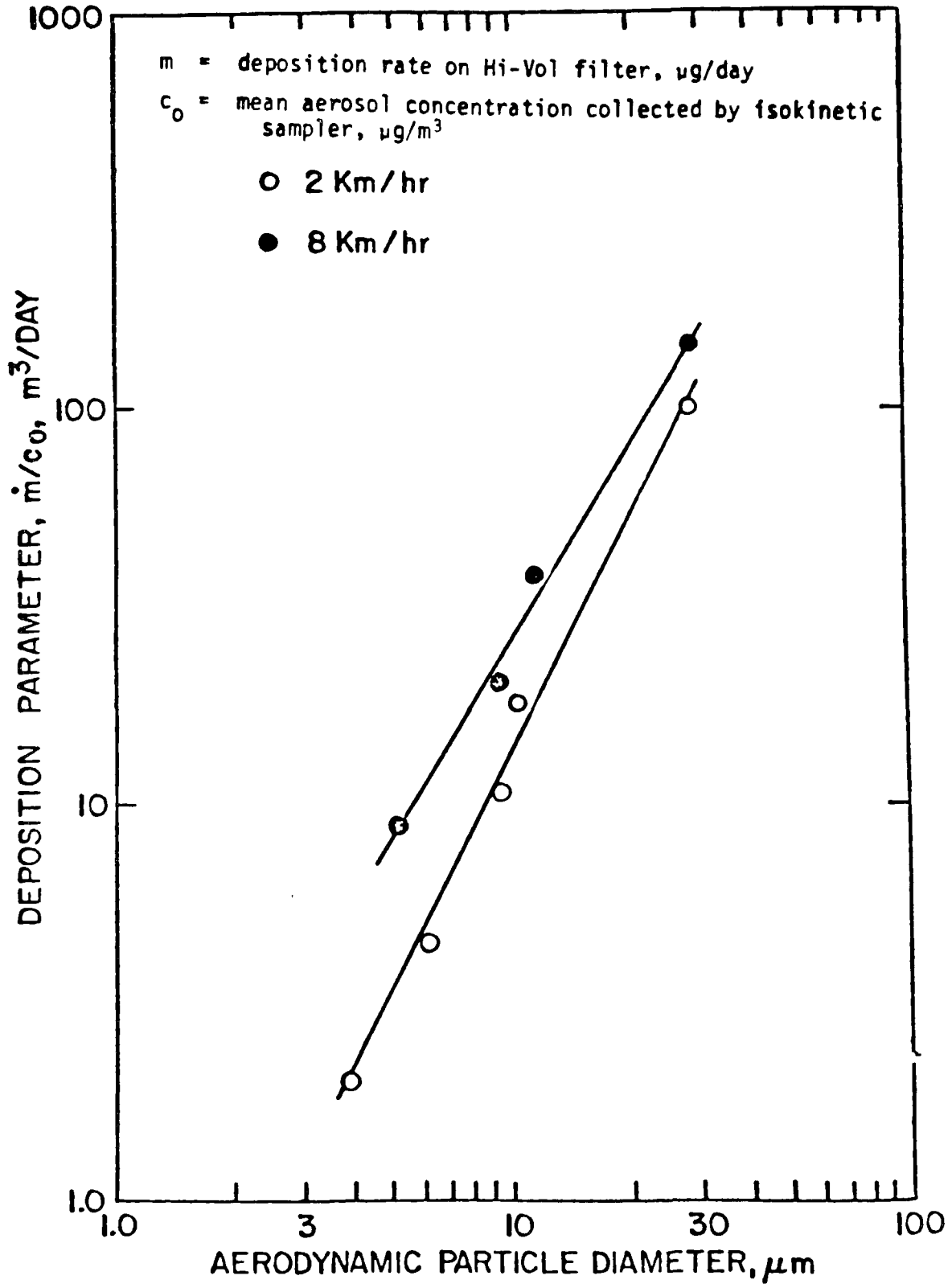



Figure 2-13. Deposition of standby mode, 11 1/2" x 14" hi-vol.

Source: McFarland and Rodes (1979)

Alternatively, installation and retrieval of filters relative to the scheduled sample period will also minimize the problem.

As shown by Coutant (1977) and Spicer and Schumacher (1979), artifact particulate matter can be formed on the surfaces of alkaline filter materials such as glass fiber by oxidation of the acid gases present in the sample air. The effect is a surface-limited reaction usually occurring early in the sample period, and is dependent on factors such as the length of the sample period, the filter pH, and the presence of acid gases in the sampled air. The magnitude and the significance of artifact mass errors are variable and dependent on local conditions. The majority of artifact mass is the sum of the sulfates and nitrates formed by filter surface reactions with ambient sulfur dioxide and nitric acid, respectively. The ambient concentration of sulfur dioxide is primarily dependent on fossil fuel combustion, while nitric acid concentration is dependent on atmospheric photochemistry. A laboratory study by Coutant (1977) has reported sulfate artifact mass for 24 hour samples from 0.3-3 $\mu g/m^3$. This is supported by the field data of Rodes and Evans (1977) who noted a 0.5 $\mu g/m^3$ artifact in Los Angeles, California. Spicer and Schumacher (1979) have reported nitrate artifacts of approximately 5 $\mu g/m^3$ for field measurements in Upland, California. These data would support a typical influence of 2-5 $\mu g/m^3$ and a worst case influence of 5-8 $\mu g/m^3$ on the total mass concentrations determined using glass fiber filters.

2.5.2.2.2 British smoke shade sampler. The design of the British Smoke Shade sampler is based upon early work by Hill (1936), who used transmitted light to assess the darkness of the stain resulting from particle collection on the filter paper. This sampler draws an air stream upward through an inverted funnel and 3 meters of nominal one-quarter inch diameter plastic tubing to an

inverted filter holder containing a Whatman Number 1 cellulose fiber filter. As noted earlier, this filter medium has been shown to be somewhat inefficient when sampling very small particles (Liu et al., 1978). A schematic diagram of a version of this sampler designed to sequentially collect samples for 8 days is shown in Figure 2-14. A bubbler is often used down stream of the filter holder for subsequent $SO_2$ measurements. The sampler is operated at approximately 1.5 liters/min, which is verified by a dry test meter built into the sampler. The filter holder can be 25, 50, or 100 mm in diameter to collect a spot of the proper darkness range for subsequent measurements by reflectance. A 1964 study supported by the Organization for Economic Cooperation and Development (OECD) established relationships between smoke shade reflectance measurements and gravimetric total suspended particulate concentrations, based on collocated sampler tests performed in Britain with the high volume sampler. These data were accepted by the World Health Organization (WHO, 1976) and compiled into a standard operating procedure, which permitted reporting of smoke shade measurements in equivalent $\mu g/m^3$.

This sampler was used extensively in early monitoring studies, and its aerosol collection properties have been examined by McFarland (1979). This examination produced the efficiency plot shown in Figure 2-15, which shows that the $D_{50}$ for particles reaching the filter is only 4.5 μm. Many large particles are either rejected at the inlet or lost in the inlet line. Since the typical ambient size distribution contains only a small amount of mass between 3.5 and 4.5 μm (see Figure 2-1), the size fraction collected by the British Smoke Shade sampler is very nearly equivalent to the 0-3.5 μm respirable suspended particulate (RSP) fraction defined by the American Conference of Governmental and Industrial Hygienists (ACGIH) Threshold Limits Values Committee (1968) and described by Lippman

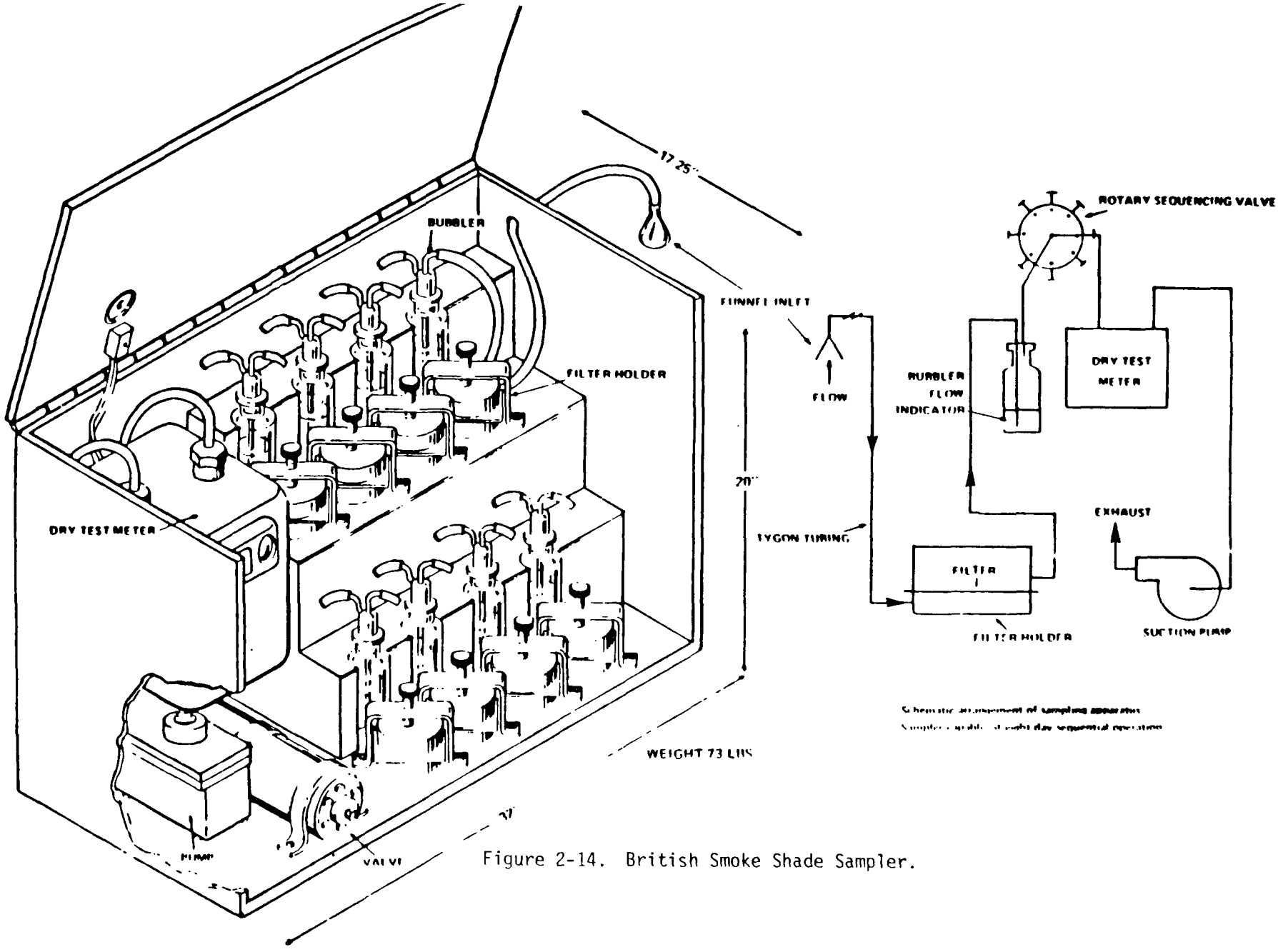



Figure 2-14. British Smoke Shade Sampler.

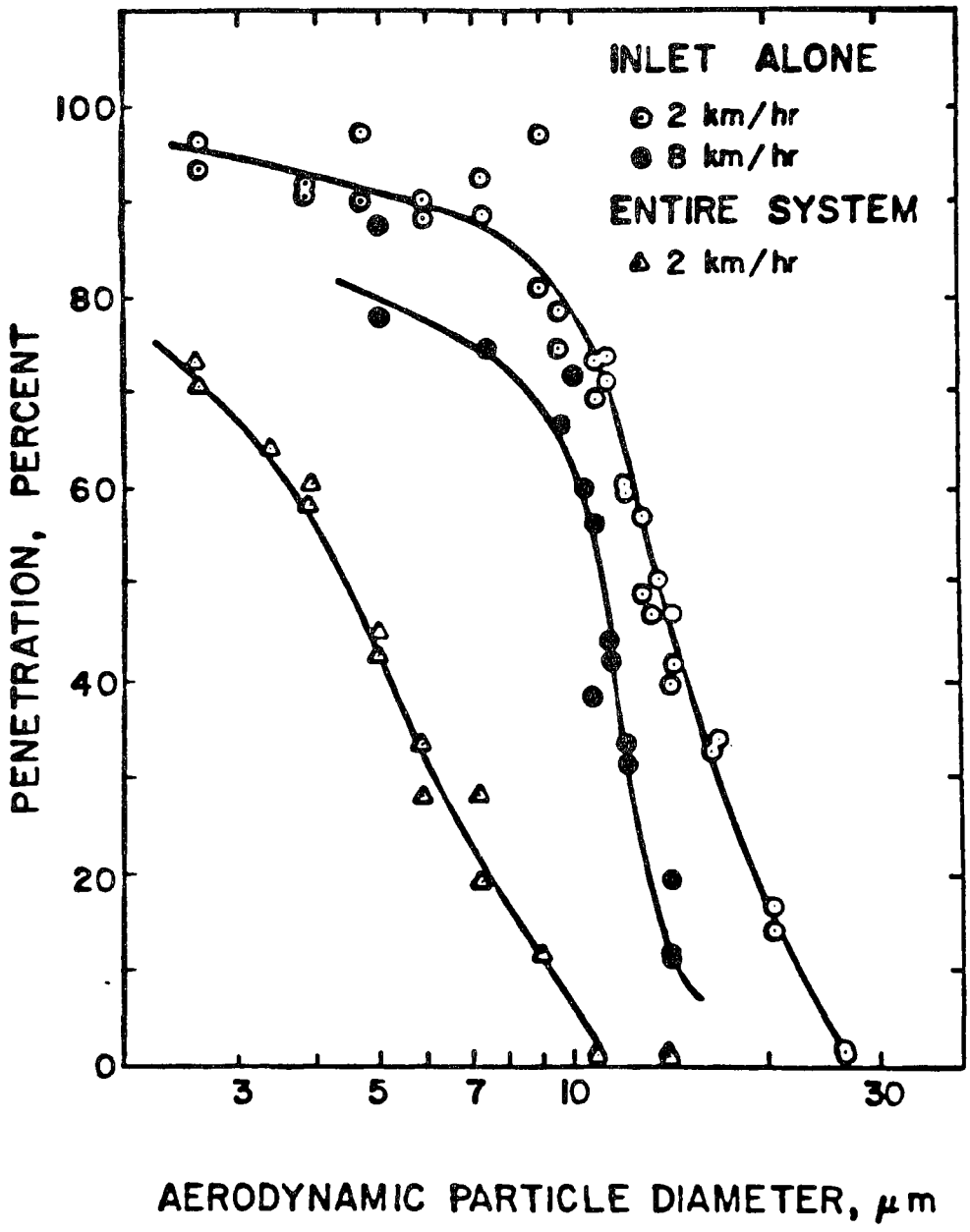



Figure 2-15. **PENETRATION OF AEROSOL THROUGH INLET ALONE AND THROUGH ENTIRE FLOW SYSTEM TO FILTER**
Source: McFarland (1979)

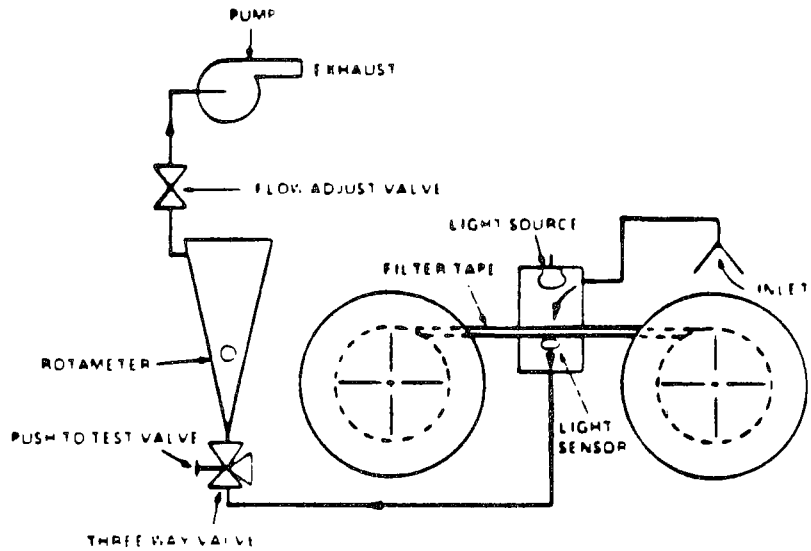
(1970). Since the size range of particles collected by the smoke shade sampler is substantially less than that collected by the high volume sampler, comparisons between the methods could be expected to be variable. This varibility is primarily influenced by the proportions of fine and coarse particles in the atmosphere (e.g., see Figure 2-8), and to a lesser degree by the inherent color of the particles. The reproducibility (CV) of collocated smoke shade sampler measurements was reported by the British Standards Institution (1964) as 6 percent.

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

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

Reflectance measurements are converted through a simple Beer's Law relationship to CoH (Coefficient of Haze) units per 1000 linear feet of air sampled. A CoH is defined as the quantity of particulate matter on the paper tape that produces a change in optical density of 0.01. The less popular RUDS (Reflectance of Dirt Shade) is equivalent to 0.1 CoH units.

The tape sampler, shown in Figure 2-16, utilizes a small diameter plastic



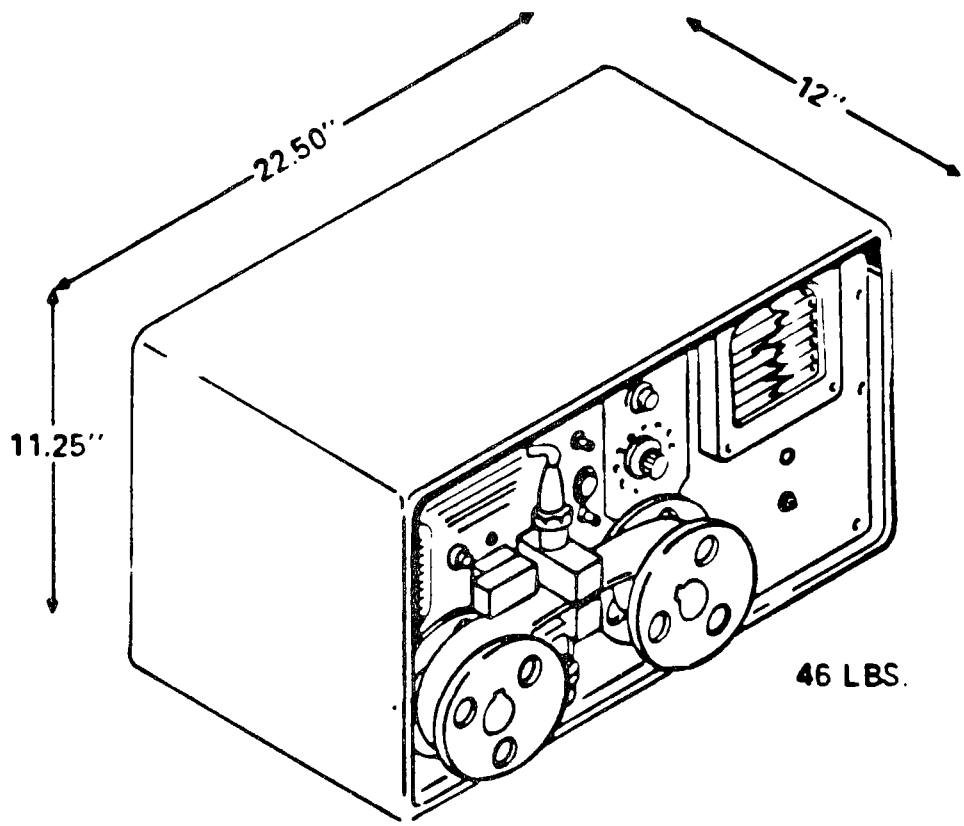




Figure 2-16. A.I.S.I. Sampler with Built-in evaluator and recorder.

inlet tube and funnel nearly identical to the British Smoke Shade sampler. Even though the two samplers operate at different flowrates, the particles reaching the filter tape will have a size range similar to that illustrated in Figure 2-15. This size range restriction plus the capability for direct real-time readout can be useful for providing a continuous measurement of fine particles during air pollution episodes. The utility of the sampler to estimate mass concentrations has been investigated by many researchers, usually in comparison with the standard high-volume sampler. Since these two samplers do not collect similar particle size ranges, such comparisons are difficult unless very few coarse particles are present. Regan et al. (1979) have shown with field data that the correlation improves when the tape sampler data are compared with smaller particle fractions.

2.5.2.2.4 Inertial impactors. Often referred to as cascade impactors when used in multiple stages, inertial impactors provide a means of collecting an ambient mass fraction which is divided into subfractions of specific particle sizes. This method involves acceleration of the ambient air stream by drawing it through one or more converging nozzles or slots. As shown in Figure 2-17, upon leaving the nozzle the jet of air is directed perpendicularly toward a collection surface. Large, high inertia particles are unable to turn with the air stream and consequently impact against the collection surface. Smaller particles follow the air stream and can be directed either to another stage of impaction or collected on a filter. Utilization of multiple stages, each with a different nozzle velocity, provides collection of particles in several size ranges.

Cascade impactors typically have 2 to 6 stages, and commercial low volume sampler flowrates range from about 0.01 to 0.04 $m^3$/min. Lee and Goranson

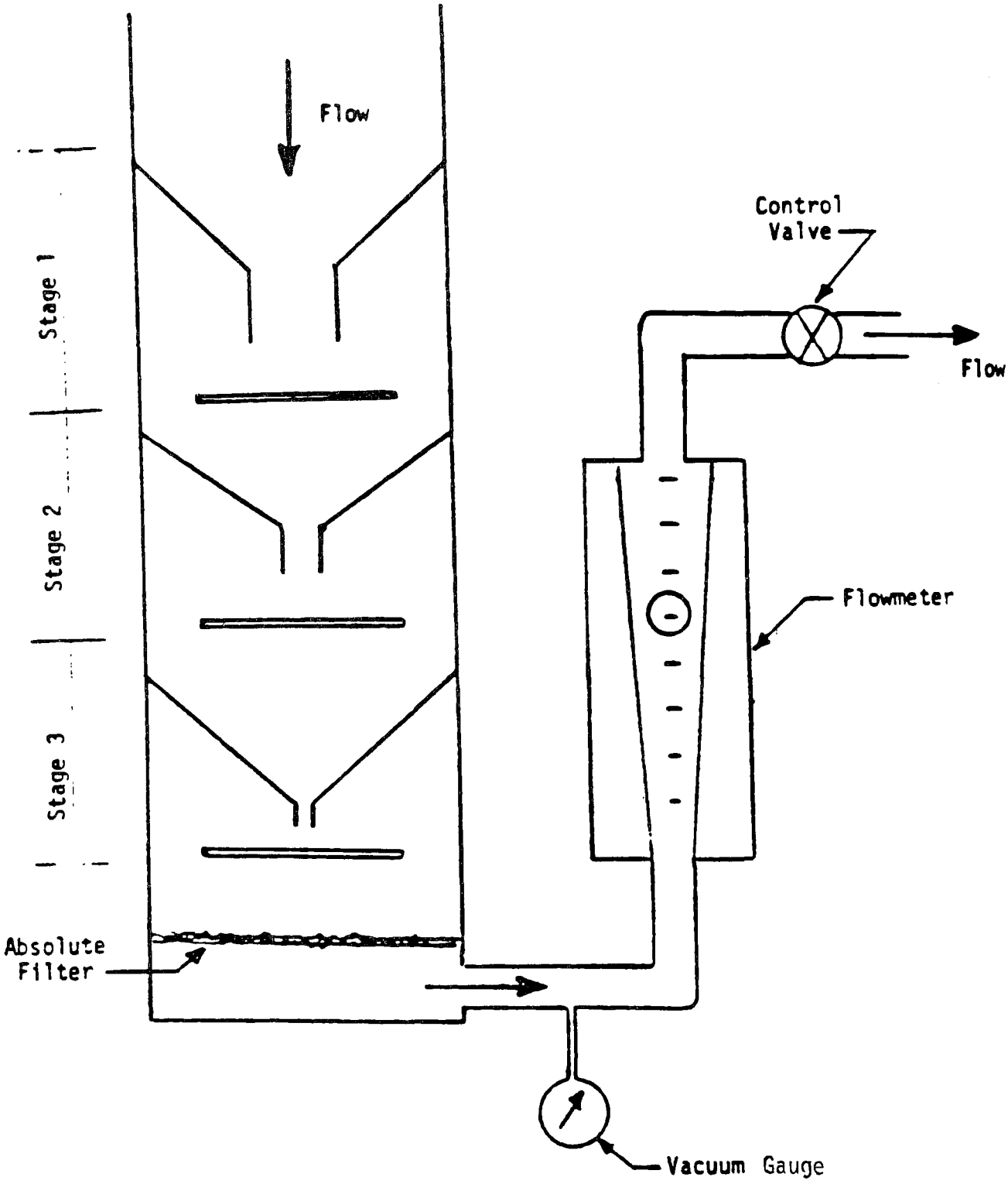



Figure 2-17. **Cascade Impactor Sampling System**

(1972) utilizing a modified commercially available 0.03 $m^3$/min low volume impactor, operated it at 0.14 $m^3$/min to obtain larger mass collections on each stage. Cascade impactors have also been designed to mount on a high-volume sampler and operate at much higher flowrates, from approximately 0.6 to 1.1 $m^3$/min. A single stage high volume impactor as shown in Figure 2-18 was utilized in the Community Health Air Monitoring Program (CHAMP) program and operated at 1.1 $m^3$/min.

The particle size cutpoints for each stage are dependent primarily on the sampler geometry factors and flowrate. The smallest practical size cutpoint is approximately 0.3 μm. Below this size, the high vacuums and small nozzle diameters required to attain the necessary jet velocities can result in changes in particle character and rapid clogging of the smaller stage nozzles. A filter is normally used after the last stage of inertial impactors to collect particles not collected on the impactor stages. The masses collected on each stage plus the backup filter mass collection are often reported as shown in Figure 2-19 from data by Lee and Goranson (1972). This cumulative distribution format permits determination of the MMD, at which point 50 percent of the mass is smaller than the indicated size.

The inlet cutoff characteristics of most impactors have not been determined resulting in uncertainty about the size range of particles sampled. McFarland (1980) has examined the inlet of the NASN low volume (0.03 $m^3$/min) cascade impactor and determined that particles larger than 10 μm were unlikely to reach the collection stages. Willeke and McFeters (1975) characterized the CHAMP high volume sampler inlet under static wind speed conditions as shown in Figure 2-20. If the impactor inlet $D_{50}$ is known, the total mass collected by the sampler can be used for comparison with other size specific measurements.

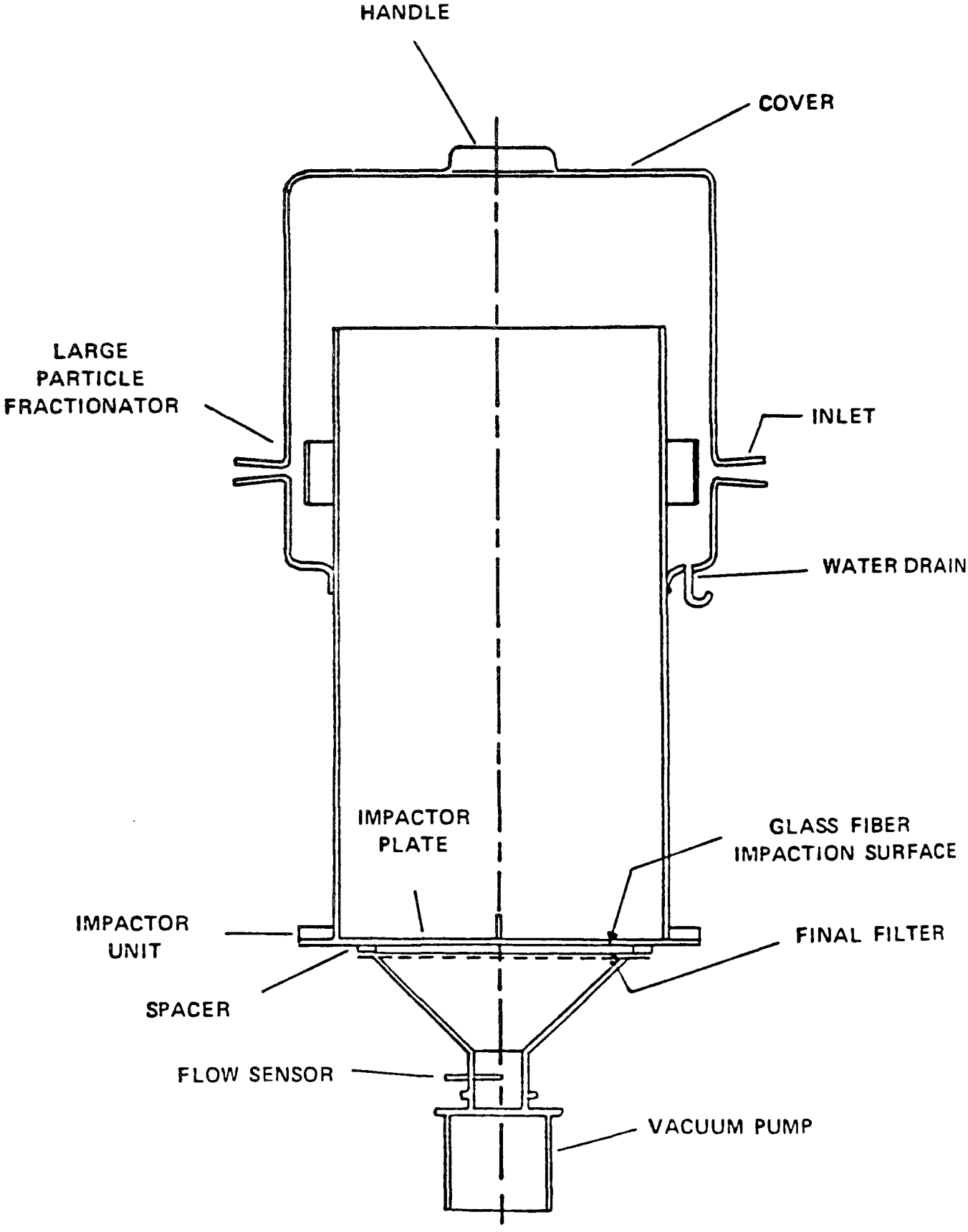



Figure 2-18. **Cross Section Schematic of the CHAMP Aerosol Sampler.**
Source: Ranade and Osdell (1978)

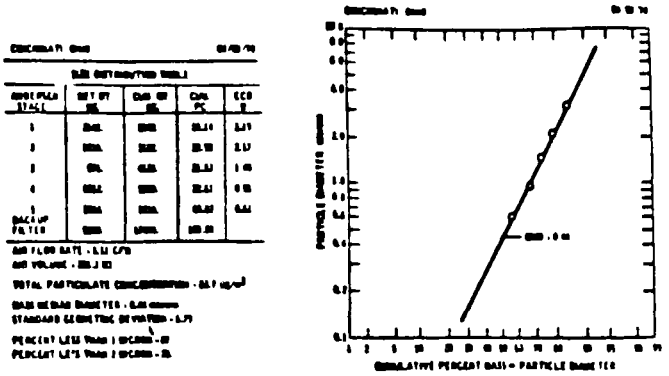


Figure 2-19. Example of computer printout and corresponding size distribution curve.

Source: Lee and Goranson (1972)

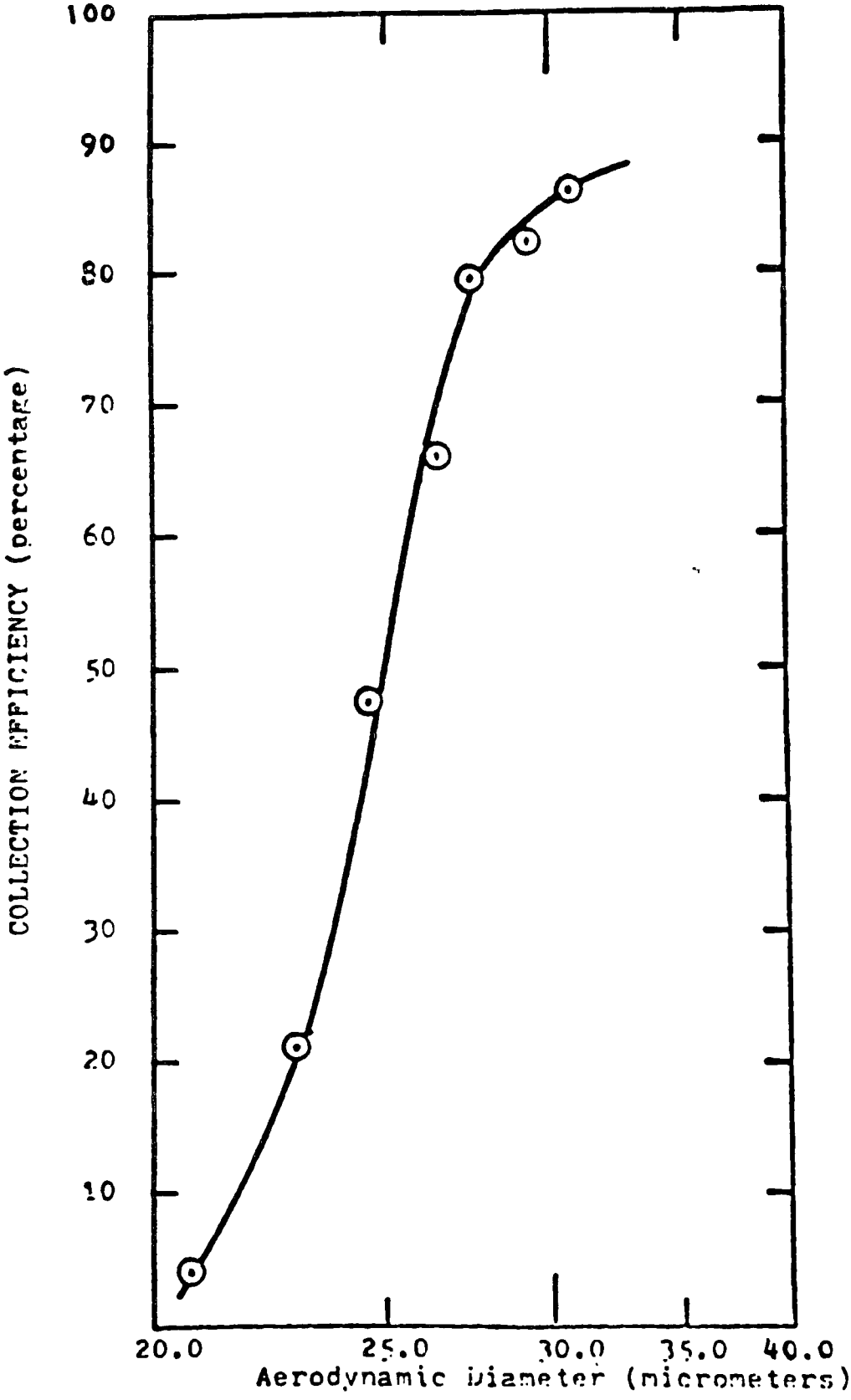



Figure 2-20. Experimentally derived collection efficiency curve of the CHAMP fractionator inlet operated at 1132.7 l/min (40 SCFM), $D_{Paero}$ = 25 $\mu$m, $\sigma_g$ = 1.16.

Source: Willeke and McFeters (1975).

Cascade impactors use removable impaction surfaces for collecting particles. Impaction substrates are weighed before and after exposure and are typically glass, metal foil or glass fiber filters. The selection and preparation of these substrates can have a significant effect on the impactor performance. Improperly coated metal surfaces can cause particle bounce to lower stages resulting in substantial cutpoint shifts (Dzubay et al., 1976). Glass fiber substrates can also cause particle bounce and are subject to the formation of artifact particles similar to high-volume sampler filters. The single impaction stage of the CHAMP high volume sampler designed to be 3.5 μm was characterized by Ranade and Van Osdell (1978) as shown in Figure 2-21.

Multiple stage impactors are more commonly used to collect discrete mass fractions in specific size ranges, from which particle mass size distributions such as Figure 2-8 are constructed. These size distributions can provide information valuable to the understanding of sources and transport of suspended particles. Cascade impactors are not normally operated in routine monitoring networks because of the manual labor requirements for sampling and analysis.

2.5.2.2.5 Cyclone sampler. Ambient particle size separation using cyclones has primarily been used to provide cutpoints in the 2 to 4 μm range. A cyclone sampler as used in the Community Health Environmental Surveillance Studies (CHESS) (Bernard, 1976) is shown in Figure 2-22. This cyclone, as characterized in Figure 2-23, provides a relatively sharp 3.5 μm separation. The inlet of the sampler is the cyclone inlet, and a single 0 to 3.5 μm particle fraction is collected on the filter. The filter medium used in the CHESS network was glass fiber. Collection of the larger particles excluded by a cyclone on a removable substrate is difficult, but alternative approaches such as that designed by John et al. (1978) and shown in Figure 2-24, are available

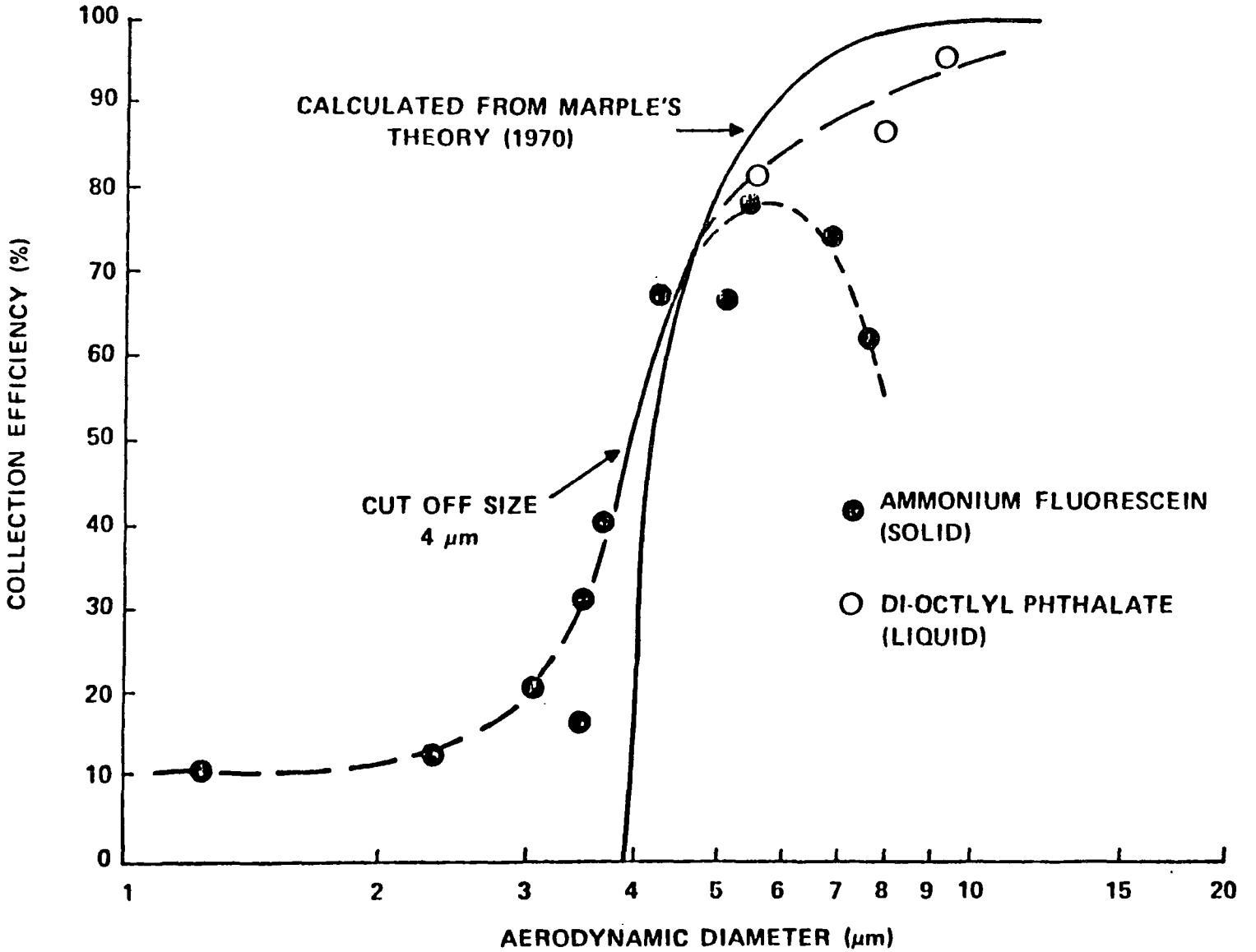



Figure 2-21. **Experimental Results for The Calibration Tests.**

Source: Ranade and Van Osdell (1978)

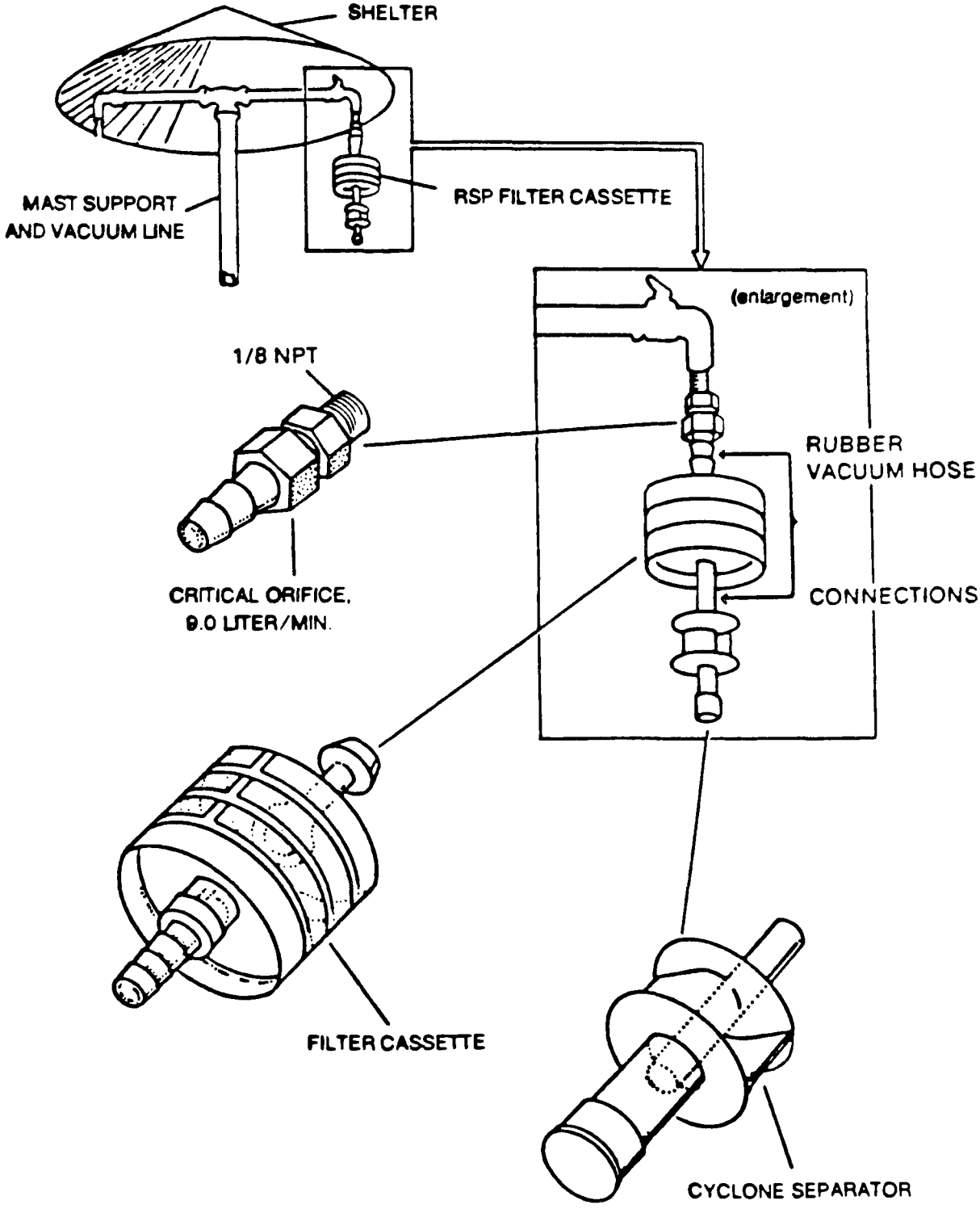



Figure 2-22. Cyclone sampler and shelter assembly.

Source: Bernard (1976).

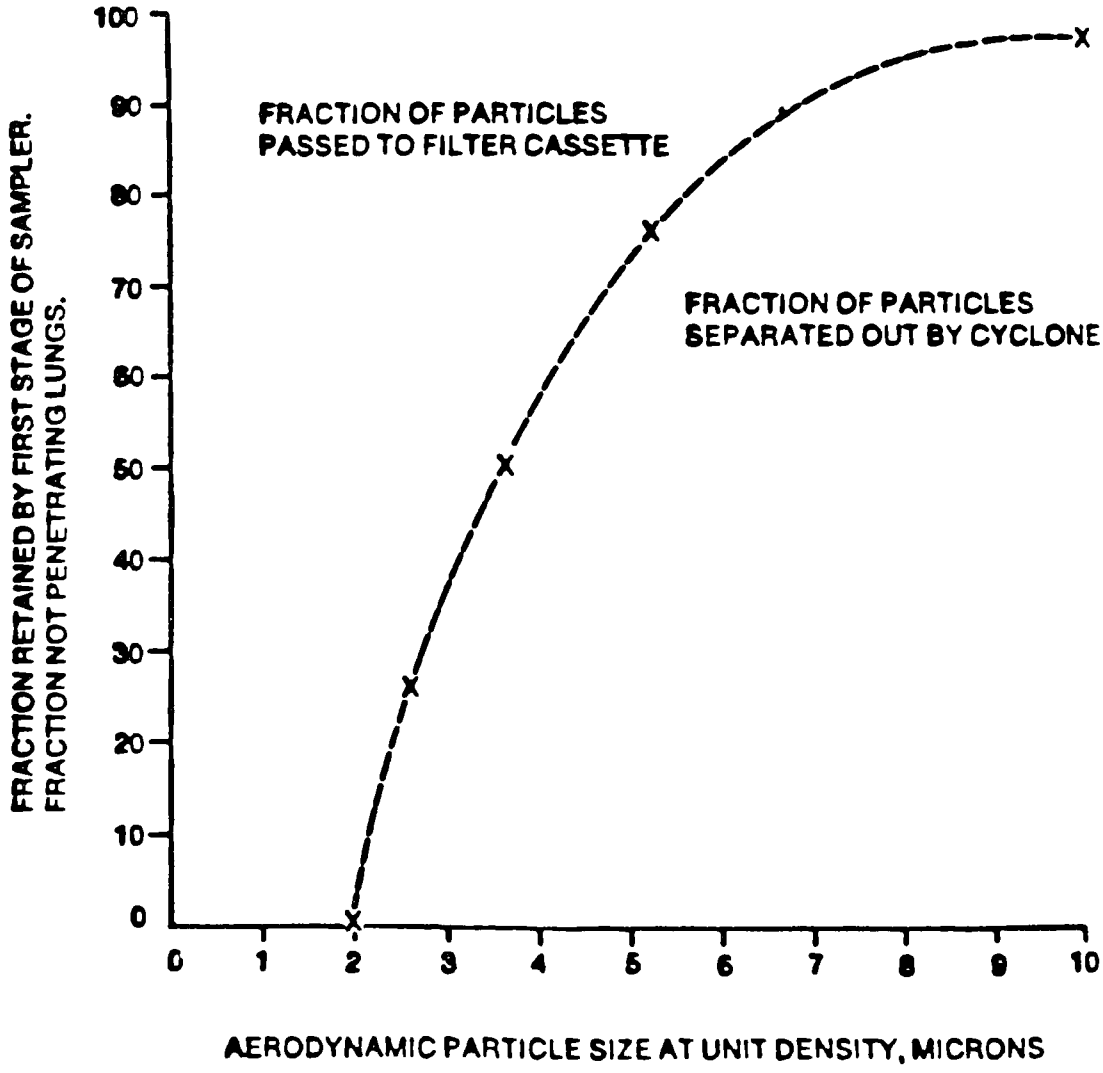



Figure 2-23. "Los Alamos" Curve for Fine Particulates.
Source: Bernard (1976).

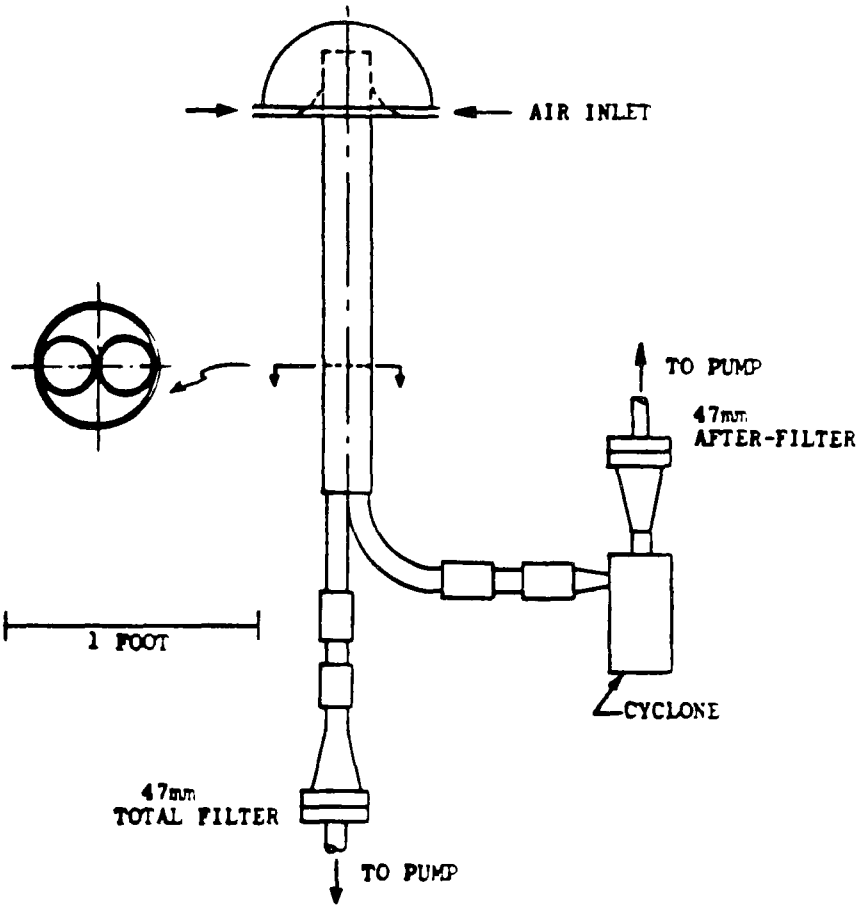



Figure 2-24. Assembly for sampling with a total filter and cyclone in parallel
Source: John et al. (1978)

to provide a total sample and a smaller subfraction sample. The efficiency data for this cyclone as a function of sampler flowrate are shown in Figure 2-25 and indicate that sharp cutpoints with current state-of-the-art units are possible. A neutral pH Teflon® filter medium was recommended to minimize artifact mass formation.

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

The principle of "virtual impaction" applied to particle separation was described by Hounam and Sherwood (1965) and Conner (1966). As shown in a simplified version in Figure 2-26, the separation principle involves acceleration of the particles through a nozzle, after which 90 percent of the flow stream is drawn off at right angles. The small particles follow the right angle flow stream, while the larger particles, because of their inertia, continue toward the collection nozzle. A separate filter is used for each fraction. The sharpness of separation is shown in Figure 2-27 from data by Loo et al. (1979) for a design cutpoint of 2.5 μm. Inherent in this separation technique is a contamination of the coarse particle fraction with a small percentage of the fine particles in the total flow stream. This is not considered a substantial problem for mass measurements, as a simple mathematical correction as described by Dzubay et al. (1977) can be applied.

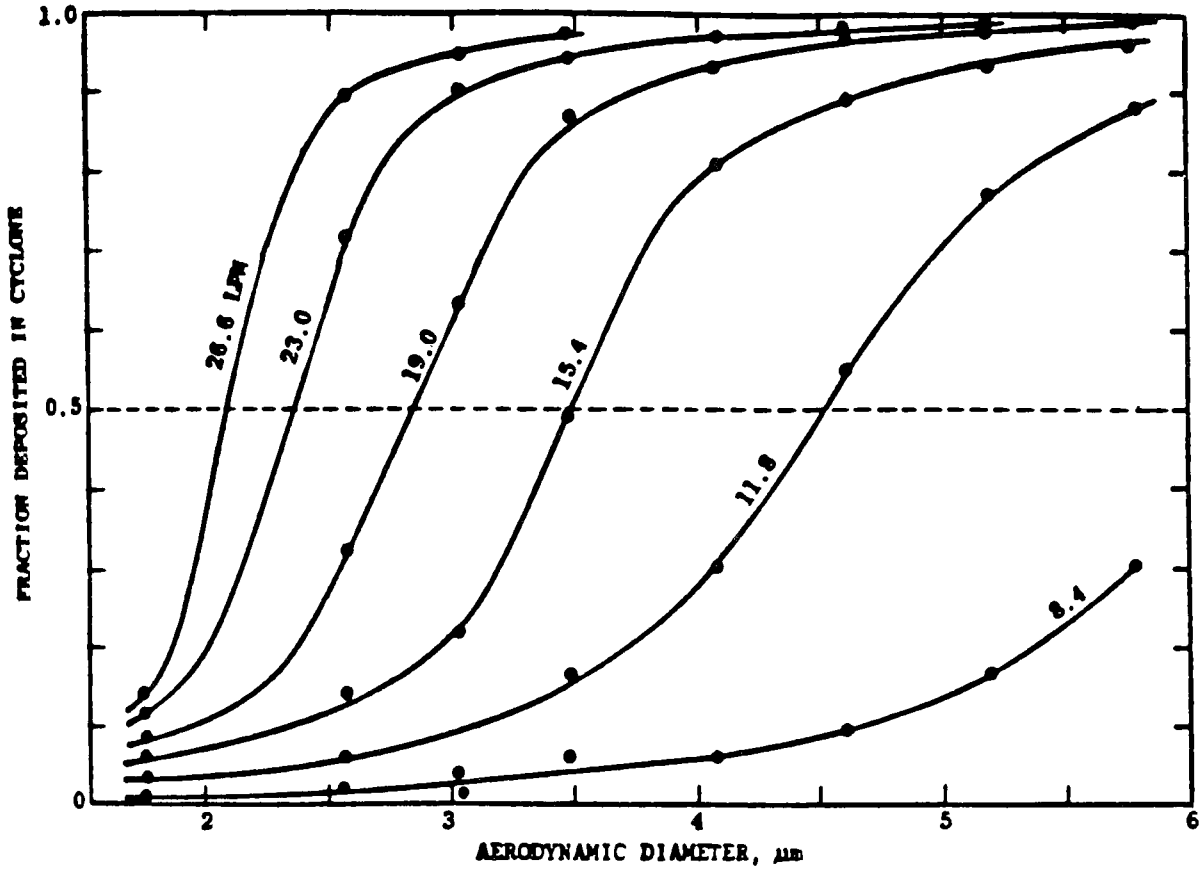



Figure 2-25.

Fraction of Methylene Blue Particles Deposited in the Cyclone as a Function of the Aerodynamic Particle Diameter. The Curves are Labelled with the Flow Rate.

Source: John et al. (1978)

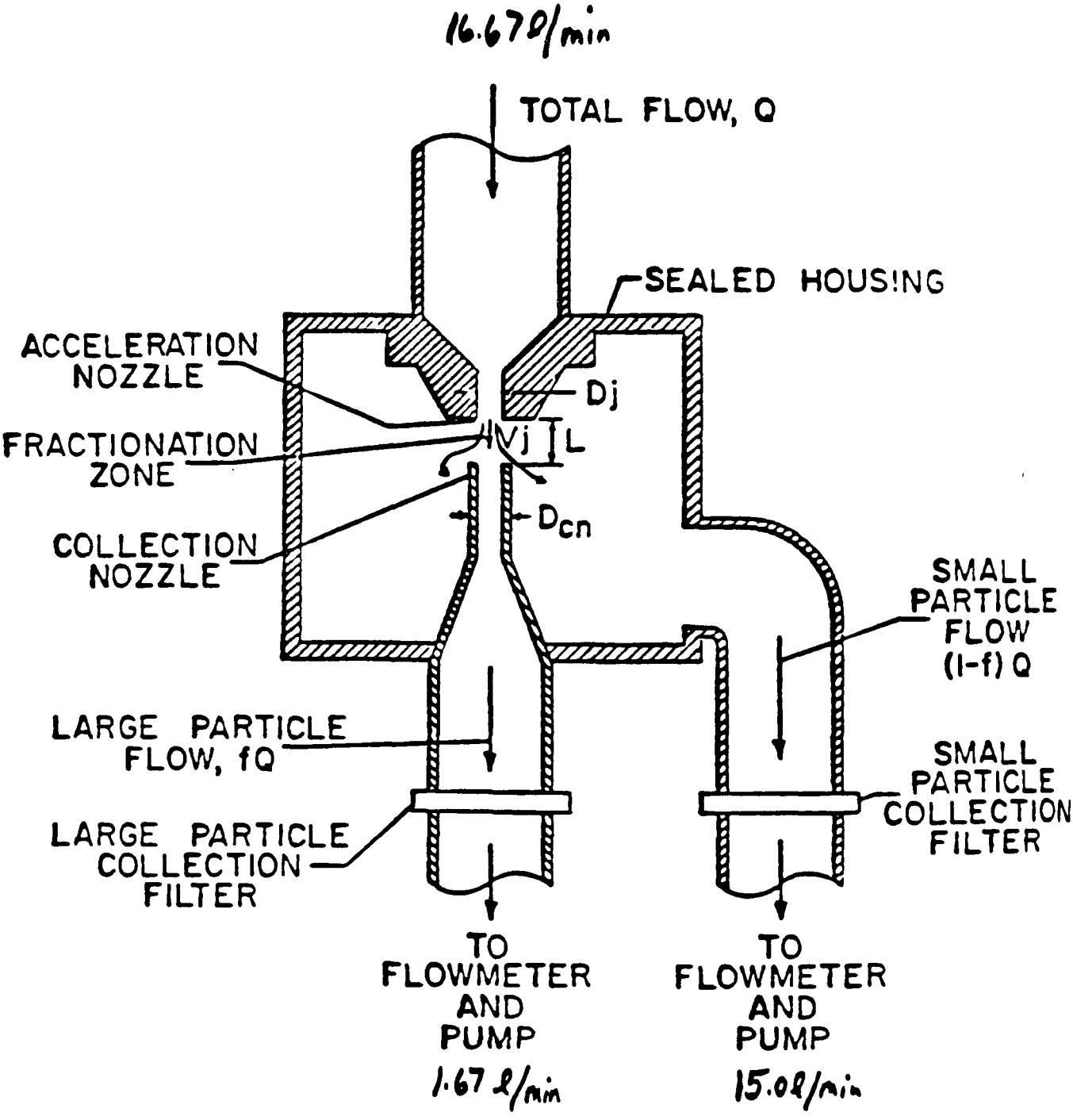



Figure 2-26. **Single Stage Centripeter**

Source: Loo et al. (1979)

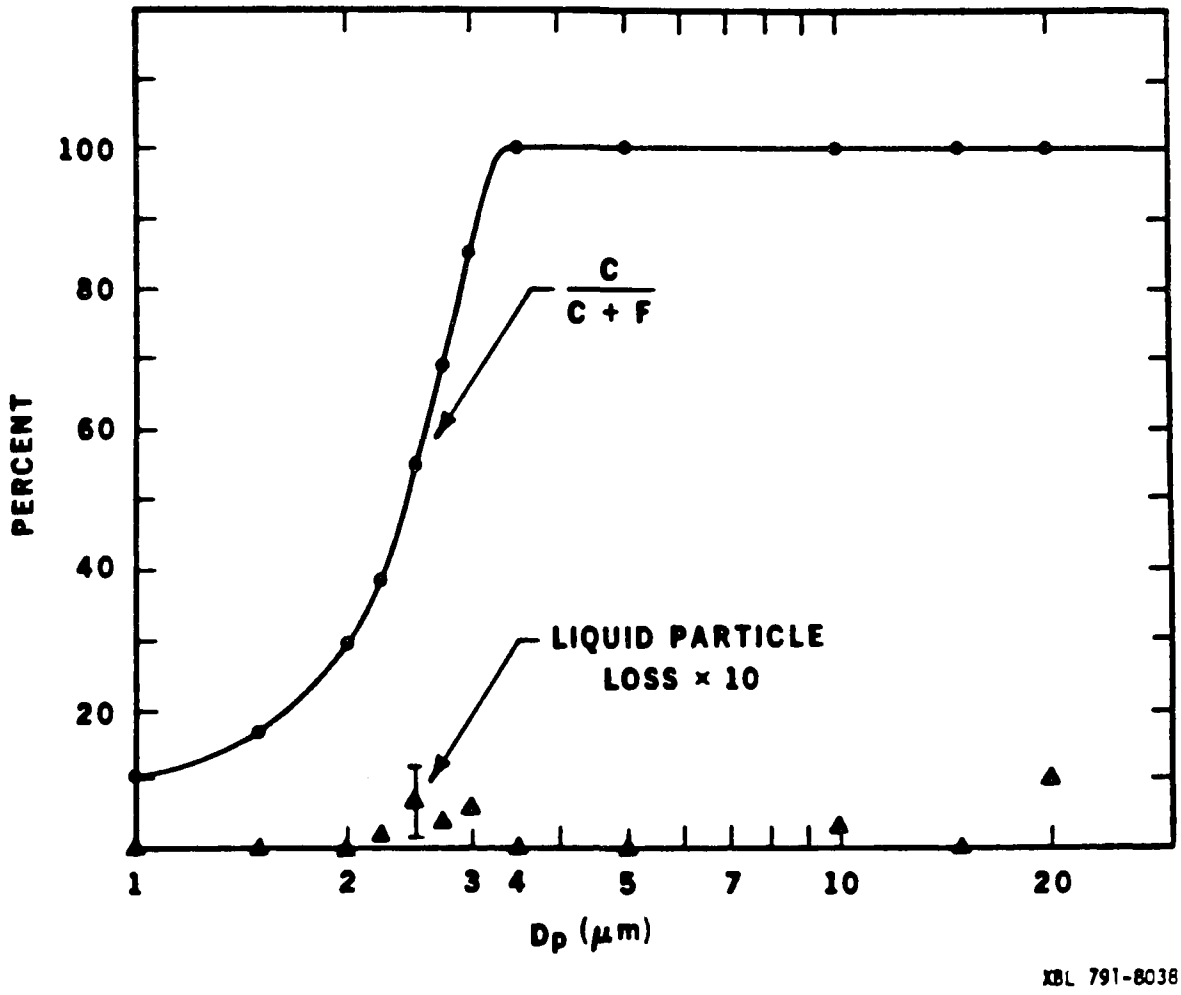



Figure 2-27. The size separation characteristics and wall loss measurement of a 2.5 μm cutpoint virtual impactor as a function of particle size Dp. C and F represent particle collections on the coarse and fine filters respectively.

Source: Loo et al. (1979)

Dzubay et al. (1977) recommend that the filter substrate be Teflon®, and nominal porosities as large as 2.0 μm have been shown to have essentially 100 percent collection efficiency for 0.3 μm particles (Liu et al. 1978). The sampler operates at a flowrate of 1 $m^3$/hr and collects approximately 1/100 of the particle mass collected by a high-volume sampler. Removal of the stickier fine particles causes the particles on the coarse filter (2.4 to 15 μm) to have a greater tendency to fall off the filter if care is not exercised during filter handling (Shaw, ~~1979~~ 1980).

The inlet typically used for this sampler has been a vertical elutriator design by Wedding et al. (1977) shown in Figure 2-28. More extensive testing by the designers has recently shown that this simple inlet is significantly wind speed sensitive, as shown in Figure 2-29.

Current automated versions of this sampler can automatically change the sample filters to provide unattended operation. Depending on atmospheric concentrations, short-term samples of 2 to 4 hours are possible with the automatic samplers to provide diurnal pattern information.

2.5.2.2.7 <u>High-volume sampler with size selective inlet</u>. To meet the monitoring requirements for a ~~new~~ possible inhalable particulate (IP) standard (Miller et al. 1979), EPA commissioned the design of a size-selective inlet suitable for existing TSP high-volume samplers to provide a single 0 to 15 μm particle size fraction. This new inlet, shown mounted on a conventional high-volume sampler in Figure 2-30, has been tested by the designers (McFarland and Ortiz, 1979) and has an inlet efficiency as shown in Figure 2-31 and a sensitivity to wind speed as shown in Figure 2-32. Dry particle bounce and re-entrainment are insignificant at the designed sampler flowrate of 1.1 $m^3$/min.

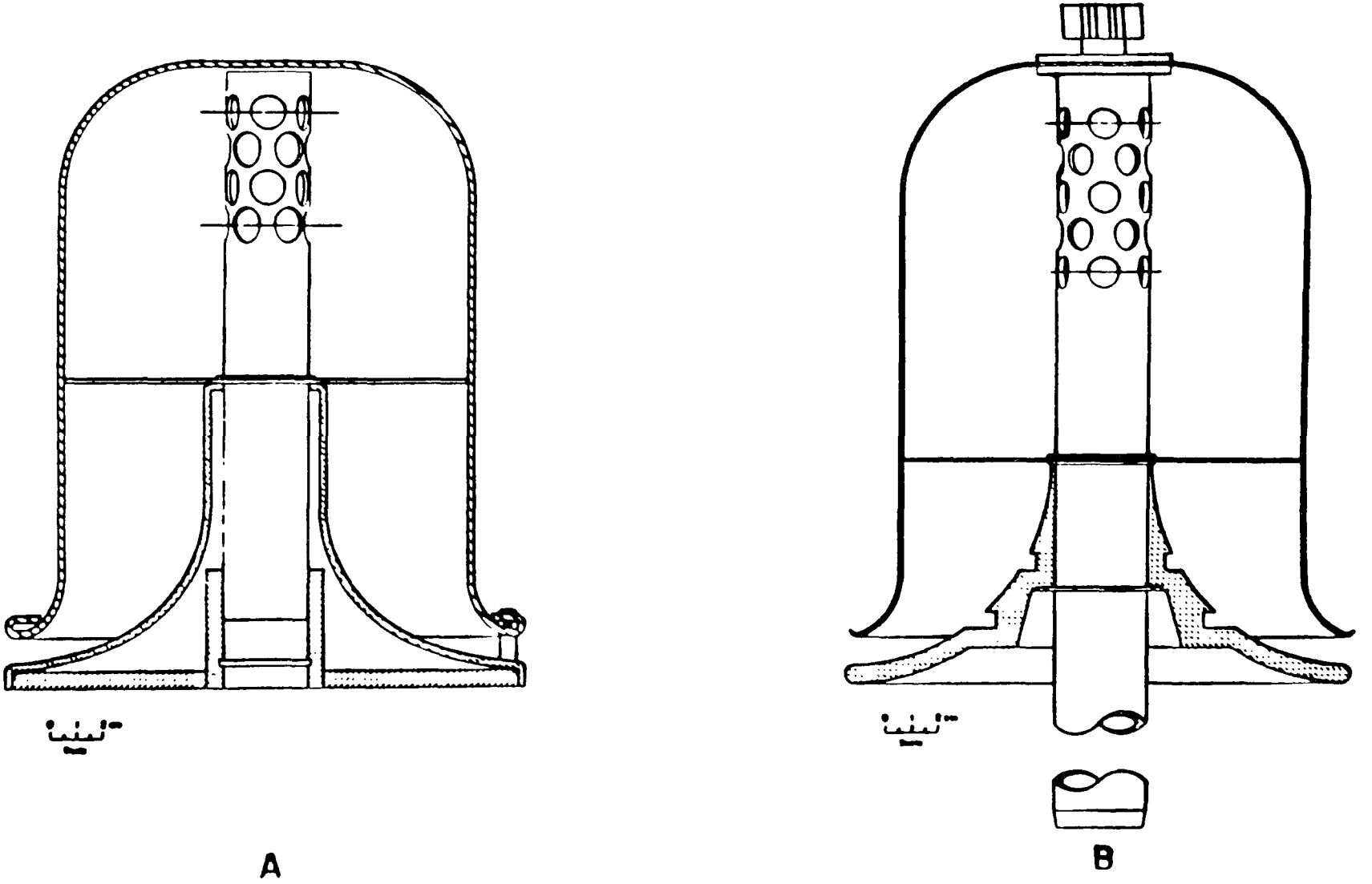



Figure 2-28. Inlets for the dichotomous virtual impactor (a) Sierra Model 244E (b) Beckman Automated Dichotomous Particulate Sampling System.

Source: Wedding et al. (1980)

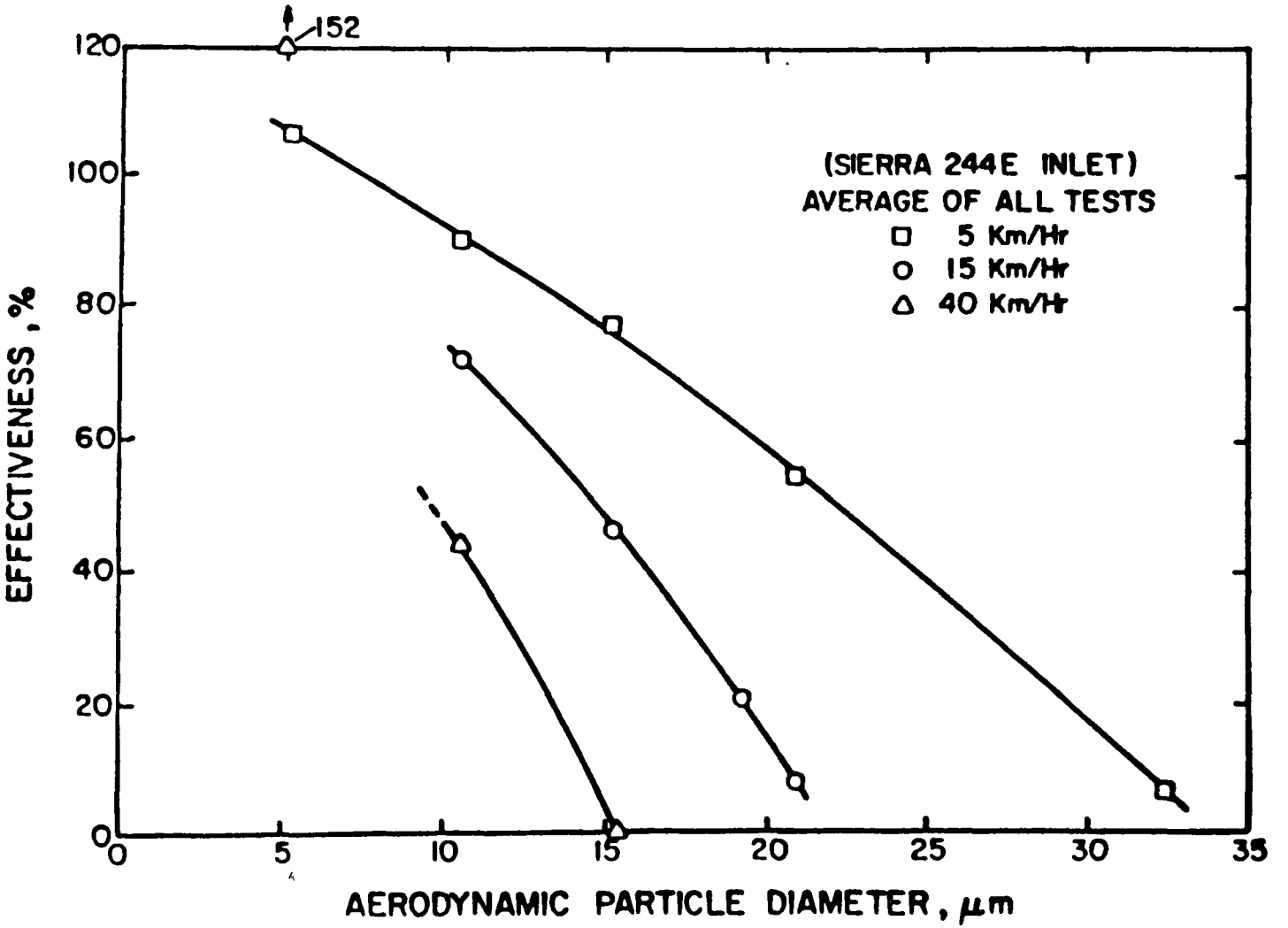



Figure 2-29. Sampling effectiveness of the Sierra Model 244E inlet vs. particle diameter for three wind speeds. The lines are arbitrary fits.
Source: Wedding et al. (1980)

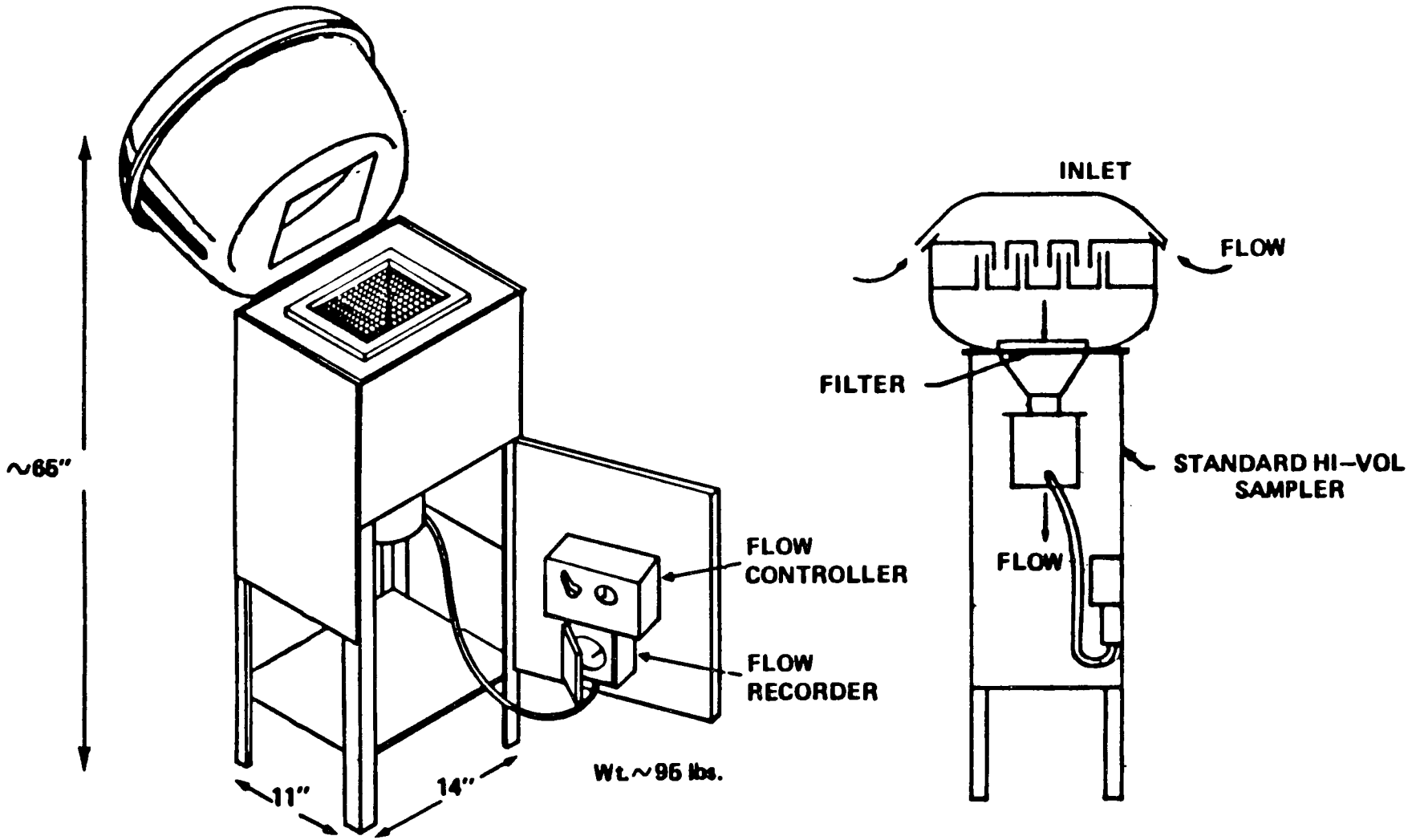



Figure 2-30. SSI hi-vol used in IP network.

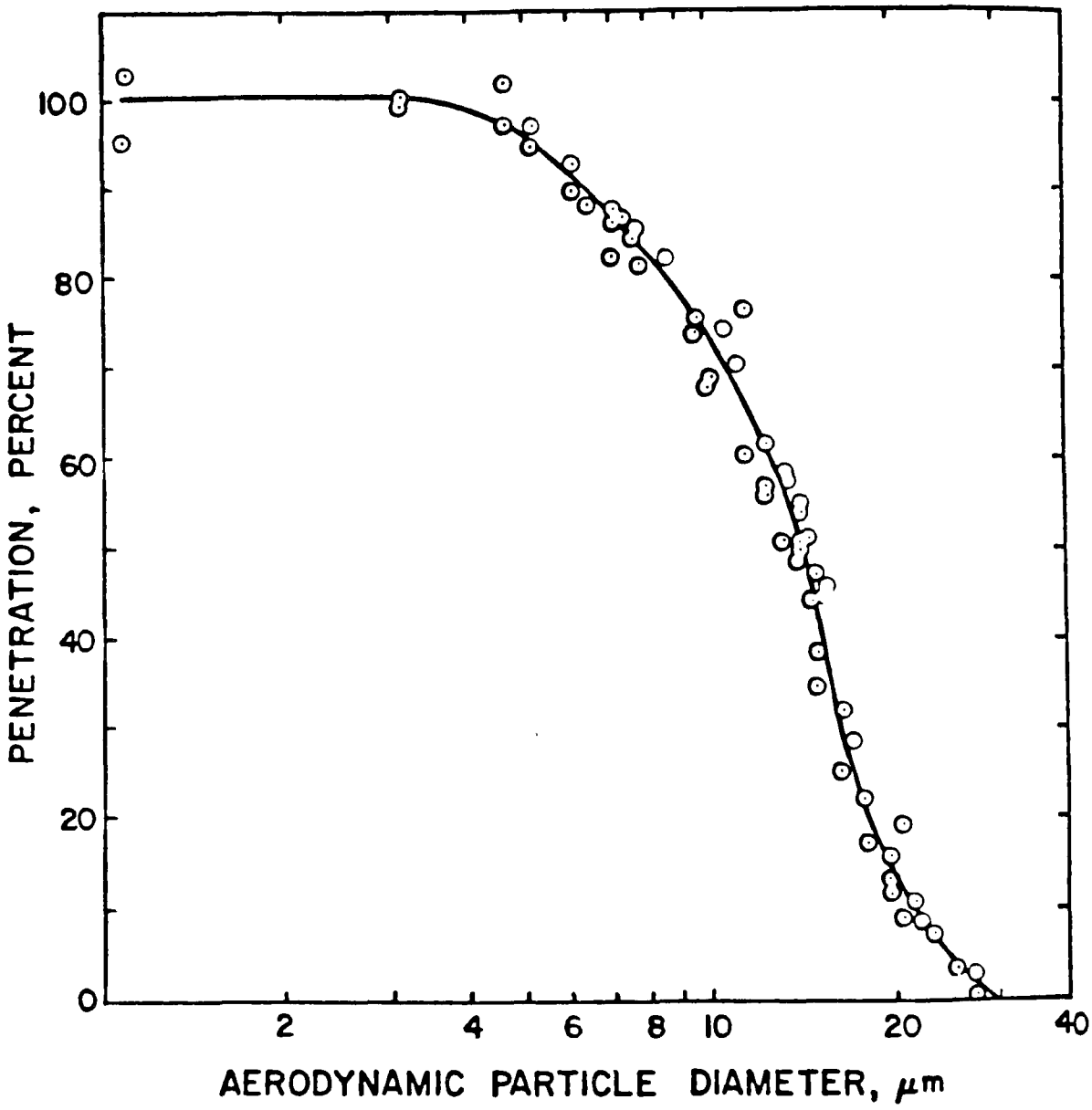



Figure 2-31. AEROSOL COLLECTION PERFORMANCE FOR THE SIZE SELECTIVE INLET HIGH VOLUME SAMPLER

Source: McFarland and Ortiz (1979).

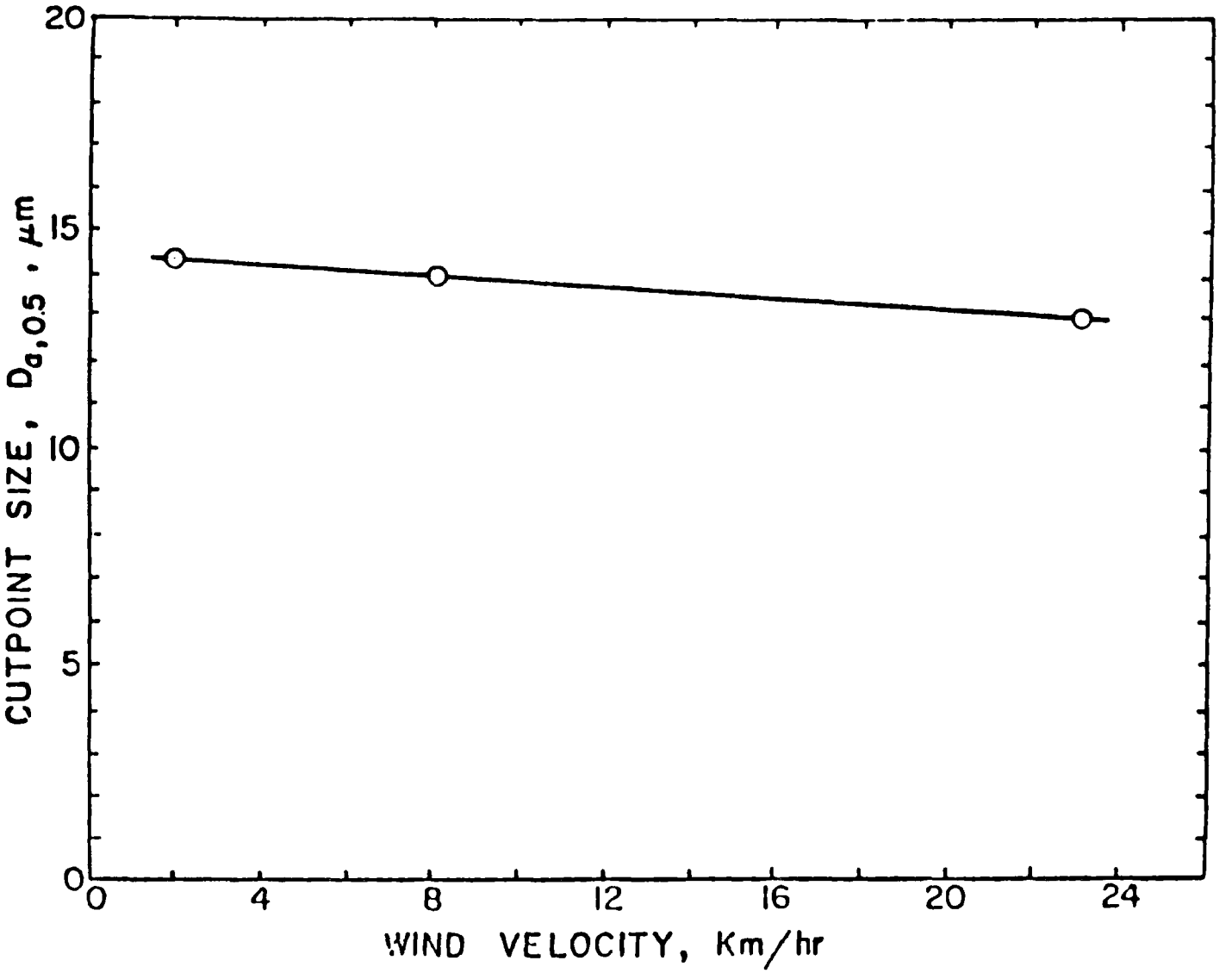



Figure 2-32. Effect of Wind Speed upon Cutpoint Size of SSI with Domed Roof

Source: McFarland and Ortiz (1979)

The glass fiber filter material is the same as that used for a TSP high-volume sampler, thereby presenting the same potential for artifact particulate formation. This size selective inlet (SSI) sampler, as with any size fractionating device, is somewhat sensitive to sampler flowrate for larger particles as shown in Figure 2-33. However, these data suggest that special flow controlling measures are not necessarily required to maintain consistent collection efficiencies over a range of sampler flowrates. The replacement of the gable roof of the TSP high-volume sampler with a size selective inlet effectively removes the directional sensitivity as well as the problem of large particle deposition when the sampler is not operational.

2.5.2.2.8 Dustfall sampling. Since the largest suspended particles have appreciable settling velocities, they are usually determined gravimetrically following collection by deposition in a dustfall jar as described by ASTM (1966). Although a cylindrical jar might be expected to collect the equivalent of the dust content of an air column of its own diameter extending to the top of the atmosphere, in fact the aerodynamic effects of the jar, the mounting brackets for the jar, and adjacent structures tend to complicate the collection pattern. As noted by Nadel (1958), only relative significance may be attached to the resulting data, and then only if conditions are carefully standardized. There is no definitive study of the effect of the height of the collector above ground on measured dustfall.

2.5.2.3 Calibration of Integrated Sampling Methods--Dynamic calibration of particle samplers by exposing the sampler inlet to known concentrations of ambient particulate matter is currently not technically feasible. Because of the variable nature of ambient particle size and shape, it is virtually impossible to accurately simulate a real situation.

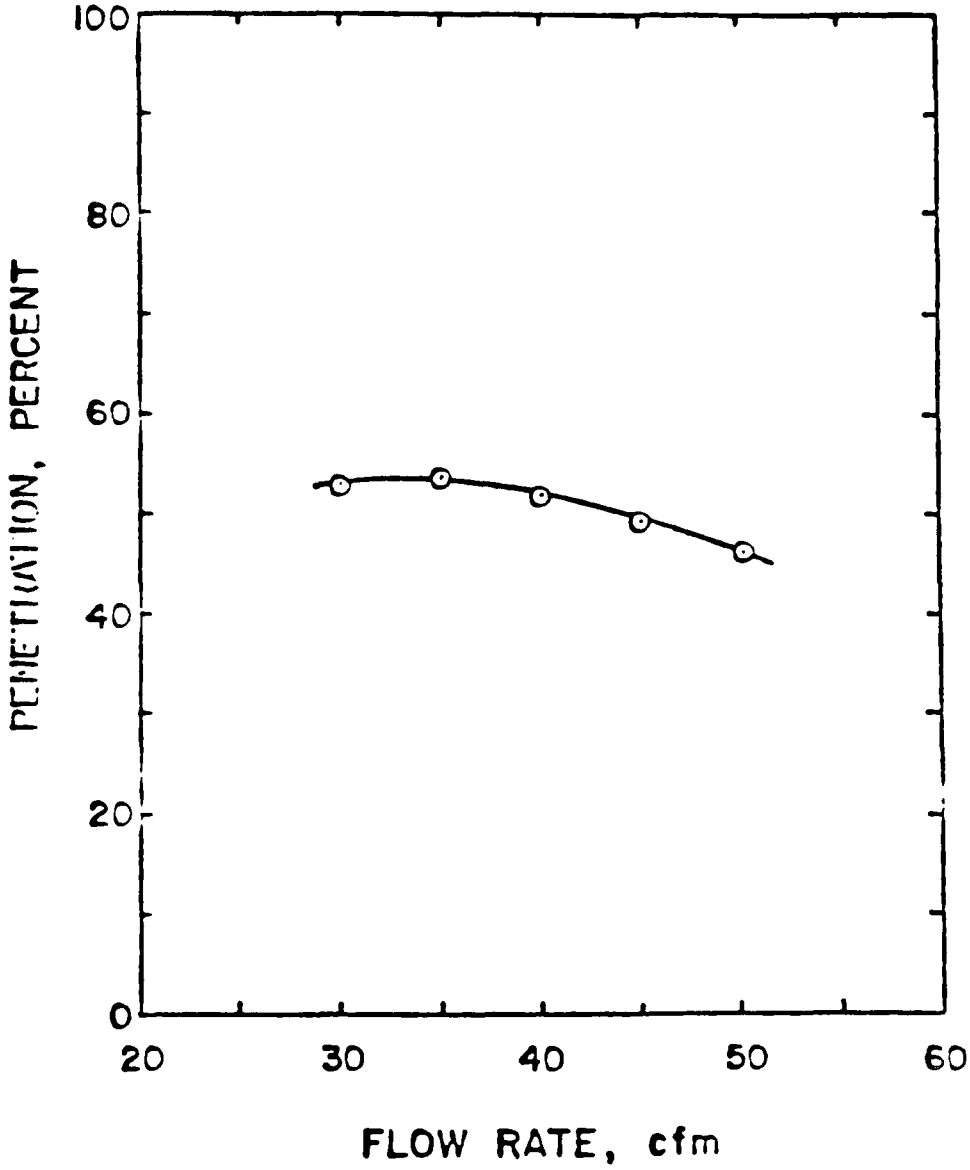



Figure 2-33. **Variation of Aerosol Penetration with Flow Rate. Particle Size = 14.1 μm. Wind Speed = 2 km/hr.**

Source: McFarland and Ortiz (1979)

Calibration of the sampler flow or volume measurement device is the only type of system calibration that can be performed in the field. Since all samplers used to measure particle concentration require a knowledge of the total volume of air sampled, the accuracy of this measurement bears directly on the concentration measurement. Typically, NBS-traceable fixed volume flowmeter standards such as spirometers are used as reference devices against which flowrate transfer standards such as orifices, mass flowmeters, or rotameters are certified. These transfer standards are then used in the field to calibrate the flow indicator device on the sampler. Correction for ambient temperature and pressure must be made properly as described by Smith et al. (1978). The EPA Quality Assurance Handbook, Volumes I and II, (von Lehmden and Nelson, 1977 a and b) provide additional guidance on quality assurance procedures.

The performance characteristics of particle samplers can be tested with monodispersed (single size) particles which are usually spherical in shape and near unit density. The sampler inlet is placed in the particle-laden air stream of a wind tunnel, and the sampler is operated to collect the artificial particles. Isokinetic nozzles in the wind tunnel are used as reference samplers against which the sampler results are compared. Wedding et al. (1977) and McFarland and Rodes (1979) describe such test systems. The results for various windspeeds, sampler orientations, and turbulence levels can be determined under controlled conditions to produce plots of particle collection efficiency versus particle size for the sampling system or its individual components. Testing with both wet and dry particles may be important to examine worst case collection characteristics such as wall loss and particle bounce.

Additional particle sampler testing needed to characterize the nature and quality of collected samples consists of side-by-side sampler tests to determine

reproducibility, and tests to determine the sensitivity of the sample collection to factors such as manufacturing tolerances and sampler flowrate.

2.5.2.4 Analysis of Particulate Samples

2.5.2.4.1 General considerations. Following collection of a particulate sample at the monitoring site, the sample must be analyzed to determine the desired quantitative (or qualitative in some cases) measurement result. For simple analytical techniques such as optical density, optical reflectance or beta density, the analysis may be carried out at the monitoring site. More commonly, the exposed filter or collection surface is returned to a laboratory for analysis. During this transfer, care must be exercised to avoid loss of fibers or particulate matter from the filter or collection surface and to protect the sample from damage or conditions that may affect the analytical result. Sometimes special filter cartridges or filter holders are used to safeguard the sample. Also transferred with the sample is an information record containing the site and sampler identification, sample air flow readings or total sample air volume, quality assurance data, and other information pertinent to the sample.

2.5.2.4.1.1 Filter conditioning. Most filter materials used for particulate sampling are reasonably insensitive to changes in humidity; however, collected particles can be hygroscopic. For samples to be analyzed gravimetrically, the weight of absorbed moisture could have a significant effect (Tierney and Conner, 1967). Therefore, such filters are normally conditioned prior to weighing. Conditioning consists of maintaining the filter in an environment with constant humidity until moisture equilibration is achieved--usually about 24 hours. The humidity level used is somewhat arbitrary, but should be less than about 50 percent relative humidity to avoid significant weight error due

to moisture (Tierney and Conner, 1967). Excessively low humidities may aggravate weighing errors due to static charges. Best results are obtained when the humidity of the weighing environment is about the same as that of the conditioning environment. For uniformity, the unexposed filters are also conditioned prior to the preexposure weighing. No conditioning is usually necessary for optical analyses, but analysis by beta attenuation may require moisture conditioning.

2.5.2.4.1.2 Artifact mass. Artifact particulate matter, which can be formed on the surfaces of alkaline filter materials such as glass fiber by oxidation of acid gases in the sample air, results in an artifically high particulate measurement. This surface-limited effect usually occurs early in the sample period and is a function of the filter pH and the presence of acid gases. While usually accounting for only a small part of the collected particulate sample, the error can be more significant for short sampling periods or where the total amount of particulate matter collected is very small. Use of a neutral pH filter material such as Teflon® minimizes the formation of artifact material on the filter; however, as noted by Pierson et al. (1980), particulate nitrates collected on inert surfaces such as Teflon® and quartz can exhibit significant metathetical losses in the presence of acid aerosols, causing an underestimation of the true concentration.

Reactions between various particulates collected on the filter are also possible. While such reactions may not significantly affect gravimetric determinations, they could affect chemical analysis of the sample.

2.5.2.4.1.3 Loss of volatiles. Volatile particles collected on the filter may be lost or partially lost during subsequent sampling, during transport to a laboratory for analysis, or during storage before the

post-exposure weighing. Filters are normally analyzed as soon after collection as is practical, but some loss of volatiles is inevitable. For gravimetric analyses, these losses may tend to compensate to some extent for artifact particulate formation.

2.5.2.4.1.4 Airflow variation. The amount of particulate material collected on the filter represents the (integrated) sum of the instantaneous products of the sample air flowrate times the particulate concentration during the sample period. Dividing the total quantity of particulate collected by the averaging sample flowrate over the sample period yields the true particulate concentration only when the sample flowrate is constant over the period. The error resulting from a nonconstant flowrate depends on the magnitude of the instantaneous changes in the flowrate and the particulate concentration.

Many high-volume samplers used in recent years are equipped with constant flow regulators to avoid air flow variation. However, measurements from older high-volume samplers, which do not have flow recorders or use flow regulators, may suffer significant error due to flow variation. Significant flow variation can be expected from heavy filter particulate loading, high relative humidity, substantial ambient temperature and pressure changes, and sample pump variation. Flowrates in low-volume samplers tend to be somewhat more stable because of characteristically higher impedance flow systems.

2.5.2.4.1.5 Air volume measurement. Another potential source of error from flowrate variation in samplers not equipped with a flow regulator is in the estimation of the total air volume sampled. Typically, an average flowrate over the sampling period is determined from measurements of the actual flowrate before and after the sample period. When the flowrate changes nonlinearly during the sample period, as may be characteristic during conditions

of filter loading, malfunction of the flow regulator, etc., the linear estimation of the average flowrate may not be accurate. The addition of a flow recorder permits exact integration of the high-volume sampler flowrate during the sampling period.

2.5.2.4.2 Mass concentration determination. Simplest of the particulate sample analyses is the estimation of the mass concentration of the particulate in the ambient air. This may be achieved directly by a gravimetric determination or indirectly by one of several nongravimetric techniques. Where the particulate sample has been fractionated by particle size, mass concentration for each size range may be determined.

Sample air volumes are determined either by measuring the total volume of air actually sampled or by estimating the total sample air volume as the product of the sampling time and the average sample flow rate. For samplers equipped with a constant flow regulator, the average flowrate is identical to the constant, controlled flowrate. However, for unregulated samplers, the average flowrate itself may have to be estimated from pre- and post-exposure flow measurements. Since an unregulated flow may be likely to change during the sample period, some error in the final computed particulate concentration may be expected, as described previously. Some samplers have a flowrate recorder to provide a continuous record of the flowrate over the sampling period, from which a better estimate of the average flowrate can be derived. In all cases, air volume measurements and particularly flowrate measurements are determined from the sampler flow or volume indicator readings via the calibration relationship for the indicator established during sampler calibration. These measurements may be further corrected for the actual temperature and pressure at the sampling point during the sampling period.

Sampled air volumes are usually corrected to a reference temperature 25°C and a pressure of 760 mm Hg (U.S. Environmental Protection Agency, 1979 b). Accordingly, mass concentration is typically reported as mass (micrograms) per standard cubic meter of air (μg/std $m^3$; however, the "std" is often omitted). If desired, the actual, physical mass concentration (μg/$m^3$) can be computed from the reported concentration by correcting back to the actual temperature and pressure that prevailed at the time and place the sample was collected.

2.5.2.4.2.1 Gravimetric determination. Mass concentration is determined directly by dividing the mass (weight) of the collected particulate by the total (standard) volume of air sampled. Filters are conditioned and weighed before and after exposure to determine the particulate mass as the net weight gain of the filter or other collection surface. In addition to potential errors described earlier, errors are possible in the weighing operation. High-volume samplers generally collect sufficient particulate matter to be weighed with a semi-micro balance and commensurate weighing techniques. However, lower volume samples, and particularly size-fractionated samples, often require weighing with a micro balance and more sophisticated weighing techniques to achieve adequate precision.

2.5.2.4.2.2 Nongravimetric methods. Several nongravimetric analytical methods are or have been used to estimate the mass concentration of particulate matter in the atmosphere. In general, such methods rely on the measurement of a property of the collected sample (as it is thinly and presumably uniformly deposited on a filter matrix) that is closely related to mass. Common examples include reduction in reflected light (British Smoke Shade sampler and tape sampler-RUDS), attenuation of transmitted light (tape sampler-CoHs), and attenuation of transmitted beta radiation. Typically, these techniques are

either used as a relative indicator of particulate levels or are "calibrated" in terms of mass units by empirical, statistical comparisons with samples collected concurrently at the same site and analyzed gravimetrically.

2.5.2.4.2.3 Optical determination. Optical analyses of integrated samples are made on samples collected by the British Smoke Shade sampler and AISI tape sampler. The reflectance measurement procedures for the British Smoke Shade filters and AISI tapes are described in detail in the World Health Organization's "Selected Methods of Measuring Air Pollutants" (WHO, 1976). The reflectance smoke shade measurements, using specific laboratory reflectance meters, are delineated along with the empirical relationships permitting conversion to equivalent $\mu g/m^3$. The smoke shade reflectance meter is calibrated at zero percent against a standard black tile and 100 percent for a standard white tile. An example of one of these calibration plots is shown in Figure 2-34. Note that this curve applies to only one spot size. As an alternative to using the standard plots, a specific site relationship can be obtained by operation of a standard high-volume sampler together with a smoke shade sampler.

Transmittance measurements of tape sampler filter spots are made with a simple white light transmissometer which is scaled from zero at total blackness to 100 percent for a clean portion of the filter. A conversion equation using the percent transmittance values, flowrates, sampling times, and spot size is used to calculate the quantitative result in CoHs/1000 linear feet (305 linear meters).

2.5.2.4.2.4 Measurement by beta ray attenuation. For projects in which an automated instrument is needed to measure large numbers of samples (Goulding et al. 1978; Loo et al. 1978) or in applications where real time mass measurements (Macias and Husar, 1976) are needed, mass measurement by beta-ray attenuation is attractive (Liliennfeld, 1970). In a device called a beta gauge, one

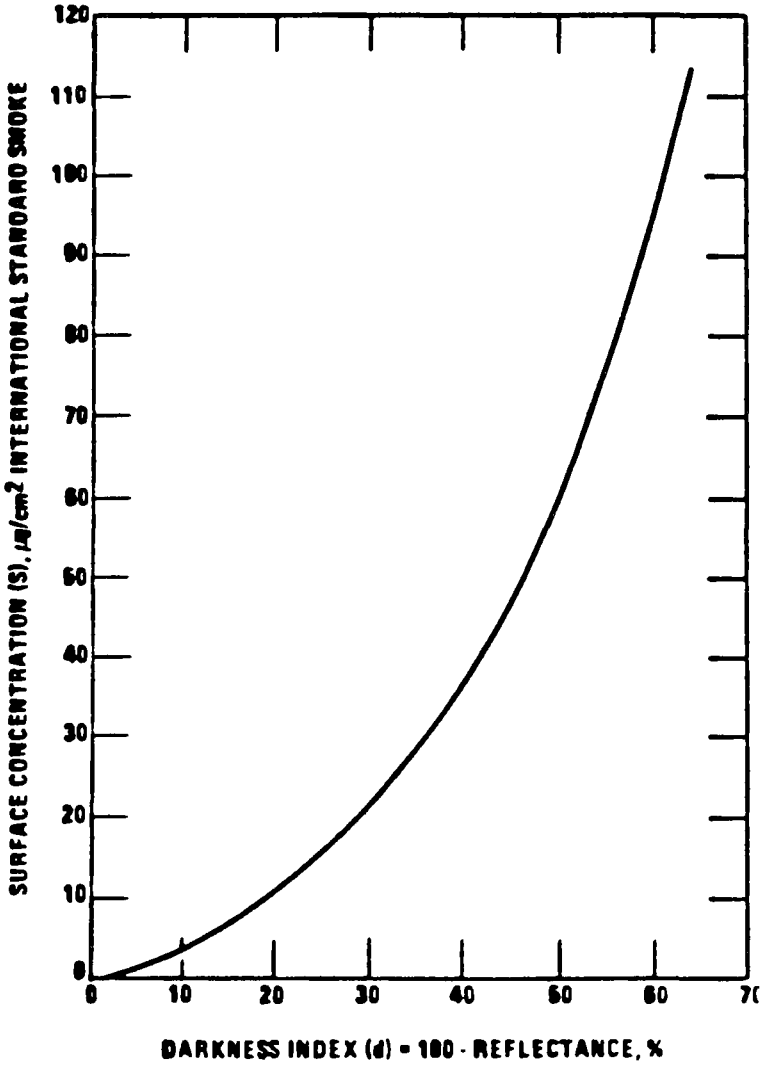



Figure 2-34. OECD proposed international standard calibration curve; Photovolt reflectometer - Whatman No. 1 filter paper, 25-mm diameter.

Source: WHO (1976)

measures the extent to which a sample attenuates beta rays from a radioactive source, such as $^{63}Ni$, $^{14}C$, or $^{147}Pm$. For aerosol measurements, the beta ray attenuation must be measured on each membrane filter before sampling and again after an aerosol deposit is collected. A set of gravimetrically prepared standards are needed to relate the results to units of mass. Investigators (Macias and Husar, 1976; Goulding et al. 1978) have studied the dependence of the beta ray absorption coefficient on elemental composition of the sample. Goulding et al. (1978) have found the dependence on composition to be very slight for the ranges of average compositions that occur in aerosol samples.

In a recent interlaboratory comparison of aerosol sampling and measurement methods (Camp et al., 1978), it was demonstrated that laboratory beta gauge measurements of ambient aerosols collected by dichotomous samplers on Teflon® filters compared favorably in precision and accuracy with gravimetric analyses. Further studies to compare beta gauge and gravimetric measurements are in progress. Principal sources of error in the method are: (1) possible changes in the geometry of the beta source, filter substrate, or detector between the pre- and post-sampling measurements, and (2) absorption of water from the atmosphere by the filter material or the collected particulate (Lawrence Berkeley Laboratory, 1975).

2.5.2.4.3 Particle sizing determination of filtered particles. Examination of polydispersed particles on filter and inertial impaction substrates to provide size distribution information is typically performed either by microscopy or by using electrical resistance counters after resuspension in a liquid medium. Microscopy is the most straightforward, and sizing is practical with a reticle-equipped light microscope for particles larger than about 0.5 μm; smaller particles cannot be differentiated with a light microscope, and must

be examined with an electron microscope. Statistical counting techniques must be applied when examining only a portion of the particles on a filter to obtain reliable number distributions by particle size. The collection substrate is also critical; a non-fibrous filter or impactor plate which maintains the particles on its surface is needed for accurate counting.

Another technique for evaluating particles collected on a surface is electrical resistance counting using the Coulter Counter®. This method requires resuspension of the particles from the collection surface in a suitable liquid medium. The liquid suspension is passed through a small orifice in a detector cell where the change in electrical resistance of the liquid suspension is measured. The change in resistance is proportional to the volumetric particle size, and use of discrete channel analysis provides a size distribution. A conversion factor is necessary to convert from volumetric size to aerodynamic diameter. The particle size range capability extends from 0.5 to 200 μm.

2.5.2.4.4 Chemical analysis. Analysis of trace elements. Most methods for trace element analysis of atmospheric particulate material utilize spectroscopic detection. They respond only to the presence of an element and provide no information about chemical compounds. Most tell nothing of the oxidation state of the element.

2.5.2.4.4.1 Atomic absorption spectrometry. Atomic absorption spectrometry (Ahearn, 1972) is widely employed for quantitative elemental analysis of airborne particles. It involves, usually, an acid extraction and excitation of the solution by a flame. Light of a wavelength characteristic of the one element of interest is made to traverse the flame. The amount of light absorbed is related to the quantity of the element present. Special high temperature furnaces can be employed instead of a flame.

Individual elements must be determined sequentially. Thus, although any element can be determined for which a lamp is available to produce the characteristic light, airborne particulate samples are often large enough for only half a dozen determinations to be made. Moreover, some trace elements present in airborne particles (including antimony and arsenic) may require the application of special methodology.

Atomic absorption is subject to significant interferences and can lead to substantial errors. If recognized, these errors can generally be overcome or eliminated to produce good quantitative analyses at the expense of additional effort on each sample. Despite its drawbacks, atomic absorption spectrometry still ranks as a useful method for elemental analysis of airborne particles. It seems likely, however, to be superceded in the future by techniques capable of multielement determinations.

2.5.2.4.4.2 Optical emission spectrometry. A variety of ways can be used to excite rather loosely bound electrons in elements and observe characteristic emissions as de-excitation occurs. The wavelength is characteristic of the element, and the intensity is an indication of the quantity of the element present. The most desirable excitation technique is argon plasma excitation of an acid extract of the particulate matter (Lambert and Wilshire, 1979).

Plasma spectrometry can be more advantageous than atomic absorption, since sample preparation and analysis rates are essentially equal. However, emission techniques can simultaneously determine up to perhaps 50 elements, with detection limits about the same as those of flame atomic absorption. It is also more interference-free than atomic absorption, although interferences are not absent.

2.5.2.4.4.3 Spark source mass spectrometry. Spark source mass spectrometry (Morrison, 1965) can analyze airborne particulates if they can be separated

from the filter and oxidized, or they can be extracted with an acid. Spectral interferences are important, but can generally be overcome by employing a spectrometer with high resolution.

The precision obtained depends on the way the analysis is performed but can be about 30 percent (relative standard deviation) in careful work. Accuracy, as with any multielement technique, may depend on the element and the matrix in question. The advantage of this technique is that it can simultaneously estimate the quantity of every nonvolatile element in the periodic table and do so with roughly equal sensitivity. Large numbers of samples, however, cannot be analyzed in a day.

2.5.2.4.4.4 Neutron activation analysis. Neutron activation analysis (Morrison, 1965; Goold, 1976) implies a variety of distinct methods all of which produce unstable nuclei which emit γ-radiation. Gamma-ray energy and intensity are indicators of the element and its quantity. Instrumental thermal neutron activation analysis is most commonly used. With this approach, a nuclear reactor is used to produce unstable nuclei. The method can simultaneously determine up to perhaps 25 elements in particulate samples collected by high-volume samplers.

An advantage of instrumental activation analysis is that airborne particles can be analyzed as received directly on the filter surface.

2.5.2.4.4.5 X-ray fluorescence spectrometry. X-ray fluorescence spectrometry (Morrison, 1965; Fassel, 1978) involves excitation of tightly bound electrons and observation of the x-ray emission as de-excitation occurs. Excitation may be done by a variety of techniques, but use of an x-ray generator is most common. Detection may either be multielement (up to perhaps 30) energy dispersive detection or only one to a few (up to perhaps 10 elements) by wavelength dispersive detection. Only elements with atomic numbers greater than that of

magnesium can be analyzed. Particles can be analyzed nondestructively directly on a filter; however, samples must be thin and of uniform surface texture or uncertain corrections must be made. Interferences are common and must be considered. Adequate calibration can be a problem, but a reasonable sample analysis rate can be achieved.

2.5.2.4.4.6 Electrochemical methods. Electrochemical methods have been used to a limited extent to determine a small number of elements in airborne particles. These methods include potentiometry with ion selective electrodes and polarography and anodic stripping voltammetry (Morrison, 1965). Electrochemical methods have few advantages for airborne particle analysis, aside from their low initial capital equipment costs when compared with other techniques.

2.5.2.4.4.7 Chemical methods. Many wet chemical procedures constitute the classical methods employed for trace element analysis of airborne particles. In general, a colorforming reagent is involved, and the amount of a given element present is determined by the extent of color development. Probably the best known of these procedures is based on the use of dithiocarbazone (dithizone) (Snell, 1978) as the colorimetric reagent for lead. Wet chemical procedures are labor intensive and slow compared with spectral techniques, particularly since only one element can be determined at a time. Interferences can also be a problem.

2.5.2.4.4.8 Analysis of sulfates and $NH_4$. Analysis of sulfates and $NH_4^-$ is covered in Section 2.4 of this chapter.

2.5.2.4.4.9 Analysis of organics. Procedures to estimate the total mass of benzene extractable organic material in TSP have been employed occasionally. A portion of a high-volume filter is placed in a soxhlet extractor and refluxed with benzene for several hours. The benzene is then volatilized, and the mass

of the residue is measured and reported. Utilization of this procedure now presents very special problems because of the requirements for handling benzene.

Methods to identify and determine individual organic species present in airborne particles abound. These schemes utilize different sequences of solvent extractions which separate groups of different organic species based on their solubility. Solutions are often subjected to chromatographic separation with mass spectral detection. For organic compounds volatile at temperatures up to about 300°C, gas chromatography-mass spectrometry (GC-MS) (McFadden, 1973) can be employed. For organic species with lower volatility, liquid chromatography might be used. High performance liquid chromatography (HPLC) (Kirkland, 1971) is typically used, but none of these procedures permit a high rate of anaysis.

For one species of longstanding interest, benzo-α-pyrene (BaP), thin layer chromatography (TLC) with fluorescence detection is often used, and HPLC procedures have been proposed. The TLC procedure requires a cyclohexane extraction, spotting, and development of a TLC plate and fluorescence detector. This procedure is more interference-free than some HLC methods and has a higher production rate (Swanson, 1978).

2.5.3 Continuous Sampling Methods for Particulate Matter

2.5.3.1 Introduction--Continuous or *in situ* measurement methods for ambient particles do not provide mass concentration directly as integrated sampling methods can. These devices examine one or more aspects of atmospheric particles, such as the particle size distribution or light scattering ability. This information is valuable in research efforts to qualify the sources, transformation, and transport of particles in the atmosphere, but may not be directly usable for regulatory monitoring to support a particle standard.

The integrating nephelometer, because of its simplicity of operation, may prove to be useful for real time determination or prediction of fine particle episode situations. Its utility as a visibility monitor, especially in areas concerned with prevention of significant deterioration (PSD), is being investigated.

2.5.3.2 Integrating Nephelometer--The most commonly used nephelometer for continuous particle monitoring is the integrating nephelometer, which measures the differences in light scatter caused by varying particle concentrations in the air stream. These differences can be related to the scattering coefficient ($b_{scat}$ with units of $m^{-1}$) and the particle size distribution present, but are normally expressed in terms of visible range in kilometers (Friedlander, 1977). The initial designs for this technique were made by Buttell and Brewer (1949) and subsequently improved by Ahlquist and Charlson (1967). Light scattering is at a maximum for particles in the 0.3 to 0.8 μm range, as shown in Figure 2-35, and hence the response of techniques based on this principle must be corrected for particle size effects. Light scattering is primarily caused by accumulation mode particles and only slightly affected by particles in the nucleation or coarse particle modes. Comparisons between nephelometer and high-volume sampler mass concentrations, such as those by Charlson et al. (1968), showed that a reasonable correlation existed under the conditions tested. Comparison with any integrated sampling method in which the coarse particle mode is variable will provide erratic, site-dependent results. As noted in Airborne Particles (National Academy of Sciences, 1979), $b_{scat}$ is also significantly affected by relative humidity and the particle refractive index.

2.5.3.3 Condensation Nuclei Counter--The condensation nuclei counter measures the total light scatter of submicron particles by increasing their size by condensing vapor from a cloud chamber onto their surface. This device is of

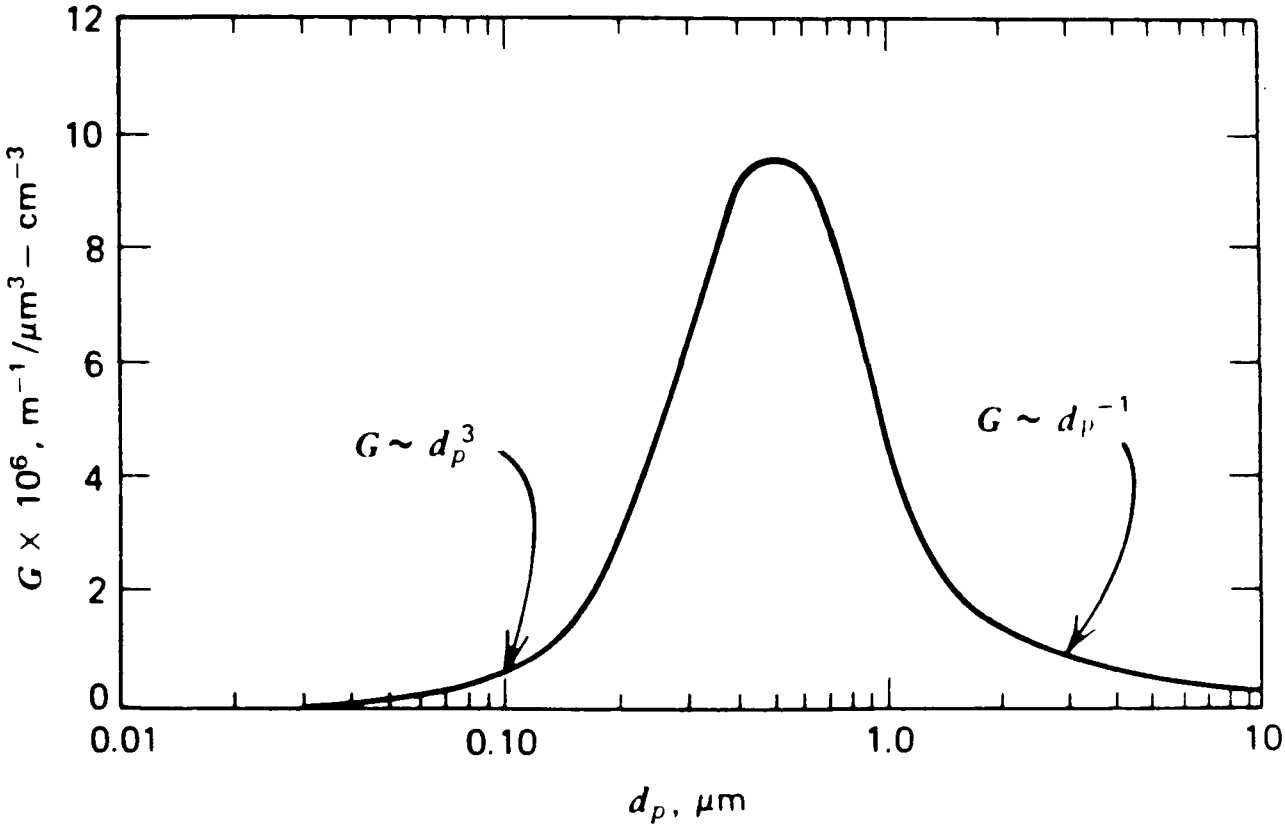



Figure 2-35. **Light scattering per unit volume of aerosol material as a function of particle size, integrated over all wavelengths for a refractive index, $m$=1.5.**
**SOURCE: BELZ and TUVE, 1970**[51]

Source: Bolz and Turve (1970)

interest in examining the number of particles in the nuclei mode, but is not useful for particle sizes above about 0.5 μm (Perera and Ahmed, 1978).

2.5.3.4 Particle Size Distribution Counters--Single particle counters provide discrete size-distribution information, but most are classed as research measurement devices, not routine monitors, and cover only selected portions of the size spectrum. The Electrical Aerosol Analyser, as originally described by Whitby and Clark (1966), measures the electrical mobility of particles as related to their size. Within several minutes, this device provides a detailed size distribution over the range of approximately 0.01 to 0.5 μm electrical diameter (Liu and Pui, 1975). The unit must be empirically calibrated to obtain the relationship to aerodynamically sized particles. The Diffusion Battery, as described by Sinclair et al. (1979), is a set of tubes through which the air stream flows to produce selected differential particle removal by diffusion to the walls as a function of particle size. A condensation nuclei counter is used as the particle counter. This diffusion separation principle is useful only in the range from 0.01 to 0.1 μm.

Optical versions of single particle counters direct the flow stream through a small nozzle such that the light scatter from single particles can be measured. This scatter produces a signal which is related to the size of a spherical particle which scatters an equal amount of light. These devices produce a size spectrum of particle sizes from about 0.5 to 10 μm (Whitby and Willeke, 1979). Calibration with monodispersed particles is required. For sampling of particles larger than 10 μm, modification of commercially available devices would be required. Mass concentrations for specific size ranges can be estimated by selecting an appropriate particle density.

2.5.3.5 Visibility Monitors--Visibility is usually interpreted to mean visual range; however, this quantity is not directly measurable as described by Malm (1979). The measurements of light scattering, color, and contrast changes can be used individually to provide a measure of visibility change, but a combination of measurements may be required to provide reliable correlation with human eye observation. In urban areas, the reduction in visual range may also be aggravated by $NO_2$ absorption. Friedlander (1977) shows that the extinction coefficient (b) is equal to the sum of the coefficients for scattering ($b_{scat}$) and absorption ($b_{abs}$). Therefore, the nephelometer, which measures only $b_{scat}$, may not provide a true indication of visible range at all locations. Another drawback to visual range estimation with the nephelometer is the fact that it is a point measurement integrated over a viewing angle range rather than an integrated measurement over a measured distance. The interrelation of $b_{scat}$ to visibility is very complex, and is discussed in detail by Malm (1979) and in Airborne Particles (National Academy of Sciences, 1979).

Long path optical measurement devices for ambient air are available to examine an aspect of visibility over a defined distance. Transmissometers measure the attenuation of transmitted light resulting from scattering and absorption in the atmosphere. These devices are similar to their in-stack counterparts, requiring either a light source and receptor or light source and retroreflector at separate locations. Telephotometers measure the contrast caused by brightness differences between a distant object and its surroundings. The advantages and disadvantages of these long path devices compared with other visibility monitors is currently under investigation by EPA.

### 2.5.4 Summary - Measurement Techniques for Particulate Matter

Measurement of atmospheric particulate matter includes quantification of the mass concentration, categorization of the particulate mass into various particle size ranges of interest, quantitative chemical analysis, and to a lesser extent, determination of direct effects such as reduction in visibility. The majority of particulate measurements are made by the integrated collection of particles from a measured volume of air over a significant time interval using either filtration or impaction on a substrate material. The collected particulate samples are usually analyzed gravimetrically to provide a direct measure of mass concentration when related to the volume of air sampled. Non-gravimetric techniques must be calibrated in mass units by empirical comparison with gravimetrically analyzed samples. Most of the mass measurement techniques are non-destructive, such that the particulate sample is available for chemical analysis if the quantity of sample permits.

Current ambient particle size discrimination is typically accomplished by specific geometrical design of the sampler inlet. Following or in conjunction with this mechanical separation, particles of one or more size ranges are collected on separate substrates. Most samplers have an inherent upper limit on the size of particles collected, since large particles are very difficult to transport to the collection surface without substantial losses. This limit may be as low as 4 to 5 μm or as high as 50 to 60 μm, depending on the sampler configuration.

The high-volume sampler as specified in the current EPA reference method is widely used for gravimetric analysis of mass concentrations. Operating for periods up to 24-hours at a flowrate of over 1 $m^3$/min, the sample is large enough to be suitable for a wide variety of chemical analyses. The sampler

design is unsophisticated and a number of shortcomings have been reported. The particle collection characteristics have only recently been quantified. A recently-designed size-selective inlet head is available for the high-volume sampler to restrict the collected particulates to the 0 to 15 μm inhalable particulate range.

The optically based British Smoke Shade and AISI tape samplers are also simple in design. These techniques have been widely used in early monitoring studies. Efforts to compare them with high-volume sampler mass concentration measurements are hampered by the differences in particulate size range collected.

Multi-stage cascade impactors segregate various particle size ranges by controlled jet velocities and impaction of the particles on collection surfaces for gravimetric analysis. Both high flow (0.6 to 1.1 $m^3$/min) and low flow (0.01 to 0.04 $m^3$/min) impactors have been used to develop particle mass size distributions, but the inlet cutoff characteristics of most impactors have not been adequately determined. The devices are not widely used in monitoring networks because of manual labor requirements for sampling and analysis. Cyclone samplers are also used for ambient particle size fractionation, usually providing a cut point in the 2 to 4 μm range.

The dichotomous sampler is of recent, more sophisticated design and provides particulate samples in two size ranges: 0 to 2.5 μm and 2.5 to 15 μm. The 15 μm cutoff coincides with the range currently defined by EPA for Inhalable Particulates (IP) and is obtained by inlet geometry. The 2.5 μm cut is achieved by the principle of "virtual impaction," and provides coarse and fine particle fractions helpful in separating the atmospheric bimodal particle distribution and identification of particulate sources. The low sample flow (about 1

$m^3$/hour) results in a small mass of collected material as compared with the high-volume sampler and requires micro-balance weighing techniques.

Dynamic aerosol calibration of particulate samplers is not feasible except under laboratory conditions, but the sampler's flow indicator can be calibrated against a reference volumetric standard. The performance characteristics of particulate samplers can be determined under laboratory conditions with artifically generated monodispersed particles using a wind tunnel.

Gravimetric analysis of particulate samples requires filter conditioning to minimize interference from moisture and static change. Other sources of error include formation of artifact particulate matter, loss of volatiles, air flow variation during sampling and weighing errors. Optical analysis involves the use of an appropriate reflectance or transmittance meter with suitable 0 and 100 percent references as prescribed in the respective procedures.

Manual wet-chemistry analyses of particulate samples are being rapidly replaced with automated spectroscopic methods. Some of the methods such as atomic absorption require transfer of the particulate matter to a liquid media. Other methods such as X-ray fluorescence spectrometry provide non-destructive analyses. Most of the methods provide elemental, cation, or anion identification and not information about chemical compounds or oxidation state. Atomic absorption is widely used for quantitative analysis for a variety of elements with each element analyzed sequentially. Optical emission spectrometry can also determine a variety of elements, but simultaneously and with fewer interferences than atomic absorption. Spark source mass spectrometry can be used for almost every nonvolatile element, but is not suitable for the rapid analysis of large numbers of samples.

Similarly neutron activation analysis is not rapid and some elements of particular interest such as lead and sulfur are difficult to determine. One of the more common non-destructive multi-element analysis techniques for elements heavier than potassium is x-ray spectrometry. Particle samples must be thinly deposited and preferably collected on a membrane filter substrate. Other less commonly used elemental analysis techniques include electrochemical methods such as potentiometry and anodic stripping voltammetry.

Analysis of a particulate sample for organics may include an estimate of the fraction of solvent (e.g., benzene) extractable organic material or identification of individual organic species. Benzo-α-pyrene (BaP) is a commonly determined organic analyzed by thin layer chromatography with fluorescence detection.

Methods for continuous or in situ monitoring of atmospheric particulates are available. Such measurements are not as closely related to mass concentration as the integrated methods, but provide useful information for studying particulate sources, transport, episodes, and effects such as visibility. The integrating nephelometer measures light scattering by atmospheric particles and is commonly used as an indicator of visibility. Its measurements are most sensitive to fine particles and show reasonable correlation with integrated samples of fine particles. Research monitoring devices which have been used to provide discrete particle number, volume, and/or surface area size distribution information include the electrical aerosol analyzer, the diffusion battery, and single-particle optical counters.

Visibility as detected by the human observer is actually a combination of factors including light scattering, color change, and loss of contrast. Visibility monitors, such as the integrating nephelometer, measure only light

scatter and do not provide an accurate indication of visual range. Long-path instruments, now under development, may provide better measurements of visibility.

Historical interpretations of total suspended particulate data as collected by the high volume sampler have often been clouded because this sampler is sensitive to ambient wind speed and direction. In situations where the mass contribution of large particles in the size distribution was very small, the effect of these errors was minimal. During periods of elevated winds or near fugitive dust sources, however, the high volume sampler can underestimate the true mass concentration substantially.

Extremely sharp inlet cutoff for size selective particle samplers are currently not a reality, and the acceptability of less than perfect size separation must be considered. Historical development work in particle separation techniques has concentrated on particle sizes less than 10 μm and specifically in the 2 to 4 μm range. Separation techniques for this latter range, including virtual impaction, inertial impaction, and cyclone separation, provide relatively sharp cutpoints. Since this size range tends to be the minimum in the size distribution between the accumulation and coarse particle modes, small differences in sharpness are often academic when considering total mass collected.

Particle separation for particles above 10 μm has been ignored until only recently when EPA defined the 0-15 μm inhalable particulate fraction. Techniques are currently commercially available to provide a 15 μm cutoff, such as the dichotomous sampler and a size selective inlet for high volume samplers. The current state-of-the-art, however, does not permit the sharpness of separation for large particles as is possible with the smaller particles. An assessment must therefore be made as to the utility of these less-than-ideal efficiencies for collection of samples to support specific monitoring objectives.

## 2.6 SUMMARY

Methods for the measurement of sulfur dioxide can be classified as integrated or continuous. Integrated methods can be direct or based on techniques involving absorption and stabilization in aqueous solution or adsorption and stabilization on a solid substrate. The analysis of the collected sample is commonly based on colorimetric, titrimetric, turbidimetric, gravimetric, and ion chromatographic measurement principles. The most widely used integrated method for the determination of atmospheric sulfur dioxide is an improved version of the colorimetric method developed by West and Gaeke and adopted as the EPA reference method in 1971. Sulfation methods, based on the reaction of $SO_2$ with lead peroxide paste to form lead sulfate, have commonly been used to estimate ambient $SO_2$ concentration over extended time periods. Continuous methods for the measurement of ambient levels of sulfur dioxide have gained widespread use in the air monitoring community. Continuous sulfur dioxide analyzers using the techniques of flame photometric detection, fluorescence, and second derivative spectrometry have been developed over the past ten years and are commercially available.

Methods for determining soluble sulfates, total sulfates and specific sulfate species involve the collection of particulate matter and its subsequent analysis by direct or indirect methods. For trace soluble sulfate determinations, a commercial method based on ion exchange chromatography exists that is specific, exceptionally accurate, and sensitive. Methods for analysis of total sulfur include x-ray fluorescence, electron spectroscopy, and flame photometry. X-ray fluorescence methods are non-destructive and applicable to the determination of large numbers of ambient aerosol samples. Procedures for determining specific sulfate species include thermal volatilization and solvent extraction

techniques, gas phase ammonia titration, infrared and visible spectrometry, flame photometry and electron microscopy. Several semiquantitative methods for estimating sulfate species include gas phase ammonia titration technique methods based on infrared spectroscopy and electron microscopy techniques.

The majority of particulates in the atom are collected using either filtration or impaction methods. The collected particulate samples are usually analyzed gravimetrically to provide a direct measure of mass concentration when related to the volume of air sampled. The most widely used method for gravimetric analysis of mass concentrations is the high-volume sampler, the current EPA reference method. Other methods include the British Smoke Shade and AISI tape samplers, multi-stage cascade impactors, cyclone samplers, and the dichotomous sampler. Chemical analyses consist of manual wet-chemistry, atomic absorption, x-ray fluorescence, optical emission spectrometry, spark source mass spectrometry, neutron activation analysis, and thin layer chromatography with fluorescence detection. Methods for continuous or _in situ_ monitoring of atmospheric particulates are also available. They are not as closely related to mass concentration as the integrated methods, but they provide useful information for studying particulate sources, transport, episodes, and effects such as visibility. The integrating nephelometer measures light scattering by atmospheric particles and is commonly used as an indicator of visibility.

## 2.7 REFERENCES


Adams, F. C., and R. E. Van Grieken. Absorption correction for X-ray fluorescence analysis of aerosol loaded filters. Anal. Chem. 47:1767-1773, 1975.

Adamski, J. M., and S. P. Villard. Application of the methylthymol blue sulfate method to water and wastewater analysis. Anal. Chem. 47:1191-1194, 1975.

Ahearn, A. I. Trace Analysis by Mass Spectrometry. Academic Press, New York, NY, 1972.

Ahlquist, N. C., and R. J. Charlson. A new instrument for evaluating the visual quality of air. J. Air Pollut. Control Assoc. 17:467-469, 1967.

American Society for Testing and Materials. Standard method for collection and analysis of dustfall. In: Book of ASTM Standards. American Society for Testing and Materials, Philadelphia, PA, 1966. pp. 785-788.

Andrezejewski, R. Les Proprietes physiques des poussiered, Ed. Slask, Katowice, 1968.

Appel, B. R., E. L. Kothny, E. M. Hoffer, and J. J. Wesolowski. Comparison of Wet Chemical and Instrumental Methods for Measuring Airborne Sulfate. EPA-600/2-76-059, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1976.

Archer, A. W. The indirect colorimetric determination of sulphate with 2-aminoperimidine. Analyst (London) 100:755-757, 1975.

Barringer Research, Ltd., A report to Department of Health, Education and Welfare of optical measurements of $SO_2$ and $NO_2$ air pollution using Barringer Correlation Spectrometers. Barringer Research Technical Report TR-69-113. Canada, 1969.

Barton, S. C., and H. G. McAdie. A specific method for the automatic determination of ambient $H_2SO_4$ aerosol. In: Proceedings of the 2nd International Clean Air Congress. H. M. Englund and W. T. Berry, eds., Academic Press, New York, NY, 1971. pp. 379-382.

Barton, S. C., and H. G. McAdie. An automated instrument for monitoring ambient $H_2SO_4$ aerosol. In: Proceedings of the 3rd International Clean Air Congress. VDI-Verlag GmbH, Dusseldorf, West Germany, 1973. pp. c25-C27.

Barnard, W. F. Community Health Environmental Surveillance Studies (CHESS) Air Pollution Monitoring Handbook. EPA-600/1-76-011, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1976.

Benarie, M., B. T. Chuong, and A. Nonat. Essai d'une Methode pour le Dosage Selectif de l'Acide Sulfurique dans l'Atmosphere de Stransbourg et Definition du Role des Particules Solides dans l'Oxydation du $SO_2$ dans l'Atomsphere. Report of IRCHA Study 7106, Centre de Recherche, Vert-le-Petit, France, January 16, 1976.

TABLE 2-11. FRACTIONAL AEROSOL PENETRATION FOR SELECTED SUBSTRATES AS A FUNCTION OF FACE VELOCITY AND PARTICLE SIZE

FILTER: Gelman Type A, glass fiber

| $\Delta P$, cm Hg | 1 | 1.5 | 3 | 10 |
|---|---|---|---|---|
| $\nabla$, cm/sec | 11.2 | 16.9 | 32.7 | 108 |
| $D_p$, μm | PENETRATION | | | |
| 0.035 | <0.0001 | <0.0001 | <0.0001 | 0.0008 |
| 0.10 | <0.0001 | <0.0001 | <0.0001 | 0.00054 |
| 0.30 | <0.0001 | <0.0001 | <0.0001 | <0.00007 |
| 1.0 | <0.0001 | <0.0001 | <0.0001 | <0.00002 |

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

| $\Delta P$, cm Hg | 1 | 3 | 10 |
|---|---|---|---|
| $\nabla$, cm/sec | 23.4 | 64.1 | 187 |
| $D_p$, μm | PENETRATION | | |
| 0.035 | <0.0002 | 0.0011 | 0.0005 |
| 0.10 | <0.00006 | 0.00008 | <0.00024 |
| 0.30 | <0.00007 | <0.00007 | <0.00022 |
| 1.0 | <0.00007 | <0.00009 | <0.00008 |

FILTER: Whatman No.1, cellulose fiber

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

Source: Liu et al., 1978

Benarie, M., T. Menard, and A. Nonat. Etude de la transformation de l'a sulfureux en acide sulfurique en relation avec les donnees climatologiques, dans un ensemble urban a caractere industriel, Rouen. Atmos. Environ. 7:403-421, 1973.

Bertolacini, R. J., and J. E. Barney II. Colorimetric determination of sulfate with barium chloranilate. Anal Chem. 29:281-283, 1957.

Blanco, A. J., and G. B. Hoidale. Microspectrophotometric technique for obtaining the infrared spectrum of microgram quantities of atmospheric dust. Atmos. Environ. 2:327-330, 1968.

Blanco, A. J., and R. G. McIntyre. An Infra-red spectroscopic view of atmospheric particulates over El Paso, Texas. Atmos. Environ. 6:557-562, 1972.

Bogen, D. C., and G. A. Welford. Radiometric determination of sulfate. J. Radioanal. Chem., 1977.

Bokhaven, C., and H. J. Niessin. Int. J. Air Water Pollut. 10:223, 1966.

Bolleter, W. T., C. J. Bushman, and P. W. Tidwell. Anal. Chem. 33:592, 1961.

Bolz, R. E., and G. E. Tuve, eds. Handbook of Tables for Applied Engineering Science. Chemical Rubber Co., Cleveland, OH, 1970. p. 159.

Bostrom, C. E. Air Water Pollut. 10:435, 1966.

Bowden, S. R. Improved lead dioxide method of assessing sulphurous pollution of the atmosphere. Air Water Pollut. 8:101-106, 1964.

British Standards Institution. Methods for the measurement of Air Pollution. Part 3. Determination of Sulphur Dioxide. B.S. 1747, Part 3, British Standards Institution, London, England, 1963.

British Standards Institution. Methods for the Measurement of Air Pollution. Part 2. Determination of Concentration of Suspended Matter. B.S. 1747, Part 2, British Standards Institution, London, England, 1964.

Brock, J. R., and Marlow. Charged aerosol particles and air pollution. Environ. Letters, No. 10, 1975.

Brosset, C., K. Andreason, and M. Ferm. _____ Atmos. Environ. 9:631- , 1975.

Brosset, C., and M. Ferm. Man-made airborne acidity and its determination. Atmos. Environ. 12:909-916, 1978.

Buttell, R. G., and Brewer _____ J. Sci. Inst. 26:357, 1949.

Cahill, T. A. Comments on surface coatings for Lundgren - Type impactors. In: Aerosol Measurement. University Presses of Florida, Gainesville, FL, 1979. p. 131.

Calvert, S., and W. Workman. Talanta 4:89, 1960.

Camp, D. C., A. L. Van Lehn, and B. W. Loo. Intercomparison of Samplers Used in the Determination of Aerosol Composition. EPA-600/7-78-118, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1978.

Charlson, R. J., A. H. Vanderpol, D. S. Covert, A. P. Waggoner, and N. C. Ahlquist. $H_2SO_4/(NH_4)_2SO_4$ background aerosol: Optical detection in St. Louis region. Atmos. Environ. 8:1257-1267, 1974.

Charlson, R. J., N. C. Ahlquist, and N. Horvath. On the Generality of Correlation of Atmospheric Aerosol Mass Concentration and Light Scatter. Atmos. Environ. 2:455-464, 1968.

Charlson, R.J., A. H. Vanderpol, D. S. Covert, A. P. Waggoner, and N. C. Ahlquist. Sulfuric acid-ammonium sulfate aerosol: Optical detection in the St. Louis region. Science 184:156-158, 1974b.

Cheney, J. L., and J. B. Homolya. Sampling parameters for sulfate measurement and characterization. Environ. Sci. Technol. 13:584-588, 1979.

Conner, W. D. An Inertial-Type Particle Separator for Collecting Large Samples. J. Air Pollut. Control Assoc.. 16:35-38, 1966.

Coutant, R. W. Effects of environmental variables on collection of atmospheric sulfate. Environ. Sci. Technol. 11(9):873-878, September 1977.

Crider, W. L. Anal. Chem. 37:1770, 1965.

Crider, W. L., N. P. Barkley, M. J. Knott, and R. W. Slater. Hydrogen flame chemiluminescence detector for sulfate in aqeous solutions. Anal. Chim. Acta 47:237-241, 1969.

Cunningham, P. T., and S. A. Johnson. Spectroscopic observation of acid sulfate in atmospheric particulate samples. Science 191:77-79, 1976.

Cushing, K. M., G. E. Lacey, J. D. McCain, and W. B. Smith. Particulate Sizing Techniques for Control Device Evaluation: Cascade Impactor Calibrations. EPA-600/2-76-280, U.S. Environmental Protection Agency, Research Triangle Park, NC, February 1978.

Davies, C. N., ed. Aerosol Science. Academic Press, New York, NY, 1966.

Dennis, E. R., ed. Handbook on Aerosols. National Technical Information Service, TID-26608, Arlington, VA, 1976.

deVeer, S. M., H. J. Bronwer, and H. Zeedijk. Presented at the 62nd Annual Meeting, Air Pollution Control Association, New York, New York, June 1969. Paper No. 69-6.

Dimitt, R. L., and E. R. Graham. Anal. Chem. 48:604, 1976.

Dionex Corporation. Dionex Analytical Ion Chromatographs. Technical Brochure, Dionex Corp., Palo Alto, California, 1975.

Dubois, L., R. S. Thomas, T. Teichman, and J. L. Monkman. A general method of analysis for high volume air samples. I. Sulphate and sulphuric acid. Mikrochim. Acta 269:1268-1275, 1969.

Dzubay. T. G., H. L. Rook, and R. K. Stevens. A chemiluminescent approach to measurement of strong acid aerosols. In: Analytical Methods Applied to Air Pollution Measurements. R. K. Stevens and W. F. Herget, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1974. pp. 71-83.

Dzubay, T. G., R. K. Stevens, and C. M. Paterson. Application of the dichotomous sampler to the characterization of ambient aerosols. In: X-ray Fluoresence of Environmental Samples. T. G. Dzubay, ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1977. pp. 95-105.

Dzubay, T. G., G. K. Snyder, D. J. Reutter, and R. K. Stevens. Aerosol acidity determination by reaction with $^{14}C$ labeled amine. Atmos. Environ. 13:1209-1212, 1979.

Dzubay, T. G., L. E. Hines, and R. K. Stevens. Particle bounce errors in cascade impactors. Atmos. Environ. 10:229-234, 1976.

Eagan, M. L., and L. Dubois. Anal. Chim. Acta 70:157, 1974.

Falkowski, J. M. Suszka i uwlaznisnije lubovoloknistych matierijalow. Moscow, GNTI, 1951.

Fassel, V. A. Quantitative elemental analyses by plasma emission spectroscopy. Science. 202:183-191, 1978.

Federal Register, 40(157):34024, 1975.

Friedlander, S. K. Smoke, Dust, and Haze. Wiley Interscience Publication, New York, NY, 1977. p. 154.

Fritz, S. J., and S. S. Yamamura. Anal. Chem. 27:1461, 1955.

Fuerst, R. G., F. P. Scaringelli, and J. H. Margeson. Effect of Temperature on Stability of Sulfur Dioxide Samples Collected by the Federal Reference Method. U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/4-76-024, May 1976.

Gales, M. E., Jr., W. H. Kaylor, and J. E. Longbottom. Determination of sulphate by automatic colorimetric analysis. Analyst (London) 93:97-100, 1968.

Gilbert, T. R., and A. M. Clay. Determination of ammonia in aquaria and in sea water using the ammonia electrode. Anal. Chem. 45:1757-1759, 1973.

Goold, R. W., C. S. Barrett, J. B. Newkirk, and C. O. Ruud. Advances in X-Ray Analysis. Kendall/Hunt, Dubuque, IA, 1976.

Goulding, F. S., and J. M. Jaklevic. X-ray fluorescence spectrometer for airborne particulate monitoring. EPA Report No. EPA-R2-73-182, U.S. Environmental Protection Agency, Washington, DC, April, 1973.

Goulding, F. S., J. M. Jaklevic, and B. W. Loo. Aerosol Analysis for the Regional Air Pollution Study. EPA-600/4-78-034, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1978.

Hager, R. N., Jr., and R. C. Anderson. J. Opt. Soc. Am. 60:1444, 1970.

Hansen, L. D., L. Whiting, D. J. Eatough, T. E. Jensen, and R. M. Izatt. Anal. Chem. 48:634, 1976.

Harris, B. Second Stage Development of an Automated Field Sulfuric Acid Sampler and the Development of a Sulfuric Acid Analyzer. Monthly Technical Progress Narrative No. 6, Cabot Corporation, Billerica, MO, December 1975.

Heard, M. J., and R. D. Wiffen. Electron microscopy of natural aerosols and the identification of particulate ammonium sulphate. Atmos. Environ. 3:337-340, 1969.

Hemeon, W. C. L., G. F. Haines, Jr., and H. M. Ide. Determination of haze and smoke concentrations by filter paper samples. Air Repair 3:22-28, 1953.

Hesketh, H. E. Understanding and Controlling Air Pollution, Ann Arbor Science Publishers, Michigan, 1974.

Hill, A. S. G. Measurement of the optical densities of smokestains on filter papers. Trans. Farad. Soc. 32:1125-1131, 1936.

Hochheiser, S. Methods of Measuring Atmospheric Sulfur Dioxide. 999-AP-6, U.S. Department of Health, Education, and Welfare, Public Health Service, Cincinnati, OH, August 1964.

Hoffer, E., and E. L. Kothny. A Micromethod for Sulfate in Atmospheric Particulate Matter. Report No. 163, Air and Industrial Hygiene Laboratory, Berkeley, CA, July 1974.

Hounam, R. E., and R. J. Sherwood. The cascade centripeter: a device for determining the concentration and size distribution of aerosols. J. Am. Ind. Hyg. Assoc. 26:122-131, 1965.

Huey, N. A. The lead dioxide estimation of sulfur oxide pollution. J. Air Pollut. Control Assoc. 18:610-611, 1968.

Huey, N. A., M. A. Wallar, and C. D. Robson. Field evaluation of an improved sulfation measurement system. Presented at the 62nd Annual Meeting, Air Pollution Control Association, New York, NY, June 22-26, 1969. paper no. 69-133.

Huntzicker, J. J., L. J. Isabelle, and J. G. Watson. The continuous monitoring of particulate sulfate by flame photometry. In: International Conference on Environmental Sensing and Assessment. Volume 2, Institute of Electrical and Electronics Engineers, Inc., New York, NY, 1976. paper 23-4.

Huntzicker, J. J., L. M. Isabelle, and J. G. Watson. The continuous monitoring of particulate sulfur compounds by flame photometry. Presented at the 173rd National Meeting, American Chemical Society, New Orleans, LA, March 20-25, 1977. paper ENVR-39.

Husar, J. D., R. B. Husar, and P. K. Stubits. Determination of submicrogram amounts of atmospheric particulate sulfur. Anal. Chem. 47:2062-2065, 1975.

Husar, R. B., J. D. Husar, N. V. Gillani, S. B. Fuller, W. H. White, J. A. Anderson, W. M. Vaughan, and W. E. Wilson, Jr. Pollutant flow rate measurement in large plumes: sulfur budget in power plant and area source plumes in the St. Louis region. Presented at the 171st Meeting. American Chemical Society, New York, NY, April 4-9, 1976. paper ENVR-14.

Huygen, C. A simple photometric determination of sulphuric acid aerosol. Atmos. Environ. 9:315-319, 1975.

Intersociety Committee. Methods of Air Sampling and Analysis. American Public Health Association, Washington, DC, 1972.

Intertech Corp. Descriptive brochure.

Jacobs, M. B. The Chemical Analysis of Air Pollutants. Wiley-Interscience, New York, NY, 1960.

Jacobs, M. B., M. M. Braverman, and S. Hochheiser. Anal. Chem. 29:1349-1957.

Johansson, T. B., R. E. Van Grieken, J. W. Nelson, and J. W. Winchester. Anal. Chem. 47:855, 1975.

John, W., G. Reischl, and J. Wesolowski. Size Selective Monitoring Techniques for Particulate Matter. Report No. ARB A5-00487 California Department of Health, Air and Industrial Hygiene Laboratory, Berkeley, CA, February 1978.

Katz, M. Anal. Chem. 22:1040, 1950.

Katz, M. In: Analysis of Inorganic Gaseous Pollutants. Air Pollution. Vol. II 2nd ed. A. C. Stern, ed., Academic Press, New York, NY, 1968. pp. 53-114.

Katz, M. Measurement of Air Pollutants--Guide to Selection of Methods. World Health Organization, Geneva, 1969.

Keay, J., and P. M. A. Menage. Analyst (London) 95:379, 1970.

Kirkland, J. J. Modern Practice of Liquid Chromatography. John Wiley, New York, NY, 1971.

Kittleson, D. B., R. McKenzie, M Vermeersch, M. Linne, F. Dorman, D. Pui, B. Liu, and K. Whitby. Total sulfur aerosol detection with an electrostatically pulsed flame photometric detector system. Presented at the 173rd National Meeting, American Chemical Society, New Orleans, LA, March 20-25, 1977. paper ENVR-42.

Klockow, D., and G. Ronicke. An amplification method for the determination of particle-sulphate in background air. Atmos. Environ. 7:163-168, 1973.

Kolthoff, I. M., E. B. Sandell, E. J. Meehan, and S. Bruckenstein. Quantitative Chemical Analysis, 4th ed., MacMillan, Toronto, Canada, 1969. pp. 992-994.

Lambert, J. P. F., and F. W. Wilshire. Neutron activation analysis for simultaneous determination of trace elements in ambient air collected on glass-fiber filters. Anal. Chem. 51:1346-1353, 1979.

Lamothe, P. J., and R. K. Stevens. Sulfuric acid analysis using low temperature volatilization. Presented at the 171st National Meeting, American Chemical Society, New York, NY, April 4-9, 1976. paper ENVR-38.

Lawrence Berkeley Laboratory. Instrumentation for Environmental Monitoring, Air. LBL-1, Vol. 1, University of California, Berkeley, CA, May 1972.

Lawrence Berkeley Laboratory. Instrumentation for Environmental Monitoring, AIR Part 2, University of California, CA, 1975.

Lazarus, A. L., K. C. Hill, and J. P. Lodge. In: Proceedings of the 1966 Technicon Symposium on Automation in Analytical Chemistry. Mediad, Inc., New York, NY, 1966. pp. 291.

Leahy, D., R. Siegel, P. Klotz, and L. Newman. The separation and characterization of sulfate aerosol. Atmos. Environ. 9:219-229, 1975.

Lee, R. E., and S. Goranson. National air surveillance cascade impactor network. I. Size distribution measurements of suspended particulate matter in air, Environ. Sci. Technol., 6:1019-1024, 1972.

Lilienfield, P. J. Am. Ind. Hyg. Assoc. 31:722, 1970.

Lippman, M. "Respirable" dust sampling. Am. Ind. Hyg. Assoc. J. 31:138-159, 1970.

Liu, B. Y. H., and D. Y. H. Pui. On the Performance of the Electrical Aerosol Analyzer. J. Aerosol Sci. 6:249-264, 1975.

Liu, B. Y. H., ed. Fine Particles, Aerosol Generation, Measurement, Sampling, and Analysis. Academic Press, New York, NY, 1976.

Liu, B. Y. H, D. Y. H. Pui, K. L. Rubow, and G. A. Kuhlmey. Progress Report - Research on Air Sampling Filter Media. Grant Report R804600, University of Minnesota, Minneapolis, MN, May 1978.

Lizarraga-Rocha, J. A. The Effect of Exposure of Filters During Non-operating Periods in the High Volume Sampling Method. M.S. Thesis, University of North Carolina, Chapel Hill, NC, 1976.

Lochmuller, C. H., J. W Galbraith, and R. L. Walter. Trace metal analysis in water by proton-induced x-ray emission analysis of ion-exchange membranes. Anal. Chem. 46:440-442, 1974.

Lodge, J. P., J. Ferguson, and B. R. Havlik. Analysis of micron-sized particles: Determination of sulfuric acid aerosol. Anal. Chem. 32: 1206-1207, 1960.

Loo, B. W., R. S. Adachi, C. P. Cork, F. S. Goulding, J. M. Jaklevic, D. A. Landis, and W. L. Searles. A second generation dichotomous sampler for large scale monitoring of airborne particulate matter. Presented at 86th Annual Meeting, American Institute of Chemical Engineers, Houston, Texas, April 1, 1979.

Loo, B. W., W. R. French, R. C. Gatti, F. S. Goulding, J. M. Jaklevic, J. Llacer, and A. C. Thompson. Large scale measurement of airborne particulate sulfur. Atmos. Environ. 12:759-771, 1978.

Lucero, D. P., and J. W. Paljug. Monitoring sulfur compounds by flame photometry. Trib. CEBEDEAU 27:139-147, 1974.

Lundgren, D. A. Mass Distribution of Larger Atmospheric Particles. Ph.D. Thesis, University of Minnesota, Minneapolis, MN, 1973.

Lundgren, D. A., M. Lippman, F. S. Harris, W. E. Clark, W. H. Marlow, and M. D. Durham, eds. Aerosol Measurement. University Press of Florida, Gainesville, FL, 1979.

Macias, E. S. Instrumental analysis of light element composition of atmospheric aerosols. In: Methods and Standards for Environmental Measurement. W. Kirchhoff, ed., National Bureau of Standards Special Publication 464. Department of Commerce, Washington, DC, 1977. pp. 179-188.

Macias, E. S., and R. B. Husar. Atmospheric particulate mass measurement with beta attenuation mass monitor. Environ. Sci. Technol. 10:904-907, 1976.

Maddalone, R. F., G. L. McClure, and P. W. West. Anal. Chem. 47:316, 1975.

Malm, W. Consideration in the measurement of visibility. J. Air Pollut. Control Assoc. 29:1042-1052, 1979.

Mamane, Y., and R. G. de Pena. A quantitative method for the detection of individual submicron size sulfate particles. In: Sulfur in the Atmosphere, Dubrovnik, Proceeding of an International Symposium, Yugoslavia, September 7-14, 1977. Atmos. Environ. 12:69-82, 1978.

Mamantov, G., E. L. Wehry, R. R. Kemerer, and E. R. Hinton. Anal. Chem. 49:86, 1977.

Martin, B. E. Sulfur Dioxide Bubbler Temperature Study. EPA-600/4-77-040, U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1977.

McCoy, R. A., D. E. Camann, and H. C. McKee. Collaborative Study of Reference Method for Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method) (24-Hour Sampling). EPA-650/4-74-027, U.S. Environmental Protection Agency, Research Triangle Park, NC, December 1973.

McFadden, W. H. Techniques of Combined Gas Chromatography/ Mass Spectrometry. John Wiley, New York, NY, 1973.

McFarland, A. R. Test Report - Wind Tunnel Evaluation of British Smoke Shade Sampler. Air Quality Laboratory Report, 3565/05/79/ARM, Texas A&M University, College Station, TX, May 1979.

McFarland, A. R. and C. E. Rodes. Characteristics of Aerosol Samplers Used in Ambient Air Monitoring. Presented at 86th National Meeting, American Institute of Chemical Engineers, Houston, TX, April 2, 1979.

McFarland, A. R., and C. A. Ortiz. Progress Report - Aerosol Characterization of Ambient Particulate Samplers Used in Environmental Monitoring Studies. Texas A&M University Research Foundation, College Station, TX, October 1979.

McFarland, A. R., C. A. Ortiz, and C. E. Rodes. Evaluation of the NASN Cascade Impactor Ambient Air Monitor. Report 3565/07/78/ARM, Texas A&M, Air Quality Laboratory, College Station, TX, 1978. Accepted Publication Atm. Environ., 1980.

McKee, H. C., R. E. Childers, and O. Saenz, Jr. Collaborative Study of Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method). APTD-0904, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1971.

Miller, F. J., D. E. Gardner, J. A. Graham, R. E. Lee, Jr., W. E. Wilson, and J. D. Bachmann. Size considerations for establishing a standard for inhalable particles. J. Air Pollut. Control Assoc. 29:610-615, 1979.

Moffat, A. J., J. R. Robbins, and A. R. Barringer. Electro-optical sensing of environmental pollutants. Atmos. Environ. 5:511-525, 1971.

Morrison, G. H. Trace Analysis Physical Methods. Wiley Interscience, New York, NY, 1965. pp. 245-263, 271-310, 325-360, 377-425.

Mudgett, P. S., L. W. Richards, and J. R. Roehrig. A new technique to measure sulfuric acid in the atmosphere. In: Analytical Methods Applied to Air Pollution Measurement. R. K. Stevens and W. F. Herget, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1974.

Mulik, J. D., G. Todd, E. Estes, R. Puckett, E. Sawicki, and D. Williams. In: Ion Chromatographic Analysis of Environmental Pollutants. E. Sawicki, J. D. Mulik, and E. Wittgenstein, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1978.

Nader, J. S. Dust retention efficiencies of dustfall collectors. J. Air Pollut. Control Assoc. 8:35-38, 1958.

National Academy of Sciences. Airborne Particles. University Park Press, Baltimore, MD, 1979.

National Air Pollution Control Administration Publication. Air Quality Criteria for Particulate Matter. AP-49, U.S. Department of Health, Education, and Welfare, Washington, DC, January 1969.

Natusch, D. F. S., C. F. Bauer, and A. Loh. Collection and analysis of trace elements in the atmosphere. In: Air Pollution Control, Part III. W. Strauss, ed., John Wiley and Sons, Inc., 1978.

Newman, L., J. Forrest, and B. Manowitz. The application of an isotopic ratio technique to a study of the atmospheric oxidation of sulfur dioxide in the plume from an oil-fired power plant. Atmos. Environ. 9:959-968, 1975.

Newman, L., J. Forrest, and B. Manowitz. Atmos. Environ. 9:969, 1975b.

Novakov, T. Chemical characterization of atmospheric pollution particulates by photoelectron spectroscopy. In: Proceedings of the 2nd Joint Conference on Sensing of Environmental Pollutants, Instrument Society of America, Washington, DC, December 10-12, 1973. p. 197.

Novakov, T., S. G. Chang, and A. B. Harker. Sulfates as pollution particulates: Catalytic formation on carbon (soot) particles. Science 186:259-261, 1974.

Okabe, H., P. L. Splitstone, and J. J. Ball. J. Air Pollut. Control Assoc. 23:514, 1973.

O'Keeffe, A. E., and G. C. Ortman. Primary standards for trace gas analysis. Anal. Chem. 38:760-763, 1966.

Organization for European Economic Cooperation. Paper EPA/AR/4283, European Productivity Agency, Paris, France, 1961.

Palmer, H. F., C. E. Rodes, and C. J. Nelson. Performance characteristics of instrumental methods for monitoring sulfur dioxide. II. Field Evaluation. J. Air Pollut. Control Assoc. 19:778, 1969.

Perera, F. P., and A. K. Ahmed. Respirable Particles: Impact of Airborne Fine Particulates on Health and the Environment. National Resources Defense Council, Washington, DC, October 1978.

Philips Electronic Instruments. Coulometric amperometric analyzers. Bull. WA-4-C13.

Pierson, W. R., W. W. Prachaczek, T. J. Korniski, T. J. Truex, and J. W. Butler. Artifact formation of sulfate, nitrate, and hydrogen ion on backup filters: Allegheny Mountain experiment. J. Air Pollut. Control Assoc. 30:30-34, 1980.

Ranade, M. B., and D. VanOsdell. Quality Assurance Evaluation of the CHAMP Aerosol Sampler, Project Report 43U-1487-59, Research Triangle Institute, Research Triangle Park, NC, July 1978.

Regan, G. F., S. K. Goranson, and L. L. Lawson. Use of tape samplers as fine particulate monitors. J. Air Pollut. Control Assoc. 29:1158-1160, 1979.

Rider, P. E., C. C. Rider, and R. N. Corning. Studies of Huey sulfation plates at high ambient $SO_2$ concentrations. J. Air Pollution Control Assoc. 27:1011-1013, 1977.

Roberts, P. T., and S. K. Friedlander. Analysis of sulfur in deposited aerosol particles by vaporization and flame photometric detection. Atmos. Environ. 10:403-408, 1976.

Rodes, C. E., and G. F. Evans. Summary of LACS Integrated Measurements. EPA-600/4-77-034, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1977.

Ross, J. W., Jr., and M. S. Frant. Potentiometric titrations of sulfate using an ion-selective lead electrode. Anal. Chem. 41:967-969, 1969.

Sajo, I., and B. Sipas. Talanta 14:203, 1967.

Scaringelli, F. P., and K. A. Rehme. Determination of atmospheric concentrations of sulfuric acid aerosol by spectrophotometry, coulometry, and flame photometry. Anal. Chem. 41:707-713, 1969.

Scaringelli, F. P., B. E. Slatzman, and S. A. Frey. Spectrophotometric determination of atmospheric sulfur dioxide. Anal. Chem. 39:1709-1719, 1967.

Scroggins, L. H. Collaborative study of the microanalytical oxygen flask sulfur determination with dimethylsulfonazo III as indicator. J. Assoc. Off. Anal. Chem. of the AOAC 57:22-25, 1974.

Shaw, R. Personal Communication to C. E. Rodes, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1980.

Sides, J. O., and H. F. Saiger. Effects of Prolonged Static Exposure of Filters to Ambient Air on High Volume Sampling Results. Kansas State Department of Health and Environment, Bureau of Air Quality and Occupational Health, Topeka, KS, May 1976.

Sinclair, D., R. J. Countess, B. Y. H. Liu, and D. Y. H. Pui. Automatic analysis of submicron particles. In: Aerosol Measurement. University of Florida Presses, Gainsville, FL, 1979. p. 544-563.

Small, H., T. S. Stevens, and W. C. Bauman. Anal. Chem. 47:1801, 1975.

Smith, A. F., D. G. Jenkins, and D. E. Cunningworth. J. Appl. Chem. 11:317, 1961.

Smith, F., P. S. Wohlschlegel, R. S. C. Rogers, and Mulligan, D. J. Investigation of Flow Rate Calibration Procedures Associated with the High Volume Method for Determination of Suspended Particulates. EPA-600/4-78-047, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1978.

Snell, F. D. Photometric and Fluorometric Methods of Analysis, Metals. Part 1. John Wiley, New York, NY, 1978. p. 1-25.

Spicer, C. W., and P. M. Schumacher. Particle Nitrate: Laboratory and Field Studies of Major Sampling Interferences. Atmos. Environ. 13:543-552, 1979.

Stalker, W. W., R. C. Dickerson, and G. D. Kramer. Atmospheric sulfur dioxide and particulate matter: A comparison of methods of measurements. Am. Ind. Hyg. Assoc. J. 24:68-79, 1963.

Stevens, R. K., and T. G. Dzubay. Recent Development in Air Particulate Monitoring. IEEE Trans. Nucl. Sci. 22: April 1975.

Stevens, R. K., J. A. Hodgeson, L. F. Ballard, and C. E. Decker. In: Determination of Air Quality. G. Mamantov and W. D. Shults, eds., Plenum Publishing Corporation, New York, NY, 1972.

Stevens, R. K., J. D. Mulik, A. E. O'Keeffe, and K. J. Krost. Gas chromatography of reactive sulfur gases in air at the parts-per-billion level. Anal. Chem. 43:827-831, 1971.

Stevens, R. K., T. G. Dzubay, G. Russwurm, and D. Rickel. Sampling and analysis of atmospheric sulfates and related species. Atmos. Environ. 12:55-68, 1978.

Stratmann, H. Mikrochim Acta 6:668- , 1954.

Swanson, D., C. Morris, R. Hedgecoke, R. Jungers, R. J. Thompson, and J. E. Bumgarner. A rapid analytical procedure for the analysis of BaP in environmental samples. Trends Fluoresc. 1:22-27, 1978.

Tanner, R. L., and Cordova. U.S. Energy Research Development Administration. Contract No. EY-76-C-02-0016, 1978.

Tanner, R. L., J. Forrest, and L. Newman. Determination of atmospheric gaseous and particulate sulfur compounds. U.S. Energy Research Development Administration. Contract No. EY-76-C-02-0016, 1978.

Tanner, R. L., R. Cederwall, R. Garber, D. Leahy, W. Marlow, R. Meyers, M. Phillips, and L. Newman. Separation and analysis of aerosol sulfate species at ambient concentrations. Atmos. Environ. 11:955-966, 1977.

Tanner, R. L., R. W. Garber, and L. Newman. Speciation of sulfate in ambient aerosols by solvent extraction with flame photometric detection. Presented at the 173rd National Meeting, American Chemical Society, New Orleans, LA, March 20-25, 1977a. paper ENVR-41.

Tanner, R. L., R. W. Garber, W. H. Marlow, B. Leaderer, D. Eatough, and M. A. Leyko. Chemical composition and size distribution of sulfate as a function of particle size in New York City aerosol. Presented at the Industrial Hygiene Conference, New Orleans, Louisiana, May 22-27, 1977b. paper No. 140.

Technicon Corporation. Sulfate method VIb via turbidimetry. Technicon Corporation, Tarrytown, NY, 1959.

Terraglio, F. P., and R. M. Maganelli. Laboratory evaluation of sulfur dioxide methods and the influence of ozone-oxides of nitrogen mixtures. Anal. Chem. 34:675-677, 1962.

Tetlow, J. A., and A. L. Wilson. Analyst (London) 89:453, 1964.

Thoen, G. N., G. G. Dehaas, and R. R. Austin. Tappi 51:246, 1968.

Thomas, R. L., V. Dharmarajan, G. L. Lundquist, and P. W. West. Measurement of sulfuric acid aerosol, sulfur trioxide, and the total sulfate content of the ambient air. Anal. Chem. 48:639-642, 1976.

Thrane, K. E. Intercomparison of analytical methods within the European monitoring and evaluation program (EMEP). In: Studies in Environmental Science, Vol. 2, Air Pollution Reference Measurement Methods and Systems. T. Schneider, H. W. de Koning, and L. J. Brasser, eds., Elsevier Scientific Publishing Company, Amsterdam, 1978. pp. 139-149.

Threshold Limits Committee. Threshold Limit Values of Air Borne Contaminants for 1968. American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1968.

Tierney, G. P., and W. D. Conner. Hydroscopic effects of weight determinations of particulates collected on glass fiber filters. J. Am. Ind. Hyg. Assoc., 1967.

Treon, J. F., and W. E. Crutchfield, Jr. Rapid turbidimetric method for determination of sulfates. Ind. Eng. Chem. Anal. Ed. 14:119-121, 1942.

Turner, J. M., and R. S. Sholtes. Laboratory evaluation of the sulfation plate for estimation of atmospheric sulfur dioxide. Presented at the 64th Annual Meeting, Air Pollution Control Association, Atlantic City, NJ, June 27-July 2, 1971. Paper No 71-39.

U.S. Environmental Protection Agency. Ambient Air Monitoring Reference and Equivalent Methods. 40 CFR 53:952-986, July 1, 1979c.

U.S. Environmental Protection Agency. National Primary and Secondary Ambient Air Quality Standards. Appendix A - Reference method for the determination of sulfur dioxide in the atmosphere (pararosaniline method). 40 CFR 50:6-11, July 1, 1979.

U.S. Environmental Protection Agency. National Primary and Secondary Ambient Air Quality Standards. Appendix B - Reference method for the determination of suspended particulates in the atmosphere (high volume method). 40 CFR 50:12-16, July 1, 1979a.

U.S. Environmental Protection Agency. National Primary and Secondary Ambient Air Quality Standards. 40 CFR 50:3-5, July 1, 1979b.

U.S. Environmental Protection Agency. Summary of Performance Test Results and Comparative Data for Designated Equivalent Methods for $SO_2$. Document No. QAD/M-79.12, U.S. Environmental Protection Agency, Research Triangle Park, NC, December 1979.

Volmer, W., and F. Z. Frohlich. Z. Anal. Chem. 126:401, 1944.

Von Lehmden, D. J., and C. Nelson. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume I: Principles. EPA-600/9-76-005, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1976.

Von Lehmden, D. J., and C. Nelson. Quality Assurance Handbook for Air Pollution Measurement System. Volume II. Ambient Air Specific Methods. EPA-600/4-77-027a, U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1977b.

Wartburg, A. F., J. B. Pate, and J. P. Lodge, Jr. Environ. Sci. Technol. 3:767, 1969.

Wedding, J. B., A. R. McFarland, and J. E. Cernak. Large particle collection characteristics of ambient aerosol samplers. Environ. Sci. Technol. 11:387-390, 1977.

Wedding, J. B., M. Weigand, W. John, and S. Wall. Sampling Effectiveness of the Inlet to the Dichotomous Sampler. Aerosol Science Laboratory, Fort Collins, CO, 1980.

Welch, A. F., and J. P. Terry. Developments in the measurement of atmospheric sulfur dioxide. Am. Ind. Hyg. Assoc. J. 21:316-321, 1960.

West, P. W., and G. C. Gaeke. Anal. Chem. 28:1816, 1956.

Whitaker Company Electrochemical Transducer.

Whitby, K. T. Modeling of Atmospheric Aerosol Size Distribution, Progress Report, EPA Grant No. R800971, 1975.

Whitby, K. T. The Physical Characteristics of Sulfur Aerosols. Paper Prepared for Presentation at the International Symposium on Sulfur in the Atmosphere, 7-14 Sept., 1977, Dubrovnik, Yugoslavia.

Whitby, K. T., and K. Willeke. Single particle optical counters: principles and field use. In: Aerosol Measurement. University of Florida Presses, Gainesville, FL, 1979. p. 145-180.

Whitby, K. T., and W. E. Clark. Electrical aerosol particle counting and size distribution measuring system for the 0.015 to 1.0 mm size range. Tellus. 18:573-586, 1966.

Willeke, K., and J. J. McFeters. Calibration of the CHAMP Fractionator, Particle Technology Publication No. 252, University of Minnesota, Minneapolis, MN, March 1975.

Willeke, K., and Whitby, K. T. Atmospheric aerosols size distribution interpretation. J. Air Pollut. Control Assoc. 25:529-534, 1975.

Wilsdon, B. H., and F. J. McConnell. J. Soc. Chem. Ind. 53:385, 1934.

Wilson, W., et al. Sulphates in the Atmosphere. Paper No. 76-30.06, 69th Annual Meeting of the Air Pollution Control Assoc., Portland, Ore., U.S.A., June 27, 1976.

World Health Organization Selected Methods of Measuring Air Pollutants. WHO Offset Publication No. 24, World Health Organization, Geneva, Switzerland, 1976.

Inhaled Particles. Environ. Sci. Technol. 12(13):1353-1355, 1978.

## 2.7 REFERENCES


Adams, F. C., and R. E. Van Grieken. Absorption correction for X-ray fluorescence analysis of aerosol loaded filters. Anal. Chem. 47:1767-1773, 1975.

Adamski, J. M., and S. P. Villard. Application of the methylthymol blue sulfate method to water and wastewater analysis. Anal. Chem. 47:1191-1194, 1975.

Ahearn, A. I. Trace Analysis by Mass Spectrometry. Academic Press, New York, NY, 1972.

Ahlquist, N. C., and R. J. Charlson. J. Air Pollut. Control Assoc. 17:467-, 1967.

American Society for Testing and Materials. Standard method for collection and analysis of dustfall. In: Book of ASTM Standards. American Society for Testing and Materials, Philadelphia, PA, 1966. p. 785-788.

Andrezejewski, R. Les Proprietes physiques des poussiered, Ed. Slask, Katowice, 1968.

Appel, B. R., E. L. Kothny, E. M. Hoffer, and J. J. Wesolowski. Comparison of Wet Chemical and Instrumental Methods for Measuring Airborne Sulfate. EPA-600/2-76-059, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1976.

Archer, A. W. The indirect colorimetric determination of sulphate with 2-aminoperimidine. Analyst (London) 100:755-757, 1975.

Barringer Research, Ltd., A report to Department of Health, Education and Welfare of optical measurements of $SO_2$ and $NO_2$ air pollution using Barringer Correlation Spectrometers. Barringer Research Technical Report TR-69-113. Canada, 1969.

Barton, S. C., and H. G. McAdie. A specific method for the automatic determination of ambient $H_2SO_4$ aerosol. In: Proceedings of the 2nd International Clean Air Congress. H. M. Englund and W. T. Berry, eds., Academic Press, New York, NY, 1971. p. 379-382.

Barton, S. C., and H. G. McAdie. An automated instrument for monitoring ambient $H_2SO_4$ aerosol. In: Proceedings of the 3rd International Clean Air Congress. VDI-Verlag 6 mbH, Dusseldorf, West Germany, 1973. p. c25.

Benard, W. F. Community Health Environmental Surveillance Studies (CHESS) Air Pollution Monitoring Handbook. EPA-600/1-76-011, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1976.

Benarie, M., B. T. Chuong, and A. Nonat. Essai d'une Methode pour le Dosage Selectif de l'Acide Sulfurique dans l'Atmosphere de Stransbourg et Definition du Role des Particules Solides dans l'Oxydation du $SO_2$ dans l'Atomsphere Report of IRCHA Study 7106, Centre de Recherche, Vert-le-Petit, France, January 16, 1976.

Benarie, M., T. Menard, and A. Nonat. Atmos. Environ. 7:403, 1973.

Bertolacini, R. J., and J. E. Barney. Anal Chem. 29:281, 1957.

Blanco, A. J., and G. B. Hoidale. Atmos. Environ. 2:327, 1968.

Blanco, A. J., and R. G. McIntyre. Atmos. Environ. 6:557, 1972.

Bogen, D. C., and G. A. Welford. Radiometric determination of sulfate. J. Radioanal. Chem., 1977.

Bokhaven, C., and H. J. Niessin. Int. J. Air Water Pollut. 10:223, 1966.

Bolleter, W. T., C. J. Bushman, and P. W. Tidwell. Anal. Chem. 33:592, 1961.

Bolz, R. E., and G. E. Tuve, eds. Handbook of Tables for Applied Engineering Science. Chemical Rubber Co., Cleveland, OH, 1970. p. 159.

Bostrom, C. E. Air Water Pollut. 10:435, 1966.

Bowden, S. R. Int. J. Air Water Pollut. 8:101, 1964.

British Standard 1747, Part 3, 1963.

British Standards Institution. Methods for the Measurement of Air Pollution. Part 2. Determination of Concentration of Suspended Matter. B.S. 1747, Part 2, British Standards Institution, London, England, 1964.

Brock, J. R., and Marlow. Charged aerosol particles and air pollution. Environ. Letters, No. 10, 1975.

Brosset, C., and M. Ferm. Man-made airborne acidity and its determination. Atmos. Environ. 12:909-916, 1978.

Buttell, R. G., and Brewer _____ J. Sci. Inst. 26:357, 1949.

Cahill, T. A. Comments on surface coatings for Lundgren - Type impactors. In: Aerosol Measurement. University Presses of Florida, Gainesville, FL, 1979. p. 131.

Calvert, S., and W. Workman. Talanta 4:89, 1960.

Camp, D. C., A. L. Van Lehn, and B. W. Loo. Intercomparison of Samplers Used in the Determination of Aerosol Composition. EPA-600/7-78-118, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1978.

Charlson, R. J., A. H. Vanderpol, D. S. Covert, A. P. Waggoner, and N. C. Ahlquist. Atmos. Environ. 8:1257, 1974a.

Charlson, R. J., N. C. Ahlquist, and N. Horvath. On the Generality of Correlation of Atmospheric Aerosol Mass Concentration and Light Scatter. Atmos. Environ. 2:455-464, 1968.

Charlson, R.J., A. H. Vanderpol, D. S. Covert, A. P. Waggoner, and N. C. Ahlquist. Science 184:156, 1974b.

Cheney, J. L., and J. B. Homolya. Sampling parameters for sulfate measurement and characterization. Environ. Sci. Technol. 13:584-588, 1979.

Conner, W. D. An Inertial-Type Particle Separator for Collecting Large Samples. J. Air Pollut. Control Assoc.. 16:35-38, 1966.

Coutant, R. W. Effects of environmental variables on collection of atmospheric sulfate. Environ. Sci. Technol. 11(9):873-878, September 1977.

Crider, W. L. Anal. Chem. 37:1770, 1965.

Crider, W. L., N. P. Barkley, M. J. Knott, and R. W. Slater. Hydrogen flame chemilurimescence detector for sulfate in aqeous solutions. Anal. Chim. Acta 47:237-241, 1969.

Cunningham, P. T., and S. A. Johnson. Science 191:77-79, 1976.

Cushing, K. M., G. E. Lacey, J. D. McCain, and W. B. Smith. Particulate Sizing Techniques for Control Device Evaluation: Cascade Impactor Calibration EPA-600/2-76-280, U.S. Environmental Protection Agency, Research Triangle Park, NC, February 1978.

Davies, C. N., ed. Aerosol Science. Academic Press, New York, NY, 1966.

Dennis, E. R., ed. Handbook on Aerosols. National Technical Information Service, TID-26608, Arlington, VA, 1976.

deVeer, S. M., H. J. Bronwer, and H. Zeedijk. Presented at the 62nd Annual Meeting, Air Pollution Control Association, New York, New York, June 1969. Paper No. 69-6.

Dimitt, R. L., and E. R. Graham. Anal. Chem. 48:604, 1976.

Dionex Corporation. Dionex Analytical Ion Chromatographs. Technical Brochure, Dionex Corp., Palo Alto, California, 1975.

Dubois, L., C. J. Baker, T. Teichman, A. Zdrojewski, and J. L. Monkman. Mikrochim. Acta 269:1268, 1969.

Dzubay. T. G., H. L. Rook, and R. K. Stevens. A chemiluminescent approach to measurement of strong acid aerosols. In: Analytical Methods Applied to Air Pollution Measurement. R. Stevens and W. Herget, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1974. p. 71.

Dzubay, T. G., G. K. Snyder, D. J. Reutter, and R. K. Stevens. Aerosol acidity determination by reaction with $^{14}C$ labeled amine. Atmos. Environ., 13:1209-1212, 1979.

Dzubay, T. G., L. E. Hines, and R. K. Stevens. Particle bounce errors in cascade impactors. Atmos. Environ. 10:229-234, 1976.

Eagan, M. L., and L. Dubois. Anal. Chim. Acta 70:157, 1974.

Edited by Lundgren, D. A., M. Lippman, F. S. Harris, W. E. Clark, W. H. Marlow, and M. D. Durham. Aerosol Measurement. University Press of Florida, Gainesville, FL, 1979.

Environmental Monitoring Systems Laboratory, Summary of Performance Test Results and Comparative Data for Designated Equivalent Methods for $SO_2$. Document No. QAD/M-79.12. U.S. Environmental Protection Agency, Research Triangle Park, NC, December 1979.

Falkowski, J. M. Suszka i uwlaznisnije lubovoloknistych matierijalow. Moscow, GNTI, 1951.

Fassel, V. A. Quantitative elemental analyses by plasma emission spectroscopy. Science. 202:183-191, 1978.

Federal Register, 40(33):7044, 1975.

Friedlander, S. K. Smoke, Dust, and Haze. Wiley Interscience Publication, New York, NY, 1977. p. 154.

Fritz, S. J., and S. S. Yamamura. Anal. Chem. 27:1461, 1955.

Fuerst, R. G., F. P. Scaringelli, and J. H. Margeson. Effect of Temperature on Stability of Sulfur Dioxide Samples Collected by the Federal Reference Method. U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/4-76-024, May 1976.

Gales, M. E., Jr., W. H. Kaylor, and J. E. Longbottom. Analyst (London) 93:97, 1968.

Gilbert, T. R., and A. M. Clay. Anal. Chem. 45:1757, 1973.

Goold, R. W., C. S. Barrett, J. B. Newkirk, and C. O. Ruud. Advances in X-Ray Analysis. Kendall/Hunt, Dubuque, IA, 1976.

Goulding, F. S., and J. M. Jaklevic. X-ray fluorescence spectrometer for airborne particulate monitoring. EPA Report No. EPA-R2-73-182, U.S. Environmental Protection Agency, Washington, DC, April, 1973.

Goulding, F. S., J. M. Jaklevic, and B. W. Loo. Aerosol Analysis for the Regional Air Pollution Study. EPA-600/4-78-034, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1978.

Hager, R. N., Jr., and R. C. Anderson. J. Opt. Soc. Am. 60:1444, 1970.

Hansen, L. D., L. Whiting, D. J. Eatough, T. E. Jensen, and R. M. Izatt. Anal. Chem. 48:634, 1976.

Harris, B. Second Stage Development of an Automated Field Sulfuric Acid Sampler and the Development of a Sulfuric Acid Analyzer. Monthly Technical Progress Narrative No. 6, Cabot Corporation, Billerica, MO, December 1975.

Heard, M. J., and R. D. Wiffen. Atmos. Environ. 3:337, 1969.

Hemeon, W. C. L., G. F. Haines, and H. M. Ide. Determination of haze and smoke concentrations by filter paper samples. J. Air Pollut. Control Assoc. 3:22-28, 1953.

Hesketh, H. E. Understanding and Controlling Air Pollution, Ann Arbor Science Publishers, Michigan, 1974.

Hill, A. S. G. Measurement of the optical densities of smokestains on filter papers. Trans. Farad. Soc. 32:1125-1131, 1936.

Hochheiser, S. Methods of Measuring Atmospheric Sulfur Dioxide. AP-6, U.S. Department of Health, Education, and Welfare, Cincinnati, OH, August 1964.

Hoffer, E., and E. L. Kothny. A Micromethod for Sulfate in Atmospheric Particulate Matter. Report No. 163, Air and Industrial Hygiene Laboratory, Berkeley, CA, July 1974.

Hounam, R. E., and R. J. Sherwood. The cascade centripeter: a device for determining the concentration and size distribution of aerosols. J. Am. Ind. Hyg. Assoc. 26:122-131, 1965.

Huey, N. A. The lead dioxide estimation of sulfur oxide pollution. J. Air Pollut. Control Assoc. 18:610, 1968.

Huey, N. A., M. A. Wallar, and C. D. Robson. Field evaluation of an improved sulfation measurement system. Paper No. 69-133 Presented at Air Pollution Control Association Annual Meeting, June, 1969. Paper No. 69-133.

Huntzicker, J. J., L. J. Isabelle, and J. G. Watson. The continuous monitoring of particulate sulfate by flame photometry. In: International Conference on Environmental Sensing and Assessment. Volume 2, Institute of Electrical and Electronics Engineers, Inc., New York, NY, 1976. Paper 23-4.

Huntzicker, J. J., L. M. Isabelle, and J. G. Watson. The continuous monitoring of particulate sulfur compounds by flame photometry. Presented at the 173rd National Meeting, American Chemical Society, New Orleans, Louisiana, March 20-25, 1977. Paper ENVR-39.

Husar, J. D., R. B. Husar, and P. K. Stubits. Anal. Chem. 47:2062, 1975.

Husar, R. B., J. D. Husar, N. V. Gillani, S. B. Fuller, W. H. White, J. A. Anderson, W. M. Vaughn, and W. E. Wilson, Jr. Pollutant flowrate measurement in large plumes: sulfur budget in power plant and area source plumes in the St. Louis region. Presented at the 171st Meeting. American Chemical Society, New York, New York, April 4-9, 1976. Paper ENVR-14.

Huygen, C. Atmos. Environ. 9:315, 1975.

Inhaled particles. Environ. Sci. Technol. 12(13):1353-1355, 1978.

Intersociety Committee. Methods of Air Sampling and Analysis. American Public Health Association, Washington, DC, 1972.

Intertech Corp. Descriptive brochure.

Jacobs, M. B. The Chemical Analysis of Air Pollutants. Wiley-Interscience, New York, NY, 1960.

Johansson, T. B., R. E. Van Grieken, J. W. Nelson, and J. W. Winchester. Anal. Chem. 47:855, 1975.

John, W., G. Reischl, and J. Wesolowski. Size Selective Monitoring Techniques for Particulate Matter. Report No. ARB A5-00487 California Department of Health, Air and Industrial Hygiene Laboratory, Berkeley, CA, February 1978.

Katz, M. Anal. Chem. 22:1040, 1950.

Katz, M. In: Air Pollution. Vol. II, 2nd ed. A. C. Stern, ed., Academic Press, New York, NY, 1968.

Katz, M. Measurement of Air Pollutants--Guide to Selection of Methods. World Health Organization, Geneva, 1969.

Keay, J., and P. M. A. Menage. Analyst (London) 95:379, 1970.

Kirkland, J. J. Modern Practice of Liquid Chromatography. John Wiley, New York, NY, 1971.

Kittleson, D. B., R. McKenzie, M Vermeersch, M. Linne, F. Dorman, D. Pui, B. Liu, and K. Whitby. Total sulfur aerosol detection with an electrostatic pulsed flame photometric detector system. Presented at the 173rd National Meeting, American Chemical Society, New Orleans, Louisiana, March 20-25, 1977. Paper ENVR-42.

Klockow, D., and G. Ronicke. Atmos. Environ. 7:163, 1973.

Kolthoff, I. M., E. B. Sandell, E. J. Meehan, and S. Bruckenstein. Quantitative Chemical Analysis, 4th ed., MacMillan, Toronto, Canada, 1969. pp. 992-994.

Lambert, J. P. F., and F. W. Wilshire. Neutron activation analysis for simultaneous determination of trace elements in ambient air collected on glass-fiber filters. Anal. Chem. 51:1346-1353, 1979.

Lamothe, P. J., and R. K. Stevens. Sulfuric acid analysis using low temperature volatilization. Presented at the 171st National Meeting, American Chemical Society, New York, New York, April 4-9, 1976. Paper ENVR-38.

Lawrence Berkeley Laboratory. Instrumentation for Environmental Monitoring, Air. LBL-1, Vol. 1, University of California, Berkeley, CA, May 1972.

Lawrence Berkeley Laboratory. Instrumentation for Environmental Monitoring, AIR Part 2, University of California, CA, 1975.

Lazarus, A. L., K. C. Hill, and J. P. Lodge. In: Proceedings of the 1966 Technicon Symposium on Automation in Analytical Chemistry. Mediad, Inc., New York, NY, 1966. pp. 291.

Leahy, D., R. Siegel, P. Klotz, and L. Newman. Atmos. Environ. 9:219, 1975.

Lee, R. E., and S. Goranson. National air surveillance cascade impactor network. I. Size distribution measurements of suspended particulate matter in air, Environ. Sci. Technol., 6:1019-1024, 1972.

Lilienfield, P. J. Am. Ind. Hyg. Assoc. 31:722, 1970.

Lippman, M. Respirable dust sampling. J. Am. Ind. Hyg. Assoc. 1970. p. 146.

Liu, B. Y. H., and D. Y. H. Pui. On the Performance of the Electrical Aerosol Analyzer. J. Aerosol Sci. 6:249-264, 1975.

Liu, B. Y. H., ed. Fine Particles, Aerosol Generation, Measurement, Sampling, and Analysis. Academic Press, New York, NY, 1976.

Liu, B. Y. H, D. Y. H. Pui, K. L. Rubow, and G. A. Kuhlmey. Progress Report - Research on Air Sampling Filter Media. Grant Report R804600, University of Minnesota, Minneapolis, MN, May 1978.

Lizarraga-Rocha, J. A. The Effect of Exposure of Filters During Non-operating Periods in the High Volume Sampling Method. M.S. Thesis, University of North Carolina, Chapel Hill, NC, 1976.

Lochmuller, C. H., J. W Galbraith, and R. L. Walter. Anal. Chem. 46:440, 1974.

Lodge, J. P., J. Ferguson, and B. R. Haylik. Anal. Chem. 32:1206, 1960.

Loo, B. W., R. S. Adachi, C. P. Cork, F. S. Goulding, J. M. Jaklevic, D. A. Landis, and W. L. Searles. A second generation dichotomous sampler for large scale monitoring of airborne particulate matter. Presented at 86th Annual Meeting, American Institute of Chemical Engineers, Houston, Texas, April 1, 1979.

Loo, B. W., W. R. French, R. C. Gatti, F. S. Goulding, J. M. Jaklevic, J. Llacer, and A. C. Thompson. Large Scale Measurement of Airborne Particulate Sulfur. Atmos. Environ. 12:759-771, 1978.

Lucero, D. P., and J. W. Paljug. Monitoring sulfur compounds by flame photometry. ASTM Committee D-22 Conference on Instrumental Monitoring for Ambient Air, Boulder, Colorado, August 14-16, 1973.

Lundgren, D. A. Mass Distribution of Larger Atmospheric Particles. Ph.D. Thesis, University of Minnesota, Minneapolis, MN, 1973.

Macias, E. S. Instrumental analysis of light element composition of atmospheric aerosols. In: Methods and Standards for Environmental Measurement. W. Kirchhoff, ed., National Bureau of Standards Special Publication 464. Department of Commerce, Washington, DC, 1977. pp. 179-188.

Macias, E. S., and R. B. Husar. Atmospheric particulate mass measurement with beta attenuation mass monitor. Environ. Sci. Technol. 10:904-907, 1976.

Malm, W. Consideration in the measurement of visibility. J. Air Pollut. Control Assoc. 29:1042-1052, 1979.

Mamane, Y., and R. G. de Pena. A quantitative method for the detection of individual submicron size sulfate particles. In: Sulfur in the Atmosphere, Dubrovnik, Proceeding of an International Symposium, Yugoslavia, September 7-14, 1977. Atmos. Environ. 12:69-82, 1978.

Mamantov, G., E. L. Wehry, R. R. Kemerer, and E. R. Hinton. Anal. Chem. 49:86, 1977.

Martin, B. E. Sulfur Dioxide Bubbler Temperature Study. EPA-600/4-77-040, U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1977.

McCoy, R. A., D. E. Camann, and H. C. McKee. Collaborative Study of Reference Method for Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method) (24-Hour Sampling). EPA-650/4-74-027, U.S. Environmental Protection Agency, Research Triangle Park, NC, December 1973.

McFadden, W. H. Techniques of Combined Gas Chromatography/ Mass Spectrometry. John Wiley, New York, NY, 1973.

McFarland, A. R. Test Report - Wind Tunnel Evaluation of British Smoke Shade Sampler. 3565/05/79/ARM, Texas A&M University, College Station, TX, May, 1979.

McFarland, A. R. and C. E. Rodes. Characteristics of Aerosol Samplers Used in Ambient Air Monitoring. Presented at 86th National Meeting, American Institute of Chemical Engineers, Houston, TX, April 2, 1979.

McFarland, A. R., and C. A. Ortiz. Progress Report - Aerosol Characterization of Ambient Particulate Samplers Used in Environmental Monitoring Studies. Texas A&M University Research Foundation, College Station, TX, October 1979.

McFarland, A. R., C. A. Ortiz, and C. E. Rodes. Evaluation of the NASN Cascade Impactor Ambient Air Monitor. Report 3565/07/78/ARM, Texas A&M, Air Quality Laboratory, College Station, TX, 1978. Accepted Publication Atm. Environ., 1980.

McKee, H. C., R. E. Childers, and O. Saenz. Collaborative Study of Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method). Southwest Research Institute, Houston, TX, June 1971.

Miller, F. J., D. E. Gardner, J. A. Graham, R. E. Lee, W. E. Wilson, and J. D. Bachmann. Size considerations for establishing a standard for inhalable particles. J. Air Pollut. Control Assoc. 29:610, 1979.

Moffat, A. J., J. R. Robbins, and A. R. Barringer. Atmos. Environ. 5:511, 1971.

Morrison, G. H. Trace Analysis Physical Methods. Wiley Interscience, New York, NY, 1965. pp. 245-263, 271-310, 325-360, 377-425.

Mudgett, P. S., L. W. Richards, and J. R. Roehrig. A new technique to measure sulfuric acid in the atmosphere. In: Analytical Methods Applied to Air Pollution Measurement. R. Stevens and W. Herget, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1974.

Mulik, J. D., G. Todd, E. Estes, R. Puckett, E. Sawicki, and D. Williams. In: Ion Chromatographic Analysis of Environmental Pollutants. E. Sawicki, J. D. Mulik, and E. Wittgenstein, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1978.

Nadel, J. A. Dust retention efficiencies of dustfall collectors. J. Air Pollut. Control Assoc. 8:35-38, 1958.

National Academy of Sciences. Airborne Particles. University Park Press, Baltimore, MD, 1979.

National Air Pollution Control Administration Publication. Air Quality Criteria for Particulate Matter. AP-49, U.S. Department of Health, Education, and Welfare, Washington, DC, January 1969.

Natusch, D. F. S., and C. F. Bauer. Collection and analysis of trace elements in the atmosphere. In: Air Pollution Control, Part III. W. Strauss, ed., John Wiley and Sons, Inc., 1978.

Newman, L., J. Forrest, and B. Manowitz. Atmos. Environ. 9:959, 1975a.

Newman, L., J. Forrest, and B. Manowitz. Atmos. Environ. 9:969, 1975b.

Novakov, T. Chemical characterization of atmospheric pollution particles by photoelectron spectroscopy. In: Proceedings of the 2nd Joint Conference on Sensing of Environmental Pollutants, ISA, Washington, DC, December 1973. p. 197.

Novakov, T., S. G. Chang, and A. B. Harker. Science 186:259, 1974.

Okabe, H., P. L. Splitstone, and J. J. Ball. J. Air Pollut. Control Assoc. 23:514, 1973.

O'Keeffe, A. E., and G. C. Ortman. Anal. Chem. 38:760, 1966.

Organization for European Economic Cooperation. Paper EPA/AR/4283, European Productivity Agency, Paris, France, 1961.

Palmer, H. F., C. E. Rodes, and C. J. Nelson. Performance characteristics of instrumental methods for monitoring sulfur dioxide. II. Field Evaluation. J. Air Pollut. Control Assoc. 19:778, 1969.

Perera, F. P., and A. K. Ahmed. Respirable Particles: Impact of Airborne Fine Particulates on Health and the Environment. National Resources Defense Council, New York, NY, 1978.

Philips Electronic Instruments. Coulometric amperometric analyzers. Bull. WA-4-C13.

Pierson, W. R., W. W. Prachaczek, T. J. Korniski, T. J. Truex, and J. W. Butler. Artifact formation of sulfate, nitrate, and hydrogen ion on backup filters: Allegheny Mountain experiment. J. Air Pollut. Control Assoc. 30:30-34, 1980.

R. F. Maddalone, G. L. McClure, and P. W. West. Anal. Chem. 47:316, 1975.

Ranade, M. B., and D. VanOsdell. Quality Assurance Evaluation of the CHAMP Aerosol Inlet, Project Report 43U-1487-59, Research Triangle Institute, Research Triangle Park, NC, July 1978.

Regan, G. F., S. K. Goranson, and L. L. Lawson. Use of tape samplers as fine particulate monitors. J. Air Pollut. Control Assoc. 29:1158-1160, November 1979.

Rider, P. E., C. C. Rider, and R. N. Corning. J. Air Pollution Control Assoc. 27:1011, 1977.

Roberts, P. T., and S. K. Friedlander. Conversion of $SO_2$ to ambient particulate sulfates in the Los Angeles atmosphere. Atmos. Environ. 10:403, 1976.

Rodes, C. E., and G. F. Evans. Summary of LACS Integrated Measurements. EPA-600/4-77-034, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1977.

Ross, J. W., Jr., and M. S. Frant. Potentiometric titrations of sulfate using an ion-selective lead electrode. Anal. Chem. 41:967-969, 1969.

Sajo, I., and B. Sipas. Talanta 14:203, 1967.

Scaringelli, F. P., and K. A. Rehme. Anal. Chem. 41:707, 1969.

Scaringelli, F. P., B. E. Slatzman, and S. A. Frey. Anal. Chem. 39:1709, 1967.

Scroggins, L. H. Collaborative study of the microanalytical oxygen flask sulfur determination with dimethylsulfonazo III as indicator. J. Assoc. Off. Anal. Chem. of the AOAC 57:22-25, 1974.

Shaw, R. Personal Communication to C. E. Rodes, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1980.

Sides, J. O., and H. F. Saiger. Effects of Prolonged Static Exposure of Filters to Ambient Air on High Volume Sampling Results. State of Kansas Report, Department of Health and Environment, Topeka, KS, May, 1979.

Sinclair, D., R. J. Countess, B. Y. H. Liu, and D. Y. H. Pui. Automatic analysis of submicron particles. In: Aerosol Measurement. University of Florida Presses, Gainsville, FL, 1979. p. 544-563.

Small, H., T. S. Stevens, and W. C. Bauman. Anal. Chem. 47:1801, 1975.

Smith, A. F., D. G. Jenkins, and D. E. Cunningworth. J. Appl. Chem. 11:317, 1961.

Smith, F., P. S. Wohlschlegel, R. S. C. Rogers, and Mulligan, D. J. Investigation of Flow Rate Calibration Procedures Associated with the High Volume Method for Determination of Suspended Particulates. EPA-600/4-78-047, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1978.

Snell, F. D. Photometric and Fluorometric Methods of Analysis, Metals. Part 1. John Wiley, New York, NY, 1978. p. 1-25.

Spicer, C. W., and P. M. Schumacher. Particle Nitrate: Laboratory and Field Studies of Major Sampling Interferences. Atmos. Environ. 13:543-552, 1979.

Stalker, W. W., R. C. Dickerson, and G. D. Kramer. J. Am. Ind. Hyg. Assoc. 24:68, 1963.

Stevens, R. K., and T. G. Dzubay. Recent Development in Air Particulate Monitoring. IEEE Trans. Nucl. Sci. 22: April 1975.

Stevens, R. K., J. A. Hodgeson, L. F. Ballard, and C. E. Decker. In: Determination of Air Quality. G. Mamantov and W. D. Shults, eds., Plenum Publishing Corporation, New York, NY, 1972.

Stevens, R. K., J. D. Mulik, A. E. O'Keeffe, and K. J. Krost. Anal. Chem. 43:827, 1971.

Stevens, R. K., T. G. Dzubay, G. Russwurm, and D. Rickel. Sampling and analysis of atmospheric sulfates and related species. Atmos. Environ. 12:55-68, 1978.

Stratman, H. Mikrochim Acta 6:668- , 1954.

Swanson, D., C. Morris, R. Hedgecoke, R. Jungers, R. J. Thompson, and J. E. Bumgarner. A rapid analytical procedure for the analysis of BaP in environmental samples. Trends Fluoresc. 1:22-27, 1978.

Tanner, R. L., and Cordova. U.S. Energy Research Development Administration. Contract No. EY-76-C-02-0016, 1978.

Tanner, R. L., J. Forrest, and L. Neurnan. Determination of atmospheric gaseous and particulate sulfur compounds. U.S. Energy Research Development Administration. Contract No. EY-76-C-02-0016, 1978.

Tanner, R. L., R. Cederwall, R. Garber, D. Leahy, W. Marlow, R. Meyers, M. Phillips, and L. Newman. Atmos. Environ. 11, 1977.

Tanner, R. L., R. W. Garber, and L. Newman. Speciation of sulfate in ambient aerosols by solvent extraction with flame photometric detection. Presented at the 173rd National Meeting, American Chemical Society, New Orleans, Louisiana, March 20-25, 1977a. Paper ENVR-41.

Tanner, R. L., R. W. Garber, W. H. Marlow, B. Leaderer, D. Eatough, and M. A. Leyko. Chemical composition and size distribution of sulfate as a function of particle size in New York City aerosol. Presented at the Industrial Hygiene Conference, New Orleans, Louisiana, May 22-27, 1977. Paper No. 140.

Technicon Corporation. Sulfate method VIb via turbidimetry. Technicon Corporation, Tarrytown, NY, 1959.

Terraglio, F. P., and R. M. Maganelli. Anal. Chem. 34:675, 1962.

Tetlow, J. A., and A. L. Wilson. Analyst (London) 89:453, 1964.

Thoen, G. N., G. G. Dehaas, and R. R. Austin. Tappi 51:246, 1968.

Thomas, R. L., V. Dharmarajan, G. L. Lundquist, and P. W. West. Measurement of sulfuric acid aerosol, sulfur trioxide, and the total sulfate content of the ambient air. Anal. Chem. 48:639-642, 1976.

Thrane, K. E. In: Studies in Environmental Science, Vol. 2, Air Pollution Reference Measurement Methods and Systems. T. Schneider, H. W. de Koning, and L. J. Brasser, eds., Elsevier Scientific Publishing Company, Amsterdam, 1978.

Threshold Limits Committee. Threshold Limit Values of Air Borne Contaminants for 1968. American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1968.

Tierney, G. P., and W. D. Conner. Hydroscopic effects of weight determinations of particulates collected on glass fiber filters. J. Am. Ind. Hyg. Assoc., 1967.

Treon, J. F., and W. E. Crutchfield. Ind. Eng. Chem. Anal. Ed. 14:119, 1942.

Turner, J. M., and R. S. Shotes. Presented at the 64th Annual Meeting, Air Pollution Control Association, 1971. Paper No 71-39.

U.S. Environmental Protection Agency. Ambient Air Monitoring Reference and Equivalent Methods. 40 CFR 53:952-986, July 1, 1979c.

U.S. Environmental Protection Agency. National Primary and Secondary Ambient Air Quality Standards. Appendix A - Reference method for the determination of sulfur dioxide in the atmosphere (pararosaniline method). 40 CFR 50:6-11, July 1, 1979.

U.S. Environmental Protection Agency. National Primary and Secondary Ambient Air Quality Standards. Appendix B - Reference method for the determination of suspended particulates in the atmosphere (high volume method). 40 CFR 50:12-16, July 1, 1979a.

U.S. Environmental Protection Agency. National Primary and Secondary Ambient Air Quality Standards. 40 CFR 50:3-5, July 1, 1979b.

Volmer, W., and F. Z. Frohlich. Z. Anal. Chem. 126:401, 1944.

Von Lehmden, D. J., and C. Nelson. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume I. Principles. EPA-600/9-76-005, U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1977.

Von Lehmden, D. J., and C. Nelson. Quality Assurance Handbook for Air Pollution Measurement System. Volume II. Ambient Air Specific Methods. EPA-600/4-77-027a, U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1977b.

Wartburg, A. F., J. B. Pate, and J. P. Lodge, Jr. Environ. Sci. Technol. 3:767, 1969.

Wedding, J. B., A. R. McFarland, and J. E. Cernak. Large particle collection characteristics of ambient aerosol samplers. Environ. Sci. Technol. 11:389, 1977.

Wedding, J. B., M. Weigand, W. John, and S. Wall. Sampling Effectiveness of the Inlet to the Dichotomous Sampler. Aerosol Science Laboratory, Fort Collins, CO, 1980.

Welch, A. F., and J. P. Terry. Developments in the measurement of atmospheric sulfur dioxide. J. Am. Ind. Hyg. Assoc. 21:316-321, 1960.

West, P. W., and G. C. Gaeke. Anal. Chem. 28:1816, 1956.

Whitaker Company Electrochemical Transducer.

Whitby, K. T. Modeling of Atmospheric Aerosol Size Distribution, Progress Report, EPA Grant No. R800971, 1975.

Whitby, K. T. The Physical Characteristics of Sulfur Aerosols. Paper Prepared for Presentation at the International Symposium on Sulfur in the Atmosphere, 7-14 Sept., 1977, Dubrovnik, Yugoslavia.

Whitby, K. T., and K. Willeke. Single particle optical counters: principles and field use. In: Aerosol Measurement. University of Florida Presses, Gainesville, FL, 1979. p. 145-180.

Whitby, K. T., and W. E. Clark. Electrical aerosol particle counting and size distribution measuring system for the 0.015 to 1.0 mm size range. Tellus. 18:573-586, 1966.

Willeke, K., and J. J. McFeters. Calibration of the CHAMP Fractionator, Particle Technology Publication No. 252, University of Minnesota, Minneapolis, MN, March 1975.

Willeke, K., and Whitby, K. T. Atmospheric Aerosols Size Distribution Interpretation, J. Air Pollution Control Assoc., 25, No. 5, 1975.

Wilsdon, B. H., and F. J. McConnell. J. Soc. Chem. Ind. 53:385, 1934.

Wilson, W., et al. Sulphates in the Atmosphere. Paper No. 76-30.06, 69th Annual Meeting of the Air Pollution Control Assoc., Portland, Ore., U.S.A., June 27, 1976.

World Health Organization Selected Methods of Measuring Air Pollutants. World Health Organization, Geneva, Switzerland, 1976.

Chapter 3 Critical Appraisal of Air Quality Measurement Applications Corrigenda

Before listing specific minor errata (insertions/deletions) for text contained in Chapter 3 of the April, 1980, External Review Draft, several major changes to be made in the chapter should be noted. The proposed changes are based in part on additional literature review and comments received since finalization and release of the April, 1980, external review draft of the chapter.

On pg. 3-84, after the first paragraph, new text is to be inserted discussing the fact that difficulties in comparing results from various bodies of epidemiologic literature (e.g., British versus American) on particulate matter health effects arise from differences in specific physical and chemical properties of particulate matter pollution indexed by different measurement techniques employed in such studies. In particular, the following points are to be noted:

(1) The British smoke (BS) sampling technique (widely used in Britain and Europe) mainly collects fine mode particles (<3-5 μm) and, using reflected light, specifically measures degree of reduction of reflectance by the collected particles. BS computed by the degree of reduction in reflectance, although sometimes highly correlated with TSP (r=0.8-0.9) and lead (r=0.8-0.9) as reported by Ball and Hume (1977) and affected by certain other materials (Pedace and Sansone, 1972), is most highly correlated with the amount of graphitic carbon* present (r=.96; Baily and Clayton, 1980). Levels of carbon or other materials affecting reflectance readings can, however, vary independently of the total mass of the collected (mainly fine mode) particles. Thus, estimation of collected particle mass indexed by BS readings is dependent upon calibration of BS readings against standard mass readings (weighing) of collected particle samples typifying

* The term "graphitic carbon" is not meant to imply the three-dimensional structure of graphite, but only to indicate a structure similar to that of carbon black contained in soot.

a given location, allowing for calculation of corresponding mass concentration levels (in $\mu g/m^3$) by taking into account sampling periods and air flow rates. Relationships between BS reflectance readings and mass concentrations ($\mu g/m^3$) for a given location are most accurately determined empirically by reflectance to mass calibrations derived on a site-by-site and, time-specific basis, given the fact that relative mixes of va ious pollutants sampled could vary on an hour to hour, day to day, or longer-term basis. However, if the relative mix of particulate matter sampled and the percentage of the total collected mass attributable to graphitic carbon and other materials affecting light reflectance remains, similar from time to time or site to site, as empirically demonstrated by representative calibration determinations, then a common standard calibration curve relating mass concentration ($\mu g/m^3$) of particulates collected to reflectance readings may be generally applicable for BS data obtained from thusly calibrated sites shown to fit the standard curve well (Wallin, 1965).

(2) Particulate matter measurements by certain American sampling techniques (e.g., the AISI tape sampler method) which uses light transmittance as the physical property measured (Katz and Sanderson, 1958), are also most strongly affected by graphitic carbon levels present among particulate matter mass collected (mainly fine mode, <5μm size-range). Thus, similar considerations and limitations as described above for the BS method apply to the AISI tape sampler light transmittance method in regard to converting transmittance readings (coefficient of haze units or COHS for the AISI method) to estimates of particulate mass collected. That is, very precise estimates of particulate mass collected or air concentration (in $\mu g/m^3$) require that the transmittance readings (in COHS) be calibrated against representative corresponding sample weights on a site-and time-specific basis.

However, practical application of the AISI light transmittance method, as in the case of BS measurements, usually precludes other than occasional representative calibrations for a given sampling site due to personnel and other resource limitations. Rather, to the extent that similar relationships of mass to transmittance readings are consistently obtained at a given site through repeated calibrations over time, then use of a standard calibration curve for converting transmittance readings (COHS units) to corresponding particle mass estimates for that site appears to be reasonably well justified.

Analogously, to the extent that a relatively similar mix of pollutants (e.g. graphitic carbon) most strongly affecting light transmittance is represented among the total mass of particulate matter collected at various other sites, it appears reasonable to employ a common standard calibration curve for conversion of transmittance values to estimates of particulate mass collected at those sites by the AISI method, especially if representative calibration data are fit well by the standard curve. Conversely, substantial variations in the pollutant mix, e.g. in the percentage of graphitic carbon represented in the overall particulate mass collected either for the same site at different times or between different sites, should be reflected by notable deviations from the more usually applicable calibration curve and would require generation of another one on a site-and time-specific basis. The likely generalizability of any particular calibration curve for estimation of collected particulate mass concentrations based on light transmittance readings appears, then, to be amenable to empirical testing in terms of: (a) assessment of goodness of fit of data for specific sites to the particular model defining the given calibration curve, and (b) assessment of similarities of chemical composition (including percentage of graphitic carbon and other substances affecting light transmittance) of atmospheric particulate matter sampled at different times at the same site or between different sites.

(3) Since both light reflectance (BS) and transmittance (AISI tape sampler) measurement methods are both most strongly affected by levels of graphitic carbon among the particulate matter mass collected, it might be assumed that results obtained by each method should be readily translatable into equivalent measurement units employed by the other method (i.e., reflectance or darkness index BS readings versus COHS units for the AISI tape sampler), using emperically-derived calibration curves. Similarly, it might be assumed that, if particles of the same size-range are collected and valid curves exist for estimation of particulate matter mass levels based on either light absorption or transmittance readings for a given site, equivalent particulate matter mass or air concentration estimates should be derivable from reflectance or transmittance readings for a given set of BS or COHS data points on a site-and time-specific basis. Those mass concentration estimates, furthermore, would then presumably provide a reasonable basis for comparisons of particulate matter levels in the same size-range from one site or time to another, where atmospheric aerosols of similar chemical composition are sampled. This might be the case, for example, in terms of samples of certain urban aerosols containing similar pollutant mixes derived from relatively similar emission sources, but not obtained from collection sites markedly dominated by different single emission sources. The interconversion (comparability), or lack thereof, of particulate matter mass estimates derived from light reflectance versus light transmittance measurement techniques, therefore, should be empirically testable in terms of goodness of fit of data from a given site or time in relation to curves or equations modeling relationships between results from the two techniques.

The particulate matter measurements (in terms of mass concentrations in $\mu g/m^3$) based on standard light reflectance (BS) or transmittance (AISI tape sampler) methods most often used in community health epidemiology studies might also be expected to approximate fine mode particulate matter mass estimates determined by gravimetric methods, in view of procedures for the former two methods being reported to result mainly in collection of fine mode fraction particles (<3 μm). However, factors influencing estimation of mass from BS reflectance or COH units could be such to result in quantitative mass estimates different from those obtained for fine particulate mass as determined by gravimetric methods.

(4) Conversion of particulate matter measurement results from either light reflectance (e.g., BS) or transmittance (e.g., AISI tape sampler) methods versus high-volume sampler results (expressed in $\mu g/m^3$ TSP) involve additional considerations beyond those outlined above. First, the high volume sampler has an inlet which is 50% efficient in collecting 25-30 μm sized particles and therefore collects coarse mode particles not sampled by the other two methods as standardly employed. Also, graphitic carbon levels and other materials most strongly affecting light reflectance and transmittance readings and fine mode particulate mass levels (indirectly indexed by the same methods) can vary independently of coarse mode particle levels. They may, therefore, increase or decrease in directions opposite to changes in total suspended particulate (TSP) matter mass. It is thusly not surprising that quite different relationships between particulate matter mass estimates based on BS or COHS readings and TSP levels can exist from site to site or from sampling time to sampling time at the same site.

Reliable determination or estimation of likely TSP levels present at particular sampling points (times/places) based on corresponding BS or COHS data, then, may only be possible or justifiable within very circumscribed limits and highly dependent upon development of applicable empirically-derived intercomparison models in a fashion analogous to obtaining calibration or interconversion curves for BS and COHS readings discussed above.

On pg. 3-102, immediately before the last paragraph and heading for Section 3.5.5, new text is to be added which notes that three recently reviewed papers (by Ledbetter and Cerepaka, 1980; Swinford and Kolaz, 1980; and Heindryckx, 1975) report on relationships between COH and TSP as determined by comparisons of results obtained from collocated high volume and AISI tape samplers. In each case, for data obtained from sampling site locations as diverse as areas in Texas, Illinois, and Belgium, considerable scatter was found for individual paired observations, suggesting great uncertainty in predicting 24 hour TSP levels from short-term (1 hour) COH readings. It may be possible to improve on the relationships by using seasonal calibrations at each site and nonlinear models calibrated in a manner similar to the ASTM method or the British Standard 1747 Part 2 procedure for smokeshade in order to convert COH readings to units of mass for comparison with TSP data. However, these studies, and other literature cited above in this chapter, all appear to indicate that COH measurements are generally not directly relatable to TSP levels.

On pg. 3-103, immediately before the last paragraph, new text is to be inserted which notes that a typical finding among the various BS/TSP comparison studies cited in the preceeding paragraph is that considerable scatter or variability

exists for individual paired observations for 24 hour BS and corresponding TSP measurements analyzed in the various studies. However, greater consistency appeared to exist for BS-TSP relationships expressed as long-term (monthly or longer) averages of the paired 24 hour observations; and efforts were made in the different studies to derive equations or models (mainly linear regression) that best fit the observed data obtained from different individual sites, cities and time periods (e.g., winter heating seasons versus summer nonheating seasons).

On pg. 3-116, immediately before the last paragraph, new text is to be inserted noting that neither the Mage (1980)* bounded nonlinear model derived primarily from the annual average (mean) BS-TSP comparison data of Commins and Waller (1967) as summarized by Holland et al. (1979) nor any other presently available model provides a generally reliable basis for interconversion of corresponding individual 24 hour BS-TSP data points, except perhaps at high levels of BS ($\geq$ 500 $\mu g/m^3$). The Mage (1980) and other models such as those discussed in Lee et al. (1972) or Pashel and Egner (1980), however, may provide better ore more reliable fits for BS-TSP monthly or annual average data.

On pg. 3-121, there is to be deleted the last three paragraphs discussing the impact of the use of a sampling flow rate of 0.72 liters per minute by Pashel and Egner (1980). Also to be deleted are Figure 3-13 on pg. 3-122, all text but the last paragraph on pg. 3-123, and Appendix C of Chapter 3. These deletions are based on a personal communication from Pashel and Egner indicating that a 0.72 liter per minute flow rate was erroneously reported in their draft 1980 Atmospheric Environment article; rather, according to their personal communication, a 1.5 l/min. flow rate more typically employed in generating BS data used by British epidemiologists was also used by them in producing the data reported in their 1980 paper.

* Manuscript now in preparation.

Detailed discussion of possible methodological errors in the Pashel and Egner study, starting on pg. 3-118, are to be moved to appendices and only brief summary statements regarding such included in the main text of Chapter 3. Also, on pg. 3-128, the paragraph immediately before the heading for Section 3.5.5.3. is to be entirely deleted and replaced with the following new text: Another possible explanation for the particular pattern of results obtained by Pashel and Egner is suggested by the fact that all of their annual mean data for rural, residential, and commercial sites studied fall on or very near the BNLM (Mage, 1980) model curve in Figure 3-15 on pg. 3-127, whereas data for seven of eleven industrial sites fall rather far to the right of the BNLM curve. The possibilty exists that high levels of either noncarbonaceous fine-mode particles, coarse mode particles, or both in fugitive dust or stack emissions from nearby industrial sources in the absence of much carbonaceous material from fossil fuel combustion, result in the relatively higher TSP readings (mostly >100 $\mu g/m^3$) obtained at those sites. If such were the case, the data would illustrate a likely general limiting factor in making meaningful comparisons or interconversions between BS and TSP data, even on a long term annual mean basis. That is, whereas the BNLM or other analogous models might fit well BS-TSP comparison readings obtained from sites sampling aerosols dominated by graphitic carbon and other particles from fossil fuel combustion sources, such models would not likely apply in markedly different circumstances, eg. in dry rural areas of the American Southwest or sites strongely affected by fugitive dust from industrial facilities. Especially highly variable BS-TSP relationships can be expected in such situations where large amounts of coarse mode crustal particulate matter or mechanically produced coarse mode particles from anthropogenic activities exists in the air in the

presence of little fine-mode carbon or other materials from fossil fuel combustion sources.

On pg. 3-141, additional sentences are to be added to the last paragraph, as follows: On the other hand, another possible explanation for the marked divergence of the data set from other published results for BS-TSP comparisons (mainly sampling urban aerosol mixes dominsted by fossil fuel combustion emission products) is that significant amounts of particles from fugitive dust or other emissions from nearby industrial facilities may have contributed to relatively high TSP readings (ca. 100 - 200 $\mu g/m^3$) in the presence of low BS readings ($\leq$ 25 $\mu g/m^3$). Such results would be illustrative of one type of circumstance severely limiting determination of reliable or meaningful relationships between corresponding BS-TSP data points.

Chapter 3 - $PM/SO_x$
Errata

| Page | Par/Line | Delete | Insert |
|---|---|---|---|
| 3-1 | 2/12 | Higgins and Ferris, 1978 | National Academy of Sciences, 1978a |
| 3-1 | 2/13 | Speizer and Ferris, 1978 | National Academy of Sciences, 1978b |
| 3-25 | 2/2 | dates | was after: which |
| 3-29 | 1/11 | Adams et al., 1971 | - |
| 3-42 | 2/6 | are | as |
| 3-44 | | air (column 4, line 17) | error |
| 3-52 | 3/2 | - | National Survey after: for |
| 3-59 | 3/5 | reflectance | darkness |
| 3-62 | 1/3 | - | Ellison (1968) after: by |
| 3-62 | 2/7 | MckEllison (1964) | Ellison (1968) |
| 3-63 | 3/4 | Page 3-52 | Page 3-57 |
| 3-67 | 1/3 | "period" after: December 15 | , since |
| 3-77 | | (column 4, line 8) Moulds, 1961 | Moulds, 1962 |
| | | (Column 5, line 14) 10 cm | 10 mm |
| 3-82 | 2/12 | | uncorrected after: usage of |
| 3-85 | 1/last | Mck | - |
| 3-89 | | (Entire table heading) | Relationship of coefficient of Haze to Particle Counts (Np), 0.3 - 2.0μm, Measured in New York City |
| 3-89 | -/last | - | Source: Ingram (1969) |
| 3-91 | 2/7 | $length^2/mass$ | $length^{-2}$-mass |
| 3-93 | 1/3 | can | could |

# CHAPTER 3. CRITICAL ASSESSMENT OF PRACTICAL APPLICATIONS OF SULFUR OXIDES AND PARTICULATE MATTER MEASUREMENT TECHNIQUES

## 3.1 INTRODUCTION

In the preceding chapter (Chapter 2) of this document, physical and chemical properties of sulfur oxides ($SO_x$) and particulate matter (PM) were discussed and numerous methods that have been developed for measuring air concentrations of those substances were described. Also, information was provided, in a general form, regarding possible sources of error associated with various $SO_x$ and PM measurement approaches, and comments were made regarding the general specifity, sensitivity, accuracy, and precision of measurement that can be attained with the different approaches.

In the present chapter (Chapter 3), ways in which some of the methods described in Chapter 2 have been put to practical use in monitoring ambient air quality will be discussed, accompanied by: (1) critical assessment of factors found to affect the quality of measurements obtained with actual applications of certain of the approaches, and (2) comparison of results obtained with key applications of those approaches. Particular emphasis will be placed in the ensuing discussion on those measurement approaches that have attained a fairly high degree of widespread usage or which have played important roles in the collection of air quality data discussed in later chapters of this document. For other discussions of $SO_x$ and PM measurement applications consult: National Research Council/National Academy of Sciences (NRC/NAS) reviews on Airborne Particles (National Academy of Sciences ~~Higgins and Ferris~~, 1978a) and Sulfur Oxides (National Academy of Sciences ~~Speizer and Ferris~~, 1978b); the WHO document, Environmental Health Criteria (8): Sulfur Oxides and Particulate Matter (1979), and the recent American Journal of Epidemiology report by Holland et al. (1979).

## 3.2 HISTORICAL PERSPECTIVE

It is important that consideration of problems associated with the practical application of $SO_x$ and PM air quality measurement techniques be undertaken against the backdrop of a historical recounting of factors that stimulated and influenced the development and practical application of these methods. By providing such a historical perspective, it is hoped that a better appreciation can be achieved concerning the indispensible utility of air quality measurements, despite their various imperfections, in helping to quantify air pollutant-effects relationships and to reduce or eliminate such effects as major public health problems.

There is little question that severe air pollution generated by anthropogenic activities has long exerted significant, even lethal, adverse effects on the health and welfare of many industrial societies. It has only been within the past 50 years or so, however, that sufficient recognition of such effects as a major public health problem has stimulated both (1) extensive research to better understand the problem and (2) strong governmental and private sector actions to control or eliminate it.

It is not surprising that the air pollution incidents most often cited as signal events precipitating great concern about the problem and strong actions in response to it occurred among the most heavily industrialized societies then extant, i.e., in Western Europe, Great Britain and the United States. It is also easy to understand the urgency associated with taking strong actions to control the problem in light of the magnitude and seriousness of the effects experienced during those incidents.

For example, in describing the effects of a thick fog that covered the industrial Meuse Valley in Belgium during early December 1930, Firket (1931)

noted that several hundred people were afflicted by suddenly appearing acute respiratory symptoms, complicated in many instances by serious cardiovascular failure. Firket (1931) further noted: "More than sixty died on the 4th and 5th of December after only a few hours of sickness. A sizeable number of livestock had to be slaughtered." Also, taking into account that mortality rates were more than 10 times normal, Firket projected that over 3,000 deaths would occur if a similar fog were to occur in a city the size of London.

Twenty-two years later, such an event did occur in London and more than 4,000 deaths appeared to be attributable to the four-day London Fog of December 1952, according to Logan (1953). Logan further noted: "The incident was a catastrophe of the first magnitude in which, for a few days, death rates attained a level that has been exceeded only rarely during the past hundred years - for example, at the height of the cholera epidemic of 1854 and of the influenza epidemic of 1918-19." Indeed, the death rate rivaled or exceeded that on many of the worst days of other catastrophic events afflicting London in its more recent past, e.g., the Battle of Britain during World War II.

Similar catastrophic air pollution incidents also occurred around the same time in the United States. Almost half of the residents of Donora, Pennsylvania, for example, were afflicted with respiratory symptoms as the result of a "smog" covering the coke- and steel-producing Monongahela River Valley during October, 1948 (Schrenk et al., 1949). Twenty people in the small town of about 10,000 population died during the final week of the "Donora Smog Episode," in comparison to the 2 or 3 deaths normally expected for the same period. Over the next few years, catastrophic air pollution incidents also affected other United States communities. One such case was a dramatic

increase in infant mortality in Detroit, Mich., attributed to a "pollution incident" in September 1952 (Int. Joint Commission, 1960). This was followed by marked increases in respiratory distress cases and fatalities attributable (Greenburg et al., 1962) to air pollution occuring on an even larger scale during a "Thanksgiving Day" pollution episode in New York City in November, 1953--an experience later to be repeated several more times in New York City during the early 1960s.

It was clear from the above incidents and others occurring elsewhere in the industrialized world that air pollution, especially under certain weather conditions leading to stagnant masses of pollutant-laden "fog" or "smog", was capable of causing incidents rivaling natural disease epidemics or man-made wartime disasters that constituted national emergencies for the affected societies. Equally clear was the urgent need to take immediate action to avert or reduce in severity future air pollution disasters. Among the first to act were two of the most severely affected countries, Great Britain and the United States.

Many parallel historical threads can be discerned regarding the paths taken by the two nations in trying to cope with the problem, including a number of similar mistakes as well as successes. In each country, for example, there occurred extensive expansion of epidemiological and toxicological research aimed at identifying components of the killer smogs or fogs responsible for the observed lethal effects and increased morbidity. Also, in each country, although occurring within different specific time frames and at different specific paces or rates, there ensued the upgrading and expansion of air quality monitoring networks. This included the expansion of monitoring networks capable of indexing high levels of various industrial pollutants implicated by

the historical data as being associated with increased incidences of both morbidity and mortality. The latter invariably included oxides of sulfur and particulate matter present in the killer fogs or smogs of the 1940s and 1950s, although the relative contributions of each could not be precisely linked to observed health effects.

It is important to note in regard to the air quality data that very precise accuracy and specificity were not then demanded; rather, "benchmark" ranges of estimates of air pollutant concentrations were acceptable, especially for indexing the rather high levels of pollution associated with severe morbidity or mortality effects. It mattered little if the exact amounts of $SO_2$, for example, were 143 or 781 or 1408 $\mu g/m^3$ plus or minus 5 or 10 percent, when one was concerned that people would begin to experience severe morbidity or even die when $SO_2$ or particulate matter exceeded several hundred $\mu g/m^3$. Being able to establish that increased mortality or severe morbidity occurred at, say, a range of 550 to 600 or even 500 to 1000 $\mu g/m^3$ of $SO_2$ or particulate matter in comparison to the incidence of such effects observed at, say, 70 to 100 or even 50 to 200 $\mu g/m^3$ of the same pollutants was, understandably, sufficient scientific evidence to support political and social measures needed to avert the worst air pollution episodes.

Nor was it particularly important whether or not $SO_2$, specifically, or particulate matter of whatever specific size-range or chemical composition could be precisely implicated as the "culprit" causing one or another very specific health effect. Rather, it was sufficient to recognize that those substances might not be any more than representative indicators of the total mix or some other potentially lethal subfraction of pollutants typically present during the dangerous past pollution episodes. Basically, the main objective, regardless of specific fine details associated with various pollution

situations, was to obtain sufficient information: (1) to allow for reasonable conclusions to be drawn regarding ranges of air levels of various pollutants (or indices) empirically linked to the occurrence of severe health effects and (2) to help serve as a guide in directing pollution control efforts toward sources emitting such pollutants (or mixes containing them).

In addition to the above developments, certain regulatory actions were taken in response to the severe air pollution situations in Britain and the United States in the 1950s. The British acted strongly on a national scale by passing the Clean Air Act of 1956 which forced implementation of very stringent controls on emissions from coal-fired combustion sources, essentially eliminating the use of coal for home-heating and many industrial purposes in heavily industrialized and congested urban areas. The effectiveness of those measures was reflected in the resulting declines seen by the early 1960's in both atmospheric sulfur oxides and particulate matter and associated mortality effects (WSL, 1967).

As for the United States, action initially tended to be taken mostly on more more restricted geographic bases and consisted mainly of local or state air pollution control ordinances being passed, often with the cooperation of local industrial leaders, to reduce air pollution. Among the more notable examples were early actions taken to control air pollution in one of the most heavily industrialized regions of the country, the Pittsburgh area. There, and in other areas of Pennsylvania, extensive steel-making and coking operations and the burning of locally produced high-sulfur coal contributed to widespread elevations in both particuate matter and sulfur dioxide air concentrations. Notable improvements in air quality in various American regions were attained as the result of such initial actions. However, simultaneous deterioration in air quality in many other communities or states lacking effective pollution

control laws, and the growing recognition of air pollution as a multi-state, regional or national problem eventually led to the passage in the United States of the Clean Air Act of 1970 and consequent promulgation of National Ambient Air Quality Standards for sulfur oxides, particulate matter, and other air pollutants of widespread concern.

Subsequent to many of the above actions taken in the 1950s and early 1960s, questions began to be raised regarding what less severe, but important, effects on human health and welfare might be caused by lower air levels of oxides of sulfur, particulate matter, and other air pollutants, especially under conditions of prolonged periods (months or years) of exposure. Again, fairly similar paths were followed in both Great Britain and the United States in trying to deal with such questions.

In both countries, epidemiologists began to design studies to either retrospectively or prospectively define in more precise terms both qualitative and quantitative relationships between elevations of various pollutants in the ambient air and specific sublethal health effects, such as acute or chronic bronchitis, respiratory infections, temporary decrements in pulmonary function, and asthma attacks. Air quality monitoring networks set up or expanded earlier to provide at least representative, but not necessarily thorough, coverage of geographic areas having varying pollution levels were often looked to by the epidemiologists to provide requisite, albeit less than perfect, quantitative estimates of air quality to help define quantitative air pollution-effect relationships. Only in relatively rare circumstances were sufficient funds or other resources available to allow for more thorough monitoring coverage to be arranged specifically for collection of community air quality data to be coupled with health endpoint measurements.

At the same time as the above expansion of research efforts, more precise estimates of air pollutant levels were being demanded or expected from existing or expanding air monitoring networks to help index progress in reductions of air pollutants. Bearing on this point, the following was later noted in Her Majesty's Report on the Investigation of Atmospheric Pollution 1958-1966 (Warren Spring Laboratory, 1967):

> The industrial provisions of the Clean Air Act 1956 had come into force by June 1958, and the first smoke control areas were declared under the domestic provisions in April 1958. This timetable added urgency to the view that the existing survey of air pollution throughout the United Kingdom was too blunt an instrument either to assess the benefits accruing from the Act or to guide its future application, and that a scientifically planned National Survey was necessary. Such a survey was designed and the co-operation of the local authorities concerned was obtained where measurements were required in addition to those already being made. Observations were started in the winter of 1962-63. Not only has the whole pattern of co-operative observations been transformed in this way, but so also has the basis of the co-operation: the local authorities and other organizations are now making measurements as required to conform to an overall statistical plan.

A growing need was also felt for establishing or maintaining monitoring systems using sufficiently uniform and reliable measurement approaches to allow for comparability of air quality data from disparate geographic sites. This need became perhaps most acutely felt in the United States in the late 1960s in light of the growing prospect of having to attain national ambient air quality standards at much lower air concentrations than were earlier envisaged. Pressure to meet such needs and demonstrate the benefits of air pollution control in the United States intensified greatly with the passage of the Clean Air Act of 1970.

Both the above needs and the anticipated use of air quality data in future epidemiology studies increased the necessity for better air quality data in terms of their specificity, sensitivity, accuracy, precision, and

reliability. Thus, it became increasingly more important to be able to distinguish with confidence between much closer absolute levels of air pollutants even at relatively low ambient air concentrations (e.g., at levels around or lower than 100 to 200 $\mu g/m^3$ of either $SO_2$ or particulate matter). In other words, the emerging demands required practical applications of available or newly developed measurement techniques to meet previously unheard-of levels of accuracy. At times expectations may have exceeded what could realistically be achieved with field applications of available technology, especially in comparison to theoretical limits of what could be achieved with particular measurement techniques under ideal laboratory conditions.

In responding to the above demands, several similar historical parallels can again be discerned between the British and American experiences, as well as some quite significant differences. In Britain, steps were taken to assure that a high degree of uniformity in measurements of pollutants was maintained or further enhanced; this included the establishment of the National Air Pollution Survey alluded to above. As part of this effort, the British Smoke (BS) filter method, widely used in Britain since the early 1900s for the measurement of black suspended particulate matter, was officially adopted to monitor air quality across the United Kingdom. The daily smoke filter has since been the standard air particulate matter measurement instrument used in the United Kingdom, and responsibility for quality assurance for the use of the instrument throughout the entire United Kingdom was assigned to the Warren Spring Laboratory (WSL) of the Department of Industry, where central coordination and evaluation of uniformity, accuracy, and reliability of all National Survey air quality measurement have been carried out since the late 1950s. Based largely on WSL evaluations, the daily smoke filter was later adopted as a standard also by the British Standards Institute and became one

of OECD's recommended procedures for measuring suspended particulate matter.

The WSL was also instrumental in selecting $SO_2$ measurement methods for the British National Survey air monitoring program. Under WSL guidance, the hydrogen peroxide method was adopted in the early 1960s as the standard approach for measuring $SO_2$. This replaced the lead dioxide gauge still in use at many sites in Britain (in 1962 there were about 1200 gauges in operation). The decision to adopt the hydrogen peroxide method was based on recommendations of a WSL-organized "Work Party" that considered both the deliberations of an OECD Working Party and detailed comparisons of the two methods under field conditions by WSL.

The above interplay between the WSL, the British Standards Institute, and the OECD is illustrative of close working relations that broadly evolved between the WSL, other British government groups, agencies of various foreign governments, international agencies and other groups having interests or responsibilities in research on or application of air pollutant measurement methods. Such close working relationships further reflect the wide international respect engendered by the WSL in the field of air pollution monitoring and broad international acceptance of rigorous standards developed by the WSL for practical applications of air pollution measurement techniques as used in the United Kingdom National Air Pollution Survey.

Turning to concomitant developments in the United States during the past twenty years, one can discern a lag in the development of a standardized nation-wide approach to air pollution monitoring and control. During the 1950s and early 1960s numerous air monitoring systems established by different governmental units sprang up around the country, often to meet needs associated with enforcement of newly enacted air pollution control ordinances. It was not until the mid-to-late 1960s that effective procedures were implemented to feed

data obtained from the multiplicity of air monitoring sites operated by city, county, state, and federal agencies into a central data bank as part of a National Air Survey Network (NASN). Even then, those data were still often derived from different measurement methods used by various agencies for monitoring of a given pollutant. Generally, the Hi-Vol TSP measurement method developed in the United States in the 1950s was used for assessing airborne particulate levels; but, at times, other methods such as coefficient of haze (CoH) measurements were also employed to assess particulate levels. Similarly, several approaches, e.g., the West-Gaeke or sulfation methods, were used to measure $SO_2$.

Considerably greater uniformity in monitoring approaches has, however, been achieved over the past decade or so through the publication of "Federal Reference Methods." Additional efforts were undertaken in the late 1960s and early 1970s by EPA and its predecessor Federal agencies to establish a new nationwide air monitoring network using uniform measurement methods. That network was established as part of what became known as EPA's Community Health and Environment Surveillance System (CHESS) Program. The "CHESS" monitoring network, set up in addition to other Federal air sampling stations used for monitoring compliance with air regulations, included monitoring sites dispersed in widespread urban and semi-rural areas of the United States to provide air quality data representative of pollutant exposures experienced by surrounding population groups. Various health endpoints were also evaluated for those population groups as part of CHESS Program epidemiology studies. Thus, the CHESS monitoring network, including sampling sites often situated near or along side local or state monitoring sites, was designed to provide air quality data from a nationwide network using uniform measuring methods that supplemented other data entered into the NASN data bank. The hi-volume TSP sampling procedure

was usually employed in the CHESS Program to monitor atmospheric particulate matter levels and the West-Gaeke method was generally employed for $SO_2$ measurements, along with additional procedures for estimating suspended sulfates discussed below. The series of major air pollution/health effects studies carried out between 1969 and 1975 as part of the CHESS Program, and coupling such aerometric measurements with community health surveys, have been considered by many experts as the most comprehensive of their kind.

It should be noted, however, that a number of methodological problems were engendered by attempts to rapidly deploy air monitoring stations at widespread sites across the United States and to bring them up to full operational status in time to collect air quality data to be coupled with health surveys as part of the CHESS Program. Of particular concern for the present discussion are problems which were detected regarding certain errors in air quality data generated from CHESS network sampling sites--several types of errors which were either not detected at all during the CHESS health endpoint data collection period (1969-75) or were only detected and corrected through improved quality control procedures implemented and applied in the last few years of the Program (i.e. 1972 or 1973 onward).*

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*As discussed in more detail later in this chapter, the matter of errors in air quality data collected as part of the CHESS Program (together with other concerns regarding the collection of health endpoint data in CHESS studies) contributed to considerable controversy regarding the validity and accuracy of results of early CHESS studies, as interpreted and reported in a 1974 EPA monograph entitled "Health Consequences of Sulfur Oxides: A Report from CHESS" 1970-71, U.S.EPA Document No. EPA-650/1-74-004 (May 1974). The controversy eventually led to the 1974 "CHESS Monograph" becoming the subject of U.S. Congressional oversight hearings in 1976. Subcommittees of the U.S. House of Representatives Committee on Science and Technology produced a report on the Monograph, other aspects of the CHESS Program, and EPA's air pollution research programs generally--a report entitled "The Environmental Protection Agency's Research Program with Primary Emphasis on the Community Health and Surveillance System (CHESS): An Investigative Report." Of primary importance for the present discussion, that report, widely referred to either as the

Improvements in the air quality data obtained during the last few years of the CHESS Program and, also, in other EPA air monitoring efforts, were accomplished via a substantially expanded in-house EPA quality assurance program. That program, conducted by EPA's Environmental Monitoring Systems Laboratory in Research Triangle Park, N.C., has since provided quality assurance backup for all of EPA's research and nationwide enforcement air monitoring activities.

From the foregoing, it can be seen that similar needs and demands as those felt by the British in conjunction with the passage of their Clean Air Act of 1956 were later experienced by the Americans with the passage of their Clean Air Act of 1970. Remarkably similar paths were also followed in both countries in responding to those needs; that is, in both cases intensive efforts were carried out to rapidly expand and improve air monitoring capabilities, including introduction of more uniformity in measurement approaches across geographic regions along with increased quality control efforts to help assure

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*(continued)

"Brown Committee Report" or the "Investigative Report" (IR), contained various comments regarding sources of error in CHESS Program air quality data and quality control problems associated with the data collection and analysis. The I.R. also contained various recommendations to be implemented by the Administrator of EPA pursuant to Section 10 of the Environmental Research, Development, and Demonstration Authorization Act of 1978 ("ERDDAA," P.L. 95-155, 91 Stat. 1257, November 8, 1977). ERDDAA also requires that EPA and the Agency's Science Advisory Board report to Congress on the implementation of the IR recommendations.

One recommendation of the IR was that an addendum to the sulfur oxides monograph be published, to be used in part to qualify the usefulness of the CHESS studies, and to apprise the public of the controversy surrounding CHESS. An addendum has been published, and is available from EPA, as announced in the Federal Register of April 2, 1980, 45 F.R. 21702. The addendum is incorporated by reference in this document in partial qualification of the CHESS studies cited herein, and is part of the public file (or docket) established for revision of this criteria document. The addendum contains the full text of the IR, reports to Congress by EPA on its implementation of the IR recommendations, and a report to Congress by EPA's Science Advisory Board on the same subject. See also Appendix A of of Chapter 14 of the present draft criteria document.

the validity of the aerometry data collected. Also, in each case it was contemplated that such improved and uniformly obtained aerometry data from throughout the two nations could serve as useful data pools to be coupled with community health epidemiology studies aimed at both (1) improving knowledge of quantitative air pollution-health effects relationships and (2) demonstrating the benefits to be accrued from implementation of the respective Clean Air Acts. In addition, as will become apparent below, remarkably similar problems were encountered and responded to with roughly comparable degrees of success in the course of practical applications of air pollution measurement techniques undertaken to achieve the above objectives.

In addition to the above developments in the United Kingdom and the United States, many analogous steps have been taken by numerous other industrialized countries over the past 30-40 years to cope with air pollution problems. In that regard, again many parallels (and dissimilarities) in the historical evolution of their air monitoring programs, epidemiologic research efforts, and political/legal regulatory control activities could be noted in comparison to developments in Britain and the United States.

However, a historical review of the evolution of such other activities or detailed analysis below of results obtained with practical applications of other sulfur oxides or particulate matter measurement approaches employed outside Britain and the United States is beyond the scope of present purposes. Rather, major emphasis is placed below on critical assessment of measurement techniques, mainly British and American, employed in collection of quantitative air quality data employed in epidemiologic or other evaluations of the health and welfare effects of sulfur oxides and particulate matter discussed in later chapters of the present document.

## 3.3 CRITICAL ASSESSMENT OF SULFUR OXIDES MEASUREMENT APPLICATIONS

Practical applications of measurement approaches employed in Great Britain and the United States for determinations of air concentrations of oxides of sulfur are critically evaluated in what follows. In both countries, lead oxide "sulfation rate" techniques were often employed prior to 1960 for the measurement of sulfur oxides. Later, other approaches used in some locations in the two countries during the 1950s were adopted in an effort to establish more uniform and improved $SO_2$ measurements for comparisons of data from widely disparate geographic sites.

The following discussion on sulfur oxides measurement applications in part alludes to published information on the relative specificity, sensitivity, accuracy, precision, and reliability of the methods discussed when used under optimum conditions in the hands of technically-expert analysts. Results actually obtained, in the course of practical applications of the measurement methods, often by less technically-skilled personnel, are also evaluated, drawing mainly upon published commentary on quality control assessments for the different applications.

### 3.3.1 British Approaches

As noted earlier, the lead dioxide gauge was used extensively in Britain during the years prior to 1960. However, use of the hydrogen peroxide method was gradually interspersed with the lead dioxide gauge during the course of the 1950s, often being coupled in tandem, as it were, with the apparatus for smoke measurements. Much of the early (1950s) British epidemiology data discussed later in Chapter 14 of this document has been related to $SO_2$ measurements obtained by the hydrogen peroxide method, especially where 24-hr $SO_2$ values are used. Nevertheless, it is useful to compare the results obtained with the

two methods, since other British air quality data of historical interest are derived from the lead dioxide method.

3.3.1.1 Comparison Between the Lead Dioxide Gauge and Hydrogen Peroxide Method-The National Survey--In 1962, as part of the establishment of the National Survey, a working party was set up to compare the lead dioxide gauge with the hydrogen peroxide method which was chosen as the standard method for use in the survey. As quoted in Atmospheric Pollution, 1958-1966 (WSL, 1967):

> The hydrogen peroxide method is subject to the limitation that its reaction is not confined to sulphur compounds; the lead dioxide method has the limitation that the extent of the reaction can be substantially influenced by weather conditions. Despite limitations, both methods estimate pollution by sulphur compounds; the hydrogen peroxide method is somewhat more complicated, but has the outstanding advantage that it can measure concentrations of pollution over short periods; the lead dioxide method is simple in operation, but it is incapable of measuring concentrations over short periods.
>
> Even so, it was considered desirable to compare the results from the two types of instrument under controlled conditions. A statistical analysis was made by Warren Spring Laboratory of results from a group of 20 sites at which both lead dioxide and hydrogen peroxide instruments had been operated over a period of 48 months. The 20 sites selected were those with a reasonably complete set of results from March 1957 to February 1961 at which the two instruments were not more than 100 feet apart.
>
> The correlation between 829 pairs of results from the 20 sites over a period of four years was highly significant, showing that both instruments were predominantly affected by the same pollutant, sulphur dioxide.

The WSL (1967) report presents a plot of these data shown below as Figure 3.1, with the lead dioxide data reported as mg $SO_3/100cm^2$ day.

The WSL fits these data with a linear regression line. Examination of these data suggests that a line $y = bx - cx^2$ might improve the fit. In this case the origin is not an absolute, since the presence of ammonia can cause a reduction in the $SO_2$ reading by the peroxide method, but ammonia would not

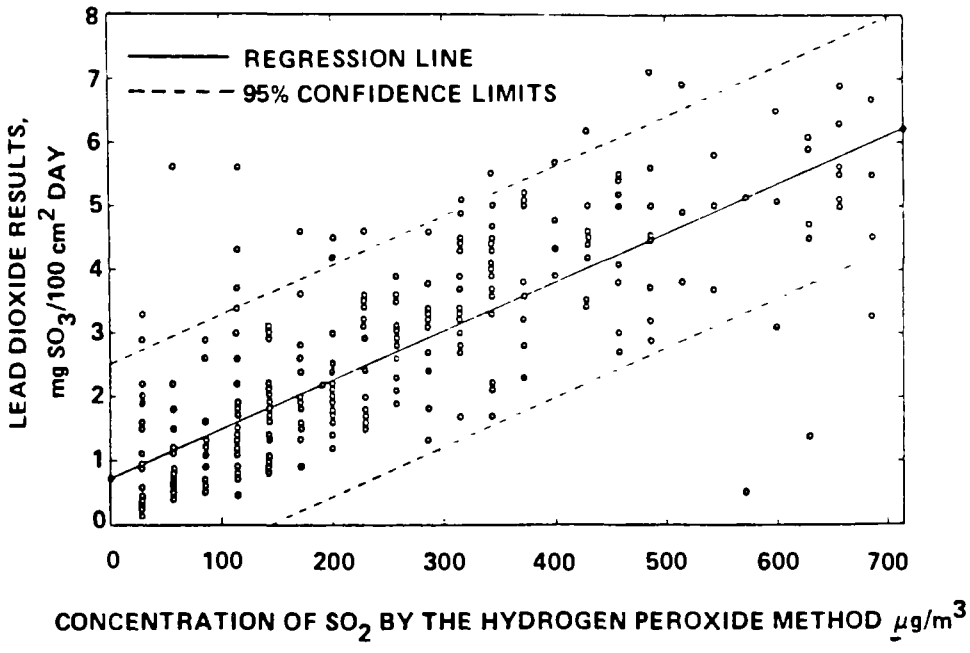



Figure 3.1 A comparison of lead dioxide and hydrogen peroxide methods for sulfur dioxide showing wide variations between simultaneous measurements. The solid line is the regression line, and the dotted lines are the 95 percent confidence limits. From WSL (1967).

influence the lead dioxide results. A correction for ammonia might shift these data to the right enough to justify a line through the origin.

The ± 2σ confidence limits shown in Figure 3.1 correspond to ± 1.8 mg $SO_3$/100 $cm^2$/day for a given hydrogen peroxide reading and ± 0.18 mg $SO_2/m^3$ for a given lead dioxide reading. The WSL (1967) report concludes:

> "The analyses carried out indicated that there is no generally applicable calibration for relating lead dioxide and hydrogen peroxide results. The conversion from lead dioxide to hydrogen peroxide reading is not recommended except to give a rough indication of the levels of concentration concerned, the degrees of approximation being as indicated by the preceding paragraphs."

In other words, estimates of $SO_2$ levels derived from lead dioxide sulfation rate measurements, especially 24-hr estimates, can only be roughly compared with $SO_2$ estimates obtained by the hydrogen peroxide method at other geographic sites or at later times at the same location(s). Also, it appears from the data in Figure 3.1, that comparisons between sulfation rate readings are only likely meaningful when such readings differ by the equivalent of about 180 $\mu g/m^3$ of $SO_2$, as measured by the hydrogen peroxide method.

3.3.1.2 Daily Sulfur Dioxide Measurements of the United Kingdom National Survey-- As noted above, when the National Survey began in 1961, it was recognized that the lead dioxide method could not provide the 24-hour $SO_2$ measurements necessary for correlation with mortality and morbidity effects investigated by epidemiology studies. The hydrogen peroxide method for $SO_2$ was, therefore, adopted as being more valid than the old lead dioxide gauge sulfation method. Because many of the staff making the measurements would be the same people who had been servicing particle deposit gauges and the lead candles without detailed technical knowledge of the analyses, however, an Instruction Manual (IM) issued by WSL in 1966 had to be quite detailed and clearly readable by people

with no training in analytical techniques. This section reviews the IM (1966) and some published studies discussing factors affecting accuracy, precision, and reliability of the British National Survey $SO_2$ measurements.

Reagents and Glassware-- In discussing reagents and glassware needed for proper use of the hydrogen peroxide method, the IM (1966) states:

> Distilled water. This should be obtained from a pharmacist or a supplier of chemicals. It need not be carbon-dioxide free; 'purified' water from an ion-exchange resin column may also be used...note that it is not necessary to use Grade A glassware. Grade B quality is often considerably cheaper and has sufficient accuracy for present purposes.

The IM (1966) also states:

> If it is considered that the cost of the extra Drechsel bottles is prohibitive other containers can be used provided they have been conditioned before use...The exposed solution should be treated as soon as possible if containers other than Dreschel bottles have been used."

The IM (1966) discusses the problem of alkali being given up by borosilicate glass and the need to condition the bottles. Polyethylene containers were permitted and a tolerable range of effect on the pH was given.

Martin and Barber (1971), however, reported that problems were found with unstable reagents in the course of practical application of the hydrogen peroxide method in the National Survey. They stated:

> In October 1966, zero daily concentrations appeared at some of the sites and in November alkaline samples were observed with no ammonia present. The cause of this situation was eventually traced to a change in the water used for making up the neutral hydrogen peroxide reagent. A large container of water had been emptied and freshly prepared demineralised water was apparently then being used. The freshly prepared water was rich in carbon dioxide. As required, the reagent was initially neutralised to pH 4.5, but as a result of a day's bubbling and a week's standing, sufficient carbon dioxide was evolved to make it alkaline. Demineralised water that stood for a week before neutralising was reasonably stable in use, but glass-distilled water was even better, and could be used as soon as it was cool. Tests with a spare sample held as long as the bubbled sample

> confirmed this stability. A comparison of results with those from nearby local authority sites indicated that the use of freshly prepared demineralised water could give monthly average results around 40 $\mu g/m^3$ low out of 50 $\mu g/m^3$.

The extent to which WSL addressed this problem with carbon dioxide is unclear, because a later report written by WSL (1977b) discussing quality control tests states:

> The tests also showed an unexpected, small, but significant, loss in acid from acidified 1-volume peroxide solutions prepared at WSL for the tests, within a few days of preparation; no explanation for these losses has been found.

It appears, then, that at least some British National Survey $SO_2$ data obtained in late 1966, and perhaps for a time afterwards, would tend to be biased toward underestimation of actual $SO_2$ air levels due to the carbon dioxide problem. The size of the error apparently could have been substantial for late 1966 and, perhaps, early 1967 data reported before the error was detected. Since then (at least up to 1977), errors due to this problem presumably were not very large, in light of the steps WSL could have taken to assure their correction.

Ammonia-- Ammonia is a negative interference since it neutralizes some of the sulfuric acid. According to the WSL (1975, Volume 5) section on accuracy of data:

> Depending on the site and the season, ammonia may be present in concentrations which cause significant under-estimation of sulphur dioxide, of up to 80 $\mu g/m^3$ on individual days, and up to 40 $\mu g/m^3$ in the monthly mean at country sites in summer (Martin and Barber, 1971). The under-estimation seldom reaches 25 $\mu g/m^3$ in urban areas. Sites have occasionally been found at which there has been interference by other gases, e.g. hydrochloric acid, but these are likely to be exceptional cases. Where gross interference with sulphur dioxide determination is suspected at National Survey sites, whether by ammonia or by some other gas, specific measurements of sulphate or of the interfering agent may be made as a check.

The 1966 IM states: "If there is any reason to believe that the presence of ammonia may be interfering with the estimation of sulphur dioxide, it is not difficult to ascertain whether this is so." However, if the operator is not adequately trained technically, the presence of alkalinity may not be suspected until it is so great that the pH is greater than 4.5 without addition of alkali. Martin and Barber (1971) also state: "The incidence of ammonia was erratic. It could appear abruptly at many sites on one day and disappear from them all on another." Thus, if a check is made a week later, ammonia might not be present on the day the test is made, and this might lead the non-technical observer to believe that no ammonia was present on the day the pH was over 4.5 and so not to repeat the test.

BS 1747: Part 3 (1969), Note 1 states that:

> The correction seldom reaches + 25 $\mu g/m^3$ $SO_2$ except in farming areas etc. This value has been exceeded in about 10 percent of samples over the last three summers, including some from town sites.
>
> For Central Electricity Generating Board (CEGB) purposes, the $SO_2$ results are corrected for ammonia, to allow comparison with conductimetric recorder results (which are virtually unaffected by these ammonia concentrations), and also because free $SO_2$ and ammonia may co-exist in air without reaction for some time at these low concentrations.
>
> Warren Spring Laboratory, on the other hand, publish uncorrected $SO_2$ values in their Monthly Summary of National Survey results, so that all their values are on the same basis, i.e., as measured by simple titration.
>
> The difference between corrected and uncorrected monthly averages at a site may be negligible or as great as 40 $\mu g/m^3$, depending on the ammonia found. Forty microgrammes per cubic metre may be the entire monthly average $SO_2$ at a country site.

From the foregoing, it can be concluded that, in general, National Survey $SO_2$ data for United Kingdom urban areas probably represent some under-estimations of actual levels due to ammonia as a source of error. Also, in rare instances where they might be so affected, the result would probably

be no more than a 25 $\mu g/m^3$ underestimation of the actual $SO_2$ level. However, for rural or small town sites with significant ammonia-generating sources (e.g., livestock barns), the ammonia impact could be quite great--causing even up to a 90 or 100 percent underestimation of actual $SO_2$ levels. Unfortunately, from the specific information available to the present authors, it could not be clearly determined as to which National Survey data from what areas or time periods are likely so affected.

Sample Line Conditioning--Martin and Barber (1971) discuss the need for lacquering to prevent wall loss of $SO_2$ to anodized aluminum and araldite in the manifolds. Analysis of the data showed that "pre-laquering monthly averages were probably low by about 25 $\mu g/m^3$ out of 50 $\mu g/m^3$." They also give an example where a leak was discovered inside a metal conduit supporting the clean PVC tubing which led to a drop of about 20 $\mu g/m^3$ out of 50 $\mu g/m^3$. Sample lines also deteriorate with time. Martin and Barber (1971) report that some PVC deteriorated when exposed to sunlight, becoming dark and sticky and absorbing $SO_2$. "To a much lesser extent the same phenomena was [sic] found to occur over 2 or 3 years on the routine surveys, inside windowless huts and even inside metal conduit...Several instances were found of spiders' webs or insect carcases, heavily sooted, inside the plastic tubing." Another potentially more serious problem can be caused by "sucking back" of the bubbler solution into the system if the air line is blocked. Martin and Barber (1971) stated:

> From time to time the air line became blocked, e.g. by kinking, with ice from freezing fog, or with insects. When this happened the pump suction sometimes caused the contents of one or more Drechsel bottles to be sucked back into the manifold, the filter assembly and the connecting lines. This meant the loss of some samples and careful cleaning and drying of the system was necessary. In some cases the air line was freed and in others it was replaced.

> However, there was an increasing suspicion during Summer 1968 that further low results were being obtained. This was partly due to the air line deterioration discussed in the previous section. However, tests with a spare instrument at two sites showed that the lacquering was also faulty and that relacquering would restore the sensitivity of the instruments. It was not clear, though, whether the original lacquering had been poor, or whether the lacquer had deteriorated with age or perhaps by the action of reagent sucked back.

The original IM (1966) does not discuss this problem. Thus, if it occurred, the operators might neither have performed the scrupulous cleaning of the entire system which Martin and Barber performed nor would they have necessarily checked for lacquer deterioration caused by the reagent action. This could presumably have led to underestimation of some $SO_2$ levels by 40 to 50 percent based on the above examples cited by Martin and Barber (1971). It is not presently possible to determine which National Survey or other British air quality data may have been so affected other than to suspect that some 1968 data may be underestimates. However, an additional source of bias likely exists from the reported adsorption and conversion of $SO_2$ to sulfate on the BS smoke filter in the line before the collection bottle. This could lead to a consistent underreporting of $SO_2$.

Evaporation of Reagent--In regard to evaporation of reagent the British Standards Institution (BSI) (1963) noted the following concerning the National Survey method for determination of sulphur dioxide:

> If the apparatus is left to run continously for more than 24 hours or in very hot weather a volume of 75 ml is preferable. Evaporation should be kept to a minimum and any loss should be made up with distilled water.

As pointed out by Fry (1970), if the bubblers are maintained inside a heated building the evaporation loss can be appreciable even in the winter. The pump also runs hot, which can lead to heating of the bubbler if they are enclosed together.

As stated in the Fry (1970) report:

> It is shown that a significant error can occur in the estimation of sulphur dioxide for localities of low pollution, due to loss of water by evaporation during sampling. This error leads to the reporting of high results and can be overcome by making up the adsorbing peroxide solution to its original volume, prior to estimating the net change in acidity.

Fry (1970) cites the following conclusion and recommendation to WSL.

> CONCLUSION
>
> It is concluded from the results presented here that evaporation of the absorbing liquid can lead to significantly higher pollution results but that this error can be eliminated by making up the collected solution to its initial volume in accordance with B.S. 1747, prior to determination of net acidity.
>
> RECOMMENDATION
>
> That the Warren Spring Laboratory pollution survey procedure be amended to include making up the collecting peroxide solution to its initial volume prior to estimating the net change in acidity.

However, indications are this recommendation was not accepted by WSL, as indicated by the following later statement by WSL (1975):

> Evaporation of the absorbing reagent introduces an error. The dilute hydrogen peroxide solution used to collect the sulphur dioxide is neutralized to pH 4.5. If evaporation occurs during exposure the pH is altered, and some of the alkali added to the exposed solution in subsequent titration is used to bring the pH back to 4.5. Sulphur dioxide concentrations are therefore over-estimated when evaporation occurs. This was realized from the start of the Survey, but it was decided that any attempt to correct this by ruling that samples be made up to 50 ml before titration might well introduce larger errors; recommendations are made regarding avoidance of overheating of the instruments to minimize evaporation. The effect is likely to be more prevalent in summer than in winter and can lead to over-estimation of sulphur dioxide by up to about 15 $\mu g/m^3$.

Fry (1970), on the other hand, reported that a direct determination of the correction could be made by simply subtracting 0.008 $(50-V_f)$ ml of 0.004 N sodium borate, where $V_f$ is the final volume in ml of solution after evaporation.

There is no apparent explanation for why WSL did not provide for the recording of the final volume on form WSL 216 AP (NS) and use of the simple correction proposed by Fry (1970).

Given the evident failure of WSL to correct for this reagent evaporation error, which ~~dates~~ was known to exist from the start of the National Survey, it might be reasonable to conclude that all National Survey $SO_2$ data would be biased somewhat high as a result. All past and present British National Survey $SO_2$ data would then have to be taken as likely representing overestimations of ambient $SO_2$ levels due to this error. The absolute magnitude of overestimation of specific $SO_2$ data points would vary with specific monitoring sites (depending on care taken by different operators to avoid overheating of pump motors) and likely be at a maximum during the summer months. Assuming a maximum 15 $\mu g/m^3$ error mentioned above (WSL, 1975), this could constitute overestimations of 15 to 100 percent for obtained $SO_2$ values under 100 $\mu g/m^3$; 7.5 to 15 percent for readings of 100 to 200 $\mu g/m^3$; 3.25 to 7.5 percent for readings of 200 to 400 $\mu g/m^3$; and $\leq$3.25 percent for readings over 400 $\mu g/m^3$.

Titration Errors--As stated by WSL (1975), "Uncertainity in the end-point of the colorimetric titration, and rounding-off of the volume of alkali added in titration to the nearest 0.1 ml, each introduce errors of up to about ± 5 $\mu g/m^3$."

At low concentrations on the order of 50 $\mu g/m^3$, where only ~0.8 ml of sodium borate solution is added, the total uncertainty from titration and round off errors is about 7 $\mu g/m^3$ or 14%. That is, 68% of the analyses would be expected to be within ±14%, 95% of the analyses within ±28%, and 5% of the analyses to be in error of more than 28%.

Temperature and Pressure Corrections--The BSI (1963) method for sulfur dioxide discusses temperature and pressure corrections as follows:

> The volume of air sampled is measured at the temperature and pressure in the gas meter; if it is desired to relate the result to external air volumes, further corrections for the temperature and pressure outside the laboratory are required . . . The concentration of atmospheric sulphur dioxide is preferably expressed in terms of the weight rather than the volume of sulphur dioxide per unit volume of air.
>
> Clause 5 expresses the concentration in microgrammes per cubic metre of air sampled, without adjusting the measured volume of air to standard temperature and pressure and without allowance for the small drop in pressure at the meter. This procedure is considered to be adequate for the general run of routine observations. Some discretion may need to be exercised if the conditions are such that clogging of the smoke filter causes an unduly large pressure-drop at the meter.
>
> Where it is considered desirable to make adjustments for temperature and pressure, the apparatus shown in Fig. 2 should be modified to provide for measurement of the pressure-drop at the meter and suitable provision should be made for recording the ambient temperature and pressure during the period of the test at such intervals as will give fair average values.

However, clogging of the smoke filter occurs most often on the most polluted days. Consequently, the volumetric flow at the meter is enhanced by the drop in pressure, and the meter will report too much flow (1 meter at 1 atmosphere occupies approximately 2 meters at 1/2 atmosphere). Consequently, the effect will be to underestimate the concentration of both $SO_2$ and the BS on the filter. For example, a 3-inch drop in pressure across the filter results in approximately a 10 percent underestimate of the $SO_2$ and BS.

3.3.1.3 Summary--The assumptions and errors discussed above may be conservative because in many cases "staff making the measurements had no training in analytical techniques" (IM, 1966). Of course, if such staff followed each and every instruction in the manual to the letter then the literature estimates cited above might be valid. However, if one allows the possibility that techniques in the field varied measurably from those set forth in the manual or likely

to be followed under laboratory conditions, then these error estimates may need to be enlarged. Taking into account all of the uncertainties due to titration, ammonia, carbon dioxide, variations in quality of distilled or demineralized water, Grade B glassware, polyethylene bottles, evaporation of reagents, anodized aluminum, insects and leaks in sample lines, sample line deterioration, improper laquering of parts in contact with $SO_2$, and other miscellaneous errors such as those due to uncertain waiting time before titration of samples not transported in Drechsel bottles, one might expect that some specific sets of British National Survey $SO_2$ data could be in error by as much as 50 to 90 percent.

Ascertaining which specific data sets might be thusly affected to a greater or lesser extent would, of course, require extensive and extremely careful reexamination of all National Survey $SO_2$ data points and associated records documenting pertinent information on operator training, individual differences in carrying out lab procedures, and day-to-day condition of the sampling and laboratory equipment, reagents, etc., on a site- and time-period specific basis.

Alternatively, one could assume that most all of the errors cited, with some operating to bias the reported data upwards and others downward, would tend to cancel out, especially when data are averaged over periods of a few months or a year or for groups of sites, as has been suggested by WSL officials in Her Majesty's Report: "National Survey of Air Pollution, 1961-71: Vol. 5" (WSL 1975). It is likely, however, based on the above WSL reports that at least some errors are generic to all National Survey measurements of a particular type and would not likely be regularly cancelled out by others. Thus, for example, the "reagent loss" error discussed above would likely cause

reported National Survey $SO_2$ values to consistently be overestimations of actual $SO_2$ levels in areas of low levels of particulates and ammonia.

### 3.3.2 American Approaches

As noted earlier, under "Historical Perspective" above, different types of measurement methods for a given pollutant were at times adopted by various local, state, and federal agencies in establishing or expanding air quality monitoring systems that proliferated across the United States during the 1950s and 1960s. It is beyond the scope or purpose of the present document to attempt a critical appraisal here of the procedures employed in, and results derived from, the practical application of $SO_x$ and particulate matter measurement techniques under the varying specific circumstances associated with the operation of all of the different American air monitoring systems. Rather, main emphasis will be placed here on the discussion of only certain key American applications of measurement methods for $SO_x$ that are of crucial importance for later discussions in the present document of quantitative relationships between health and welfare effects and atmospheric levels of sulfur oxides and particulate matter. These include applications of $SO_2$ measurement methods as employed in the EPA "CHESS Program" as the single largest attempt to define quantitative relationships between air pollution and health effects. Also, as appropriate, certain pertinent information will be discussed regarding air quality measurements associated with the operation of some local (city or county) and state air monitoring programs.

In regard to sulfur oxides measurement approaches used in the United States, lead dioxide or other "sulfation rate" measurement methods were, as in Britain, widely employed prior to the early 1960s for assessing $SO_2$ air levels. However, probably to a somewhat greater extent than in Britain, sulfation rate measurement techniques continued to be used later into the mid or late 1960s by some

monitoring programs in the United States or in connection with certain community health epidemiology studies, as discussed later in Chapter 14 of this document. As shortcomings of the "sulfation" methods of the type discussed in Chapter 2 became more widely recognized, their use was generally abandoned and more specific methods for the measurement of $SO_2$ or other sulfur oxide compounds were adopted, as was done in Britain. The hydrogen peroxide acidimetric method (see OECD, 1965) selected for use in the British National Air Pollution Survey, however, was not very widely adopted in the United States for $SO_2$ measurements. Rather, versions of West-Gaeke (1956) colorimetric procedures were much more widely used in the USA. Conductivity measurements for $SO_2$ ~~(Adams et al., 1971),~~ based on an acidimetric method adaptation often used in automatic instruments and most suitable for measuring periods of around 24 hours, later began to be applied in the operation of some American air monitoring networks in the 1970s.

The West-Gaeke method was the method mainly employed in the EPA "CHESS Program" for determining $SO_2$ air levels for inclusion in analyses of community health end point data in "CHESS" epidemiology studies. The application of that method in the CHESS Program is accordingly most thoroughly discussed below. Applications of other measurement approaches for sulfur oxide compounds other than $SO_2$ (such as suspended sulfates) as employed in the CHESS Program are also discussed below. Much of the information provided is derived from a 1976 Congressional Investigative Report (IR) which contained a thorough evaluation of EPA CHESS Program air quality measurements and other aspects of the Program.

3.3.2.1 Sulfur Oxides Measurements of the U.S. EPA CHESS Program--As indicated in Section IV A of the IR (1976), the attainment of precise, reliable, reproducible, and real-time air quality measurements in the field (e.g., $SO_2$ and particulates) was a critical purpose of the EPA CHESS Program. The IR (1976) further notes

that the methods selected for use in CHESS to meet these objectives, especially in 1970-71, were probably as good as any available at the time; and attempts were made to gradually introduce better quality control procedures into the CHESS program. Thus, the use of the particular methods selected (the best available), and the goal of implementing quality control procedures in the Program cannot be criticized. However, the lack of sufficient quality control efforts to ensure the best possible application of those methods in the field and the resulting errors in measurement, especially in the early (1970-71) years of the Program, were and are matters of considerable concern that led to criticisms of the type voiced in the 1976 IR. Some of the more salient points raised by the IR regarding CHESS approaches to measurement or estimation of $SO_2$ or suspended sulfate levels are discussed below.

3.3.2.1.1 The West-Gaeke Method for Measurement of Ambient $SO_2$. As briefly described in Section IVB of the IR (1976), the West-Gaeke colorimetric procedure for $SO_2$ measurements used in CHESS is:

> The designated Reference Method (Federal Register, 36, No. 84, 6168, April 30, 1971). Atmospheric $SO_2$ is collected by bubbling air through a solution of potassium tetrachloromercurate (TCM). The product of the reaction between $SO_2$ and TCM is the nonvolatile dichlorosulfitomercurate that is then determined quantitatively by reaction with formaldehyde and pararosaniline hydrochloride, followed by photometric measurement of the resulting intensely colored pararosaniline methyl sulfonic acid.

The IR further noted that the field apparatus and sample collection procedures employed were as follows:

> Outside air is drawn through a sample line at the rate of 200 ml $min^{-1}$, then through a 6-inch long glass bubbler stem (tip diameter of 0.025 in.) immersed in 35 ml (50 ml after January, 1974) of 0.1 M TCM solution contained in a 32 mm diameter by 164 mm long polypropylene sample container. The exhaust air passed through a glass wool moisture trap, then through a hypodermic needle used as a critical orifice to control the flow, through another moisture trap,

and finally through a vacuum pump. A sample consisted of a 24-hour collection. Collected samples were stoppered, and mailed to EPA/RTP for analysis."

IR comments concerning the validity of the method as a laboratory procedure included:

> A collaborative study by McKee et al. (H. C. McKee, R. E. Childers, and O. Saenz, Southwest Research Institute, SWRI Project 21-2811, EPA contract CPA 70-40) indicates that "the method cannot detect a difference smaller than 10 percent between two observations by the same analyst in the range of 0 to 1000 μg $m^{-3}$. A difference of 20 percent or less may be detected above 300 μg $m^{-3}$, and a difference of less than 50 percent may be detected above 100 μg $m^{-3}$." For analyses conducted by different laboratories on the same sample, "the method cannot detect a difference of less than 20 percent betweem single-replicate observations of two laboratories in the range of 0 to 1000 μg $m^{-3}$. At a level of 100 μg $m^{-3}$, a difference of less than 100 percent is not detectable." The National Primary Ambient Air Quality Standard for $SO_2$ is: For 24 hour average, 365 μg/$m^3$. For annual average, 80 μg/$m^3$. Thus if the standard is met, most values will be around or below 80 μg/$m^3$, no more than one will be above 365 μg/$m^3$.
>
> Regarding the lower limit of detection, the authors cited above propose a value of 25 μg $m^{-3}$ as a practical figure. "A single determination less than this value is not significantly different from zero" (Instrumentation for Environmental Monitoring, Air-$SO_2$, Instrumentation, Lawrence Berkeley Laboratories, March 1972).
>
> It is therefore evident that a single analysis is of little use, considering that the expected concentrations of $SO_2$ will usually be less than the ambient air quality standard of 80 μg $m^3$. Results should be regarded as valid only in terms of the mean of multiple determinations, and only when the analytic method has been followed rigorously by experienced analysts.

The IR (1976) further noted the following regarding sources of errors in CHESS $SO_2$ measurements and their likely impact:

> In an attempt to standardize the methodology and to eliminate problems associated with interlaboratory errors, a CHESS policy was instituted whereby all air sampling equipment was assembled and tested at the central EPA research laboratory and then shipped to the contractors for field use. Also, bubbler tubes were prefilled with the appropriate absorber solution, shipped to the contractor for their daily monitoring use, and shipped back to the central laboratory for chemical analysis. It was this long distance shipment of the chemical solutions that led to the first of a series of field-use problems with the procedure. These problem areas will be

summarized below with an attempt to evaluate their net effect on the resultant CHESS $SO_2$ data. Following this summary of individual problem areas, an assessment of the overall $SO_2$ data quality will be given.

a. Spillage of Reagent During Shipment

The first field data were obtained in New york City and the Salt Lake area (Utah) in November, 1970. By mid-1971, field personnel at the Utah site reported to their CHESS field engineers that severe spillage was occurring during shipment. Many bubbler tubes were arriving partially filled with reagent and some were completely empty. At the Salt Lake area an attempt was made to refill with solution from extra tubes those tubes that were low. However, due to insufficient reagent, this was only partially successful. This problem was not officially recognized until October, 1972, at which time an internal EPA/CHESS memo was written outlining the problem and suggesting corrective action. The magnitude of the problem can be best assessed by quoting from the memo. "The present reagent tubes for $SO_2$ and $NO_2$ leak during shipment . . . . The $SO_2$ leakage rate (was found to be) 18% of the total volume, 50% of the time. . . . It follows therefore, that the resultant pollution data are unreliable." Recommendations were made in this memo as to possible corrective measures. These recommendations were not instituted until March, 1973.

During the subsequent years, many attempts were made to correct this leakage problem. However, none were wholly successful and as late as January 1975, another EPA memo described losses of solution in $SO_2$ bubblers during shipment and suggesting appropriate corrective action.

The effects of the reagent spillage problem on the $SO_2$ data can be only grossly estimated. Certainly, many samples were totally lost. These lost samples were not the major problem. Of more significance was the undetermined amount of daily $SO_2$ data that were in error due to the loss of sample by spillage and yet included in the network system.

If the reagent was partially lost during shipment to the sampling site and used as received, an increased concentration of TCM-$SO_2$ complex would occur relative to normal sampling. This potential positive bias would be corrected by for the analytical procedure used (Page A-6 CHESS monograph--Analysis Procedure). "At the laboratory, the sample is brought back to its original volume by the addition of distilled water to compensate for water loss during sampling." If however, the reagent spillage occurred after sampling, the required addition of water would result in data that were biased low in proportion to the amount spilled relative to the total volume of solution. According to the EPA Memo of October, 1972, one half of all $SO_2$ data taken between November, 1970 and March, 1973 are likely to have been biased low by an average of 17%. This problem was corrected after April, 1973.

b. Time Delay of the Reagent--$SO_2$ Complex

The Reference Method as originally described in the Federal Register, was to be conducted at 20° C. There was a known error in the method associated with time delay between sampling and analysis which was dependent on temperatures. This error was derived from the spontaneous decomposition over time of the TCM-$SO_2$ complex as a function of temperature. The magnitude of the error and its exact dependence on temperature was not known but a brief study was conducted to determine its magnitude by scientists of the CHESS monitoring group in November, 1971. As a result of this study, a correction factor of +1.5% per day was arithmetically applied to all CHESS $SO_2$ data to compensate for the time delay between sampling and analysis.

A more recent and comprehensive study has been carried out within the Quality Control Branch, Environmental Monitoring Laboratory at EPA on the effect of temperature on "The Stability of $SO_2$ Samples Collected by the Federal Reference Method." This study indicated a much more severe problem than was estimated by the original CHESS study. The evaluation was carried out over the range of 35 to 278 $\mu g/m^3$ $SO_2$ concentration. The following findings were presented in the report:

> Over a normal range of temperature, the rate of decay of the TMC-$SO_2$ complex increases five-fold for every 10°C increase in temperature, respectively.
>
> The rate of decay is independent of $SO_2$ concentration. At 20, 30, 40, and 50°C the following $SO_2$ losses were observed: 0.9, 5, 25, and 74% loss per day, respectively.

This study makes abundantly clear a second and even more severe error associated with $SO_2$ measurements conducted by CHESS. During the summer months, when the $SO_2$ absorber solutions were subjected to high and unknown temperatures between field sampling and laboratory analysis, significant degradation of the samples did occur. Estimates of time delay between sampling and analysis range from 7 to 14 days. Estimates of summer temperature exposures range from 25 to 40°C being most severe for the Utah CHESS sites. Thus, CHESS $SO_2$ data can be estimated to be negatively biased, mainly during the summer months. It would normally be difficult or impossible to estimate the magnitude of the bias except to say that it is probably large. However, simultaneous $SO_2$ measurements were taken by the New York City Department of Air Resources and by the Utah State Division of Health. These results were obtained by an independent method not susceptable to the temperature related error. A consistent pattern emerged when side by side data are compared. From May to October, the CHESS $SO_2$ data were low with the largest error occurring in the middle three summer months. The magnitude of the error varied from month to month and year to year, but the CHESS data were consistently low and represented only a portion of the true ambient $SO_2$ concentration.

c. Concentration Dependence of Sampling Method

The $SO_2$ reference method was subjected to a collaborative study program in 1973. Four participating laboratories tested the 24-hour version of the Federal Reference Method. A previously unknown source of error was documented that applies to the CHESS $SO_2$ data. It was found that the 24-hour sampling method does have a concentration dependent bias which becomes significant at the high concentration levels (200 $\mu g/m^3$). Observed values tend to be lower than the expected (known) $SO_2$ concentration levels. This error source will yield a negative bias on the daily CHESS $SO_2$ data when they exceed 200 $\mu g/m^3$ and on all monthly and yearly average data.

d. Low flow correction

The determination of atmospheric $SO_2$ concentration was dependent on, among other factors, the accurate measurement of air that passed through the TCM solution. This flow was controlled by a critical flow orifice in the form of a standard hypodermic needle. In practice, the air flow through the sampling system was measured at the start and end of each 24-hour sampling period. This was done to detect low flow due to needle blockage. The Federal Register Method (Reference Method) calls for an air low of 200 ± 20 ml/min. In field operation, the CHESS procedure substantially broadened these tolerances. Replacement needles were installed if the initial air flow was greater than 220 ml/min which is consistent with the Reference Method; however, needles were not replaced nor were samples voided until the measured flow dropped below 100 ml/min. Integrated flows were calculated by assuming a linear decrease in flow between the start and end of the 24-hour sampling period. If, however, the needle was partially blocked near either the beginning or the end of the sampling period, the linear flow correction would be in error. Using the Reference Method flow tolerance, only small errors would be introduced by this correction (less than 10%). Using the CHESS procedure, however, errors as large as 50% could be introduced and not detected. These errors would be random (either positive or negative) depending on when during the sampling period the needle blockage occurred. Thus a large random error component was added to the $SO_2$ daily data but this component was somewhat damped statistically in the monthly or yearly averages.

The modification of flow tolerance by the CHESS aerometric group is a procedure that would not have withstood the critical review of a competent quality assurance program.

e. Bubbler train leakage

The West-Gaeke method, as described in the Federal Register, employs a vacuum bubbler train. That is, the sampled air is drawn through the bubbler train by a vacuum pump rather than being pushed through by a positive pressure pump. There are many advantages to the vacuum procedure, most important is that

the air does not come in contact with any internal pump mechanism. However, there is a modest pressure differential between the atmosphere and the internal bubbler; thus all fittings and joints must be gas tight. The bubbler train used in the CHESS program had two points where frequent air leak problems were encountered. One was around the rubber stoppers for the bubbler tube and moisture trap and the other was the rubber tubing used to hold the glass assembly pieces together. Field operators reported consistent problems with leakage in the routine field use of the bubbler train. In a severe leak situation, the samples were voided due to out of tolerance (Low) flow rates. There were many cases however, where small leaks occurred but the final flow was within specifications so the sample was included as valid. In cases where the leaks formed around the rubber stoppers, no significant error would be introduced except due to the linear flow correction as applied to instantaneously developing leaks. This error is similar in nature to that discussed in the flow section. In the case of leaks upstream of the bubbler train, room air instead of outside air is drawn through reagent. In normal situations, it has been observed that room air is significantly less polluted than outside air. (See page 6-6, CHESS Monograph--comparison of school air to outside air). This effect may not be large for the small buildings used to house CHESS stations, but a somewhat decreased pollutant level would undoubtedly be sampled. The absolute magnitude of this error cannot be adequately assessed but it can be stated that the error would be in a negative direction, that is, again to underestimate $SO_2$ levels.

An overall assessment of CHESS $SO_2$ data from Section IV C 2 of the IR (1976), is as follows:

The $SO_2$ data, accumulated at "official" CHESS sites, followed a remarkably uniform trend as the program progressed. The method used was the EPA Reference Method which is specific for the chemical species, $SO_2$. Thus, regional changes in pollutant mix, i.e., the proportion of other pollutant species relative to $SO_2$, had minimal effect on the $SO_2$ data. However, the sum effect of the errors detailed in this section did have a profound effect on both the accuracy and the precision of the data.

Under normal circumstances, a retrospective evaluation of a monitoring effort that occurred a number of years in the past and which had been terminated, could yield only the broadest of estimates of data quality. Fortunately for this review, two geographically different locations with six different monitoring sites were involved in the collection of simultaneous $SO_2$ data. Further, the groups responsible for the two data sets were managed independently and the methodology used was also independent. This fortunate circumstance enabled the reviewers to acquire a quantitative understanding of absolute differences among data sets as well as correlations with respect to time.

The locations where side by side data existed were the New York City sites at Bronx and Queens and the Salt Lake Basin sites at Ogden, Salt Lake City, Kearns, and Magna. In these locations, the local environmental monitoring agencies had sites located within 50 meters of the CHESS sites and at similar elevations. At these sites, the local agencies collected daily $SO_2$ and TSP data for the entire life of the CHESS program. The $SO_2$ methodologies used by both State agencies were variations of the peroxide bubbler method in which twenty-four 1-hour samples were integrated to form a single 24-hour $SO_2$ measurement. In New York the samples were measured acidimetricly and in Salt Lake City they were quantified conductiometrically. Neither method is as specific for $SO_2$ as is the Reference Method, that is, pollutants that are in a significant concentration, relative to $SO_2$ and that also oxidize to form an acidic compound will be interpreted as $SO_2$. For this reason, when the NYC Department of Air Resources initially brought to the attention of the CHESS Aerometric team the large discrepancy between their respective data, the discrepancy was dismissed as method bias on the part of the New York method. An EPA memo dated November 3, 1971 described a limited study into the Reference Method. The conclusion reached was "On the basis of (this study). . .I feel there is no sound basis for discrediting the EES (Environmental Exposure System) methodology.

No further attempt was made to uncover the cause of the discrepancy in $SO_2$ data. Had the CHESS EES team obtained and compared the Salt Lake Basin data, especially that from Magna site, a disturbing similarity would have been immediately apparent. This data confirmed in detail the discrepancies observed in New York. It is important that the Magna site data were confirmatory since it was in a region of single source pollution, that from the nearby copper smelter. In this site very low levels of other pollutants existed relative to $SO_2$, thus the peroxide method was capable of giving reasonable reliable estimates of $SO_2$ concentration. Of equal importance the general pollutant mix was very different between this rural smelter site and the urban area of New York City. Despite these diffences the comparison of side by side Federal-State data indicate the same discrepancies in both trends and absolute concentrations. The following conclusions as to $SO_2$ data validity can thus be reasonably drawn from the review of methodological errors and the comparison of existing side by side data.

The following conclusions regarding CHESS $SO_2$ data validity were drawn in Section IV C 2 of the IR (1976), based on the above review of methodological errors and the comparison of side by side data:

From November 1970 until December 1971 the $SO_2$ data generated from CHESS sites using the modified Reference method were biased low by 50 to 100 percent in the High Exposure sites when compared with existing State $SO_2$ data. Thus, the 1971 annual average $SO_2$ exposure estimates of 60 $\mu g/m^3$ as reported for Magna in the CHESS monograph (page 2-24) are more likely in the vicinity of 100 $\mu g/m^3$. Also, the same phenomenon occurred in New York and the reported values are also in similar error.

A confirming fact is that during cool months after 1971 $SO_2$ data correlated well both in trends and absolute concentrations between State and Federal analyses. It thus seems likely that the State data were reasonably accurate throughout that time period. However, one consideration must be applied here: namely, that due to the difference between the independent methods an error bar of at least one hundred percent must be applied to the data and explicity correct data cannot be drawn from these observations. In other words, where two or more independent observations are in disagreement by a significant amount it cannot be said by inference alone that one data set is more correct than the other. It is reasonable to assume, however, from our review of all State and Federal data in the time period of 1970 through 1971, that the Federal $SO_2$ data as collected in the CHESS program were substantially low and went through an abrupt upward transition in concentration in December 1971 at all CHESS sites and Federal data taken before that time may reasonably be expected to have a large unknown negative bias.

In November 1971, the CHESS monthly mean $SO_2$ data underwent an abrupt change in the positive direction. The cause of this change is not apparent. However, the result was profound. From that time until the conclusion of the CHESS program in July of 1975, the fall-winter data were in very good agreement with other exisiting data and very likely gave reliable estimates of $SO_2$ exposures.

Throughout the entire program, the CHESS $SO_2$ data had an associated negative bias during the summer months, becoming most severe during the hottest periods of July and August. This error usually reached a maximum of 60 to 80 percent underestimation of exposures and was variable. As a result, even though wintertime monthly $SO_2$ averages appear valid from 1972-1975, annual averages of the same data are biased low due to the inclusion of the summer errors. The best estimate of error in the annual average data 1972-1975 is approximately minus 15-20 percent relative.

The individual daily $SO_2$ levels, when compared to city or State data or to replicate CHESS measurements taken after 1973 had so large a random error component that they are not useful to assess daily $SO_2$ exposure (as attempted in the asthma panels). The random errors associated with the daily values were much larger than the differences observed over time.

Due to inherent methodological errors, the following may be considered as minimum differences between High and Low $SO_2$ exposures which may be considered "real." These are based on EPA's collaborative study of the reference method and used a 95 percent confidence interval.

> Below 100 $\mu g/m^3$ $SO_2$, a difference of at least 50 $\mu g/m^3$ is necessary to be statistically significant.
>
> Between 100 and 300 $\mu g/m^3$ $SO_2$, a difference of at least 60 $\mu g/m^3$ is necessary to be significant.
>
> Below 25 $\mu g/m^3$, a single determination is not significantly different from zero.

3.3.2.1.2 <u>CHESS program suspended sulfate measurements</u>. Determination of suspended sulfate (SS) concentrations in the air as part of CHESS aerometry efforts was carried out as methodological extension of the Hi-Vol TSP method employed in the CHESS Program. That is, subsamples were cut from the exposed Hi-Vol filters and analyzed for total water soluble sulfate as a class (but not according to specific chemical species). The manual turbidimetric method was used from November, 1970, to September, 1971; and the methylthymol blue (MBT) method was employed from September, 1971, to July, 1975. To the extent that the SS measurements were derived as an extension of the TSP sampling, all errors associated with the TSP monitoring, as discussed later below, also apply to CHESS SS measurements. In addition, some more specific considerations pertaining to the SS measurements can be cited.

Section IV C 4 of the IR (1976), for example, noted the following:

> The turbidimetric method is subject to interferences, many of them being other common pollutants. In areas like the Salt Lake Basin where the pollutants are dominated by a single source, the procedure may be adequate. However, in urban areas like Cincinnati or New York City, where the pollutant mix is derived from many independent sources and is variable even within the city, the method is capable of only the crudest estimates of sulfate levels. It should not be thought of as an accurate measurement of atmospheric sulfate. Especially, small differences between High and Low exposure communities, such as were reported in the Cincinnati Study in the

CHESS Monograph (page 6-5) cannot be identified as real differences. When a realistic error estimate is applied to the reported sulfate concentrations, the difference becomes statistically insignificant. Any correlation of CHESS health effects with sulfate levels where the sulfate data were obtained using the turbidimetric method must be carefully qualified.

The MTB method is basically a better measurement method because most of the aerometric interferences have been eliminated by its revised methodology. The two remaining interferents, phosphate and barium, are not normally found in atmospheric concentrations high enough to cause inordinate problems. However, problems associated with the sampling aspect of the method have been documented and do impact on the general CHESS sulfate data quality.

First, problems associated with sulfate blanks (the level of sulfate on the filter pad as manufactured) were reported to be high and variable. In the 1971-1973 time period, problems of variable blanks within the EPA NASN program were documented. The general blank level was equivalent to an atmospheric sulfate concentration of 1-2 $\mu g/m^3$. However, the major problem was variability of the blank among manufactured lots of the filters. The blank level often varied by more than 100 percent among lots so that routine and continuous blank assessment should have been mandatory.

No evidence of routine sulfate blank determination was found in the CHESS monitoring program until 1974. From that time period on, adequate blank assessment and correction were applied to the data. From 1971 until 1974 however, the blank contribuiton to the CHESS sulfate data was not adequately assessed and consequently a positive and highly variable bias of unknown magnitude was included in the data.

Second, adsorption of atmospheric $SO_2$ onto the fiberglass filter material followed by spontaneous oxidation of the $SO_2$ to sulfate had been well documented. A 1966 publication by R. E. Lee and J. Wagman provided results of their investigation of the problem. The conversion was clearly documented with severe effects demonstrated on four-hour samples. The conversion did appear to be an active-site catalytic conversion that decreased in magnitude after an initial saturation of sites. Thus, 24-hour samples were much less affected by this problem than were those taken for shorter time intervals. Even so, the paper by Lee and Wagman presented data in which routinely 0.5 to 1 $\mu g/m^3$ of the measured sulfate was derived from $SO_2$ conversion products. The maximum conversion presented was 2.1 $\mu g/m^3$ derived from $SO_2$; this constituted a 10 percent positive bias of the sulfate data. A more realistic average bias is likely in the 5 percent range. However, there is clear evidence that in regions of high levels of $SO_2$, relative to sulfate, the positive measurement bias becomes much more severe. This is probably the case in the Salt Lake Basin area.

The third and most devastating problem associated with the CHESS sulfate data occurred when the laboratory analysis of sulfates was contracted to an outside firm. During this time period (October 1972-June 1974) the reported sulfate data underwent a sudden and sustained decrease in apparent atmospheric sulfate level. Upon investigation it was determined that the laboratory analysis of all sulfate data from all CHESS sites were biased low by approximately 50 percent. The reason for this negative bias was and still is not completely clear, but the continued dissemination of poor data was clearly due to inadequate quality controls. An interim EPA report on a retrospective quality assurance evaluation of CHESS Sulfate Data states:

> A quality control protocol was designed for CHESS chemical analysis but has not been implemented as per the contract.....The quality control protocol should be implemented immediately.

In a series of following studies the magnitude of the affected data and of the error were documented and an attempt was made to correct and therefore recover the data. This type of procedure is difficult at best and impossible in most cases. The validity of this data correction was again assessed by the EPA Quality Assurance Branch. Their finding was:

> The basic question.....is--How does one make bad data good? Whatever is tried will be attacked for a multitude of (justifiable) reasons. Using the existing data set for relative pollution level assessment will be acceptable, but statements concerning absolute levels will not be. It would not be wise to submit these data to the NADB,[1] but rather answer all requests for these data internally.

Their statement gives a reasonable assessment of the CHESS sulfate data between 1972 and 1974. The assessment of other year CHESS sulfate data is more difficult. No comparative sulfate data exists from the local agencies as it did for $SO_2$ and TSP. Based on the intrinsic capabilities of the methods, and the error assessment of the field use procedures, it can generally be stated that:

1. From 1970 to September 1971 the sulfate data were obtained using the turbidimetric method. It should be used only as a sulfate level indicator. Due to interferences, there will be severe problems if an attempt is made to correlate sulfate levels in one part of the country with sulfate levels in another.

2. From October 1971 until October 1972, the data are subject to the following considerations:

   a. The data are likely biased in the positive direction from 1-2 $\mu g/m^3$. This bias may be more severe in areas of high $SO_2$ concentration relative to sulfate.

b. The random error component of the measurement is probably in the order of ±25% at an atmospheric concentration of 10 $\mu g/m^3$.

3. From October 1972 until June 1974, all CHESS sulfate data were biased negatively by approximately 50% on an annual average basis due to improper laboratory analysis by the contractor. These data should be used only on an adjusted annual average basis to establish local trends within site locations. The unknown cause of the bias prohibits use of the data in shorter time structure (i.e., day, week, month) increments.

4. From July 1974 until July 1975, CHESS sulfate data underwent a marked improvement and was somewhat better than that collected in the 1971-1972 era. The positive bias of the data is probably similar to that of the earlier period but the random error component was improved due to improved sulfate blanks on the TSP filters.

3.3.2.2 Summary--The above discussion of the findings of the 1976 Congressional Investigative Report represents a fairly complete cataloguing of the types of quality control problems and resulting errors generic to EPA CHESS Program sulfur oxides measurements, and it likely applies generally to all such data collected as part of the Program during particular time periods. Certain other errors, of varying relative magnitude, were detected and discussed in the IR in connection with specific CHESS studies reported in the 1974 "CHESS Monograph." Some of these are alluded to in discussions of such studies contained in Chapter 14 of this document. The reader is also directed to the 1976 IR for more information pertaining to errors in $SO_2$ measurements for specific CHESS studies.

In general, it can be seen from the above that errors in measurement for $SO_2$ under the CHESS program likely included some that would lead to a consistent underestimation of actual atmospheric $SO_2$ levels by 30 to 40% in some instances and up to around 100% under other circumstances. Fortunately, other local or state aerometry measurements, often obtained from monitoring sites side by

side with CHESS sites and judged to be more accurate and valid than the CHESS measurements, were at times available and provide very useful "benchmarks" by which to define the most likely outer bounds of CHESS measurement errors.

### 3.3.3 Summary of Assessment of Sulfur Oxides Measurement Applications

Tables 3-1 and 3-2 respectively summarize the above information pertaining to the sources, magnitudes and directional biases of errors associated with British and American $SO_2$ measurements over the past 30 to 40 years. Versions of the lead dioxide "sulfation rate" technique were used in both countries before the 1960s, with the lead dioxide gauge (candle) being employed widely in both countries and sulfation plate methods ~~are~~ as well, especially in the United States. As shown in both Tables 3-1 and 3-2, however, several problems (e.g., temperature and humidity effects) with applications of the lead dioxide method result in their being essentially useless for 24 hr measurements and in their having rather large ± error bands associated with readings taken over longer periods of time, i.e., up to 30 days. Thus the main value of the sulfation rate data, in its time, was to provide at least a rough index of sulfur dioxide (or $SO_2$) by which to gauge large increases in sulfur compound air pollution that came to be recognized as being associated with mortality or severe morbidity effects.

In the early 1960s, the British adopted the hydrogen peroxide method as the standard method to be employed for sulfur dioxide measurements as part of the United Kingdom National Air Pollution Survey. That method was selected because its sensitivity, reliability and precision were demonstrated to be much better than that obtained in comparison to the lead dioxide method. More specifically, the British Standard for sulfur dioxide determination by the hydrogen peroxide method states that replicate determinations can be expected

TABLE 3-1. SUMMARY OF EVALUATION OF SOURCES, MAGNITUDES, AND DIRECTIONAL BIASES OF ERRORS ASSOCIATED WITH BRITISH $SO_2$ MEASUREMENTS

| Time period | Measurement method | Reported source of error | Direction and magnitude of reported error | Likely general impact on British $SO_2$ data |
|---|---|---|---|---|
| Pre-1961 | Lead Dioxide | Humidity (RH) | Reaction rate increases with RH. | Variable positive bias, especially in summer. |
| | | Temperature (T) | Reaction rate increases 2% per 5° rise. | Variable positive bias, especially in summer. |
| | | Wind speed (WS) | Reaction rate increases with WS. | Variable positive bias, under high wind cond. |
| | | (Overall errors) | | Can be up to ± 180 $\mu g/m^3$ ($2\sigma$). |
| 1961-1980 (British National Air Pol. Survey) | Hydrogen Peroxide | Siting of Sample Line Intake: | | |
| | | a. too near boiler chimneys | 50 - 100 $\mu g/m^3$ overestimation. | Occasional (prob. rare) positive bias. |
| | | b. too near vegetation | 50 - 70 percent underestimation. | Occasional (prob. rare) negative bias. |
| | | Sample Line Adsorption: | | |
| | | a. Good care & cleaning | 10 $\mu g/m^3$ underestimation. | Possible general 10 $\mu g/m^3$ negative bias. |
| | | b. Average care | 20-25 $\mu g/m^3$ low from 50 $\mu g/m^3$. | Occasional 40-50% negative bias.[a] |
| | | c. Poor care (insects, dirt) | Probable greater underestimation. | Likely rare 50-90% negative bias. |
| | | Flow Meter Problems: | | |
| | | a. Daily normal conditions | ± 3 percent variation. | Negligible impact. Presumed ±3% precision of data. |
| | | b. 8-port unit with only one weekly flow reading | ± 5 percent variation. | -5% negative bias on high $SO_2$-BS days. +5% positive bias on low $SO_2$-BS days. |
| | | Allowable Filter Clamp Leakage | 1-2 percent underestimation. | Negligible impact. Presumed ±2% precision of data. |
| | | Poor Clamp Care & Technique | 5-10 percent underestimation. | Likely occasional 5-10% negative bias. |
| | | Grade B Glassware Usage | 2-5 $\mu g/m^3$ underestimation. | Negligible impact. |
| | | Improper Alkalinity Buffering | 5-10 $\mu g/m^3$ underestimation. | Occasional 5-10 $\mu g/m^3$ negative bias. |
| | | $CO_2$ in Demineralized in $H_2O$ | 40 $\mu g/m^3$ low from 50 $\mu g/m^3$ monthly mean. | Occasional negative bias of up to 80%.[b] |
| | | Atmospheric Ammonia | 25 $\mu g/m^3$ underestimation on 10% of summer samples in urban areas. | $\geq$25 $\mu g/m^3$ neg. bias on 10% of summer samples in urban areas. |
| | | | $\leq$80 $\mu g/m^3$ low ind. days & 40 $\mu g/m^3$ low monthly summer mean in country areas. | Occasional neg. bias in country areas- up to 80 $\mu g/m^3$ daily data & up to 100% monthly mean in summer. |
| | | Titration Error: | | |
| | | a. Normal-sharp color change of indicator at pH 4.5 | ±5 $\mu g/m^3$ error in determination. | Presumed ± 5 $\mu g/m^3$ precision of data. |
| | | b. Gradual color change of indicator at pH 4.5 | ±10 $\mu g/m^3$ error in determination. | Actual ± 10 $\mu g/m^3$ precision level.[c] |
| | | c. Rounding off to 0.1 ml of alkali volume added. | ±5 $\mu g/m^3$ error in determination. | Added ± 5 $\mu g/m^3$ precision error.[c] |
| | | Evaporation of reagent: | $\leq$15 $\mu g/m^3$ over estimation, especially in summer months. | 15-100% pos. bias for $SO_2$ data <100 $\mu g/m^3$. 7.5-15% pos. bias for $SO_2$ of 100-200 $\mu g/m^3$. 3.25-7.5% pos. bias for $SO_2$ of 200-400 $\mu g/m^3$. $\leq$3.25% pos. bias for $SO_2$ data >400 $\mu g/m^3$. |
| | | Temperature and Pressure: | | |
| | | a. Corrections - normal | 5% underestimation. | General 5% neg. bias in $SO_2$ data. |
| | | b. Large $\Delta P$ at filter | 10% underestimation. | Occasional ~ ±10% negative bias in $SO_2$ data. |

[a]Data from 1965-1968 most clearly impacted.

[b]Data from 1966-1967 most clearly impacted.

[c]At $\leq$50 $\mu g/m^3$ uncertainty due to these two errors is ~ 7 $\mu g/m^3$ or 14%. That is, 68% of the data are within 14% and 5% are >28% in error.

TABLE 3-2. SUMMARY OF EVALUATION OF SOURCES, MAGNITUDES, AND DIRECTIONAL BIASES OF ERRORS ASSOCIATED WITH AMERICAN $SO_2$ MEASUREMENTS

| Time period | Measurement method | Reported source of error | Direction and magnitude of reported error | Likely general impact on American $SO_2$ data |
|---|---|---|---|---|
| 1944-1968 | Lead dioxide. | Humidity (RH). | Reaction rate increases with RH. | Variable positive bias, especially in summer. |
| | | Temperature (T). | Reaction rate increases 2% per 5° rise. | Variable positive bias, especially in summer. |
| | | Windspeed (WS). | Reaction rate increases with WS. | Variable positive bias, especially in summer. |
| | | Saturation of Reagent (sulfation plate mainly). | Variable underestimation beyond pt. where 15% of $PbO_3$ on plate reacted. | Possible large negative bias, especially for 30-day samples for summer monthly readings. |
| | | (Overall Errors). | | Generally wide ± error band associated with data. Possible negative bias up to ≥100%, mainly in summer, with 30-day reading. |
| 1969-1975 (EPA CHESS PROGRAM) | West-Gaeke Pararosanaline. | Spillage of reagent during shipment. | 18% of total volume 50% of time; occasional total loss | Half of $SO_2$ data likely negatively biased by mean of 17%; some up to 100%.[a] |
| | | Time delay for reagent-$SO_2$ complex. | $SO_2$ losses of 1.0, 5, 25, and 75% at 20, 30, 40, and 50°C, respectively. | Usually small (<5%) negative bias, but consistent negative summer bias up to 25% at 40°C temp, extreme.[b] |
| | | Concentration dependence of sampling method. | Underestimation of unspecified magnitude at daily $SO_2$ >200 $\mu g/m^3$. | Probable general negative bias in daily, monthly, and yearly $SO_2$ data.[b] |
| | | Low flow correction. | ±10% to 50% variable error. | Usually error of < ±10%; occasionally up to ± 50% in daily, but dampened statistically in annual mean.[b] |
| | | Bubbler train leakage. | Small underestimation ~~air~~ error of unspecified magnitude. | Slight negative bias suspected.[b] |
| | | (Overall errors). | | From Nov., 1970, to Dec., 1971, data biased low by 50-100%.[c] From Nov., 1971, to conclusion of CHESS Program[c] in 1975, fall-winter data appear valid but summer data biased low by maximum of 60-80%.[c] From 1972 to 1975 annual average data approximately 15-20% low.[c] Daily data highly random, not useful. |

[a]November, 1970, to April, 1973, CHESS Program data impacted before error corrected.
[b]Applies to CHESS Program $SO_2$ data from all years 1970-1975.
[c]As summarized by Congressional Investigative Report (IR, 1976).

to be within ±20 $\mu g/m^3$ for concentrations up to 500 $mg/m^3$ and within ±4 percent for concentrations above 500 $\mu g/m^3$; and an OECD Working Parting stated the accuracy of the method to be ±10% at levels >100 $\mu g/m^3$. However, as summarized in Table 3-1, numerous sources of errors have been encountered in the practical application of the method in collecting data for the British National Survey over the past 15-20 years.

Certain of the sources of error listed in Table 3-1, it can be seen, resulted in relatively small errors, whereas others produced errors ranging up to 50-100% in magnitude. Also, some errors appear to have been restricted to affecting data from only limited locations (usually unspecified as to specific names of localities) or during only limited time periods. Many of these types of errors appear to have been detected fairly quickly and steps taken to successfully correct or minimize them. Still other sources of errors exist (e.g., those from reagent evaporation), which have likely affected essentially all British National Survey $SO_2$ data. Some of these appear to remain uncorrected to this date, in some cases more than 10 or 15 years after they were first detected and brought to the attention of Warren Spring Laboratory officials responsible for overseeing quality control for the entire National Air Pollution Survey.

Taking the above information into account for present purposes, it would be extremely difficult to determine precisely which errors affected particular National Survey data sets employed in British epidemiology and other studies discussed later in this document. That would likely require a thorough examination, on a time- and site-specific basis, of records detailing information on how each pertinent data set was collected and the full WSL quality control assessment reports for each data set. Alternatively, in later evaluations of

British epidemiology studies one could accept the following overall evaluation and set on conclusions by the WSL (1975) regarding British National Survey air pollution data (emphases added):

> The actual degree of accuracy attained in the Survey is not known. Input data are scrutinized by WSL staff, and subjected to computer checks, and any reflectances, titres, or air flows which are abnormally high or low or show unusually abrupt changes from one day to the next are queried and data known to be invalid are excluded from the annual summary tables. Such checks can however eliminate only some of the gross errors. More information will become available on accuracy when current (1974) plans to institute additional quality control, e.g., on reagent solutions, are put into operation. <u>However, although the accuracy of the Survey data cannot at present be quantified, many of the errors discussed in the previous paragraphs will cancel out when data are averaged over periods of a few months or a year, or for groups of sites. The remainder tend to show up as anomalies when data are compared with past or subsequent data at the same site or with data from other sites</u>; anomalies of this kind have been commented upon throughout the Reports. Members of Warren Spring Laboratory staff have devoted a large effort over the years to site visiting and checking on procedures. It is their experience that the vast majority of the instruments are maintained and operated with reasonable care and accuracy. <u>The Laboratory is therefore confident that the accuracy is sufficient for the type of data analyses carried out in the present series of reports</u>.

Presumably, it is the opinion of the WSL and British epidemiologists that the accuracy of the survey data is also sufficient to meet the original objectives of the Survey, ie. to assess the benefits accruing from the Clean Air Act of 1956, which requires use of the survey air quality data along with community health endpoint evaluations in order to define quanititative air pollution/health effects relationships. This presumption is supported by the long history of reliance on these data by British epidemiologists, such as in the making of statements regarding such quantitative relationships in innumerable journal articles and reviews appearing during the past twenty years, up to and including the very recent review by Holland et al. (1979).

Turning to American applications of $SO_2$ measurements since the widespread abandonment of sulfur dioxide sulfation rate methods in the mid to late 1960s, one finds summarized in Table 3-2 the several different types of errors identified as being associated with EPA CHESS Program $SO_2$ measurements used as part of the single largest and most comprehensive community health survey of air pollution effects conducted in the United States. The types of errors listed in Table 3-2 were those detected via a thorough evaluation of the CHESS Program by a Congressional Investigative Committee, as reported in the IR (1976). As can be seen, the magnitudes of some errors in CHESS $SO_2$ measurements spanned about the same range as those seen for British National Survey $SO_2$ measurements and, at times, derived from analogous sources of error, e.g., evaporation or other loss or reagents. In the case of the American CHESS Program data, however, the specific overall impact of the various detected errors on particular CHESS data sets appears to have been much better defined due to the work of the IR (1976) which constitutes in one publication a rather comprehensive review of measurement errors. More specifically, it appears that the CHESS data generally tended to be somewhat negatively biased in comparison to other local or state $SO_2$ data from monitoring sites proximal to the CHESS sites, with the local and state data judged by the IR (1976) to be reasonably accurate and reliable. The specific magnitude of the negative bias for particular years of CHESS data is summarized in Table 3-2, and more information on the point can be found in Appendix A of Chapter 14 of this document.

## 3.4 CRITICAL ASSESSMENT OF PARTICULATE MATTER MEASUREMENT APPLICATIONS

This section presents a critical assessment of principal measurement approaches used for determination of air concentration of particulate matter in Britain and the United States. These measurement methods involve: weighing of filters; measurement of air flow through filters; measurement of the time

of collection; and measurements of temperature and pressure. In addition, the British method requires a measurement of reflectance that is converted to a surface loading on the filter ($\mu g/cm^2$), which in turn is converted into a mass concentration ($\mu g/m^3$).

In preparing this critical assessment, the "official" instructions for respective measurements are discussed as a starting point. In addition, whenever a reference was cited to support a computation in the official procedure, the report referenced was obtained, examined, and critiqued. A literature search was then performed for comparison studies and methods evaluations which discussed accuracy, precision, and comparability between methods. This assessment, therefore, represents a synthesis of many studies over many years. With the accuracy of hindsight it presents an overall picture of two methods being developed along parallel lines to accomplish similar purposes. It is not surprising that many of the same problems arose along each path and common misconceptions may have occurred.

The in-depth analysis contained in this section is provided to address, and answer where possible, questions raised about the accuracy and precision of particulate matter measurements employed as aerometry data in the key quantitative community health studies performed in the United States and Great Britian, as discussed in Chapter 14 of this document.

### 3.4.1 British Approaches

3.4.1.1 Daily Smoke Measurements of the United Kingdom National Survey--The general technique for the British Smoke shade (BS) measurement was described previously in Chapter 2. This section provides a critical review of the measurement procedure so that one may obtain an appreciation for the precision, accuracy, and reliability of the measurements. The details of the BS measurements are provided by the Instruction Manual (Warren Spring Laboratory, 1966),

hereafter referred to as IM. At the start of the National Survey in 1961 (WSL, 1961) it was recognized "The daily instrument, while comparatively simple in design and operation gives reliable results in good hands* and seemed the best choice for the National Survey." WSL circulated the specifications of the apparatus and methods to all the cooperating organizations as careful, uniform work was essential if the results from the different sites throughout the country were to be comparable. However, WSL found that detailed instructions were necessary as most of the Local Authority staff making the measurements had no training in analytical techniques. These methods were reviewed by an O.E.C.D. Working Party and a report "Methods of Measuring Air Pollution" (OECD, 1964) was prepared, which was accepted into the British Standards Specification 1747, Parts 2 and 3. The Manual of Instruction (WSL, 1966) incorporated the improvements in techniques, "but apparatus and procedures are specified in much greater detail to assist operation by observers with no technical knowledge."*

3.4.1.1.1 Sources of imprecision in measurement: physical layout. The question of the effect of sampling tube length was addressed by Moulds (1962). The results were reported for a long length (35 feet) and a small length (7 feet) of polyvinyl tubing. The mean concentration for the long tube was 32 $\mu g/m^3$ and the mean for the short length was 36 $\mu g/m^3$. Moulds (1962) states "these differences are not significant", but does not mention if this conclusion was from a statistical test or not. Because the levels sampled (36 $\mu g/m^3$) are relatively low, the question of whether the loss is 5 $\mu g/m^3$ or 10% is not addressed, nor is it clear that the loss could not be greater at higher BS concentrations when the flowrate falls due to mass collection on the filter.

*Underline added for present emphasis.

It is now recognized (McFarland, 1979), however, that significant gravitational settling of particulate matter can occur in a long run of tubing when laminar flow is occurring. The larger particles, which may be suspended in a turbulent ambient atmosphere by vertical motions, will be affected by gravity and even thermal gradients in the inlet tube, if the top of the tubing is differentially heated by solar radiation or differentially cooled by radiation to the sky (Katz, 1958). Since the recommended PVC tubing has an internal diameter of approximately 6.5 mm, and the recommended flowrate is 1.5 liter/min (25 cc/sec), the linear velocity in the tube is approximately 0.75 m/sec. Because the IM (1966) originally allowed lengths of tubing up to 40 ft (12.2 m), the time to reach the filter in some instances may have been as high as 16.3 seconds. Consequently, with a 12.2 m inlet line, no particle with a terminal velocity greater than 0.65 cm/16.3 sec = 0.04 cm/sec could reach the filter. In addition, particle losses can be caused by sharp bends in the tubing.

As stated in the IM (1966):

> The distance from the funnel to the filter clamps should be kept as short as possible but there is no critical length under about 40 ft (12 m). It is important that the apparatus should be protected from sunlight and from undue heating by radiators or boilers; sunlight and warmth accelerate the decomposition of hydrogen peroxide, and excessive heating leads to evaporation of the liquid in the bubbler.
>
> The run of the connecting tubing should be kept as straight as possible without kinks or dependent loops. Where the connecting tubing has to change direction it is essential to keep the radius of the bend at least 1 in (2.5 cm) and preferably 2 in (5 cm) or more. A sharp bend causes marked turbulence in the air stream and consequent deposition of some smoke particles on the walls of the tube.

Because the air is still in turbulent flow for approximately 40 tube diameters (26 cm) before laminar flow is fully developed, there probably will

be secondary flow patterns at the 90° bend over the funnel inlet. The particles may then be preferentially deposited on the glass surface of the bend. An electrostatic charge on the PVC tubing is another possible source of uncertainty since this could also cause particles to settle out faster than computed by Stokes' Law (B.S. 1747, Part 2, 1964). Because there is no uniformity required by the IM (1966) for either tube lengths or number and size of bends, uncertainty between measurements must be considered a distinct possiblity.

Leakage--The smoke filter unit consists of two heavy brass cylinders called filter clamps, drilled out to provide a fixed area for the exposed filter paper. The seal of the BS filter by the filter clamps is a major source of possible error. According to WSL (1961): "At one time weights were used to hold the clamps together, but so many failures occurred that a screw-down clamp holder is now regarded essential."

As stated by the IM (1966):

> By the nature of their construction, filter clamps and 8-port valves are prone to leakage which cannot be detected without a special test. The resistance of the filter paper and bubbler to the airflow means that the side of the clamp assembly or valve connected to the pump is under a slight vacuum, and a badly seating clamp or dirty valve will allow air to enter. Leakage can also occur edgewise through the filter paper if inadequate pressure is applied to the clamps.
>
> If such an inward leak occurs, the amount of air registered by the gas meter includes air from the room where the apparatus is kept and which has not passed through the filter paper in the normal way. This should not be permitted to exceed the limits quoted below.

Those limits for leakage are 1 to 2 percent, depending on clamp size.

This leakage problem was also observed with the early American Iron and Steel Institute (AISI) CoH instrument when the clamps were out of alignment by as little as one-thousandth of an inch, according to a 1962 WSL report (WSL AP/70, 1962). In the early development of the WSL automatic sequential

samplers, it was discovered that a gross irreproducibility of measurements with models similar to the AISI instruments was almost certainly caused by variable leakages at the filter clamps (WSL AP/70, 1962). Thus, first generation (1959-1961) WSL automatic sampling models were declared unsuitable for an early survey in Sheffield until the reproducibility could be improved. For example, one pair of readings of co-located samplers during a test gave 282 and 1065 $\mu g/m^3$.

In order to prevent a significant error due to leakage, the IM (1966) provided a section entitled Measurement of Leakage and instructions as to how to determine that the leakage is in the acceptable ranges of <1 percent for a 1/2-inch or 1-inch filter clamp or <2 percent for a 2-inch or 4-inch filter clamp. The leakage rate data, however, are apparently not used to make a correction to the final recorded value of BS, which would be raised by 1 to 2 percent.

Flow measurements--The Whatman No. 1 filter paper used in collecting samples for National Survey smoke measurements is quite porous to submicron particles when it is clean (Liu et al., 1978). As the pores begin to fill up, however, the "window" closes and the efficiency of the filter increases. The IM (1966) warns against using a 1/2-inch clamp except in clean areas.

> The use of 1/2-in clamps should be confined to extremely clean areas in open country where 1-in clamps regularly give reflectometer readings of 90 and over. The main disadvantage of using 1/2-inch clamps is that the smoke deposit builds up very quickly, soon causing the reflectometer reading to fall below 40. At the same time the resistance to the flow of air rises and the flow rate at the end of the sampling period may be only one-third of that at the beginning, when the filter paper was clean.

Another, potentially more serious error is described in WSL (1975, Volume 5)

> In the case of 8-port instruments, for which gas meters are read only once a week, concentrations are calculated on the assumption that the volume of air sampled was the same every day. When the throughput of air is less than average on days of high particulate pollution, because of back pressure at the filter, concentrations are underestimated, and they are overestimated on the other days of the week. (For the same reason diurnal variations in back pressure may lead to under-estimation of pollution when some hours of high pollution follow hours of low pollution.) This effect is kept to a minimum if the clamp is sufficiently large, having regard to season and type of area, and it is unlikely to be significant now that smoke concentrations are much less than they used to be, except occasionally at sites with 1/2-inch clamps.

This was recognized in the IM (1966) where it is clearly stated:

> In principle, the 8-port valve demands a constant air flowrate through the system, since meter readings are normally taken at intervals of several days. Obviously if one of a number of stains obtained between two meter readings is dark, the airflow for that day will be below the calculated average, and the calculated concentration, based on the average daily flow over the whole period, will be too low.

To correct for this problem, the IM (1966) states:

> Charles Austen (Pumps) Ltd have developed a constant flow pump capable of being set to work at a constant rate of 1.5 l/min (approximately 3 $ft^3$/h) over a wide range of pressure variations in the system. It is preferable to use this pump in place of the Dymax pump and air pollution meter.

This recommendation was not made a requirement by WSL, and it is quite possible that local authority personnel with no training in analytical techniques or sufficient technical knowledge ignored it. Re-examination of pertinent records would be required to ascertain which National Survey data may have been affected by flow measurement errors.

3.4.1.1.2 <u>Reflectance measurements</u>. The WSL quality control report (1977b) states:

Tests have shown that two WSL operators using different reflectometers to measure the darkness of a set of smoke stains differ on average by less than 1 unit of reflectance, the standard deviation being about 1 unit. Differences of 3 or 4 reflectance units in readings of individual stains occur occasionally. Co-operating bodies are therefore contacted regarding their smoke stain assessment if their reading of an individual stain differs by more than 4 reflectance units (about 20% of the concentration) from the WSL reading, or if the mean difference for 4 readings exceeds 3 reflectance units (about 15% of the concentration). Over 15 percent of the co-operating bodies involved in the first series of tests, and 15 percent of those in the second series, were contacted on the basis of these criteria (22 bodies altogether).

The absolute error in $\mu g/m^3$ associated with this reading difference increases in magnitude with reduction of the reflectance value. We can derive the error rate by differentiating the equation for smoke concentration with respect to reflectance. The results show that the error associated with a ± 1 unit reflectance reading is: ± 10% at R = 90; ±7% at R = 80; falling to ±4% at R = 40. The smoke concentration formulae used for converting reflectance readings are reported in the IM (1966) as:

$$C_{sm} = \frac{F}{V} (91{,}679.22 - 3{,}332.0460\ R + 49.618884\ R^2 - 0.35329778\ R^3 + 0.0009863435\ R^4)$$

where

$C_{sm}$ is the concentration of smoke ($\mu g/m^3$),

V is the volume of air ($ft^3$),

R is the reflectometer reading, and

F is a factor which depends on the size of clamp used (1/2-in clamp, F=0.288; 1-in clamp, F=1.00; 2-in clamp, F=3.68; 4-in clamp, F=12.80)

For darker stains with reflectometer readings below 40, an <u>approximation</u> of the smoke concentration can be derived from the following formula:

$$C_{sm} = \frac{F}{V} (214{,}245.1 - 15{,}130.512\ R + 508.181\ R^2 - 8.831144\ R^3 + 0.0628057\ R^4)$$

The extensive usage of significant figures in these formulas may lead a casual reader to believe that they are highly accurate and represent a scientifically valid formulation. In fact, these 5 factors were chosen to fit 5 observations exactly, which is an unusual procedure. The polynomial fit can lead to strange behavior, such as the inflection point in the first formula at R = 43.

The factors {F} above deserve particular scrutiny. They arise from the OECD (1965) report referenced in the IM (1966). The pertinent OECD (1965) report section states verbatim:

> The surface concentration of the smoke in terms of "international standard" smoke is first obtained from the reflection factor by reference to the calibration curve appropriate to the filter paper and reflectometer used. Curves for Whatman No. 1, Schneider CA 32 and fibreglass GF/A filter papers, and Eel and Photovolt reflectometers are given in Figures 2 to 6.

A discussion of the basis, derivation, and use of these curves is given in Part 3 of the OECD (1965) report, as stated below:

> Let S be the derived surface concentration of the smoke on the filter paper, in $\mu g/cm^2$,
> A be the area of the appropriate filter stain, in $cm^2$,
> V be the volume of air sampled, in $m^3$,
> C be the concentration of the smoke in the air, in $\mu g/m^3$,
> then C = SA/V
>
> The following formulae should be used for 2-in and 4-in diameter stains on Whatman No. 1 filter papers to allow for the lower linear velocity of the air as it meets the filter paper in these filters causing less penetration of the smoke particles into the pores of the paper. This leaves more of the smoke on the surface so that a given amount produces a darker stain.
> C = 0.92 SA/V for a 2-in filter
> C = 0.80 SA/V for a 4-in filter.

The factor "F" referred to in the IM (1966) appears to have been derived from the above OECD (1965) formulae and the IM specifically lists the following values for F as a function of filter clamp size:

| OECD correction values | Filter clamp size | IM "F" values |
|---|---|---|
| 0.80 | 4-inch | 12.8 |
| 0.92 | 2-inch | 3.68 |
| 1.00 | 1-inch | 1.00 |
| ? | 1/2-inch | 0.288 |

The unreported correction factor from OECD for the 1/2-inch filter clamp is apparently interpreted by WSL to be 1.15, but its derivation is unknown and is unreferenced in the IM (1966). This appears to be identical to 0.92/0.80 = 1.15, as might be derived from the OECD (1965) report, but it is quite different from 1.00/0.92 = 1.09, which could also be reasonably interpreted from the OECD (1965) figures.

Thus, the 1/2-inch clamp factor of 1.15 is apparently required by WSL in their 1966 IM to be used to account for particle deposition deeper into the filter at higher velocities. They therefore assume that the 1/2-inch filter clamp collects "less" on the surface than the 1-inch filter clamp, and the other factors are less than 1.0 because they collect more on the surface than the 1-inch BS filter. This is not easily reconciled with the results of Clayton (WSL, 1977), and Liu et al. (1978) who both report a <u>decrease</u> in collection efficiency at lower face velocities followed by increasing collection efficiency with increasing face velocities for the 0.32 to 1.0 μm particles at all velocities tested. That would imply that the particles penetrate through the filter more readily at low velocities than at the higher velocities such that the particles would not tend to be trapped on the surface.

Moulds (1962) compared the penetration of the "smooth" and "rough" sides of the BS Whatman No.1 filter paper. She reported:

> A composite filter was used to compare stains on alternative sides of the paper so that one half of the collecting surface was the "Rough" side, and the other half the "Smooth" side, with its closer more regular surface. The stains were uniform within each half and that on the "Rough" side was never darker than the on the "Smooth" side, which may allow less penetration or present less surface area for the deposit.

This statement appears to imply that the smooth side gave <u>less</u> penetration and the stain was <u>darker</u>. The OECD (1965) report implied that in the case where <u>less</u> penetration was caused by a higher velocity the stain would be <u>lighter</u>.

In a further WSL report by Bailey and Nicholson LR 89 (AP) dated October 1968, a factor "F" is developed for a 10 mm filter clamp. The summary of the report states:

> The calibration curve of standard smoke quoted in B.S. 1747: Part 2: 1964 is derived for a 2.54-cm filter holder. If the diameter of the stain is reduced whilst the air flow is held substantially constant the velocity of impact of the smoke particles on the filter paper is increased causing deeper penetration; hence an increased concentration per unit area is required to obtain a particular darkness index. This effect has been examined for a stain of 1-cm diameter and it was found that, over a range of smoke concentrations from 5 to 20 $\mu g/m^3$, the 2.54-cm calibration could be used with a multiplying factor of 1.30.

These authors ran some British High Volume Samples (B.S. 1747: Part 2) simultaneously with the standard smoke samples and reported that "The ratio of the concentration by direct weighing to the concentration in terms of equivalent smoke varied from 0.59 to 0.90 with an average value of 0.76." These values are shown in Table 3-3 below.

TABLE 3-3. CONCENTRATIONS BY DIRECT WEIGHING COMPARED WITH CONCENTRATIONS OF STANDARD SMOKE - 10 mm CLAMP

| Test No. | Volume, $m^3$ | Weight mg | Concentration, $\mu g/m^3$ by weight (a) | Concentration, $\mu g/m^3$ Standard Smoke (b) | Ratio a/b |
|---|---|---|---|---|---|
| 4 | 19.74 | 4.8 | 243 | 285 | 0.85 |
| 5 | 19.20 | 6.0 | 312 | 410 | 0.76 |
| 6 | 19.18 | 2.5 | 130 | 220 | 0.59 |
| 7 | 19.74 | 4.1 | 208 | 319 | 0.65 |
| 8 | 20.45 | 5.4 | 264 | 312 | 0.85 |
| 9 | 8.77 | 2.0 | 228 | 253 | 0.90 |
| 10 | 9.03 | 3.5 | 387 | 621 | 0.62 |

Thus, the standard smoke, which includes the 1.30 factor, is 1/0.76 or 30 percent higher than the concentration collected and weighed. This inconsistency also appears in a discussion by Appling et al. (1977) of a difference between a BS reading of 1000 $\mu g/m^3$ at the MRC site and 850 $\mu g/m^3$ at the WSL site in Endell street, Holburn, on December 15, 1975. Appling et al. state:

> The fact that the hourly concentrations were higher at the MRC site than at the Endell Street site could be wholly or partly due to a slight difference in the method of measurement at the MRC site, the instrument there having twice the air throughput rate of the standard smoke instrument.

However, the reasoning given in the OECD (1964) report for the WSL correction factors for various filter sizes is that the higher face velocity cause the particles to penetrate deeper into the filter, thereby producing a relatively lighter stain. It is not reported what factor, if any, was used at the MRC (Medical Research Council) to correct for the higher velocity.

In light of the above information, an ambiguity presently appears to exist in regard to the basis for the "F" correction factor in the IM (1966) and the correction values in the OECD (1965) Manual for the 1/2, 2, and 4-inch filter clamps. One possible explanation for the apparent inconsistencies may be that the correction factors {F} are related to a certain computer error. Figure 3-2 from WSL (1967) shows four different curves. As described in WSL, (1967):

> The National Survey data for 1961 to 1964 were, as described, processed by computer and after some little time it was discovered that the computer was not following the curve it was intended to, and that, in fact, the smoke concentrations were being calculated from the lowest of the calibration curves shown in Figure 3-2. This set of data has now been re-calculated to the standard curve and re-issued.

Examination of Figure 3-3 from Moulds (1962), shows that the deviation of the ratio of 1-inch filter to 2-inch filter concentrations diverges from unity at a reflectance of 50, where the 1961 DSIR curve labeled C in Figure 3-2 (i.e., Figure 44 from WSL, 1967) diverges from the British Standard Curve (A). For example, at ~~reflectance~~ darkness order 90, the curve A gives about twice as much mass as curve C, which we presume Moulds used. Consequently, the ratio would be about 1.0 also. As quoted above, WSL went back and re-computed and re-issued the 1961 to 1964 National Survey data. However, it appears that WSL may not have gone back and re-computed all the 1961 to 1964 data, including their data sets which were used to derive the factors {F} of 1.15, 0.92, and 0.80 (which were also computed during this period). Of course, if the computer made these calculations by curve D, the error would be even greater than the 50 percent difference that Moulds reported.

In summary, the information presently available does not seem to support the usage of the factors 1.30, 1.15, 0.92, and 0.80, which are apparently

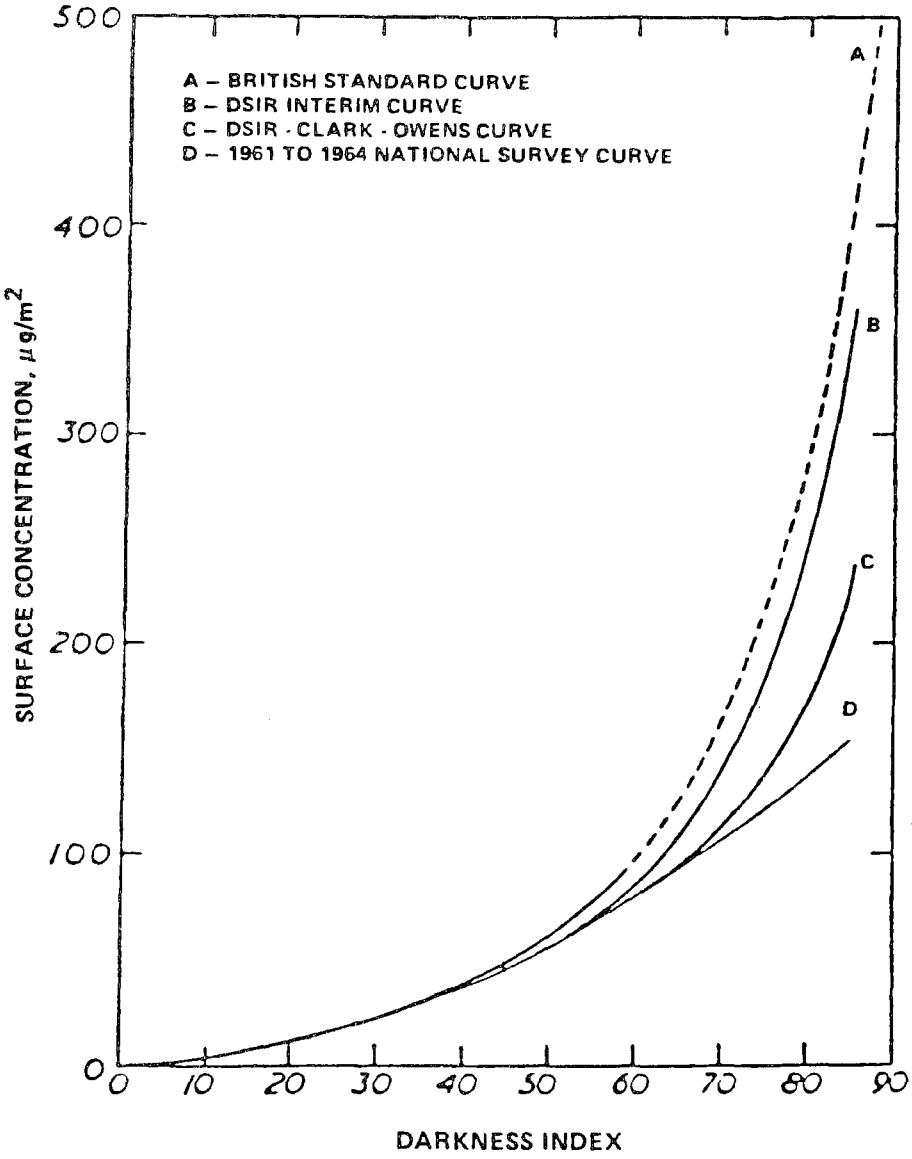



Figure 3-2. Comparison of smoke calibration curves for Eel reflectometer, Whatman No. 1 paper and a 1-in. diameter filter. From WSL (1967).

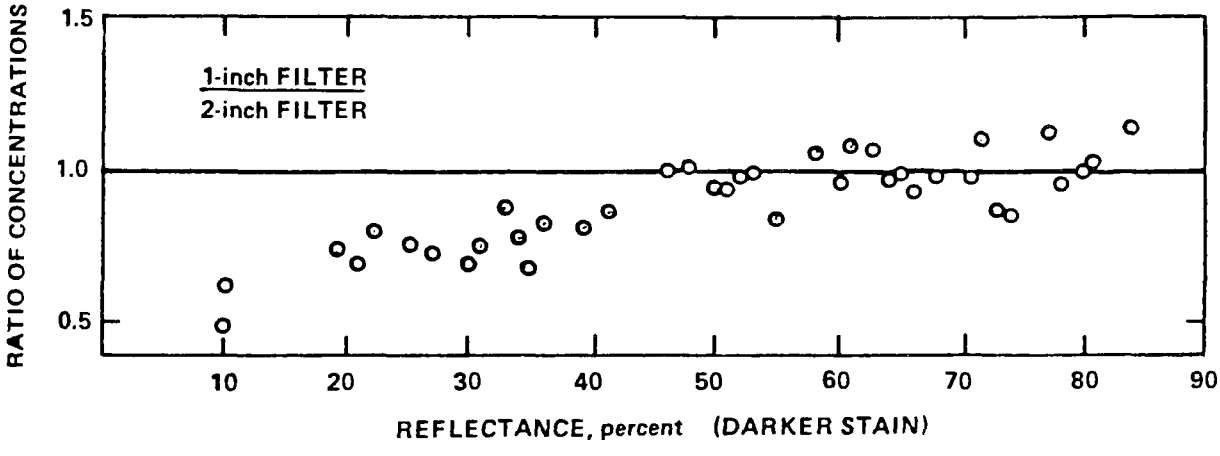



Figure 3-3. Comparison of simultaneous BS measurements using 1-in. and 2-in. filter clamps, showing that the reflectance ratio (1-in./2-in.) decreases below approximately 45 percent reflectance of the 1-inch filter clamp. From Moulds (1962).

still in use up to this present day. This could have a substantial impact on BS measurements if the use of the stated corrections cannot be supported in view of the above physical observations by Ellison (1968) WSL (1968), WSL (1977), and Liu et al. (1978).

3.4.1.1.3 Form of the Reflectance Curve. The International OECD expert curve may also be improperly based. The reflectance R is the dependent variable, and the concentration of particulate matter on the filter $C_{sm}$ must be treated as the independent variable. Consequently, the regression relation might better be $R = f(C_{sm})$ not $C_{sm} = f^{-1}(R)$. As can be seen from inspection of the two calibration equations, they can lead to an upper limit at R = 0 of [$C_{sm} = \frac{F}{V}$ (214245.1)] or about 3000 μg/m$^3$. However, Ellison (1968) reports that the reflectance must approach a constant finite value equal to the reflectance of the particle mixture. That is, $C_{sm} \rightarrow \infty$, $R \rightarrow R_\infty \neq 0$. Along with the condition $C_{sm} = 0$, R = 100, there are also alternate forms for the equations. If variables are changed to D = 100 - R, where D is the percent decrease in reflectance, then $D = f(C_{sm})$. A simple equation that places D = 0 @ $C_{sm} = 0$ and $D = D_\infty$ @ $C_{sm} \rightarrow \infty$ is:

$$D = D_\infty [1 - \exp(\alpha C_{sm} + \beta C_{sm}^2)]$$

Tests for values of $D_\infty$, $\alpha$, and $\beta$ can be made to satisfy the curve and the boundary conditions.

3.4.1.1.4 Averaging error. The IM (1966) states:

> On the larger stains, it may sometimes be advisable to take meter readings on different parts of the stain. If the readings are found to vary slightly the mean value should be taken as representative.

The British Standards manual (1747, Part 2, 1964) also states: "Take a reading at three different positions of the reflectometer head on the stain and determine the mean."

However, this procedure will lead to incorrect results. The readings must be converted to $\mu g/cm^2$ and the average filter loading must be computed. Because the reflectance curve is nonlinear the mean reflectance will lead to an underestimate of the true filter loading.

3.4.1.1.5 Filter handling. One of the most important aspects of the BS smoke measurement relates to the handling of the filter in the measurement system. The Whatman #1 filter is not isotropic. There is a smooth side to the filter which should face the direction of the airflow and a coarse side which faces downstream. The IM (1966) procedure calls for the operator to identify the smooth side thrice, in setting the filter into the clamp properly (smooth side upstream), again when a clean filter reflectance is measured in order to establish the 100 percent reflectance point and also when the stain is read. However, the British Standard instructions (B.S. 1747, Part 2, 1964) only say: "adjust the reading on a single sheet of clean filter paper" without reference to smooth or coarse side. A comparison of reflectance of coarse side versus smooth side shows the coarse side of Whatman #1 paper to be slightly darker than the smooth side by less than one unit of R (personal communication, D. T. Mage, 1980).

Failure to distinguish the smooth side from the coarse side in either or both of these measurements results in an error, since the standard curve being compared to is smooth filter-smooth filter, both ways. Moulds, (1962) demonstrated this effect in the experiment described on Page 3-52 of this section as: "Values of the quantity Concentration 'Smooth'/Concentration 'Rough' expressed as a percentage varied between 100 and 122, with a mean of 106.8 and a standard deviation of 6.15. An even larger error could exist if the filter was read in the reflectometer incorrectly, i.e., not on the impact stain side

but on the opposite side where a lowgrade stain appears from the particles pulled into the filter paper.

A WSL report (WSL, Vol. 5, January 1975) states on page 113: "Stains have occasionally been found to have been read the wrong way up, i.e., with the exposed face of the paper downwards, and the darkness has then been seriously underestimated." The IM (1966), upon close reading, does not actually say place the filter stain side up. It says

> "Replace the clean filter paper by a stained paper. Position the stain centrally over the white tile and place the masking unit over the stain, with the hole as near the centre as possible. Insert the measuring head into the unit while keeping it in position and record the reading directly on to Form WSL 216 against the date on which the filter paper was removed from the apparatus. Repeat this procedure for each stain."

Apparently WSL did not consider reading the stain backwards to be a serious problem or did not take adequate steps to avert its occurrence, because a later 1977 report (WSL, 1977) still included the following references to such errors: "Since the reading of smoke stains on the wrong side of the paper is the source of the largest errors in smoke assessment, more publicity should be given to this hazard and how to avoid it." This type of error is a clear matter of concern if accurate smoke readings are to be obtained, but it is not possible to determine precisely what National Survey data may have been affected by such error without a case-by-case examination of the original records for various monitoring sites during specific time periods (For example, one monitoring site operator is reported to have read the unstained side of BS filters for three years).

3.4.1.1.6 Filter weighing procedure. Another question can be raised regarding the procedure used for providing a weight of smoke in the calibration procedure

outlined by BS 1474, Part 2, 1964. A control on the weighing is provided by handling a second filter in an identical manner as the stained filter paper. The manual states:

> The increase in weight of the exposed paper is a measure of the weight of the dry deposited material or smoke and any change in weight arising from the handling procedure. A correction for the error due to handling is made by adding or subtracting the difference between the initial and final weights of the control paper.

This procedure is quite correct if the handling errors are positively correlated. If the handling errors are random and independent of each other then the variance of the error is increased. If, however, the errors are negatively correlated, i.e., if it is more likely to lose particles from a stained filter than make it heavier and if it is more likely to soil a clean filter than make it cleaner, then this procedure could lead to a reduction in the recorded weights.

3.3.1.1.7 Filter shipment losses. Another possible uncertainty may occur when filters are shipped to WSL to be read for quality assurance. If the filters lose particles in the mail, the filters will have a higher reflectance when they are read at WSL. In the WSL report, "The National Survey of Smoke and Sulphur Dioxide-Quality Control Tests on Analysis of Samples, October 1975 to February 1977, results of a study of filter readings by the field operators and WSL are described. The operators sent their filters to WSL to be reread and WSL reports "More operators under-estimated the reflectance than over-estimated it." No statistical analysis, however, was reported to test the hypothesis that no weight was lost in shipment.

3.4.1.1.8 Choice of clamp size. The WSL Instruction Manual (1966) leaves it to the operators' judgement as to which clamp size to use in anticipation of

varying pollution levels. For example: "When the stain produced with 1-inch clamps is close to the 'danger level' for a 24-hour period, it is obvious that a darker stain will result from a 2- or 3-day exposure over the weekend. In such cases, a change should be made to 2-inch clamps for the weekend." However, the IM states: "The daily servicing of the instrument is a simple routine task; it is often found that a caretaker or other person on duty can undertake this servicing, leaving the exposed filter paper and hydrogen peroxide to be collected at a convenient time." However, if the caretaker is not a technically trained person, then the "danger level" may not be noticed. Thus, the retrospective analysis of filters may not provide the feedback necessary to anticipate sudden increases in pollution.

This situation may have actually arisen during a December, 1975, episode in London when an excess mortality of 100-200 persons occurred (Holland, et al., 1979). As described in WSL, LR 263(AP) the period December 14-17, 1975, produced the highest smoke pollution levels seen since 1967. Because a surface inversion formed on Sunday the 14th, the network operators had no notice that an episode was occurring until they came to work on Monday the 15th.

In greater London, during December 1975, 111 monitoring sites were available for measurement of smoke stain (BS). On Friday, December 12, 1975, only 46 sites were equipped with operational 8-port instruments capable of giving 24-hour samples automatically and the other 65 sites had instruments which either required daily servicing or they had inoperational 8-port instruments.

The Instruction Manual (1966) allows for manual weekend operations by providing direction to the operators to use 4-inch diameter clamps for a 72-hour period to prevent "too dark a stain" from being produced by a 2-inch clamp.

However, the stations without the 8-port instruments apparently were not run over the 72-hour period between 11 a.m. Friday, December 12, through 11 a.m. Monday, December 15, since WSL, LR 263 AP makes no mention that these 72-hour data were available. Thus, 3 days of data were likely lost because of the weekend at each of the manual sampling sites. Unfortunately, this complicates the data analysis. For example, during the period 11:00 Sunday, December 14, to 11:00 Monday, December 15, 1975, the maximum observation out of 46 stations reporting was BS 696 $\mu g/m^3$. On the following day, 11:00 Monday, December 15 to 11:00 Tuesday, December 16, 1975, the maximum observation out of 104 stations reporting was BS 811 $\mu g/m^3$. If all 111 stations had operated Sunday to Monday, instead of only 46 stations, then the missing 65 observations might have included an actual maximum reading greater than BS 811 $\mu g/m^3$.

The episode report also makes no mention as to whether any of the 46 8-port instruments which operated over the weekend were not equipped with a constant flow pump. As described in the IM, lack of such an instrument would probably lead to underestimated values, because the flow on the episode Sunday would not be one-seventh of the total weekly flow.

In addition, the WSL report LR 263 (AP) makes no mention whether all the operators made the necessary changes from 2-inch clamps to 4-inch clamps on Monday December 15, 1975; thus, it seems possible that the same 2-inch clamps were used through the weekend as during the immediately preceding and following weekdays. If this is so, then standard procedures for changing clamp sizes would have been violated. More specifically, the WSL IM (1966) states:

> In an extremely severe episode of 'smog', when accurate knowledge of peak levels is desirable, the filter paper should be changed and the meter read at suitable intervals during the day.

Further indications that these instructions were not followed at all the stations during the episode can be derived from the Apling et al. (WSL, 1977) report. That is , in that report, hourly peak values are only reported for a few stations for the 24-hour period from Monday December 15 to Tuesday December 16, 1975. Examination of the report (WSL, 1977) further reveals that most of the stations in the borough of Kensington-and-Chelsea were reporting significantly lower BS values than the neighboring borough stations, some less than 1 km away. Since the wind was reported as ~1.5 m/s, the air-mass flight time between the Kensington-and-Chelsea stations and the neighboring stations was only 10 minutes, which would lead one to expect similar values between these upwind and downwind stations. Apling et al. (WSL, 1977) state that this difference may be produced by differences in distance to the street, but they make no special analysis of the "cold spot" in Kensington-and-Chelsea.

3.4.1.2 Summary--Similarly to what was indicated earlier for the $SO_2$ measurements, the assumptions and errors discussed here for National Survey BS measurements may be conservative because in many cases "staff making the measurements had no training in analytical techniques" (IM, 1966) and may not have followed closely the instructions in the IM (1966). Even if they did, however, given the nature of certain ambiguities concerning the origin and derivation of the recommended filter clamp correction factors, substantial errors may still have been made for that portion of the National Survey BS data base not obtained by the use of 1-inch filter clamps. Other errors mentioned above, such as, the "computer error of 1961-64" can be more definitely identified as likely affecting certain British BS data sets obtained during specific periods of time. Although this "computer error" was reported (WSL, 1967) as being corrected in the National Survey data base at an unspecified

time, it is neither clear nor likely that all publications in the peer review literature which employed these incorrect data have been corrected.

### 3.4.2 American Approaches

As discussed earlier, the hi-volume TSP sampler, since its development in the early 1950s, has been the instrument most commonly used in United States for measurement of atmospheric particulate matter; and hi-vol TSP readings have most typically been used in epidemiologic evaluation of associated air pollution effects relationships. In contrast, other particulate matter measurement approaches (e.g., the coefficient of haze method) saw only relatively limited application during the 1950s and early 1960s in certain American locations and were infrequently used in estimating quantitative relationships between airborne particulate matter and health or welfare effects. Accordingly, major emphasis is placed below on the critical appraisal of certain key applications of hi-volume TSP measurements in the United States; less extensive attention is accorded to evaluation of other particulate measurement applications in the United States.

As before, in discussing American applications for measurement of oxides of sulfur, the present discussion will focus most heavily on evaluation of applications of hi-volume TSP measurement methods that occurred as part of the EPA "CHESS Program" as the single most extensive and comprehensive use of such methods as part of American community health epidemiology studies. Some consideration of local or state monitoring applications of pertinent hi-volume TSP measurements is also included as part of the discussion of CHESS TSP monitoring. Much of the information provided is derived from the 1976 Congressional Investigative Report (IR) which included thorough analysis of EPA CHESS Program TSP measurements and comments regarding certain local or state TSP measurements.

3.4.2.1 Hi-Volume TSP Measurements of the U.S. EPA CHESS Program--Restating earlier background information, the 1976 Congressionsl Investigative Report (IR) noted that the attainment of precise, reliable, reproducible, and real time air quality measurements for particulate matter and other pollutants was a key objective of the CHESS Program. Also, as stated in the IR (1976), the air measurement methods selected for use in the CHESS program to meet that objective were probably as good as any available at the time; and attempts were made to introduce and implement better quality control procedures for air monitoring into the CHESS Program as it progressed. However, quality control problems with air quality measurements, especially in the earlier years of the Program, did occur and led to controversy and critisms of the type discussed in the IR (1976). Most of the more salient points raised by the IR concerning CHESS TSP measurements are discussed below.

As briefly described in Section IV B 2 of the 1976 IR for the CHESS Program:

> Total suspended particulates (TSP) were measured using the EPA Reference Method as specified in the Federal Register (36 (84): 8191-8194, April 30, 1971†).
>
> Total suspended particulates (TSP) were measured by drawing air through a preweighed 8 x 10 inch glass fiber filter for a period of 24 hours. The apparatus used for this procedure was the standard High Volume Sampler. At the end of the 24 hour time period, the filter was reweighed, and the TSP computed on the basis of total air flow. The air flow rate was approximately 60 $ft^3 min^{-1}$ at the start, and must be not less than 40 $ft^3 min^{-1}$ at the end for the measurement to be acceptable. The average air flow rate was computed on the basis of a straightline interpolation between beginning and ending flow rates.

Comments concerning the validity of the method as a laboratory procedure included the following from Section IV C 3 of the IR (1976):

The Reference Method for the determination of total suspended particulate matter (TSP) is probably the simplest and most reliable method used by CHESS. It has been well studied and most error sources are known. However, it is a method that measures an arbitrary and poorly defined portion of the total atmospheric particulate burden and the portion measured has unknown relevance to the human respirable portion. The size fraction measured is somewhat dependent on the design of the shelter used for Hi-Volume sampler. The design and dimensions of the Reference Method shelter are specified in the Federal Register, thus the portion of TSP that is collected by the method is generally uniform. Best estimates of particle size range included in the Reference Method are from 0.05 to 60 μm diameter. Above 60 μm diameter, the particle fall velocity is too great to navigate the bend around the roof of the shelter. Below 0.05 μm the collection efficiency of the glass fiber used in the method diminishes.

A collaborative study was conducted on the Reference Method using 12 different groups sampling ambient air at a common location. The results of this study indicate the method is capable of reproducible measurements with less than 5 percent error at the 95 percent confidence level. Also, the minimum detectable amount of TSP is approximately 2 $\mu g/m^3$ for a 24-hour sampling period. This sensitivity is more than sufficient for most 24-hour TSP measurements.

Section IV C 3 of the 1976 Investigative Report further noted the following regarding sources of error in CHESS TSP measurements and their likely impact:

The TSP measurement method, as used in CHESS, had one notable difference from the laboratory procedure which was collaboratively studied. The weighing procedure to determine TSP was performed at EPA/RTP laboratory not by the CHESS contractors on site. This necessitated the shipment of individual filter samples through the mail and the subsequent storages of the samples at EPA. During laboratory reorganizations at RTP, periods as long as 6 months elapsed between actual field sampling and laboratory analysis.

The following is a summary of individual errors and an assessment of overall TSP data quality.

<u>Loss of particulate matter before weighing</u>

In the TSP methodology there were field-related procedures that resulted in partial loss of particulate matter from the Hi-Volume filter samples. Due to the exposed location of the Hi-Vol TSP samplers, wind and cold sometimes made it very difficult to remove the filter paper from the apparatus without losing part of the sample. No estimate has been made of loss due to this problem; it would, of course bias the reported results only in the direction of lower-than-actual atmospheric loadings. This was not a constant problem among CHESS sites. It was noted by field operators as being a particularly severe problem in the Salt Lake City area during the winter months.

Two other error sources have been identified in the determination of TSP, both of which would also produce a low-side bias: (1) the shaking-off of particles from the filter during transit from the field site to EPA/RTP, and (2) the evaporation of organic substances. In an attempt to quantify the mass loss during transit, David Hinton, EPA/RTP, made a comparison of filters collected in Utah, before and after mailing from Salt Lake City to RTP (22). He found that there was an average 4 percent loss. Carl Broadhead, of the Utah Division of Health, conducted a similar comparison; however, he noted an apparent loss of approximately 25%. This difference may, in part, be due to the time of year the studies were conducted. During the dry summer months in the Salt Lake City area, much of the TSP loading is due to windborn crustal material (sand). This material is much more easily lost in sample handling that is the finer anthropogenic particulate material.

A final error source, one more difficult to assess, derives from wind velocity versus collection efficiency. On days with relatively high wind (>15 mph), the HiVol sampler is more susceptible to the inclusion of large diameter particulate material. To compound this problem, the design of the shelter makes the magnitude of the error dependent on the wind direction relative to the orientation of the shelter. The main result of this problem is that two side by side HiVol samplers, oriented 90 degrees relative to each other, will produce dissimilar measurements with the discrepancy increasing as the daily wind velocity increases.

The overall effect of the summed errors with the HiVol TSP measurement is a slight negative bias. This bias may be as small as 10% or may be as large as 30%. Side by side data from New York and Salt Lake indicate that this assessment is reasonable. These data also indicate that the TSP data were by far the best quality data taken in the CHESS monitoring program. Differences measured between High and Low sites are probably reasonable estimates of the differences of TSP exposures as received by populations within these areas. Some local source variations undoubtedly did occur, but average annual exposures were reasonable.

In any overall assessment of the CHESS TSP data it should be noted that all of the sources of errors mentioned previously related almost exclusively to the loss of large particulate matter and most likely that matter is associated with crustal weathering. This material is outside of the normal human respirable size fraction and by composition, it would be unlikely to be associated with aggravated health. Thus, loss of that portion of the total material may not have diminished the quality of data for health effects studies. It may in fact have rendered that data a closer estimate of the respirable TSP exposure to which the CHESS population groups were subjected.

3.4.2.2. Other CHESS Program Particulate Matter Measurements--The 1976 IR noted that four other methods for estimating particulate concentrations were used at various times to yield aerometry data employed as part of CHESS Program evaluations of quantitative air pollution/health effects relationships. Comments relating to each of these other methods (i.e. the dustfall bucket, the tape sampler, the cascade impactor, and the cyclone sampler) were reported in Section IV B 4 of the IR (1976) as follows:

> (a) The name 'dustfall bucket' is adequately descriptive. It is basically an open-topped cylinder, with some protection against wind and rain loss, that is left out in the open, close to the ground or on a rooftop, for a month. At the end of that time the dry matter collected is weighed, and sometimes analyzed for trace metals. The dustfall bucket method is very crude and misses almost completely the very significant part of the aerosol, including the respirable aerosol, that does not settle rapidly. It must be considered here, however, because dustfall measurements were extrapolated to obtain estimates of suspended sulfates and sulfur dioxide in New York City during the period 1949-58 ((Table 5.2.1, CHESS Monograph), and intermittently in Chicago (Table 4.1.A.3), CHESS Monograph). Dustfall measurements were used as the basis for these extrapolations because there was no other basis for such estimates, but it must be remembered that the relationship between suspended sulfates and dustfall is unknown, and that between sulfur dioxide and dustfall is another step removed from reality.
>
> (b) Coefficient of Haze (CoH) is determined by the automatically operating tape sampler. It is determined by measuring the optical density of an aerosol deposited on a filter tape. The aerosol deposit is obtained by drawing air at a given flow rate through white filter paper tape for a known period of time. If one could assume that the composition and physical characteristics of the aerosol in a given location did not change with time--that only atmospheric loadings would change--then the COH would give a fairly good approximation of the variations of particulate loading and visibility.
>
> However, this assumption is seldom justified, and even at a given location the CoH only roughly approximates the true particulate loading. The CoH method is worthless, or nearly so, for comparisons between areas with dissimilar aerosols. For example, the aerosols collected at the Utah sites are primarily the light-colored aluminosilicate dust, whereas the aerosol collected within the inner core of large cities has a predominantly sooty character. For a given

particulate loading the Utah aerosol will often have as little as one-tenth the optical density of the urban aerosol.

(c) The cascade impactor operates on the principle that particles in an air stream will tend to follow a straight line when the air stream is deflected, and thus can be impacted on a surface in their path. The cascade impactor consists of a series of parallel plates separated by precisely determined spaces. Alternate plates contain a certain number of holes of a size that is decreased as one goes through the series of plates from entrance to exit. Alternating plates contain a certain number of holes of a size that is decreased as one goes through the series of plates from entrance to exit. Alternating with the plates containing the calibrated holes are plates without holes. These may be coated with a medium for the trapping of impinged particles. Air is drawn through the apparatus at a known rate, and the particles are collected in decreasing size fractions related to the decreasing size of the holes in the plates.

(d) The cyclone sampler is a device for the collection of the respirable size fraction of an atmospheric particulate loading. It operates on the principle that the inertia of individual particles will tend to keep the particles moving in a straight line when the air stream in which they are carried is deflected. By this means the larger size particles are removed by impaction and settling, while the respirable particles are carried along with the air stream and are subsequently collected on a filter.

The 1976 IR contained very little information beyond the above remarks concerning the use of these different particulate matter measurement methods in CHESS. The few pertinent additional comments made, which also relate to certain community health studies discussed later in this document, concerned the fact that dustfall measurements from a Manhattan monitoring site were used as city-wide values for New York City. Also, note was made of the fact that such values, together with measured values for suspended sulfates for 1956-1970, were used to estimate suspended sulfate levels in Queens and New York as part of CHESS community health studies in New York City. Thus, some values on which important conclusions from CHESS were based, e.g., sulfates may be harmful to health, were actually estimated values partly derived in the above manner.

3.4.2.3 Additional Sources of Uncertainty in Hi-Volume TSP Measurements--In addition to the above sources of error noted by the IR (1976) regarding CHESS Program TSP measurements (which the IR concluded resulted in a "slight negative bias" of CHESS data), a certain other nuance of procedures included in the Federal Reference Method (40 CFR 50, Appendix B) may have resulted in the introduction of an additional slight negative bias in TSP data obtained by EPA CHESS Program investigators and other American researchers. This, more specifically, pertains to the manner in which flow rate calculations are made upon which final TSP concentration determinations are based.

The procedure calls for the averaging of the initial and final recorded airflow rates. However, as described in Appendix 3-A of this chapter, the uncontrolled flow rate drops more rapidly at the start of the run than at the end of the run. Therefore, a linear approximation leads to an overestimate of the flow rate, which will reduce the measured value. Consequently, all TSP data computed in this manner have an additional negative bias which is likely usually of the order of 5 percent; on occassion, however, under circumstances where the flow rate may have fallen below 40 $ft^3$/min, larger errors (up to approximately 15 percent) may have been introduced. Assuming that monitoring site operators in the United States adhere to the recommended Federal Reference Method procedures, then this type of bias is likely inherent in all American TSP data collected without flow rate control or recording.

Also, a recent note by Patterson (1980) reports that hi-volume sampler exhaust appears to be able to recirculate to the hi-volume air intake as shown by large copper concentrations found on hi-volume filters. This effect may be important during periods of calm or low wind speed, but its impact on reported TSP measurement data cannot yet be fully evaluated.

### 3.4.3 Summary for American Hi-Volume TSP Sampling

As indicated above in the discussion of the IR (1976) evaluation of CHESS Program TSP measurements, certain sources of error (e.g., mailing of hi-volume sampler filters) led to a slight negative bias in CHESS TSP data. That bias, according to the IR (1976) was typically about 10 percent but, on occassion, could have ranged up to 20 or 30 percent. It is thusly necessary, when considering reported CHESS Program TSP data, to take into account the possibility that it may be slightly biased low by as much as 10 to 30 percent.

In addition, such CHESS data may be biased low by 5 percent or so due to the flow rate averaging procedure discussed above. Similarly, other TSP data sets reported in the American literature may also be biased low by about 5 percent where automatic flow rate control or recording were absent. On rare occassions, probably only occurring at very high particulate levels when saturation of the sampling filter might result in a flow rate drop below 40 $ft^3$/min, the TSP data may be negatively biased by up to about 15 percent.

### 3.4.4 Summary of Assessment of Particulate Matter Measurement Applications

Tables 3-4 and 3-5, respectively, summarize the sources, magnitudes and directional biases of errors associated with major British and American applications of particulate matter measurement techniques during the past 30 to 40 years. Examination of Table 3-4 reveals that numerous sources of error have been encountered in the course of British application of methods for measurement of black smoke (BS). For example, prior to 1961, the use of weights for sealing purposes led to highly variable errors in BS measurements due to leakage at filter clamps, and steps were taken to require screw-down clamps as standard procedure as part of the later British National Survey work implemented after 1961. It is not clear to what extent any specific British BS data sets

TABLE 3-4. SUMMARY OF EVALUATION OF SOURCES, MAGNITUDES, AND DIRECTIONAL BIASES OF ERRORS ASSOCIATED WITH BRITISH SMOKE (PARTICULATE) MEASUREMENTS

| Time period | Measurement method | Reported source of error | Direction and magnitude of reported error | Likely general impact on published BS data |
|---|---|---|---|---|
| 1944-1950s | Smoke filter | Leakage at clamp. Weights used to make the seal. | Highly variable under-estimation of BS levels. | Probable widespread highly variable negative bias. |
| Pre-1961 | | Comparing reflectance to photographs of painted standard stains. | Depending upon observer and value of R. | Probable widespread relatively small negative bias. |
| | | Reflectance (R) below 25%, stain too dark with use of Clark-Owens DSIR curve. | 50-100% underestimation. | Occasional 50-100% negative bias in some data sets. |
| 1961-1964 | | Computer not following proper calibration curve. | ≤80% underestimation at low R if not corrected by WSL (See Moulds, 1962) and discussion of clamp size correction factor. | Negligible for BS <~100 μg/m$^3$. Increasing negative bias up to 80% as BS values increase over 100 μg/m$^3$. |
| 1964-1980 | | Clamp correction factor for other than 1-inch clamp. | Uncertain; derivation cannot be verified. Possible ±20%. | Possible underestimate for 2-inch and 4-inch clamps. Possible overestimate for 1/2-inch and 10 cm clamps. |
| | | Flow rate - normal 1 day. | ±3% variation. | Presumed ± 3% precision level. |
| | | Flow by 8-port with 1 reading per week. | -10% underestimation. +10% overestimation. | 10% negative bias on high BS days. 10% positive bias on low BS days. |
| | | Variability of reading reflectance. | ±2 units of R | Error increases with BS level from ±10% at 50 μg/m$^3$ up to ±20% at 400 μg/m$^3$. |
| | | Averaging reflectance instead of averaging mass/cm$^2$. | Highly variable under-estimation due to non-linearity of R. | Probable small negative bias at low BS levels, could be large at high BS. |
| | | Use of coarse side of filter facing upstream. | 6-15% underestimation. | Occasional negative bias of 6-15%. |

TABLE 3-4 (continued).

| Time period | Measurement method | Reported source of error | Direction and magnitude of reported error | Likely general impact on published BS data |
|---|---|---|---|---|
| | | Reading of wrong side of stained filter. | 50-75% underestimation. | Occasional negative bias of 50-75%. |
| | | Leakage at filter clamp | | |
| | | a. Normal, with good care | 1-2% underestimation. | General 1-2% negative bias. |
| | | b. With inadequate care. | 2-8% underestimation. | Occasional 2-8% negative bias. |
| | | c. Careless loading where uneven stains are produced. | 10-20% underestimation. | Occasional 10-20% negative bias. |
| | | Use of wrong clamp size | | |
| | | a. Stain too light R>90%. | Highly variable overestimation. | Data usage not recommended. |
| | | b. Stain too dark R<25%. | Highly variable underestimation. | Data usage not recommended. |

TABLE 3-5. SUMMARY OF EVALUATION OF SOURCES, MAGNITUDES, AND DIRECTIONAL BIASES OF ERRORS ASSOCIATED WITH AMERICAN TOTAL SUSPENDED PARTICULATE (TSP) MEASUREMENTS

| Time period | Measurement method | Reported source of error | Direction and magnitude of reported error | Likely general impact on published TSP data |
|---|---|---|---|---|
| 1954-1980 | Staplex Hi Vol TSP | Time Off (Due to power failure). | Variable underestimation. | Negligible impact, rare negative bias. |
| | | Weighing error. | ±2% random variation. | Negligible impact. |
| | | Flow measurement (with control). | ±2% random variation. | Negligible impact. |
| | | Flow measurement (without control). | | |
| | | a. Constant TSP--Average of flows. | | |
| | | 1. Low TSP level. | 2% underestimation. | Negligible impact. |
| | | 2. High TSP level. | 5-10% underestimation. | Possible 5-10% negative bias. |
| | | b. Rising TSP-Average of flows. | 10-20% underestimation. | Possible 10-20% negative bias. |
| | | c. Falling TSP-Average of flows. | 10-20% overestimation. | Possible 10-20% possible bias. |
| | | Aerosol evaporation on standing. | 1-2% underestimation. | Probable negligible impact. |
| | | Condensation of water vapor. | 5% overestimation. | Possible 5% positive bias. |
| | | Foreign bodies on filter (Insects). | Generally small overestimation. | Possible 5% positive bias. |
| | | Windblown dust into filter during off-mode. | Generally small overestimation. | Occasional (rare) positive bias. |
| | | Wind speed effect on penetration of dust into the Hi-Vol shelter. | Less penetration at high windspeed. | Occasional (rare) negative bias. |
| | | Wind direction effect due to Hi-Vol Asymmetry. | Higher penetration when normal to sides. | Probable increase in random (±) error. |
| | | Artifact formation, $NO_3^-$ $SO_4^=$. | 5-10 $\mu g/m^3$ overestimation. | Occasional positive bias. |

TABLE 3-5 (continued).

| Time period | Measurement method | Reported source of error | Direction and magnitude of reported error | Likely general impact on published TSP data |
|---|---|---|---|---|
| 1969-1975 (EPA CHESS Program). | Fed. Reference Method Standard Hi-Vol Sampler | Loss of sampling material in field. | No specific estimate of magnitude of error; but would be underestimation. | Probable slight negative bias in Utah winter data. No known impact on other CHESS TSP data. |
| | | Loss of sampling material in mailing. | Reported 4-25% apparent loss; max. likely due to crustal (sand, etc.) fall-off from selected Utah sampling sites. | Probable general small <10% negative bias; occasional 25% negative bias. |
| | | Evaporation of organic substances. | No specific estimate of error magnitude, but not likely to exceed 5% underestimation. | Probable slight negative bias of <5% for TSP data from urban/industrial areas. |
| | | Windflow velocity and asymmetry. | No specific estimate of error magnitude; but most likely to increase random variation of small underestimation. | Negligible impact or slight negative bias. |
| | | (Overall errors). | | Generally <10% negative bias; occasional 10 to 30% negative bias. |

from the 1950s may have been affected by the clamp leakage problem, but one must assume that such errors could not have often been very large or serious and that the WSL took appropriate steps to eliminate or invalidate any data in gross error as they were detected via their quality control efforts in the late 1950s. Analogously, there is evidence that WSL did take steps to inform users of pre-1961 BS data of errors arising from (1) comparing reflectance on filters to photographs of painted stains and (2) use of reflectance readings below 25 percent, where the stain was too dark to use the Clark-Owens DSIR curve. However, it also appears that only a few investigators (e.g., Commins and Waller, 1970) took steps to go back and correct published reports based on the affected pre-1961 data and to publish revised analyses taking into account corrections for the pre-1961 data errors.

Probably of much greater concern than the pre-1961 BS measurement errors are those encountered after the establishment and initial implementation of the British National Survey in 1961. These include certain errors, e.g., the "computer error of 1961-1964," which were eventually detected by WSL and resulted in steps being taken to correct affected BS data in National Survey data banks. However, although users of the affected data may have been informed of such errors by WSL, virtually none of them have taken steps to (1) alert recipients of publications containing analyses based on the affected data of the likely inaccuracies or ranges of error involved; (2) to reanalyze the study results based on the affected data sets; or (3) to reissue or publish anew any revised analyses. Moreover, even some Warren Spring Laboratory quality control literature prepared and published during the 1960s or 1970s and still in use may contain incorrect information and recommended standard procedures for BS measurements based on analyses "contaminated" by computer

errors or other problems summarized in Table 3-4 and discussed in the accompanying text.

In regard to determining which British BS data sets and related epidemiology studies are affected by different post-1961 National Survey errors, it is again presently very difficult, as was the case with British $SO_2$ measurements, to specify with any confidence the nature and magnitude of specific errors impacting particular studies. This would probably require thorough examination of records and WSL quality control reports concerning each of the pertinent data sets. On the other hand one can project that certain data sets and British epidemiology studies were almost certainly affected by some subset of BS measurement errors and these can be taken into account in evaluating such studies later in Chapter 14. For example, published reports of the "Ministry of Pensions" (1965) and Douglas and Waller (1966) studies contain specific reference to usage of uncorrected National Survey data from the 1961-64 period and, therefore, the results of those studies should be reevaluated in light of measurement errors reported by the WSL for that period.

As for errors associated with American particulate matter measurements, most of those reported to affect TSP data gathered prior to, during and after implementation of the EPA CHESS Program are summarized in Table 3-5. As seen in that table, a number of the different types of errors listed are potentially applicable to essentially all measurements using the Staplex Hi-Volume TSP sampler widely used in the United States. The general range of uncertainty derived from these various errors is estimated to be less than 20 percent, in either a positive or negative direction or on a random (±) basis.

Other errors, in addition to such general errors for TSP measurements, which were found by the 1976 Congressional Committee Investigative Report (IR, 1976) to affect CHESS Program TSP measurements during 1969-1975 are broken out and listed seperately in Table 3-5. Some of those errors (e.g., loss of sample materials in filter removal from the field monitoring apparatus) were reported by the IR (1976) as likely affecting only very restricted CHESS data sets. Others, e.g., errors due to loss of sample in mailing, appear to have been more widespread and presumably impacted on many CHESS data sets. The IR (1976) concluded, however, that the net effect of all of the errors was to introduce, in general, a slight negative bias of 10 to 30 percent into CHESS TSP data. Such a range of potential error is not far beyond the range of different types of errors (e.g., linear flow corrections) more generally associated with American applications of TSP measurements. Section IV C 3 of the IR (1976) further concluded that:"...the TSP data were by far the best quality data taken in the CHESS monitoring program. Differences measured between High and Low sites are probably reasonable estimates of the differences of TSP exposures as received by populations in these areas." Accordingly, we concur with the IR (1976) evaluation that CHESS TSP measurements are reasonable estimates of TSP exposures of CHESS Program community health study populations, taking into account that such data may by biased low by no more than 10 or, at most, 30 percent.

## 3.5 COMPARISONS OF PARTICULATE MATTER MEASUREMENTS

From the preceding discussions, it can be seen that numerous measurement approaches have been developed in order to quantify concentrations of airborne particulate matter. Also, as will become apparent upon reading later chapters of this document, the practical application of the different techniques for measuring airborne particulate matter in studies on health or welfare effects has often made it difficult to compare results from different studies. This in turn has, at times, contributed to the generation of considerable controversy and disagreement over the interpretation of literature concerning the adverse effects of atmospheric particulate matter pollution. Critical evaluation of the existing literature and emerging new studies on the comparison of different airborne particulate matter techniques and resolution, if possible, of differenc among resulting conclusions are crucial in order to interpret and understand information discussed on effects of particulate matter later in this document.

The air pollution literature is replete with comparisons between different measurement methods for airborne particulate matter. Examination of that literature reveals that the tendency has been to use a linear regression, $y = a + bx$, to the exclusion of all other models in making comparisons, even if the physical theory or boundary conditions call for a different type of model. Many analysts use a linear model because it is simple and it allows easy visual comprehension of graphical depictions of comparisons. However, if the data are not linearly related, by forcing a straight line through the data erroneous conclusions are apt to be drawn. Significant errors can also be made by extrapolating comparison data beyond the range of the initial study observations. In the following sections, various comparison studies are critically evaluated and alternative nonlinear models are proposed by which to reassess earlier findings.

### 3.5.1 Theoretical Considerations

3.5.1.1 Boundary Conditions and Dependent Variable Selection--In order to compare measurements such as TSP, CoH, BS, and $B_{scat}$, it must be recognized that each of these measurements have a common point. That is, when TSP is zero and there are no particles in the air, CoH and BS will be zero and the residual $B_{scat}$ will be from the scattering of clean air, $B_o$. Therefore, any comparison model based upon physical theory must go to 0 in the limit TSP → 0 and $B_{scat} \rightarrow B_o$. It must also be decided what is to be the dependent variable and what is to be the independent variable in making a comparison. In the comparison of TSP mass versus CoH readings, for example, CoH should be the dependent variable because the collected mass does not depend on its optical properties but the transmitted light depends upon the mass in its path. The simplest nonlinear equation to use which satisifies the boundary condition is $CoH = a\ TSP + b\ TSP^2$. Dividing through by TSP we obtain CoH/TSP = a + b TSP. By plotting (CoH/TSP) versus TSP we obtain a straight line if the model is a good approximation of the data set. However, if we had chosen TSP as the dependent variable we would have,

$$TSP = a\ CoH + b\ CoH^2 \qquad (1)$$

and

$$CoH = \frac{-a + \sqrt{a^2 + 4bTSP}}{2b} \qquad (2)$$

Note this is quite different from the equation

$$CoH = a\ TSP + b\ TSP^2 \qquad (3)$$

Thus with only two adjustable constants we can fit y versus x data which has substantial curvature. Other considerations may be made at the high concentration end as well. Ellison (1968) observed:

> The calibration curve for transmittance measurements may be substantially different from that for reflectance measurements even if allowance is made for the fact that however thick a deposit is collected, the reflectance will never fall below a limiting value whereas the transmittance will approach zero asymptotically as soiling increases.

Therefore, CoH versus TSP is a monotonically increasing function which eventually saturates because at some particular mass loading the transmitted light is below the minimum detectable level of the photocell.

In the calibration of an AISI sampler, as another example, percent transmittances have been reported for different materials as a function of mass loading (see Figures 3-4 and 3-5). Figure 3-4 is an example of inappropriate data analysis because (as plotted) mass is the dependent variable (y), and transmittance is the independent variable (x), and the origin (0,0) is no used in the relation. Each observation has an experimental error associated with it; and the intercept of the linear regression is a measure of the lack of fit of the model and the pure error in the data. An alternative should be used to fit the data in line with the boundary conditions described above.

The CoH measurement should have a relation to Beer's Law which predicts $T_o/T = \exp(k_1 m)$, where $k_1$ is a constant and $T_o$ is the initial value of the transmitted light when the mass on the filter $m_o = 0$. According to the theory, CoH is proportional to the Optical Density; therefore, $\ln(T_o/T)$, should be proportional to m. By inspection we might expect CoH to be a power series in m and $CoH = k_1 m + k_2 m^2 + \ldots$ .

Table 3-6 is a listing of % T and Np (number of particles) collected by Ingram (1969) in a study later reported by Ingram and Golden (1972).

Figure 3-6, a semilog plot of T versus Np shows curvature downward indicating that light is being blocked out faster than predicted by Beer's Law

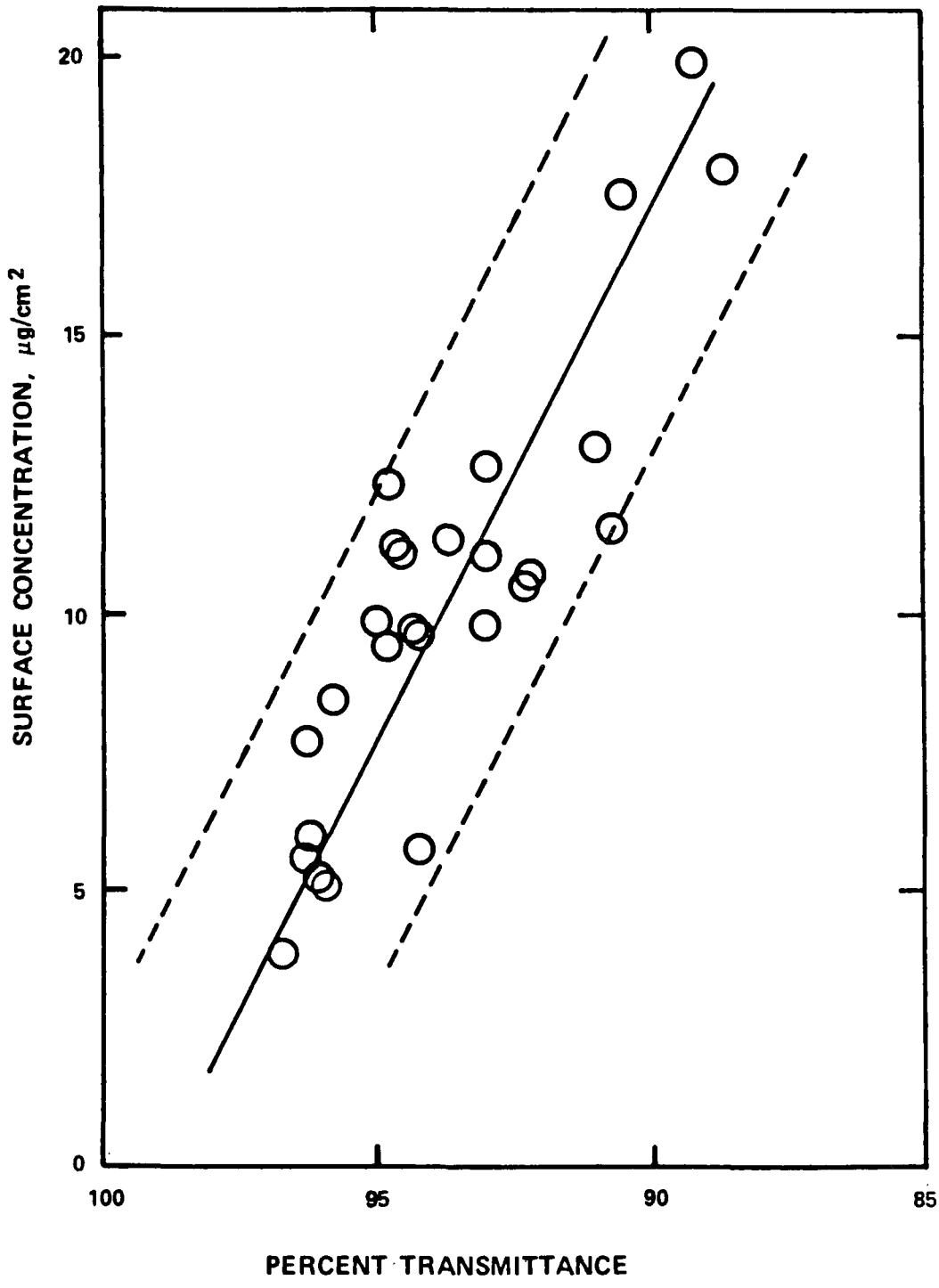



Figure 3-4. Surface concentration of particulate matter on filter vs percent transmittance showing lack of fit at the origin.

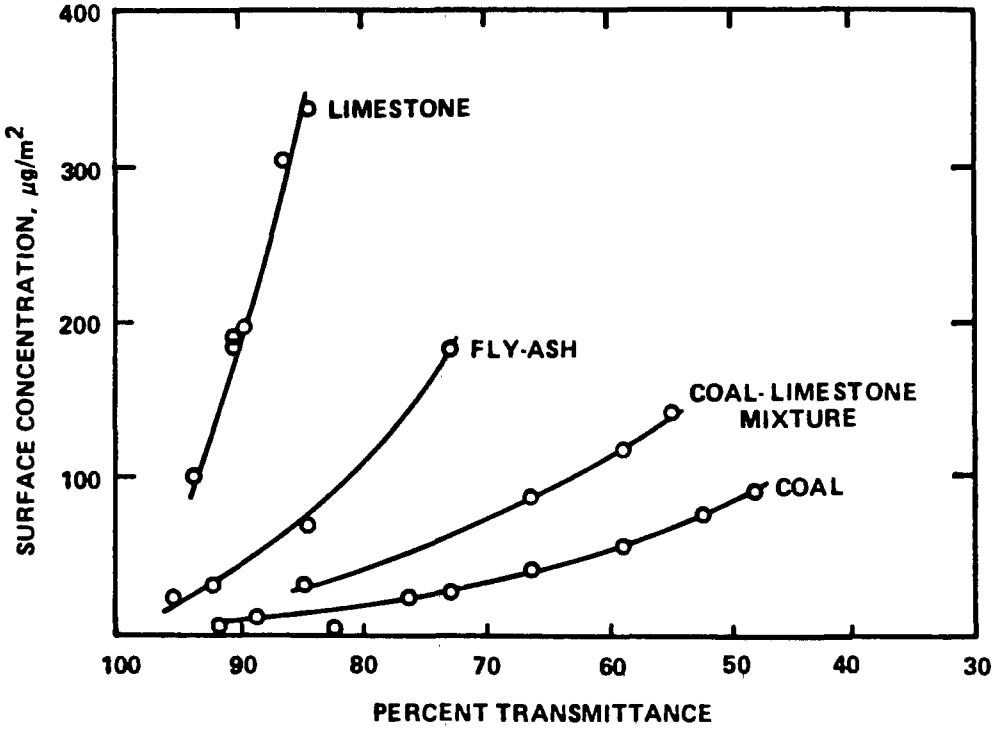



Figure 3-5. Surface concentration of particulate matter on filter vs percent transmittance showing a family of related curves.

Relationship of Coefficient of Haze to

TABLE 3-6. PARTICLE COUNTS (Np)
0.3 - 2.0 μm, measured in New York City

| Date | Time | Run | T% | CoH | Np x $10^{-3}$ | CoH/Np x $10^{-4}$ | Relative humidity (avg) |
|---|---|---|---|---|---|---|---|
| 3/10/69 | 1405-1605 | 3 | 94 | 0.62 | 85 | 7.28 | 40% |
| 3/12/69 | 0925-1125 | 4 | 92 | 0.83 | 94 | 8.87 | 47% |
| 3/14/69 | 0925-1125 | 5 | 95 | 0.51 | 58 | 8.84 | 47% |
| 3/17/69 | 0915-1115 | 6 | 78 | 2.48 | 244 | 10.18 | 31% |
| 3/17/69 | 1335-1535 | 7 | 88 | 1.28 | 177 | 7.22 | 23% |
| 3/18/69 | 0600-0800 | 8 | 55 | 5.98 | 448 | 13.34 | 45% |
| 3/18/69 | 0815-1015 | 9 | 56 | 5.80 | 464 | 12.50 | 32% |
| 3/19/69 | 1206-1406 | 10 | 84 | 1.74 | 187 | 9.32 | 40% |
| 3/20/69 | 1135-1335 | 11 | 82 | 1.98 | 224 | 8.86 | 68% |
| 3/20/69 | 1900-2100 | 12* | 71 | 3.42 | 123 | 27.84 | 86% * |
| 3/21/69 | 1720-1920 | 13 | 95 | 0.51 | 78 | 6.58 | 42% |
| 3/22/69 | 1520-1720 | 14 | 94 | 0.62 | 87 | 7.11 | 43% |

*Run not valid because of humidity effect.

Source: Ingram (1969)

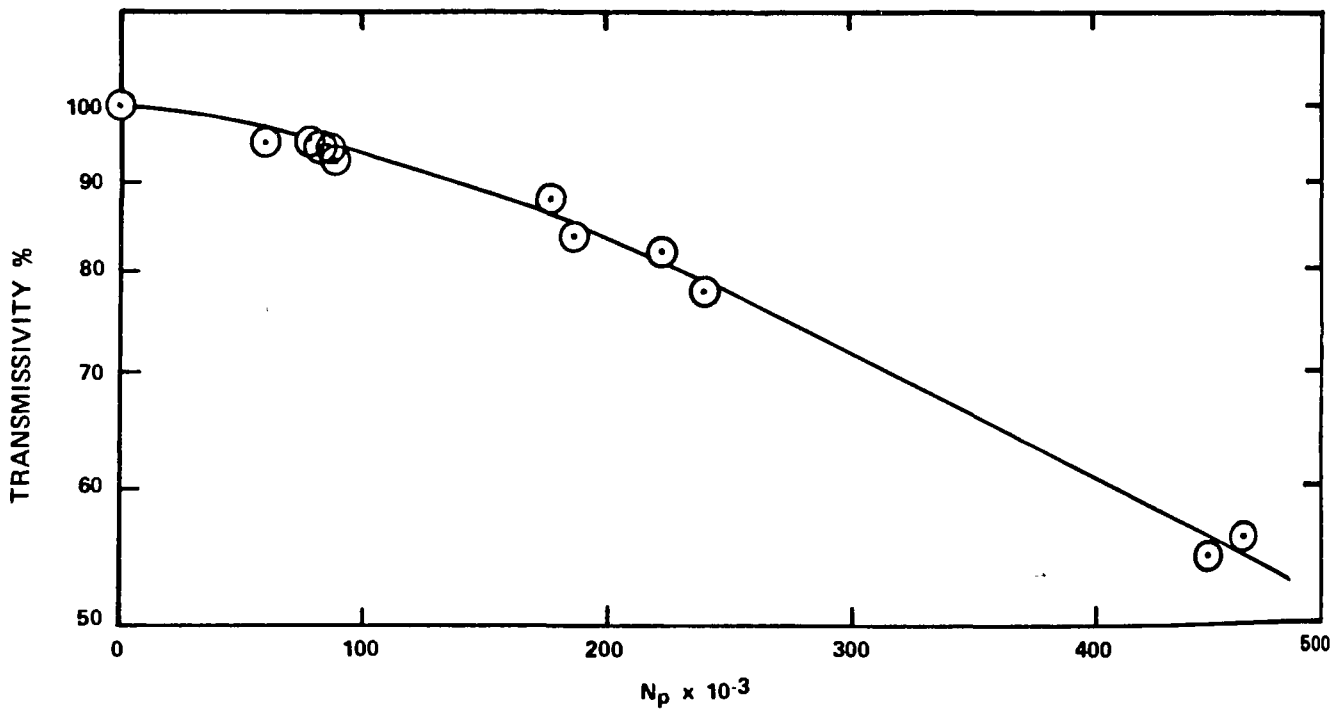



Figure 3-6. CoH vs particle count showing deviation from Beers Law.

and that a power series may be used to model it. By way of example we plot CoH/Np versus Np in Figure 3-7. The line shown is the quadratic $CoH = k_1 Np + k_2 Np^2$ where $k_1 = 6.241 \times 10^{-6}$, $k_2 = 13.73 \times 10^{-12}$, and $r^2 = 0.81$. If the accuracy of the fit is not sufficient for the intended purpose we can "bootstrap up" by plotting $(CoH-k_1Np)/Np$ versus Np and get new values for $k_2$ and $k_3$. This procedure can be performed indefinitely until the needed accuracy is attained.

3.5.1.2 Dimensional Analysis--In Figure 3-5 we have a family of curves with upward curvature. Since they are all representative of the same phenomenon, the same equation should be used to fit all the curves. That is, the use of $y = a x + b x^2$ for one curve and $y = a x + b x^3$ for another curve based solely on which equation gives a better fit is not necessarily appropriate. Not taken into account is the fact that the terms a and b may not be constants because they have dimensions. For example, 'a' has dimensions of $length^2/mass$ so it does not represent a pure number. The coefficient 'a' may be a function of products of variables which have these dimensions. We could hypothesize that the transmittance depended only on the average particle diameter (D) and the average particle density ($\rho$) (Horvath and Charlson, 1968) such that $a = kD\rho$ where k is a dimensionless constant. If we compare measured values of $(a/D\rho)$ we have a measure of k and can begin to predict the value of 'a' for another arbitrary dust from knowledge of its particle size and density. The literature contains several different studies on the value of the parameters of $TSP = a\ CoH + b$ in various cities that do not consider boundary conditions and dimensions. Also, many journals have published articles which compare the

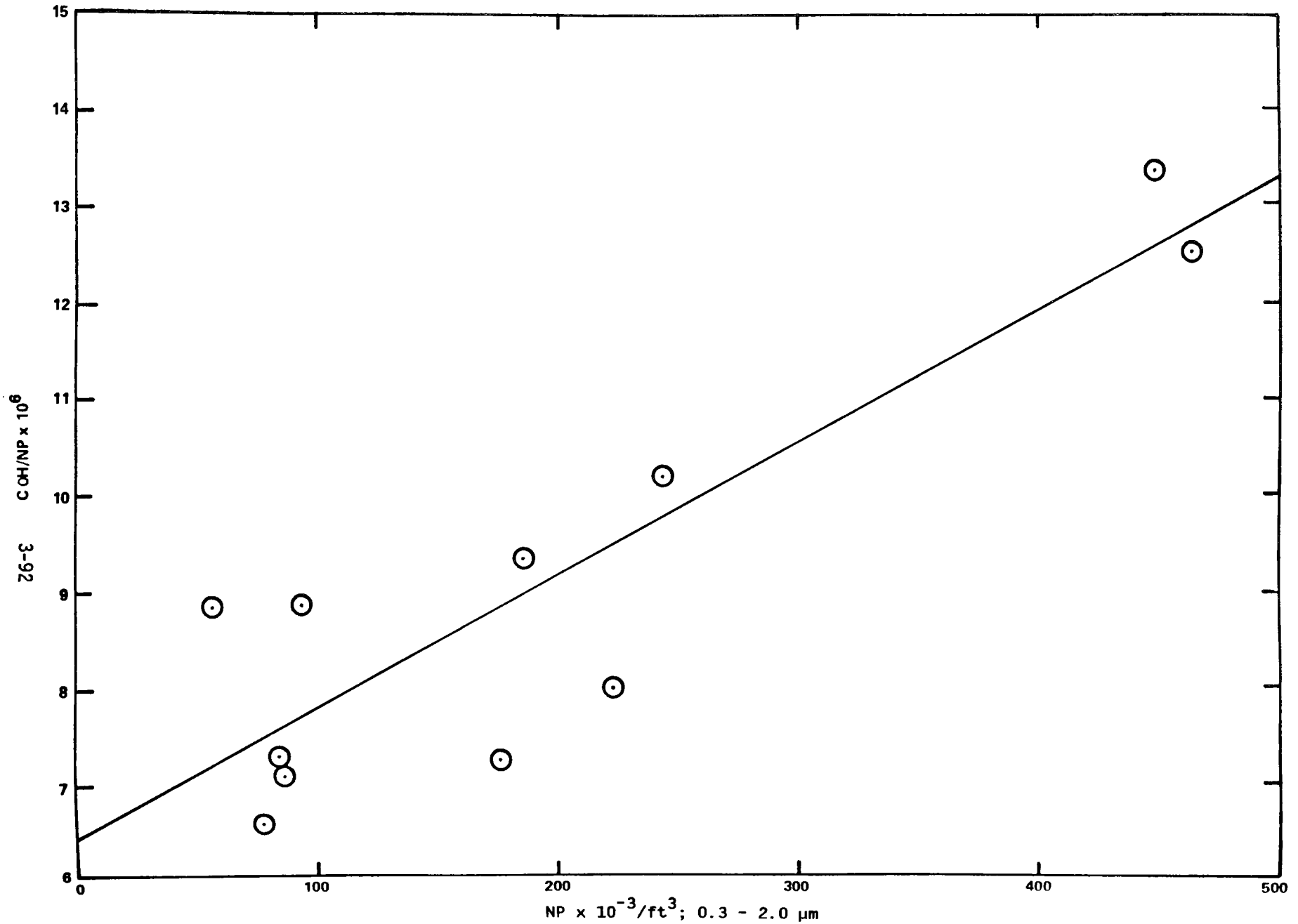



Figure 3-7. CoH/Np vs Np showing evidence of a quadratic relation.

value of 'a' in city X to published values of 'a' in city Y, and statements are made about the differences in air pollution between them. If the hypothesized model is valid, however, the unity of all cities ~~can~~ could be demonstrated by plotting a/D versus ρ which will result in a line with slope k through the origin. Therefore, this chapter on particulate matter measurement comparisons will not simply compare regression coefficients from published models but it will also attempt to develop more appropriate models where necessary.

### 3.5.2 Comparison Between TSP and Other Gravimetric Measurements

Recently, the American hi-volume sampler has been compared to a European version of the high volume sampler, the LIB Hi-Vol Filtergerät described in Herpertz (1969). It is significantly different from the U.S. type Staplex Hi-Vol. The LIB has the filter facing downward, exposed directly to the air. Consequently, the flow pattern is upwards, which will prevent capture of unusually large particles which could enter the Hi-vol sampler.

Laskus (1977) reported a detailed study in seven German cities of the Staplex TSP Hi-vol, a multiple stage Anderson non-viable impactor, the LIB Hi-vol Filtergerät, and several other devices. The relations of importance to the United States comparisons are given in Table 3-7.

The most important observation is that the U.S. type Staplex TSP Hi-vol recovers only 82 percent of the total mass collected by the modified Anderson non-viable impactor. Laskus (1976) modified the Andersen first two stages to prevent internal losses and increased the mass collection by about 25 percent. (A similar modification has also been reported by Wedding, McFarland, and Cermak, 1977). Laskus (1977) states: "The Staplex filter method (high volume air sampler) proved to be particularly reliable when variations of wind speed were considered.

TABLE 3-7. COMPARISON OF TSP RESULTS OBTAINED BY DIFFERENT HI-VOLUME SAMPLERS TESTED IN GERMAN CITIES BY LASKUS (1977)

| Instrument | Number of comparisons | Mean $\mu g/m^3$ | Std | r | Regressions |
|---|---|---|---|---|---|
| LIB (x) | 87 | 87.5 | 48 | 0.93 | y = 2.1 + 0.98 x |
| Staplex - TSP (y) | | 87.5 | 49 | | |
| A-n.v.-imp (x) | 13 | 115 | 41 | 0.83 | y = 3.4 + x |
| Staplex - TSP (y) | | 118 | 40 | | |
| Staplex without gable roof (x) | 54 | 90 | 47 | 0.88 | y = 0.7 + 0.98 x |
| Staplex - TSP (y) | | 88 | 47 | | |
| Modified A-n.v.-imp (x) | 80 | 107 | 46 | 0.86 | y = 9.5 + 0.91 x |
| Staplex - TSP (y) | | 88 | 50 | | |

However, this apparatus, like the other instruments, did not record the total particulate content as separation effects occur at the suction aperature due to external movement of air." This may not be of great importance to human health if the particles the Staplex TSP does not capture have aerodynamic diameters which cannot be inhaled by the mouth or nose breathing patterns (Stöber, 1979).

Eickelpasch and Hotz (~~1968~~ 1978) also compared the Staplex TSP with the LIB Hi-Vol Filtergerät. They found that the ratio TSP/LIB varied from 1.0 at wind speed 2 m/s, up to a ratio of 2.0 and greater at wind speeds over 5 m/s. The same qualitative effect was found by Laskus (1977) as described in Table 3-8, but above 5 m/s the LIB dropped only 10 percent below the Staplex TSP in the range of TSP <200 $\mu g/m^3$. A possible explanation for the difference in the factor of 2 reported by Eickelpasch (1968) and 1.1 reported by Laskus (1977)

TABLE 3-8. EFFECT OF WIND SPEED ON COLLECTION EFFICIENCY. From LASKUS (1977),

| | | Number of Pairs, n | Average $\mu g/m^3$ | s | Correlation Coeff, r | Regression |
|---|---|---|---|---|---|---|
| | | | Windspeed: 0-2 m/s | | | |
| Modif. Anderson n.v.-Imp. | (x) | 22 | 103 | 41 | 0.71 | y = - 23.3+1.06 x |
| Staplex | (y) | | 85 | 43 | | |
| LIB-Gerät | (x) | 24 | 87 | 43 | 0.93 | y = - 0.4+0.99 x |
| Staplex | (y) | | 86 | 43 | | |
| Staplex without gable roof | (x) | 18 | 90 | 44 | 0.82 | y = - 4.7+0.98 x |
| Staplex | (y) | | 84 | 47 | | |
| | | | Windspeed: 3-4 m/s | | | |
| Modif. Anderson n.v.-Imp. | (x) | 40 | 113 | 46 | 0.90 | y = - 8.7+0.90 x |
| Staplex | (y) | | 93 | 50 | | |
| LIB-Gerät | (x) | 44 | 97 | 47 | 0.83 | y = - 0.6+0.98 x |
| Staplex | (y) | | 94 | 47 | | |
| Staplex without gable roof | (x) | 27 | 94 | 46 | 0.89 | y = - 6.6+0.92 x |
| Staplex | (y) | | 93 | 43 | | |
| | | | Windspeed: >5 m/s | | | |
| Modif. Anderson n.v.-Imp | (x) | 18 | 98 | 50 | 0.90 | y = - 15.6+0.96 x |
| Staplex | (y) | | 79 | 60 | | |
| LIB-Gerät | (x) | 19 | 66 | 57 | 0.94 | y = 2.1+1.08 x |
| Staplex | (y) | | 73 | 55 | | |
| Staplex without gable roof | (x) | 9 | 75 | 61 | 0.95 | y = 3.8+1.15 x |
| Staplex | (y) | | 83 | 64 | | |

may be the difference in locations of the comparative sampling. Laskus sampled in 7 cities at various places ranging from the runway at Frankfurt Airport to heavy industrial, light industrial, and residential areas. If Eickelpasch and Hotz sampled at a location where windblown dust could be an appreciable factor, there could be more large particles which would not be able to enter vertically upward into the LIB. The Hi-vol operates with flow slightly upward through louvered panels, and there is only a slight rise before turning down to the filter. Consequently, one would expect the LIB to collect less of the larger particles and subsequently correlate better with the CoH and BS than the hi-volume sampler at high loadings of relatively large diameter particles.

3.5.3 Comparison of Gravimetric Methods (TSP) with Light Scattering Nephelometry ($B_{scat}$)--The integrating nephelometer described previously in Chapter 2 measures the light scattering properties of the particulate matter in a fixed light path. Because the wave length of visible light is in the region 0.3 - 0.8 μm, particles of this size "physical diameter" will preferentially scatter the light and the manufacturer calibration is based on a Freon aerosol (1 $B_{scat}$ = 38 μg/m$^3$) of that size. Because the $B_{scat}$ is measuring "physical diameter" and the BS, TSP, and CoH are measuring in a manner related to "aerodynamic diameter" these three "mass" measures appear to have more relation to each other than they have to $B_{scat}$. Of particular importance is the interference from water vapor condensation which requires the use of heated inlets to reduce relative humidity to at least 50 percent. Ruppersberg (1971) performed theoretical calculations of the changes of the scattering coefficient of maritime haze with humidity. In Table 3-6 a data set on AISI CoH versus particle count from Ingram (1969) shows such an outlier at 86 percent RH caused by condensation of water vapor.

Horvath and Charlson (1969) performed a detailed study of the nephelometer and found the factors that influence the $B_{scat}$ measure to be as follows:

1. The density of the aerosol particles,
2. The size frequency distribution of the aerosol,
3. The refractive index of the particles,
4. The shape of the particles,
5. The wave length of the light,
6. The relative concentrations of different types of aerosols.

Figure 3-8 describes the variability of measured mass concentration and $B_{scat}$. Variations of more than ±50 percent are common, indicating that this method which measures "visibility" can only be expected to approximate atmospheric particle loading.

When comparing the nephelometer to BS and TSP, Muylle et al (1978) applied linear regression and failed to force the fit through the origin as required by theory (TSP → 0, $B_{scat} \rightarrow B_o$ of clean air). The data were also inverted and TSP was treated as being dependent on $B_{scat}$ rather than $B_{scat}$ a function of particle mass in the atmosphere. Although Muylle reports that the relation 1 unit of $B_{scat}$ = 38 μg/m$^3$ gives accurate results in the mean concentration range, it underpredicts at low concentrations and overpredicts at high concentrations From Figure 3-8 it is likely that a curve is necessary to reach the origin and we should try $B_{scat} = A\ TSP + B\ TSP^2$ and plot $B_{scat}$/TSP versus TSP. Kretzschmar (1975) reports similar results from a study where a hi-volume sampler and nephelometer were 400 m apart, and also forces a line through nonlinear data.

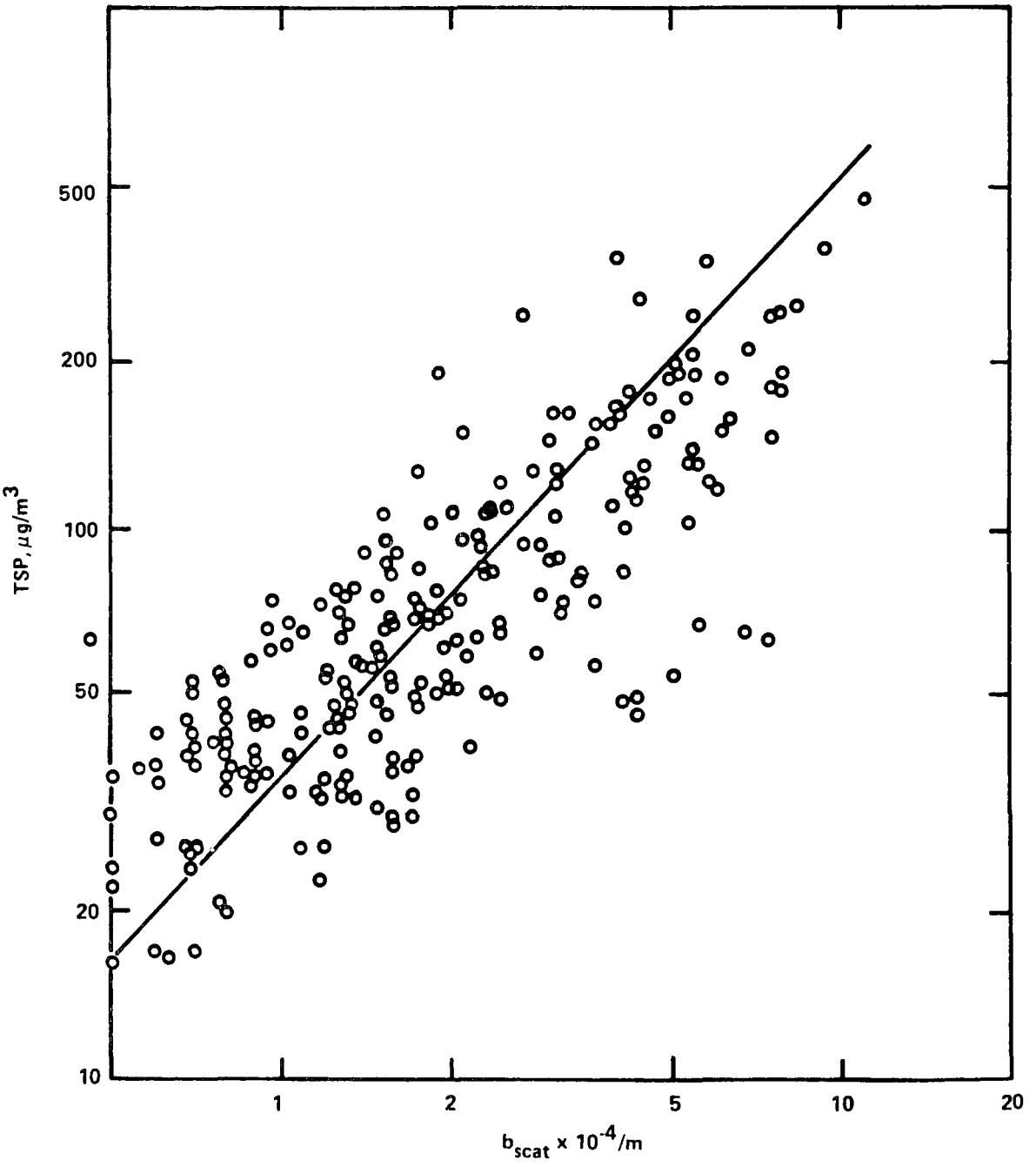



Figure 3-8. Measured mass concentration and light-scattering coefficient for atmospheric aerosols at different locations. Showing frequent variations of more than 50%.

### 3.5.4 Comparison of Hi-Vol TSP Method With ASTM (CoH) Method

The ASTM coefficient of haze (CoH) method was described previously. Park et al. (1960) found that flow rates of the AISI samplers varied linearly with optical density and that a correction could be made to the flowrate quite easily which would make a significant improvement in accuracy of the measured CoH values. They also found that ten AISI samplers gave widely different initial flowrates, varying from 0.30 to 0.40 cfm, while sampling the same filter paper spot. The flow rates also varied among spots on the same filter paper roll (0.31 to 0.37 cfm). It seems these findings were ignored in later papers since the correction for flowrate variation was never adopted in the references cited herein. Hale and Waggoner (1962) compared CoH versus CoH by running 12 AISI samplers simultaneously. They found the most variability to be caused by the inhomogeneity of the paper and the bias of the individual recording the readings. The variabilities ($\sigma$) between instrument-reader combinations of a single CoH observation were in the range 0.20 to 0.25 CoH unit. The variabilities ($\sigma$) of 12 CoH units averaged to produce a 24 hr average CoH were close to the expected value ($\sigma/\sqrt{12}$) CoH for relating the variability in CoH to variability in mass. Ingram and Golden (1973) report that this averaging process leads to an error when data are not linear, so these error estimates may be conservative.

The comparisons of CoH vs hi-volume sampler available in the literature all report somewhat different relationships. The references most often cited are Lee et al. (1972), Ingram and Golden (1973), Pedace and Sansome (1972), and Dalager (1975). Another problem that occurs in data analyses is the fact that it is theoretically incorrect to compare a regression of CoH on TSP in

City 1 with a regression of TSP on CoH in City 2. This comes from the fact that a least squares fit of y vs x gives a different result than when x vs y is used. For example, if we assume

$$y = ax \tag{4}$$

or

$$x = by \tag{5}$$

then in general

$$a = \Sigma xy/\Sigma x^2 \text{ and } b = \Sigma xy/\Sigma y^2. \tag{6}$$

Then $a \neq 1/b$ unless $\Sigma x^2 \Sigma y^2 = (\Sigma xy)^2$

Therefore one could have the same set of CoH and TSP observations in 2 different cities and have one city report $y = ax$ compared with $y = x/b$ in the other city. The differences can be very large if there are outliers in the data set, which is not an unusual occurrence (Lee et al., 1972).

Lee et al. (1972) reported that there were significant differences between the regression coefficients for the heating season and non-heating season when CoH was fit against TSP, and the relation also varied from place to place. Regan et al. (1979) reported a comparison of fine particle fractions collected near a coal burning power plant, location unspecified. They used a TSP hi-volume sampler equipped as an Andersen 2000 5-stage particle sizing fractionator. Although they report correlation coefficients of CoH vs particulate >0.95 there are some apparent problems with the reported results.

(1) The authors fit mass vs CoH instead of CoH versus mass. As described previously for a least squares analysis, $y = f(x)$ is not the same as $x = g(y)$;

(2) The inclusion of an intercept is theoretically incorrect. When TSP = 0, CoH ≡ 0;

(3) In order to compare twelve (12) daily 2-hour CoH samples with one 24-hour mass sample, the average of twelve CoH values was computed. Unfortunately a warning by Ingram and Golden (1973) to "Let mass be a function of CoH." was not considered. That is, if we have 12 values of x then the correct value of $\bar{x}$ is found by the following relationship:

$$\bar{x} = f^{-1}(\bar{y}), \quad \text{where} \quad \bar{y} = \frac{1}{12}\sum_{1}^{12} f_i\ (x) \qquad (7)$$

Because Regan et al. assumed that the fraction of mass <15 μm was 92 percent of the total mass then their reported regression of

Mass <15 μm = 18.4 + 424 CoH could be transformed to TSP = 20 + 460 CoH.

These results are 3 times the averages reported by both Lee et al. (1972) and Ingram and Golden (1973) of approximately 150 $\mu g/m^3$ per CoH and these results even fall outside the $-2\sigma$ limit for the non-heating season in England reported by Lee (1972). This extreme high TSP/CoH may be caused by the combination of factors cited previously or it may be caused by a site specific property of the local source.

Certain studies by Simon (1976) and Lisjak (1977) cited in Holland et al. (1979) should also be evaluated here. Simon (1976) searched the literature and brought forth eight internal reports and memoranda of the Allegheny County Health Department, Bureau of Air Pollution Control. Simon said: "The earliest report was written by Ed Tredway to Ron Chleboski on March 30, 1972 covering the months October, 1971 to February 1972." This is likely to be the first such study produced because, as Mr. Tredway states: "tape sampler data prior to October 1971, is considered unreliable." The Simon (1976) report does not cite the Ingram and Golden (1973) paper, which demonstrates that the

procedure of averaging CoH values was incorrect. Papers by Sullivan (1962) and Katz (1958) also not cited by Simon (1976), demonstrate that CoH was independent of the mass of large particles on the filter and that CoH vs TSP relations could be fit by a power curve.

These references demonstrated linear regression was not appropriate, especially if it did not go to zero CoH at zero TSP. The Lisjak paper (1977) is even more concise, since it moves directly to the point by only citing the Simon (1976) report. Consideration of Simon (1976) and Lisjak (1977) alone may have led Holland et al. (1979) to conclude: "One could not expect any general relationship between CoH readings (transmittance), smoke filter measurements (reflectance) and high volume measurements (gravimetric)." The CoH transmittance and British Smoke Reflectance are highly related and Saucier and Sansone (1972) report a detailed comparison of the two (BS versus CoH). However, they relied on linear regression without the requirement of fitting at the origin. (Note that the figures in Saucier and Sansone (1972) are mislabeled as R vs T, but the text and figure description cites T vs R.)

3.5.5 Comparison of American Hi-volume (TSP) and British Smoke (BS) Measurements

3.5.5.1 Introduction--Hi-vol TSP and British Smoke (BS) measurement approaches, frequently used in community health studies of the type discussed in Chapter 14 were developed to measure two distinctly different properties of atmospheric particulate matter. The TSP measure was intended to represent the total mass of particulate matter suspended in the atmosphere, whereas the BS measure was designed to more specifically estimate the relative concentrations of coal smoke, that is, black staining particles in the air thought to be more closely tied to health effects occurring during times of elevated particulate pollution in England. These basic differences in measurement approaches have contributed

to considerable confusion and controversy regarding (1) how airborne particulate matter data obtained with the two methods relate to each other; and (2) possible interrelationships between associated quantitative dose-effect or dose-response information from studies using TSP measurements vs those using BS data. It is important, therefore, to evaluate available studies comparing TSP and BS measurements, key conclusions that have been or can be derived from the results of those studies, and supporting information on physical phenomena associated with the TSP and BS measurement approaches that may help to explain observed comparison relationships.

Numerous studies have been published during the past decade or so, which report on comparisons of American Hi-vol TSP and BS measurements from colocated monitoring units at widely dispersed locations in Britain, other European countries, and the United States. Such studies include those by Commins and Waller (1967), Lee et al. (1972), Ferris et al. (1973), Kretzschmar (1975), Dalager (1975), and Ball and Hume (1977). In addition, other recently conducted studies, by Pashel and Egner (1980) and Bourbon (1980) have yielded extensive data on comparisons of side-by-side TSP and BS measurements obtained at widely disparate geographic locations in the United States and France.

Commins and Waller (1967) obtained side-by-side Hi-vol TSP and BS measurements at a site in central London over the 8 yr period 1955-1963. When 24-hr TSP readings usually taken once per week, or more frequently during high pollution episodes, were compared with corresponding BS readings, it was found that the TSP readings tended to average about 100 $\mu g/m^3$ higher than the BS measurements. The differences were most notable in the summer (non-heating) season and under windy conditions, but there was a closer correlation between the readings during winter (heating) season high pollution periods. The latter periods

were usually associated with low wind speed weather conditions during times of high particulate emissions from coal fires used for heating of homes. Initially, no attempt was made by Commins and Waller (1967) to mathematically describe the complex variation of the TSP/BS relationship in conjunction with season and wind speeds, but a later unpublished regression analysis (by Waller) of the overall data set (334 pairs of observations) was reported by Holland et al. (1979) to have yielded results that can be simply expressed as follows:

$$\text{TSP } (\mu g/m^3) = 119 + 0.824 \times \text{BS } (\mu g/m^3)$$

In a later study reported by Lee et al. (1972), side-by-side Hi-vol TSP and BS readings were obtained during 1970 from 11 sites in the United Kingdom, including some in London and its suburbs as well as several other industrial cities. Comparison of daily readings over a 5-month study period covering both non-heating and heating seasons, revealed a generally close relationship between the readings in areas not under smoke control regulation but there was a tendency for the Hi-vol TSP readings to be distinctly higher than BS measurements elsewhere. Regression analysis for measurements taken at the London sites sampled, where smoke ranged from 20 to 140 $\mu g/m^3$ BS, yielded the equation:

$$\text{TSP } (\mu g/m^3) = 44 + 1.61 \times \text{BS } (\mu g/m^3)$$

Another regression analysis for all 11 United Kingdom sites combined, including London and elsewhere, yielded the following equation:

$$\text{TSP } (\mu g/m^3) = 5.09 + 0.618 \text{ BS } (\mu g/m^3) \text{ and}$$

$$\text{BS } (\mu g/m^3) = 36.25 + 0.608 \text{ TSP } (\mu g/m^3)$$

Ball and Hume (1977) have since reported findings obtained with side-by-side Hi-vol TSP and BS sampling at one site in central London during the 1-yr period May 1975, to April 1976, with 24-hr samples being taken 4 days per wk. Again, TSP readings were generally higher than the BS readings, with greater

divergence being seen during the summer than in the winter when airborne particulate matter concentrations tend to be much higher. The following equations were derived from regression analyses by Ball and Hume (1977) to describe these relationships mathematically:

Summer $\quad TSP\ (\mu g/m^3) = 22 + 1.64 \times BS\ (\mu g/m^3)$

Winter $\quad TSP\ (\mu g/m^3) = 37 + 1.23 \times BS\ (\mu g/m^3)$

Ball and Hume (1977) further noted a close correlation was found between the amount of smoke (BS) and that of lead in the air during their 1975-76 sampling, which they interpreted as indicating that much of the smoke was derived from traffic sources, e.g., diesel engine smoke and gasoline engine lead emissions.

This would be consistent with what would be expected in terms of highly probable changes in the particulate matter content of London air following the enactment of the 1956 Clean Air Act and marked reductions in coal fire emissions already seen in the early 1960s. That is, as coal fire emissions decreased tremendously during the 1960s in response to smoke control orders and oil-based home heating increased along with an ever-growing traffic volume, the particulate matter content of the air over London and other British cities must have shifted distinctly toward that typically seen in many large American cities. Thus, by the 1970s, it should be expected that smoke (BS) measurements, and any TSP readings taken as well in London, should more closely correspond to the atmospheric particulate matter found in "American air" long characterized by notable particulate emissions from vehicular traffic and other oil combustion sources.

In addition to the above comparison studies relating TSP to BS readings obtained in London and elsewhere in Britain, several other published studies have reported on analogous comparisons carried out in other European locations

and the United States. In regard to the latter, for example, Ferris et al. (1973) reported on TSP-BS comparisons obtained at two sites in Berlin, New Hampshire, and found discrepancies between the absolute values obtained that were, in general, similar to those observed in the above studies. That is, at low arithmetic mean BS levels of 19 $\mu g/m^3$ (for March to December, 1966) and 20 $\mu g/m^3$ (for January to December, 1967), the respective side-by-side TSP readings were 101 and 91, which represent differences of about the same magnitude as those seen at British locations where BS readings were below 100 $\mu g/m^3$.

As for other published studies, Dalager (1975) reported comparisons of TSP and BS readings obtained in an urban (København) area and a semi-industrial (Ålborg) region of Denmark. Again, discrepancies were found between the two measurements, with the TSP readings always being considerably higher (around 60 to 70 $\mu g/m^3$) than the invariably very low (<5 $\mu g/m^3$) BS readings obtained in Ålborg, with similar but smaller percentage differences percentage being seen at higher BS readings from København. Kretzschmar (1975), too, reported on comparisons of TSP and BS readings, but from sites in Antwerp, Belgium. Unfortunately, however, the Hi-vol sampler used for obtaining TSP readings was sited 15 meters above the ground 400 meters away from the OECD apparatus situated 3 meters above ground level from which the paired BS readings were obtained.

Holland et al. (1979) recently reviewed the published literature comparing American Hi-vol (TSP) and British Smoke (BS) measurement results. The review, however, is limited to discussion of the studies of Commins and Waller (1967), Lee et al. (1972), Ferris et al. (1973), and Ball and Hume (1977). All of these studies share a common thread, in that they used linear regression procedures in attempting to define relationships between the two measurement

approaches. In discussing the results of the above studies Holland et al. (1979) concluded:

> The several methods in common use for the determination of suspended particulates cannot be related to one another in any simple way.

and further that

> the British smoke filter (BS), and the high volume sampler (HV) do not measure the same properties, and the results are clearly not directly interchangeable. Relationships between them can only be of an empirical nature, and those found at a particular site and time cannot be expected to apply to other sets of circumstances.

Commenting further on the studies, Holland et al. (1979) noted that:

> Their results showed clearly, however, that where there is little of the black smoke characteristic of the incomplete combustion fuel, there are likely to be huge discrepancies between the British (smoke) and the US (HV) figures.

Carrying the implications of the above conclusions to a logical endpoint, in discussing the Ferris et al (1973) comparison results for a study in Berlin, New Hampshire, Holland and colleagues stated:

> "Clearly, the characteristics of the suspended particulates must have been very different in Berlin, New Hampshire, from those of smoke in British towns."

Holland et al. (1979), therefore, suggest that consistent or meaningful relationships between Hi-vol (TSP) and BS measurement results are difficult to discern. Their report, however, concludes:

> Nevertheless, some general guidance can be obtained about how best to 'translate' British smoke filter results, as cited in epidemiologic studies carried out over the past 20 years, into equivalent high volume sampler figures.... For sites in London, where many of the epidemiologic studies reported in the following sections were carried out, each of the studies indicates that, on average, smoke (BS) values of 100 $\mu g/m^3$ correspond with HV values of about 200 $\mu g/m^3$. The ratio of HV to smoke (BS) result is greater than 2 at still lower smoke concentrations, and in the other direction it decreases towards unity for relatively high smoke concentrations, above about 500 $\mu g/m^3$.

Holland et al. (1979), in describing the Ball and Hume (1977) study, however, also noted: "simple linear regression equations were calculated ... even though it seemed likely that there would be divergences from linearity." However, Holland et al. (1979) did not go on to discuss or develop any nonlinear models capable of better accounting for the pertinent data relationships analyzed.

An in-depth analysis of all of the available data (including those from studies cited by Holland et al., 1979), which takes into account the nonlinear character of TSP-BS relationships as a sina-qua-non, leads to the proposal of a "bounded nonlinear (BNLM) model" that appears to fit the available data over the entire range of existing observations. The proposed model, the rationale underlying it, evaluation of its ability to predict TSP-BS relationships, and physical phenomena underlying observed TSP-BS relationships accounted for by the model are all discussed below in the ensuing text.

3.5.5.2 Development of a Bounded Nonlinear (BNL) Model--The theoretical basis for proposing a BNL model arises through consideration of boundary conditions that generally appear to hold for essentially all of the above published comparison studies. For example, Dalager (1975) earlier noted that a clear boundary condition exists at the lower limit of atmospheric particulate matter concentrations. That is, in the limit as TSP goes to zero, BS must also go to zero because it is a subset of TSP. Also, at the high concentration end, in the limit, as BS $\rightarrow \infty$, BS $\rightarrow$ TSP. This arises from consideration of the fact that for the high BS pollution periods to occur, wind speed must be low and the air must be relatively stable. Therefore, the larger particles will settle out and only the small particles, which are usually optically black, will remain suspended. Consequently, a model defining a linear relation with an intercept such as BS = a + b TSP is theoretically incorrect. Rather a

nonlinear model should be fit within the above boundary conditions. The model should also fit representative emperically-derived data. One could, for example, choose a model designed to fit, at a minimum, the consensus values cited by Holland et al. (1979) as summarizing relationships observed at London sites: "at smoke concentrations of the order of 100 $\mu g/m^3$, the corresponding high volume results (in London) are about double those of the smoke figures, while around 250 $\mu g/m^3$ smoke (BS) the ratio is about 4:3, and by 500 $\mu g/m^3$ smoke (BS), it is approaching unity."

A simple nonlinear model that fits both the above boundary conditions for BS/TSP and the above consensus values can be stated as:

$$BS = TSP^3/(C^2 + TSP^2) \qquad (8)$$

Equation 8 fits both the 100 and 250 $\mu g/m^3$ BS consensus data points with almost identical values of C (200 $\mu g/m^3$ and 193 $\mu g/m^3$) for both low and high BS values; the equation also, by design, meets the boundary constraints. The model is therefore chosen, for simplicity, with C = 200 $\mu g/m^3$. This function, equation 8, is plotted on Figure 3-9 as the curve labeled "BNLM" for a bounded nonlinear model (See Appendix B for a dimensional analysis of this relationship)

This type of equation may also be applicable to a data set of total Dustfall versus Water Insoluble Dustfall in Stalker, Dickerson and Kramer (1963). In these dustfall data, the water insoluble dust (WID) must go to zero when total dustfall (TD) goes to zero and these data suggest a linear relation at high levels of TD. This model would have 2 parameters, a and B,

$$WID = \frac{aTD^3}{B^2 + TD^2} \qquad (9)$$

where a <1, and B, TD, and WID have units of Tons/mile$^2$/month.

Data used to fit the BNLM model from Holland et al. (1979) fall on the BNLM curve, as expected by their use in the fit and as shown by the symbol (θ) in Figure 3-9. In addition, data from several other studies reviewed by Holland et al. (1979) are also plotted on this figure. The data (Δ) from Commins and Waller (1967), based on means, are fit well by the model over the entire range 50 < BS < 500, and the London data (□) from Lee et al. based on means (BS = 44 + 1.61 TSP) also fit well over the range of their measurements (20 to 140 μg/m$^3$ BS). The maximum data point recorded by Ball and Hume (1977) as shown on Figure 3-10 (at 490 μg/m$^3$ BS, 600 μg/m$^3$ TSP), is plotted in Figure 3-9 as (-O). A fourth, U.S., data set (⊕), shown in Table 3-9 from Ferris et al. (1973) and obtained in Berlin, New Hampshire, is also fit well by the BNLM model even though it is in a lower concentration range than the English data sets. Three additional data sets not reviewed by Holland et al. (1979) are also plotted in Figure 3-9.

TABLE 3-9. ARITHMETIC MEAN CONCENTRATIONS OF SMOKE (BS METHOD) AND TOTAL SUSPENDED PARTICULATE (HV METHOD) AT TWO SITES IN BERLIN, NEW HAMPSHIRE*

| | 10 months Mar. - Dec. 1966 | | 12 months Jan. - Dec. 1967 | |
|---|---|---|---|---|
| Site | Smoke μg/m$^3$ | TSP μg/m$^3$ | Smoke μg/m$^3$ | TSP μg/m$^3$ |
| Fire station | 19 | 101 | 20 | 91 |
| Brown School | 6 | - | 9 | - |

*Data from Ferris et al. (1973) The authors do not report the Hi-vol TSP data from the Brown School but the BNLM model predicts ~60 μg/m$^3$ TSP at 6 μg/m$^3$ BS and ~70 μg/m$^3$ TSP at 9 μg/m$^3$ BS. (The authors note that they used a linear average in computing Hi-vol flow rates. For these relatively low mass loadings the correction would appear to be very small.)

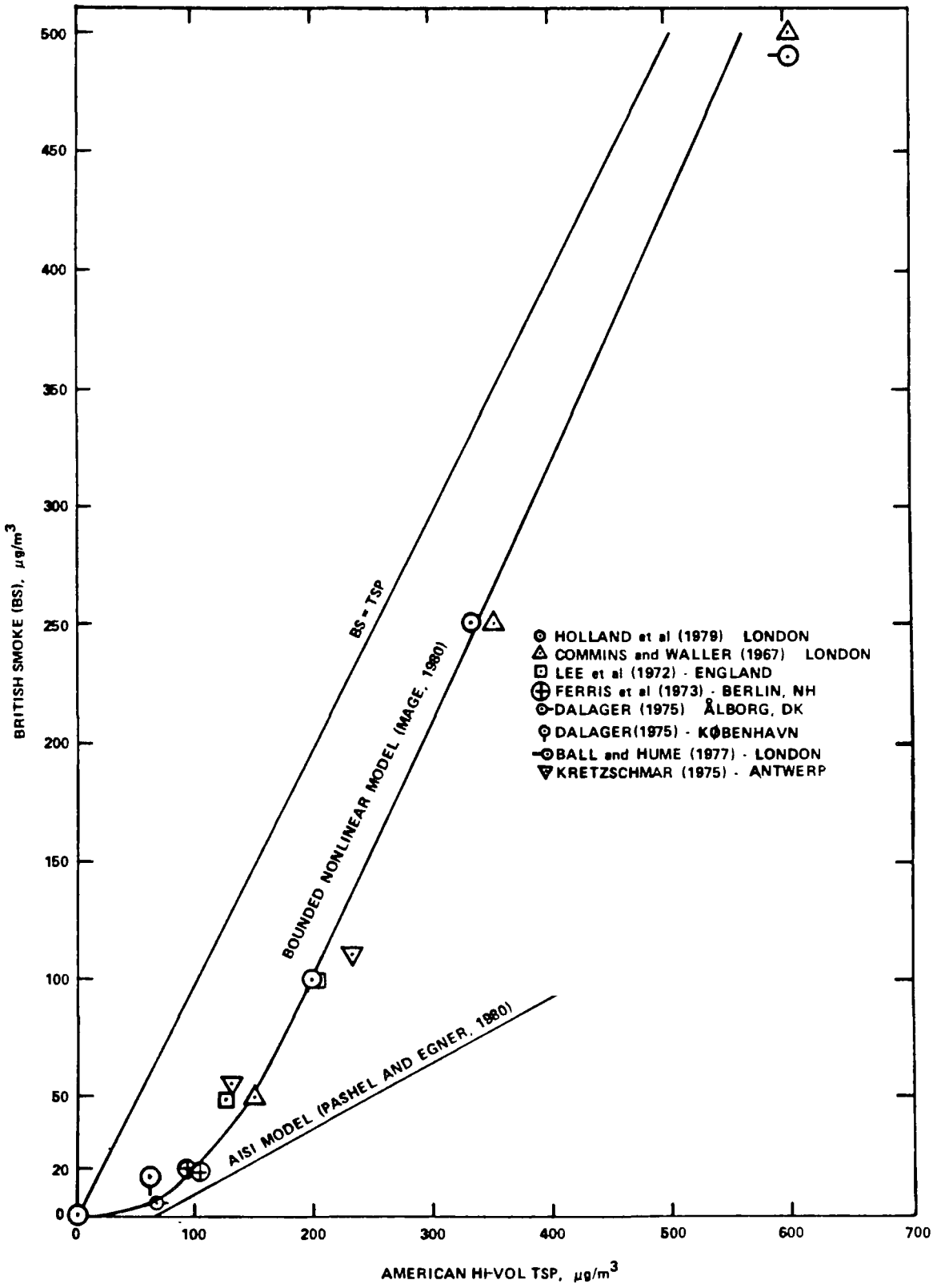



Figure 3-9. Measurements of British Smoke vs Hi-vol TSP, showing a consistent relation between these measures over the entire range of reported observations. Most points shown are annual mean values; see text for discussion.

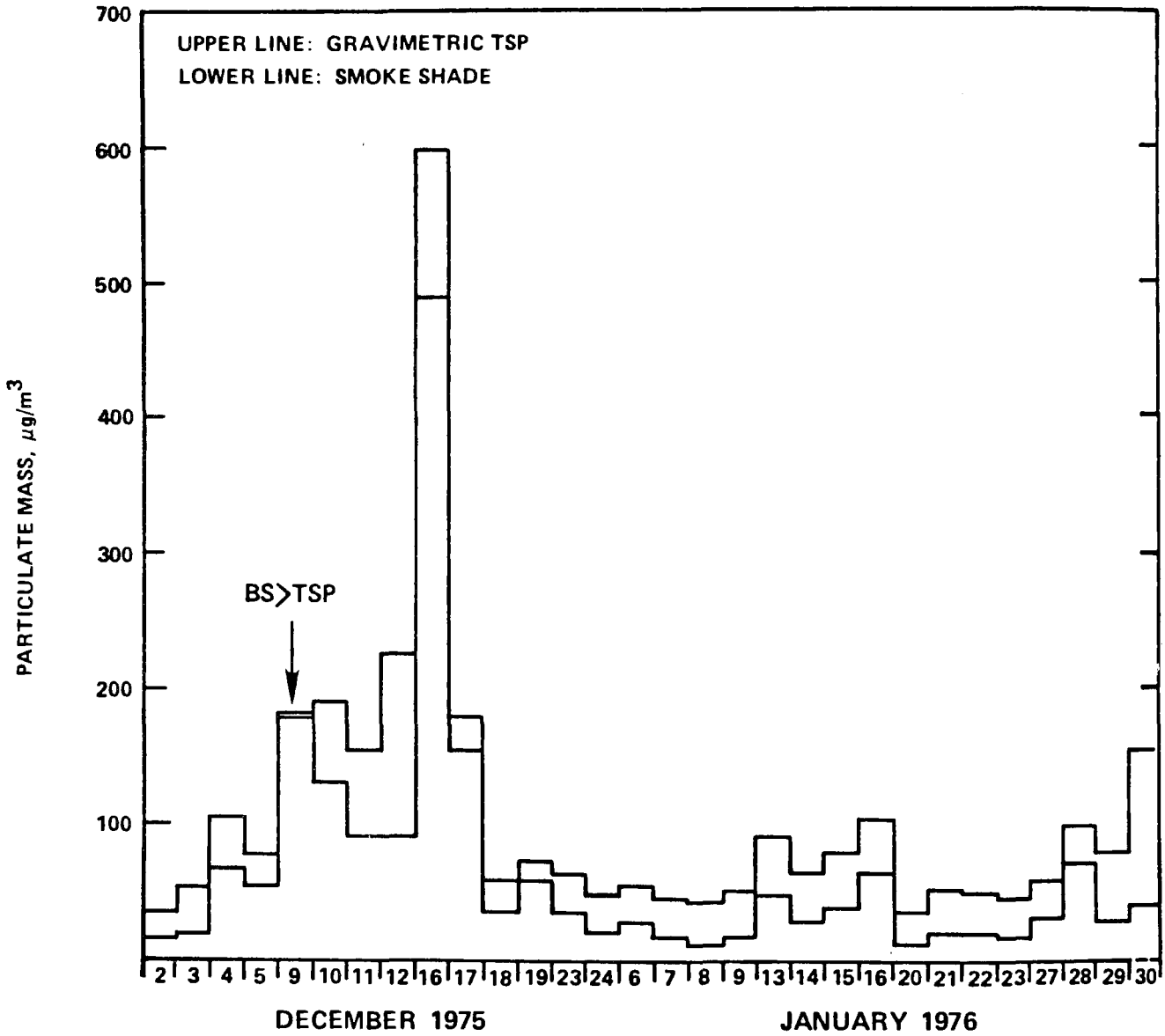



Figure 3-10. Daily gravimetric and smokeshade data for two representative periods as measured at the London County Hall. On December 9th, the two curves cross, and BS is greater than TSP. From Ball and Hume (1977).

As noted earlier, Dalager (1975) reported on BS versus TSP relationships for two locations in Denmark: (1) Dejligt København, and (2) Nørresundby, Ålborg. The TSP was measured by the LIB Hi-vol sampler described previously in this chapter. Laskus (1977) compared the LIB with the Staplex used in the United States and British studies and reported that Staplex = 2.1 + 0.98 LIB with a correlation coefficient of 0.93. In København, the relation is TSP = 1.27 BS + 43 $\mu g/m^3$ and, with a force fit through the origin, TSP = 3.9 BS. These lines intersect at TSP = 64, BS = 16.4, close to their mean values which are designated as (Q) in Figure 3-9. The value lies 10 $\mu g/m^3$ above the BNLM model line. The air in Ålborg is much cleaner than København, and Dalager (1975) does not report the Ålborg correlation because "the Hi-vol sampler often gives figures which are 50 times the OECD-smoke concentration (BS)." This condition is predicted by the BNLM model at TSP = 28 and BS = 0.56. Ferris (personal communication, 1980) also reported a similar situation of extremely high TSP/BS ratios at the Brown School in Berlin, New Hampshire, as shown in Table 3-9. At the Brown School, the BS was often below the minimum detectable level of the reflectometer while a TSP mass was in the measurable range. Figure 3-11 from Dalager (~~1975~~ 1974), shows that the weekly average BS in Nørresundby, Ålborg, is usually below the minimum detectable level; but it increases at times up to a maximum of about 5 $\mu g/m^3$, whereas the LIB Hi-vol fluctuates between 60 and 70 $\mu g/m^3$ over the same time period. This point (5 $\mu g/m^3$ BS, 65 $\mu g/m^3$ TSP) is plotted (O-) on Figure 3-9 and falls slightly below the BLN model curve.

Also, as alluded to earlier, Kretzschmar (1975) compared BS with a modified Hi-vol, using cellulose filters as reported by Dams and Heindryckx (1973). However, the Hi-vol was at a height of 15 meters above ground level, 400

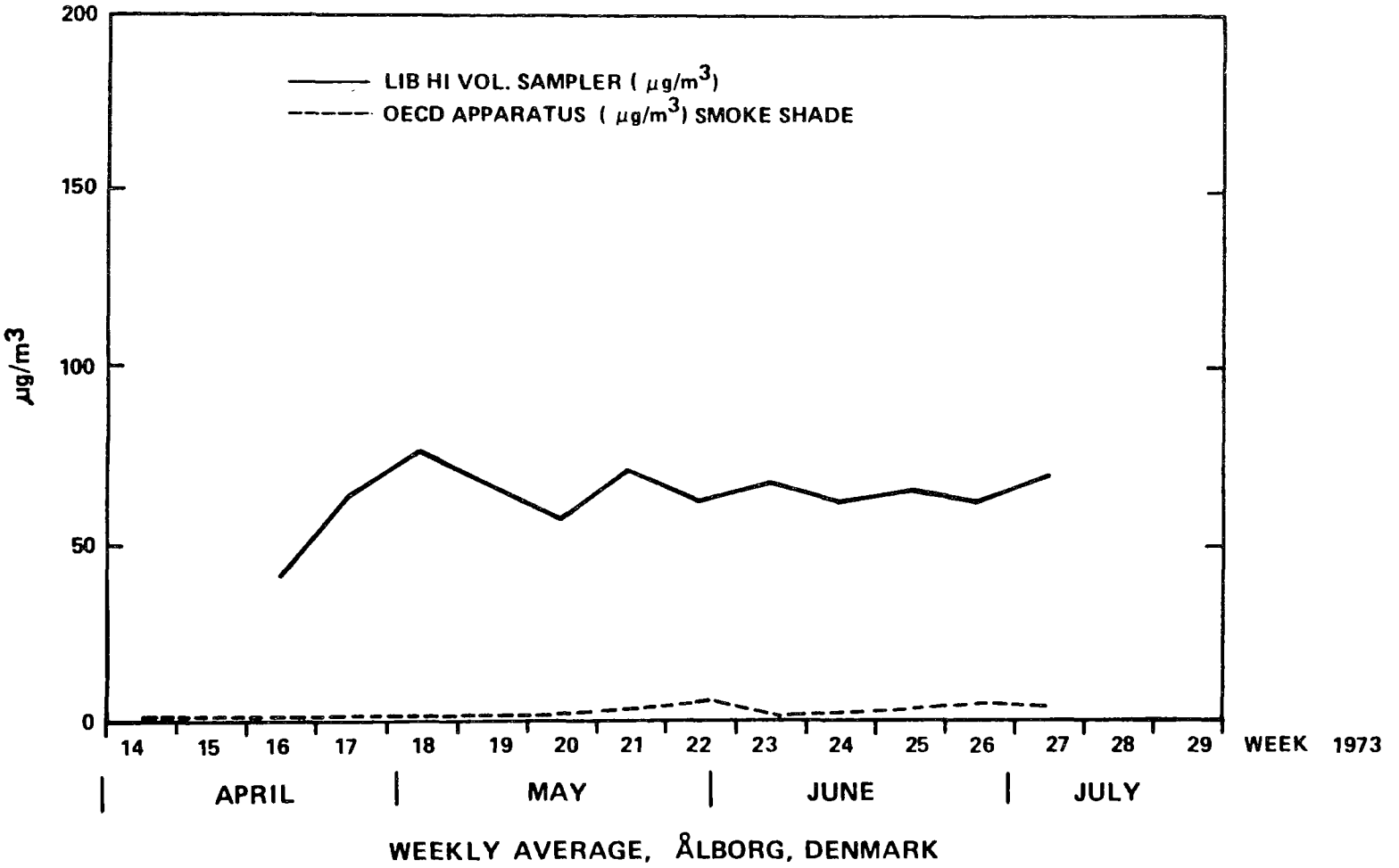



Figure 3-11. Comparison of weekly average LIB Hi-vol and smokeshade from Alborg, Denmark, showing negligible smoke and appreciable TSP. From Dalager (1975).

meters away from the OECD sampler, which was 3 meters above ground level. Since particle concentrations tend to decrease with elevation in a gravitational field, the TSP probably would have been greater if it had also been measured at 3 meters, the same elevation as the OECD samplers. Because the Hi-vols were run by Dams (1973), the corrections for flow variations described by him (Dams, 1973) were utilized so that the flow rate variation effect would not enter into this comparison. Kretzschmar (1975) reported a linear relationship of BS = 10 + 0.37 TSP, which places the regression well above the BNLM curve. At higher BS levels, which are indicative of lower wind speeds, the 95th percentile points of the TSP and BS cumulative frequency distributions are 225 $\mu g/m^3$ and 110 $\mu g/m^3$, respectively. This point is plotted (∇) on Figure 3-9 and it is consistent with both the BNLM Model and the Commins and Waller (1967) equations. The arithmetic mean for BS (55 $\mu g/m^3$) and TSP (125 $\mu g/m^3$) from Kretzschmar's (1975) study are plotted as a single point (∇) on Figure 3-9, where it falls above the BNLM model line.

A recent draft report by Bourbon (1980) discusses the comparison of (French) Smoke Shade, Hi-volume TSP and a gravimetric low volume collection (1 $m^3$/hr). Although the simultaneous TSP and smoke shade data are not listed, the report states that there appears to be no consistent relation between the gravimetric and reflectometric measurements. However, a plot of the low-volume sampler versus smoke shade data averaged over an entire city for each year appears to fall between the BNLM curve and the BS = TSP line. This is not inconsistent per se with the British Smoke versus TSP data because at a given BS, a low-volume sampler will collect less mass than the hi-volume sampler. Even so, it appears that a curve of the type of equation (8) could be used to fit the means of the French data. The report by Bourbon (1980) states that

Schneider CA32 filter papers are used with a photovolt reflectometer 610Y Tristmulus green filter. However, Bourbon (1980) reports that the reflectance is fixed at 92.5 percent by a standard off-white enameled tile; that is, "s = 92.5; Reflectometre calé sur étalon en grés ḿmaillé (sic) blanc"). It is not clear how this calibration point relates to both the OECD (1964) report and WHO (1977) report, which define an international curve with the Photovolt reflectance set to 100 on a pile of clean Schneider CA 32 filter paper.

In summary, we have analyzed comparative BS versus TSP data described previously from England, the U.S.A., Denmark, Belgium, and France. All these data, from disparate locations and independent investigations, appear to be well fit by the ~~one~~ two-parameter empirical BNLM model, which meets applicable boundary constraints and also fits well the "consensus" observations described verbally, but not mathematically, by Holland et al. (1979).

In contrast to the consistent fit of the above data achieved by the BNLM model (Mage, 1980), only the reported values from one recent study appear to diverge from the curve defined by the model. More specifically, in a study supported by the American Iron and Steel Institute (AISI) in cooperation with five AISI-member steel companies and described in a draft report by Pashel and Egner (1980) accepted for publication in Atmospheric Environment, comparisons were made between BS and TSP readings obtained from side-by-side BS and hi-volume samplers at 16 locations in the United States. The key conclusions arrived at as a result of the study are graphically depicted in Figure 3-12, a duplicate of Figure 7 of the Pashel and Egner report. That is, it could be inferred that the relationship between BS and TSP readings taken in the United States is as defined by the "AISI (1977)" line in the figure. This appears to be markedly different from the relationship defined for BS/TSP

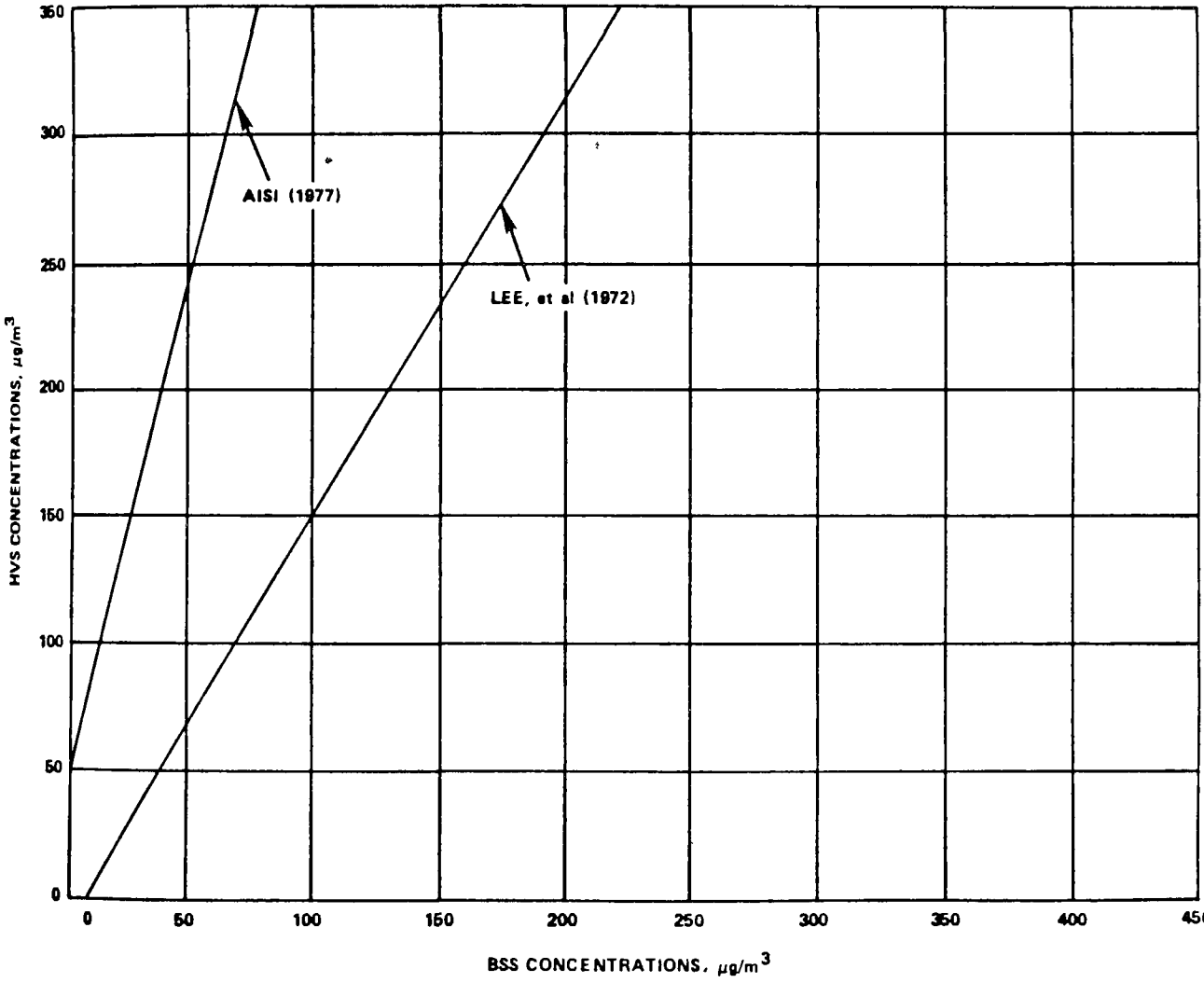



Figure 3-12. Comparison of hi-volume sampler TSP vs British smoke (BS) relationship defined by data from United States sampling sites (AISI, 1977) in contrast to analogous comparison relationship defined by data from England (Lee, et al., 1972). From Pashel and Egner (1980). Note that the Lee et al. (1977) line, as plotted here from the original Pashel and Egner (1980) paper, is incorrect.

readings obtained in England as depicted by the other line in the figure (which is incorrectly derived from the original relationship reported by Lee et al., 1972). Based on this apparent discrepancy and the precise slope of the "AISI (1977)" line, it is implied: (1) that American measurements of airborne particulate matter concentrations cannot be meaningfully compared with "British Smoke" measurements, thus negating any possibility of making meaningful comparisons between American and British epidemiological studies demonstrating quantitative relationships between various health effects and air particulate matter concentrations measured by different (Hi-vol or BS) techniques; and (2) that "no general relationship between smoke and TSP exists which would be applicable to all sampling sites."

Interpretation of this AISI study, characterized by the authors as being "the first large scale, long term attempt to study this relationship in the United States," requires in-depth critical analyses of its findings and basic information on the physical underpinnings of BS and TSP measurements, in order to understand the obvious discrepancy between the reported relationship defined by the AISI model (see Figure 3-9) the BNLM model curve (Mage, 1980) and other available data.

Sampling for the AISI study was performed by personnel from several different steel corporations throughout the United States. The TSP filters were weighed on-site, whereas the BS filters were mailed to Bethlehem, Pennsylvania, for reflectance readings. The reflectance readings were also "duplicated" at Warren Spring Laboratory (WSL) again following mailing of the filters to England (after they were read in Bethlehem). As stated by Pashel and Egner (1980):

> Reflectance readings were taken at Warren Springs (sic) to assure their comparability with data related to the British epidemiological studies of the 1950's. The Bethlehem reflectance readings were taken in order to evaluate what impact, if any, transporting the filters through the mail had on the stain reflectivity. The mean of the Bethlehem reflectance readings was 91.4% with a standard deviation of 5.36 while the mean WSL reading was 91.9% with a standard deviation of 5.99. This indicates that mailing the filters had no significant impact on filter reflectance.

Apparently, Pashel and Egner (1980) did not follow certain IM (1966) procedures requiring on-site reflectance readings in order to ascertain that the reflectance is maintained below 90 percent. When reflectance approaches 90 percent, the IM (1966) calls for changing to a smaller size filter clamp in order to keep the reflectance below 90 percent. As quoted from the IM (1966):

> If the concentration of smoke is to be obtained with reasonable accuracy it is essential that the stain should have a reflectometer reading in the range 40 to 90. During normal conditions, the readings should be above 70 so that sudden increases in pollution can be accommodated within the acceptable limits. With dark stains, the particles form more than one layer so that the concentration obtained represents only a minimum value, and the flow rate is affected by the accumulation of material.
>
> The use of 1/2-in clamps should be confined to extremely clean areas in open country where 1-in clamps regularly give reflectometer readings of 90 and over. The main disadvantage of using 1/2-in clamps is that the smoke deposit builds up very quickly, soon causing the reflectometer reading to fall below 40. At the same time the resistance to the flow of air rises and the flow rate at the end of the sampling period may be only one-third of that at the beginning, when the filter paper was clean.

Because Pashel and Egner (1980) report a mean reflectance greater than 90 percent, their study may have used too large a clamp size and 1/2-inch, or even 10 mm, clamps should have been used.

Establishing the lack of statistically-significant differences in reflectance readings due to the mailing of BS filters is essential in order to establish the reliability (or credibility) of the basic data derived from sampling and

related analytical procedures employed in the study. These data, in turn are, of course, crucial determinants in development of the overall AISI "BS/TSP relationship" model arrived at in the report of Pashel and Egner (1980) and shown in Figure 7 of their report (Figure 3-12).

Examined next is the crucial assertion that the mailing of samples had "no significant impact on filter reflectance," i.e., their BS readings in $\mu g/m^3$.

In order to apply a statistical test of the null hypothesis of no reflectance increase for the mailed filters, we can let reflectance measurements be represented by the general model:

$$X_{ij} = \mu_i + \varepsilon_{ij} \qquad \begin{array}{l} i = 1,2 \\ j = 1, \text{----} 860 \end{array} \qquad (10)$$

where $\mu_1$ represents the true reflectance before shipment and $\mu_2$ the true reflectance after shipment and $\varepsilon_{ij}$ represents a random error term with zero mean and finite variance. The average reflectance before shipment was reported as $\bar{x}_1 = 91.4\%$ with a standard deviation of $S_1 = 5.36$. After shipment, the reflectance was $x_2 = 91.9\%$ with a standard deviation of $S_2 = 5.99$. Estimates are based on n = 860 samples.

To test the null hypothesis Ho: $\mu_i = \mu_2$ versus the alternative hypothesis $H_a$: $\mu_2 > \mu_i$ a basic one-tailed t-test, outlined by Steel and Torrie (1960), was calculated:

$$t = \frac{\bar{x}_2 - \bar{x}_1}{\sqrt{\frac{S_1^2}{n} + \frac{S_2^2}{n}}} = \frac{0.5}{0.27} = 1.82$$

This test showed significance at the $\alpha = 0.05$ significance level. It must, therefore, be concluded that the reflectance readings after shipment were significantly higher than reflectance before shipment.

Reference to Waller (1964) indicates that the correction $[\partial(BS)/\partial R]\ \Delta R$ is small at R = 91.4% reflectance so the BS correction is not as large as it would be at R $\lesssim$50%. However, this was the second mailing for most of the filters since all filters except the Bethlehem filters were apparently mailed to Bethlehem for analysis. We would expect the most weight loss to occur in the first mailing since the most loosely bound particles would fall off quickly, and the weight loss should decrease with each subsequent mailing.

Also, Pashel and Egner (1980) did not use the 1.5 liter/min flow required by the IM (1966). That 1.5 l/min flow rate was cited by Holland et al. (1979) as typically being employed in generating BS data used by British epidemiologists and was used in almost all of the other BS/TSP comparison investigations discussed here. Instead, Pashel and Egner (1980) used a flowrate of 0.72 liters per minute, which likely causes a significant change in the character of the particulate matter collected, since it will cause relatively less material of each size to be collected than the standard BS sampler using the 1.5 liter/minute flow rate.

This assertion is supported by data from the report by Liu et al. (1978) summarized in a table showing the effect of pressure drop on penetration for clean Whatman No. 1 filters (see Table 2-11 in Chapter 2). In that table, there appears to be an anomalous point in the Dp = 1.0 row at either $\Delta P$ = 1 or 3 cm Hg since penetration increases as velocity increases from 6.1 cm/sec to 17.4 cm/sec.

Figure 3-13, a plot of pressure drop versus flow velocity shows that for a 1-inch (2.54 cm) filter spot the pressure drop will be 0.82 cm Hg for the standard BS method and 0.40 cm Hg for Pashel and Egners low flow conditions. Table 2-11 also indicates that Whatman No. 1 filter paper has a relatively high penetration for small ($\leq$1 μm) particles at low flowrates. This large

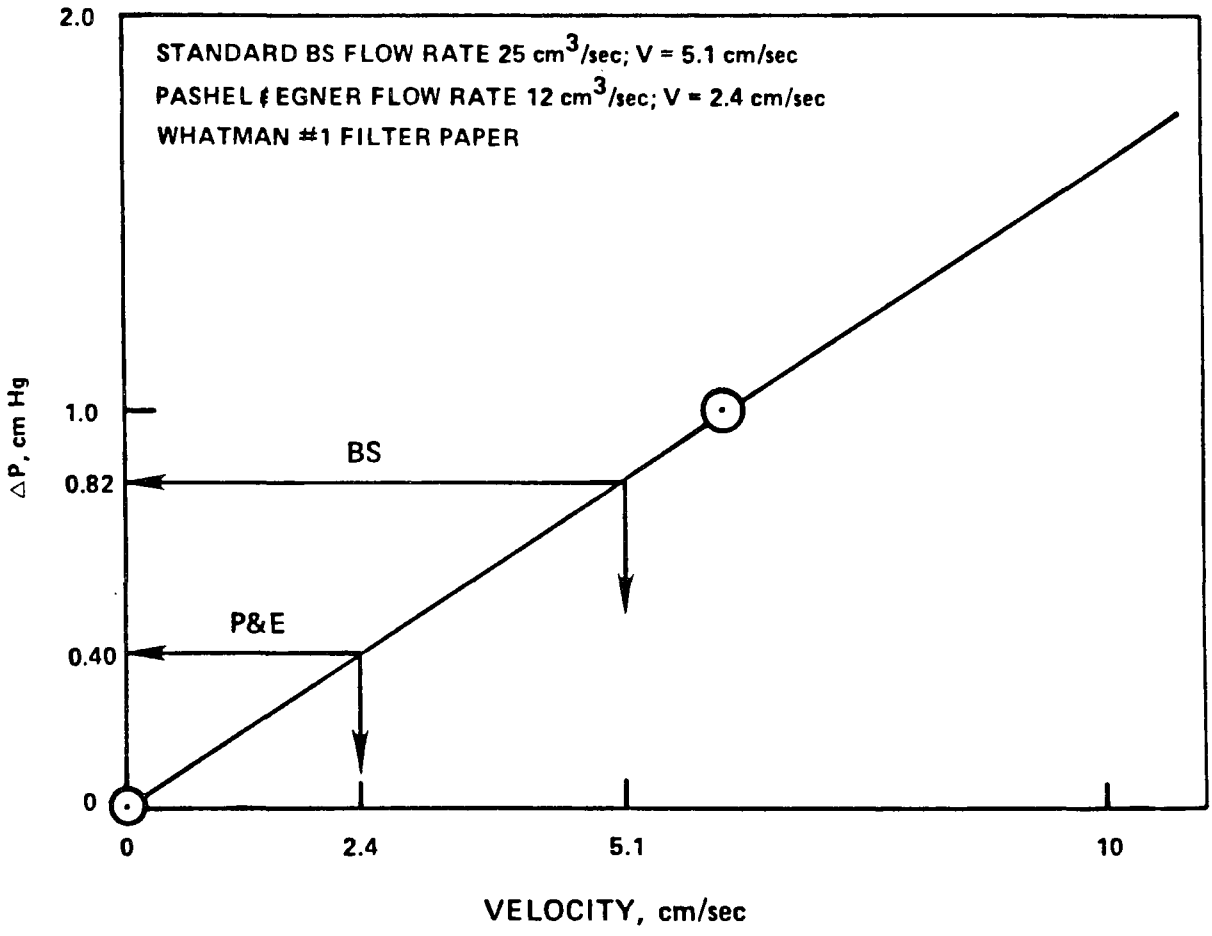



Figure 3-13. Pressure drop on Wahtman #1 filter vs flow rate showing effect of use of lower flow rate than recommended by IM (1966).

potential penetration at these low diameters means that some BS will escape capture although one expects the "window" closes as particles begin to fill the pores and coat the surface.

In a similar manner, the lower flowrate also manifests itself in changing the penetration of particles into the funnel and through the inlet tubing. In order to correct these penetration data for the lower flowrate used by Pashel and Egner (1980), it is necessary to perform a detailed analysis of the BS flow system to estimate what their results would have been if they had sampled at 1.5 liter/min. This analysis is given in Appendix C.

Using Figure 3C-1 from Appendix C, the BS has a penetration to the filter of 98.6% at Dp = 1 μm when $\bar{u}$ = 79 cm/sec. When the lower flow is used the penetration at 1 μm is 97 percent. However, if we consider the wind speed, as shown in Figure 2-15 from McFarland (1979) the inlet line penetration curve will be shifted further to the left to lower penetrations still. As stated later in the discussion of Sullivan (1962), only the particles below 1.5 μm have an appreciable effect on the BS. Consequently, the main effect of the lower flowrate is to reduce the penetration of particles less than 1.5 μm in an indeterminate manner.

Another test can be made of the hypothesis that the mailing caused a BS weight loss. Pashel and Egner report BS data from a monitoring site in Bethlehem identified as Main Office Garage (MOG) - Industrial. Since this site is in Bethlehem and the BS filters probably were not mailed, we expect these 60 filters to have a relationship consistent with Ferris (1973) and Holland (1979). Figure 3-14 is a frequency distribution of the ranked observations, which is in effect a smoothing process and the data do not appear to be inconsistent with the BNLM model. The 95 percent values appear to be almost

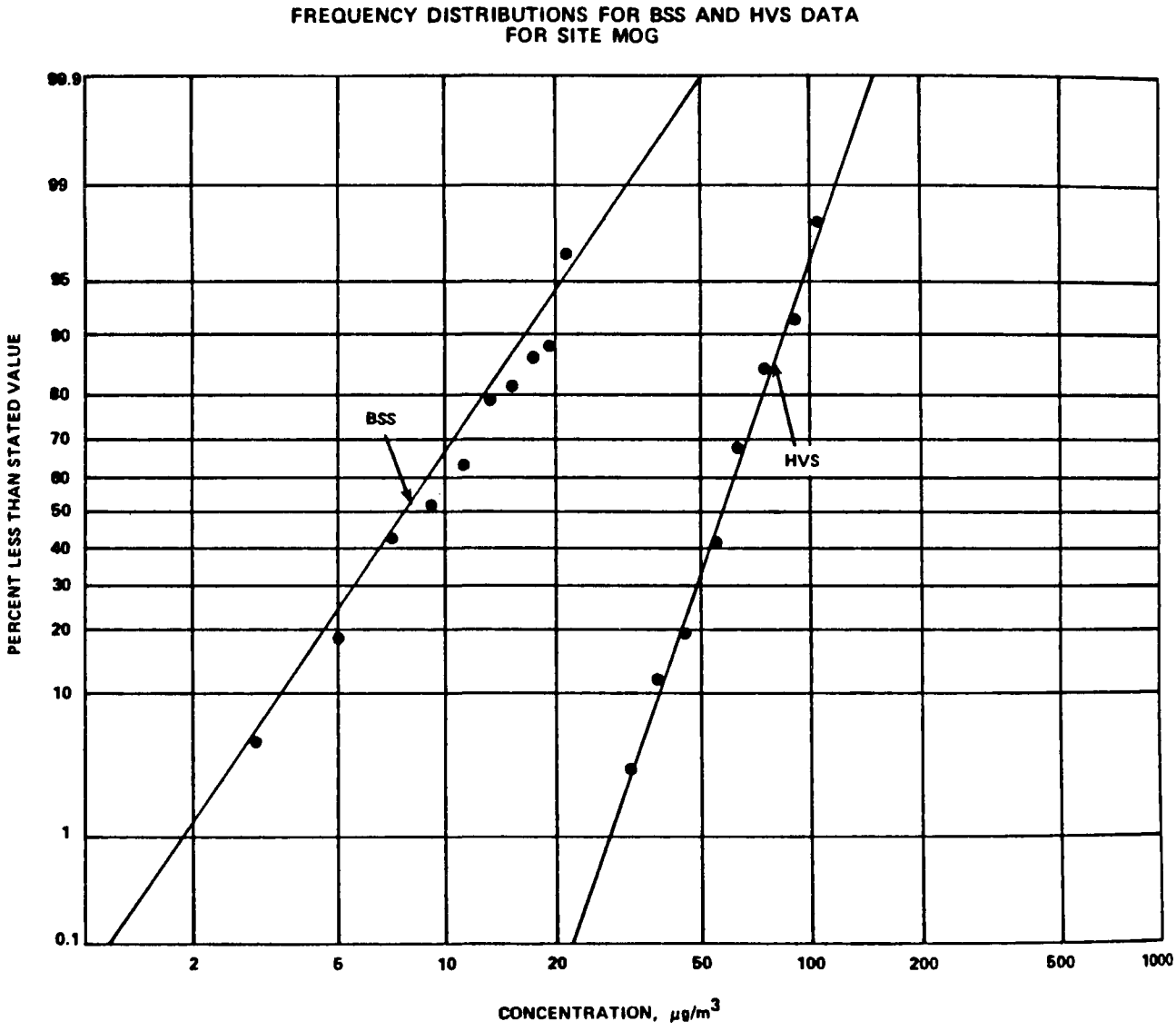



Figure 3-14. Frequency distributions of British Smoke and Hi-volume sampler data for site MOG in Bethlehem, PA, reported by Pashel and Egner (1980).

identical to the Ferris values of 20 BS and 91 TSP for 1967. The lower values diverge in a manner to place them above the EPA BNLM, indicating relatively high BS/TSP in comparison to the other stations.

Yet another test suggests itself from the geographical distribution of the sampling sites. Eight of the sixteen sites used in deriving the "AISI" line shown in Figure 3-9 are in Pennsylvania and the other eight are in Ohio (6), Kansas City, Missouri, and Colorado. The hypothesis to be tested is that the data for the eight locations in Pennsylvania are closer to the BNLM curve than the data from the eight more distant locations from which the filters were mailed. The median value of the distribution was chosen as a robust parameter for this test. Although Pashel and Egner do not list the median value they do list the geometric means and standard deviations of the distributions. One suspects that the geometric mean is a reasonably good estimator of the median, since the data for the MOG station appear to be fit by a lognormal distribution well and the data points shown do not lead to the rejection of the lognormal distribution by the Kolmogorov-Smirnov test (Mage, 1980c). Of course the lognormal distribution does not fit the physical boundary conditions for air pollution so it must only be considered as a first approximation. For example, the Johnson $S_B$ model (Mage, 1980a,b), which provides an upper and lower boundary, could be used to prevent the modeled concentration from either reaching 2 million ppm for a gas or 1 gm/cc for a TSP level which is predicted by the lines on Figure 3-14 to occur at a finite frequency. Figure 3-15 is a plot of the geometric means shown in Table 3-10. Of the eight points closest to the EPA BNLM curve, 6 are Pennsylvania (P) points and the two non-Pennsylvania points (non-P) are from Ohio. We can apply a Chi-Square test to these results as shown in Table 3-11.

TABLE 3-10. SUMMARY OF PASHEL AND EGNER (1980) BS AND TSP DATA FROM REPRESENTATIVE LOCATIONS IN THE U.S.A.

| Location | Site code | Geometric mean | | Geometric standard deviation | |
|---|---|---|---|---|---|
| | | TSP | BS | TSP | BS |
| Kansas City, MO | KAN-Industrial | 110.9 | 5.6 | 1.45 | 1.84 |
| Middletown, OH | RYS-Industrial | 212.3 | 11.4 | 1.72 | 1.94 |
| Bethlehem, PA | HAJ-Industrial | 76.2 | 8.1 | 1.63 | 1.80 |
| | MOG-Industrial | 57.3 | 7.8 | 1.36 | 1.86 |
| | NOR-Commercial | 50.4 | 7.5 | 1.40 | 1.97 |
| Pittsburgh, PA | HAZ-Industrial | 153.0 | 22.9 | 1.62 | 2.44 |
| | LAB-Residential | 64.9 | 5.4 | 1.46 | 2.22 |
| | MEL-Commercial | 89.8 | 11.1 | 1.45 | 1.80 |
| Anneville, PA | ISS-Rural | 59.2 | 4.7 | 1.51 | 1.81 |
| Cleveland, OH | DOR-Industrial | 167.6 | 18.3 | 1.64 | 1.66 |
| | RIT-Industrial | 151.4 | 16.7 | 1.48 | 1.55 |
| | RRC-Commercial | 55.2 | 5.8 | 1.72 | 1.94 |
| | STD-Industrial | 69.8 | 9.1 | 1.59 | 2.02 |
| | WTP-Industrial | 217.3 | 20.8 | 1.47 | 1.61 |
| Steelton, PA | MOR-Industrial | 69.1 | 8.6 | 1.55 | 1.82 |
| Pueblo, CO | HRS-Industrial | 79.2 | 4.0 | 1.77 | 1.96 |

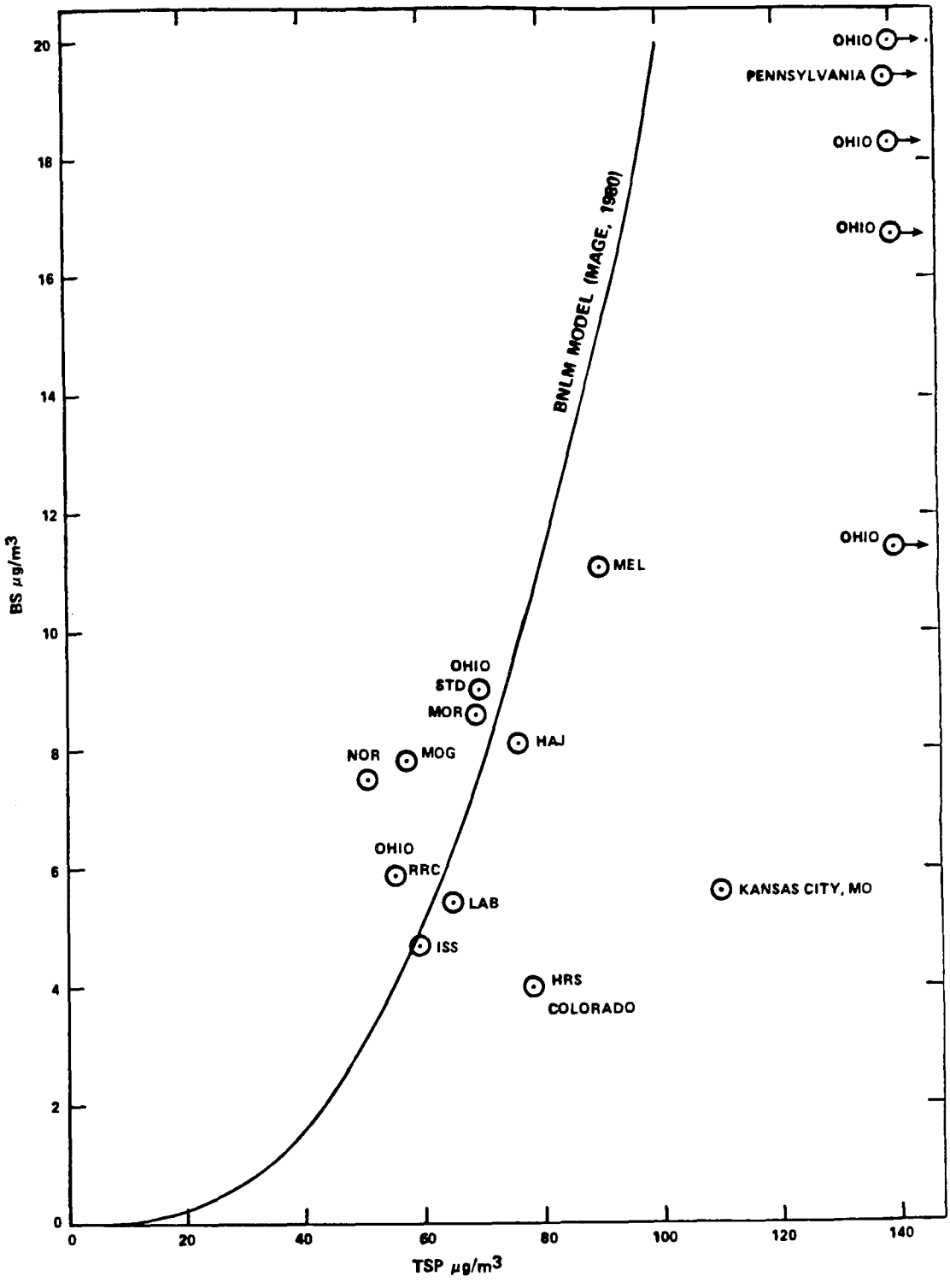



Figure 3-15. Pashel and Egner (1980) British Smoke vs Hi-volume sampler TSP data from sixteen locations in the USA plotted in relation to BNLM model of Mage (1980) and showing possible effect of filter mailing. Note that six of eight data points (MOR, MOG, NOR, HAJ, LAB, ISS) from Pennsylvania sites fall closer to the BNLM curve than data points indicated as being mailed over long distances from Ohio, Colorado, and Kansas City, Missouri.

TABLE 3-11. CHI-SQUARE TEST SUMMARY TABLE FOR PASHEL AND EGNER POINTS PLOTTED IN FIGURE 3-15

| Grouping | Expected | Observed |
|---|---|---|
| Closest to EPA BNLM Model | 8 P | 6 P + 2 non-P |
| Farthest from EPA BNLM Model | 8 non-P | 6 non-P + 2 P |

With 1 degree of freedom, the ~~sum of~~ chi-square statistic $\chi_1^2$ is 2 $(8-6)^2/8 = 1$ which is not significant. Consequently we cannot reject the hypothesis that mailing the filters influenced the BS values.

It thus appears that the AISI study results reported by Pashel and Egner (1980) are subject to the same types of criticisms, concerning measurement errors due to the mailing of particulate matter sampler filters, as were advanced in the 1976 Congressional Investigative Report (IR, 1976) in regard to TSP data obtained as part of the U.S. Environmental Protection Agency CHESS Program community epidemiology research studies. Taking into account the errors introduced by the mailing of samples in the Pashel and Egner (1980) AISI study and the other types of errors discussed above, the likely result would be underestimation of BS readings. Also, accounting for these errors, one can project that appropriate correction would bring the AISI results back into closer alignment with the mainstream of other available data and that the "AISI line" plotted in Figure 3-9 would become more consistent with the BNLM model curve.

3.5.5.3 Physical Phenomena Underlying TSP-BS Relationships--In the preceding discussion, it was demonstrated that the bounded nonlinear model proposed above describes or fits well essentially all presently available TSP-BS

comparison data in the mean. It is also important, however, to discuss physical factors or phenomena which likely underly the observed emperical relationships and to see how they relate to various specific components of the proposed model. Of particular importance is the understanding of how both BS and TSP measurements are impacted by variations in size fractions of the air particulate matter sampled and meteorological conditions, such as wind speed, present at the time of sampling.

For example, several studies have shown that removal of coarse particles, D >> 1 μm, has a negligible effect on the BS measurement of the sample. Hemeon (1953) reported that removal by settling of 84 percent of TSP from a stack sample produced no measurable difference in smoke stain optical density when compared to an in situ sample. Sullivan (1962) confirmed these results for ambient air in Australian samples by measuring the BS smoke reflectance using colocated samplers with and without a prefilter cascade impactor or cyclone to remove larger particles before they could reach the final BS filter (Table 3-12). Sullivan (1962) showed that a filter stage with a mass median diameter (MMD) cut of 1.5 μm (Lippman, 1959) had slight effect on the sample reflectance (Table 3-13). However, when another stage prefilter with a MMD cut of 0.6 μm was inserted the reflectance of the stains was greatly enhanced (Table 3-14). Sullivan concluded that "only particles of the order of a micron or less have significant effect on the production of smoke stains on filter samples." In addition, Waller, Brooks, and Cartwright (1963) reported electron microscope studies of particulate matter collected by BS devices during an epidemiological study begun in 1954. During the episode periods with documented evidence of excess mortality and excess morbidity the MMD of the particles estimated from the microscopy studies ranged from 0.5 to 1.0 μm.

TABLE 3-12. COMPARISON BETWEEN FILTER PAPER STAINS WITH AND WITHOUT CYCLONE PRE-FILTERS USING TWO-INCH DIAMETER HOLDER AND SAMPLING RATE OF 44 LITERS PER MINUTE

| No. of Test | Reflectance of Stains | | Transmission of Stains | |
|---|---|---|---|---|
| | With Cyclone | Without Cyclone | With Cyclone | Without Cyclone |
| 1 | 78.5 | 78.0 | 77.5 | 78.0 |
| 2 | 84.0 | 84.0 | 83.5 | 82.0 |
| 3 | 80.0 | 80.5 | 78.0 | 79.0 |
| 4 | 73.5 | 71.0 | 71.5 | 72.5 |
| 5 | 76.0 | 76.0 | 73.5 | 75.0 |
| 6 | 81.5 | 80.5 | 79.0 | 79.5 |

TABLE 3-13. COMPARISON BETWEEN FILTER PAPER STAINS WITH AND WITHOUT THREE STAGES OF CASELLA CASCADE IMPACTOR IN SERIES AS PRE-FILTER USING ONE-INCH DIAMETER HOLDERS AND SAMPLING RATE OF 17.5 LITERS PER MINUTE

| No. of Test | Reflectance of Stains | | Transmission of Stains | |
|---|---|---|---|---|
| | With Pre-filter | Without Pre-filter | With Pre-filter | Without Pre-filter |
| 1 | 74.5 | 74.5 | 72.5 | 73.0 |
| 2 | 79.0 | 78.5 | 77.0 | 76.0 |

Very few particulate aggregates of equivalent diameter greater than 2 μm were observed in their samples. On the other hand, other studies suggest that the size of particles sampled by BS measurement methods depend upon the precise size of the intake funnel used and may range upwards to 3 μm or more in some cases.

TABLE 3-14. COMPARISON BETWEEN FILTER PAPER STAINS WITH AND WITHOUT FOUR STAGES OF CASCADE IMPACTOR IN SERIES AS PRE-FILTER USING ONE-INCH DIAMETER HOLDERS AND FLOW RATE OF 17.5 LITERS PER MINUTE

| No. of Test | Reflectance of Stains | | Transmission of Stains | |
|---|---|---|---|---|
| | With Pre-filter | Without Pre-filter | With Pre-filter | Without Pre-filter |
| 1 | 92 | 78.5 | 90 | 77 |
| 2 | 90 | 76.0 | 89 | 73.5 |

Because the BS is a stochastic subset of the TSP there is little reason to expect BS measurements to be linearly related with TSP measurements. The ratio of BS to TSP should be bounded, $0 < BS/TSP < 1$. The lower limit of zero corresponds to the British summer conditions with minimal combustion processes upwind and relatively large amounts of light colored earth crustal material suspended in the atmosphere. Prior to establishment of smokeless zones in London the upper limit of unity corresponded to the British winter conditions when the temperatures fell to 0°C, the air was calm, and strong temperature inversions existed at the ground surface extending upwards above the chimneys of the neighboring houses. In the summer case, TSP is much greater than BS. However, in the extreme winter case, TSP is almost entirely BS since all the large particles would be removed from the atmosphere by Stokes law settling and the predominant particles present would be those particles that settled slowly or were small enough to remain suspended by Brownian motion. This

relationship was also shown by Lawther, Lord, Brooks and Waller (1973, 1977) who reported that after the introduction of smokeless zones in London TSP and BS reading were still similar on days of high pollution and calm or low wind speed, though widely divergent at most other times. This is an important factor to be understood because several of the incidences of high pollution which produced mortality and morbidity data discussed in Chapter 14 arose at the upper limit of BS/TSP $\cong$ 1.

In practice, circumstances can also arise which will lead to the paradox of BS measures being even greater than TSP. This will be briefly discussed here, because this situation illustrates some deficiencies in the TSP measurement when flow rate is uncontrolled or when TSP concentration is changing rapidly. At least four studies in the literature report data with British smoke greater that TSP. Results obtained in one study by Waller and Lawther (1955), are shown in Table 3-15. As shown in that table, data obtained in London at St. Bartholomew's Hospital, between 4 p.m. and 7 p.m., indicated that the BS level was 3980 $\mu g/m^3$ and the co-located TSP level was 3580 $\mu g/m^3$. Note that this table is cited incorrectly in Holland et al. (1979) on page 582: "At that time, the concentrations, as expressed in $\mu g/m^3$, were similar to one another [TSP (HV) 4700 $\mu g/m^3$ (sic), with smoke (BS) 4640 $\mu g/m^3$ (sic) over a 6-hour period]." Between 4 p.m., and 10 p.m. the correct values are BS = 4700 $\mu g/m^3$ and TSP = 4640 $\mu g/m^3$.

In a second study done by Lee, Caldwell and Morgan (1972) during the heating season at Salford, England, the smokeshade data were often significantly greater than the Hi-vol data as shown in Figure 3-16. In a third study, by Ball and Hume (1977), at London County Hall they report that, between 1600 hours on Dec. 8th and 1600 hours on Dec. 9th, 1975, the Hi-vol TSP was 178 $\mu g/m^3$ and BS was 182 $\mu g/m^3$, as was shown in Figure 3-10. The fourth study (WSL, 1968) is discussed elsewhere in this chapter (see page 3-58).

TABLE 3-15. CONCENTRATION OF SMOKE AND SULPHUR DIOXIDE ON JANUARY 19/20, 1955. COMPARISON OF METHODS*

| | Smoke Concentration, mg. per cubic meter | | | Sulphur Dioxide p.p.m. | |
|---|---|---|---|---|---|
| Period** | Standard D.S.I.R. Method | Short-period filter Paper | High-volume Sampler | Standard D.S.I.R. Method | Short-period Colori-metric |
| 11:30 a.m. - 4 p.m. | 1.35 | 1.94 | --- | 0.44 | --- |
| 4 - 7 p.m. | 3.98 | 3.18 | 3.58 | 0.66 | 0.63 |
| 7 - 10 p.m. | 5.42 | 5.08 | 5.70 | 0.66 | 0.52 |
| 10 p.m. - 10:30 a.m. | 1.27 | --- | --- | 0.52 | --- |

*From Waller and Lawther (1955).
**The periods quoted here refer to those for the standard D.S.I.R. method. Those for the other two methods are similar, but the terminal times differ slightly in some cases.

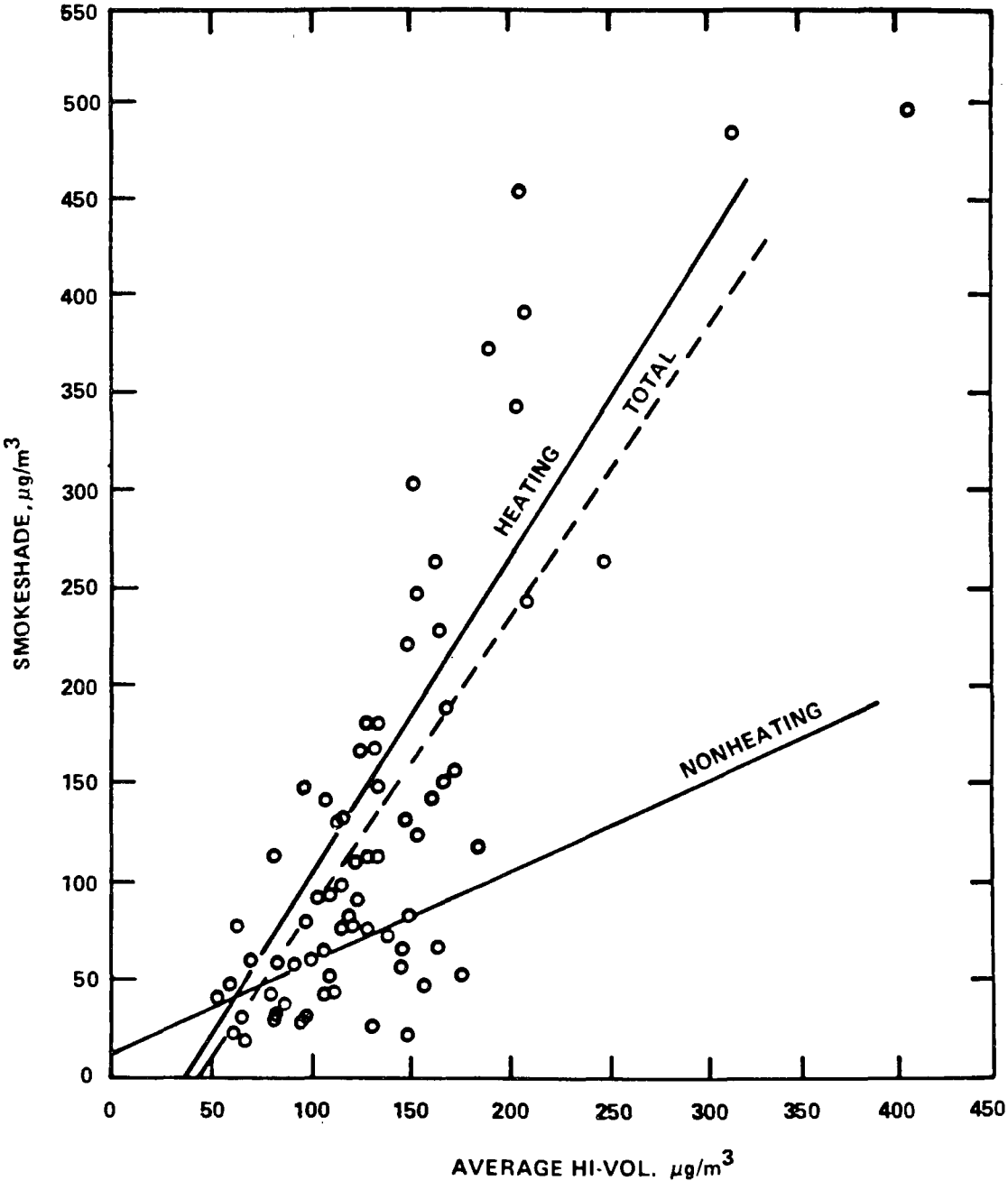



Figure 3-16. Smokeshade Hi-vol correlations for Salford, England showing occurrences of a significant number of days with smokeshade greater than total suspended particulates. From Lee et al. (1972).

The ratio of 1.022 in the study by Ball and Hume is probably due to the joint occurrence of a large negative weighing error of the TSP filter and a large negative reflectance error of the BS filter. This can be clearly seen by inspection of the regression plots of duplicate reflectometric and duplicate gravimetric measurements reported by Muylle, Hachez and Verduyn (1978). As shown in Figures 3-17 and 3-18 below, an infrequent joint occurrence of ±25 $\mu g/m^3$ is quite possible.

Several possible explanations occur for the high ratios of the Salford data reported by Lee et al. (1972). One possibility may be that in Salford, the particles may have been darker than the particles used in the original smoke shade calibration so that an equivalent mass reads as a higher BS level. However, an equally likely explanation may be due to the variation in Hi-vol flow rates.

When a Hi-volume sampler is run without flow control, the flow rate decreases nonlinearly with time as particulate matter builds up on the filter, according to Harrison, Nader, and Fugman (1960) and Dams and Heindryckx (1973). Cohen (1973) reported that the penetration of the hi-volume sampler increased by 7 percent as flowrate fell from 60 cfm to 30 cfm. This is indicative of higher particle wall losses and impactions on the asymmetric hi-volume shelter at the higher flowrates. Consequently, due to the flowrate reduction, the hi-volume collects more air to sample in the first half of the run than in the second half. Therefore, if the pollution level is increasing with time during the run, the hi-volume will likely sample in a biased manner; i.e., comparatively more of the cleaner portion than the dirtier portion would be sampled. As described in more detail in Appendix 3A, this may result in an underestimate of the true average pollution during the whole period and the assumption that

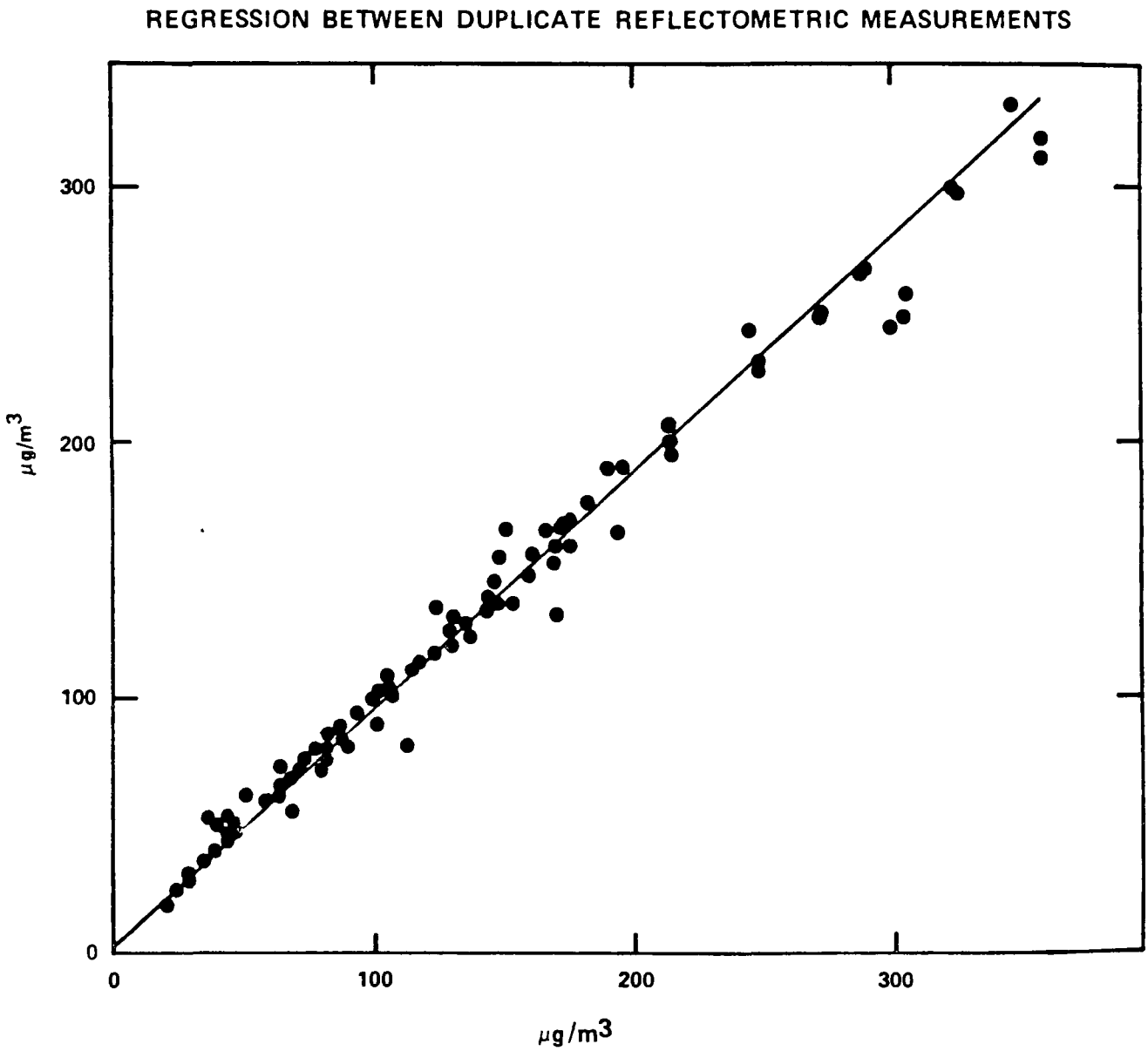



Figure 3-17. Correlation between duplicate reflectometric measurements showing deviations of up to 25 $\mu g/m^3$. From Muylle et al. (1978).

REGRESSION BETWEEN DUPLICATE GRAVIMETRIC MEASUREMENTS

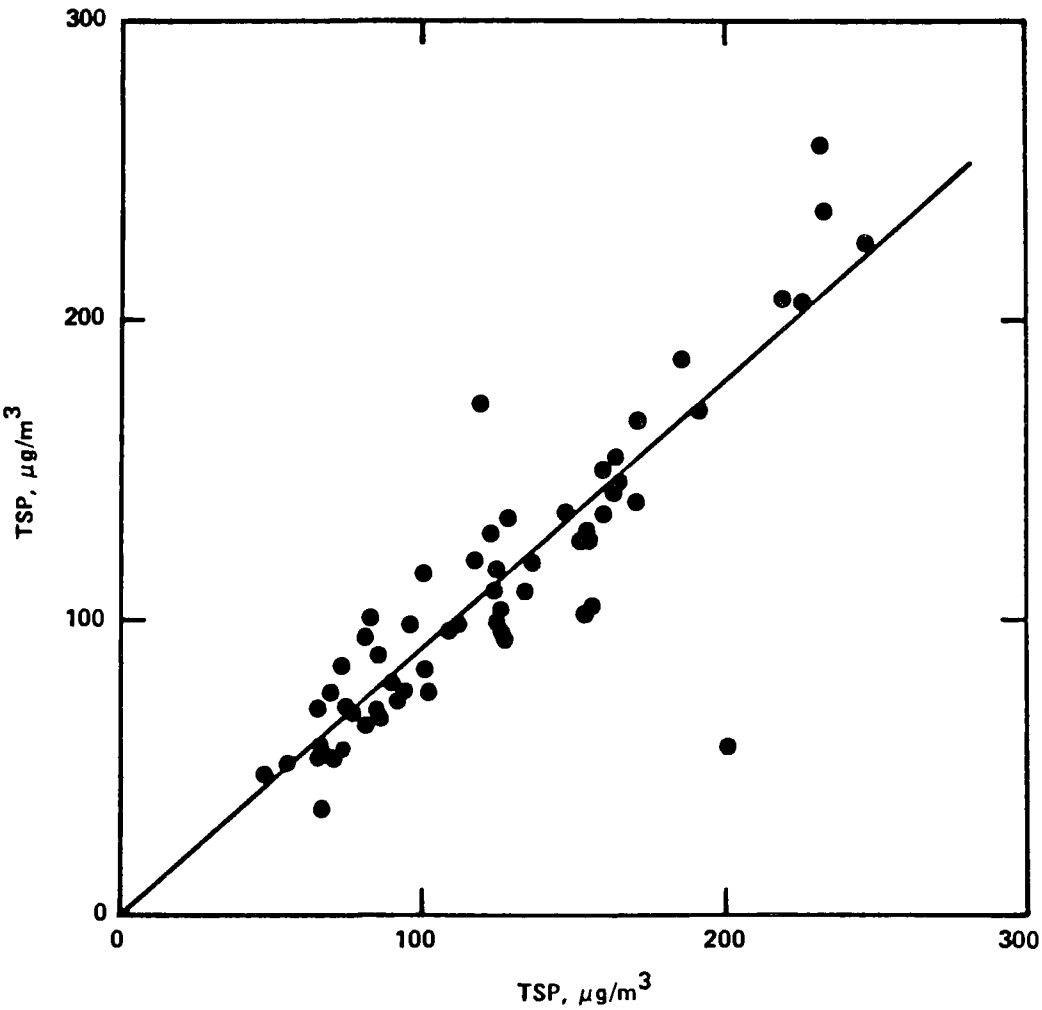



Figure 3-18. Correlation between duplicate gravimetric measurements showing deviations greater than 25 $\mu g/m^3$. From Muylle et al. (1978).

the average flow rate during the sampling period is half of the initial flow rate plus final flow rate also leads to an underestimate. Lee et al. (1972), Ferris et al. (1973), and most other United States researchers, however, routinely averaged the initial and final flow rate readings for most of the Hi-vol sampler data taken without flow control (Lee, 1974). The result will usually be an underestimate of the TSP, but the BS method sampling at an order of magnitude lower flow rate, would not likely be affected as greatly. If BS $\cong$ TSP and the TSP measurement is biased low, then BS/TSP > 1 is possible, creating a paradox of a part being apparently greater than the whole. Such "paradoxical" observations, however, have in fact been made in a number of studies, as alluded to above.

If the average flow rate is computed correctly by integrating $\bar{v} = \frac{1}{T} \int_0^T v \, dt$, then $x = M/V\,T$, and the Hi-vol value will be the same value for x computed by the BS method. Fortunately, the TSP data reported by the British workers Ball and Hume (1977 ~~1972~~) and Waller and Lawther, (1955) were analyzed by integrating the flowrate versus time so this factor does not influence their reported results discussed earlier in this chapter.

In summary, as stated by Harrison et al. (1960), the effect cited will reduce the measured TSP during periods of rising pollution. Similarly, an opposite effect occurs when the pollution levels are falling. The measured TSP will be greater than the BS due to enhanced flow in the dirtier beginning period and lower flow in the cleaner end period. Since Lee et al. (1972) were using the average of initial and final flow rates for the TSP flows, a correction to the data from the recorded ratio of initial to final flow would tend to raise the TSP values. The Salford data, where BS > TSP, could be explained if the points above the BS = TSP line occurred with increasing pollution levels and the points below occurred with decreasing pollution.

The most likely explanation for the case cited by Waller and Lawther (1955) is that the rising pollution could have biased the Hi-vol data toward lower readings. The use of 3-hour samples with heavy pollution present was intended to prevent both the Hi-vol from burning out and the BS from reaching optical saturation which would stabilize the BS readings (increase in mass on the BS filter produces no change in reflectivity). In some cases, Waller reported that a heavy wet fog could saturate the filter paper and restrict flow. When flow decreased in this manner, it would not be related to the mass of particles on the filter and the correction procedures outlined by Dams (1973) could not be followed. Dams and Heindryckx (1973) determined "weight factors" for initial and final flow rates so the volume sampled could be obtained without either averaging or integration of variations in flow rate over the sampling period.

3.5.5.4 Summary and Conclusions for BS-TSP Comparisons--In the above discussion, information was reviewed on BS-TSP comparisons derived from a number of studies published over the past twenty years and reporting results obtained from the sampling of air in many disparate geographic areas (Britain, other European countries, and the United States) and varying time periods (from the early 1950s to the mid 1970s). It was earlier hinted at and is now clear from a present perspective, with the advantage of viewing the various BS-TSP comparison data sets together in relation to each other, that a nonlinear relationship exists between BS and TSP measurements obtained with colocated samplers. That is, regardless of where or when such readings were obtained, TSP values were usually found to be two or more times higher than corresponding BS readings up to BS levels of about 100 $\mu g/m^3$. At higher levels, however, the TSP and BS readings tend to converge toward each other, such that TSP/BS approaches unity

at BS levels of 500 $\mu g/m^3$ or more. Thus, above 500 $\mu g/m^3$ or so, BS and TSP readings from colocated samplers are essentially identical.

In carrying out analyses of BS-TSP comparison data sets, various investigators in the past generally employed linear regression analyses in an effort to define straight lines that best fit data points obtained by them over a limited range of BS-TSP values. They also often extrapolated the thusly defined straight lines to BS-TSP values beyond the range of their emperical observations and found inconsistencies between the BS-TSP relationships implied by their line(s) and those defined by linear analyses of different BS-TSP comparison data sets obtained at other times or locations. Such apparent inconsistencies between BS-TSP relationships, arising from linear regression analyses of various data sets obtained over limited and often different ranges of BS-TSP values, have contributed to and reinforced the view that no consistent relationships exist between BS and TSP measurements obtained at different locations or even at different times at the same location. Paradoxically, this view has gained widespread credence despite the concurrent realization that corresponding BS-TSP readings are nonlinearly related.

Recognition of the acknowledged nonlinearity of BS-TSP relationships and the necessity to meet certain boundary conditions defined by emperical observations and certain theoretical considerations as sine-qua-non starting points led to the formation of a "bounded nonlinear model" (BNLM) proposed in this chapter as a unifying concept or means by which to interconvert monthly or annual average BS and TSP values obtained under vastly different circumstances. The BNLM essentially employs a power function defining a nonlinear relationship that meets the boundary conditions of (1) BS $\rightarrow$ 0, where TSP $\rightarrow$ 0 and (2) BS $\rightarrow$ TSP,

as BS → ∞; or, in other words, when there is no particulate matter in the air, both TSP and BS readings must be zero or tend toward zero and, also, they must tend to converge toward each other as BS values become very large as observed in empirical BS-TSP comparison studies. In addition, the particular BNLM model chosen defines a curve which fits other empirically-derived observations to the effect that TSP/BS = 2 at 100 $\mu g/m^3$ BS and TSP/BS = 4/3 at 250 $\mu g/m^3$ BS. Plotting of corresponding BS-TSP values from numerous published BS-TSP comparison studies reveals that the BNLM model fits well virtually all presently available BS-TSP comparison data, in the mean.

Only the reported results from one recently obtained data set comparing BS and TSP values from colocated samplers at 16 locations in the United States appear, at first sight, to be greatly inconsistent with the BNLM model. Closer inspection of the study, however, reveals that numerous methodological errors were made in conducting the study, including the failure to follow published standard procedures employed in the collection of BS data earlier used in British epidemiology studies on the health effects of particulate matter and, also, in most other BS-TSP comparison studies. Nevertheless, when the particular methodological errors and other deficiencies are evaluated, it becomes apparent that some of the basic observations reported may not be as inconsistent with other published results and the BNLM model as initially seems to be the case.

## 3.7 REFERENCES


Apling, A. J., Keddie, A. W. C., M-L. P. M. Weatherley, and M. L. Williams, The High Pollution Episode in London, December, 1975. LR263(AP), Warren Spring Laboratory, Stevenage, England, 1977a.

Bailey, D. L. R., and H. L. Nicholson. Smoke Filter Calibration Curve: 1-cm Filter Holder. LR 89 (AP), Warren Spring Laboratory, Stevenage, England, October 1968.

Ball, D., and R. Hume. The relative importance of vehicular and domestic emissions of dark smoke in Greater London in the mid-1970's, the significance of smoke shade measurements, and an explanation of the relationship of smoke shade to gravimetric measurements of particulate. Atmos. Environ. 11:1065-1073, 1977.

Barnes, R. Duplicate measurements of low concentrations of smoke and sulphur dioxide using two "National Survey" samplers with a common inlet. Atmos. Environ. 7:901-904, 1973.

Bourbon, P. A Propos de la Mesure des Poussieres et de l'Anhydride Sulfureux, Étude Réalisée a la Demande de la C.E.E., 1980.

British Standards Institution. Methods for the Measurement of Air Pollution. Part 2: Determination of Concentration of Suspended Matter. B.S. 1747, British Standards Institution, London, 1963.

British Standards Institution. Methods for the Measurement of Air Pollution. Part 3: Determination of Concentration of Sulphur Dioxide. B.S. 1747, British Standards Institution, London, 1963.

Cohen, A. L. Dependence of Hi-vol measurements on airflow rate. Environ. Sci. Technol. 7:60-61, 1973.

Clayton, P. The Filtration Efficiency of a Range of Filter Media for Sub-Micrometre Aerosols. LR280(AP), Warren Spring Laboratory, Stevenage, England, 1978.

Commins, B. T., and R. E. Waller. Observations from a ten year study of pollution at a site in the city of London. Atmos. Environ. 1:49-68, 1967.

Dalager, S. Correlations between methods for measuring suspended particulates in ambient air. Atmos. Environ. 9:687-691, 1975.

Dalager, S. Sammenligning af metoder til maling of svaevestov og svovldioxide. Environplan A/S, Copenhagen, 1974.

Douglas, J. W. B., R. E. Waller. Air pollution and respiratory infection in children. Br. J. Prev. Soc. Med. 20:1-8, 1966.

Additional References Recommended for Consideration in Chapter 3, $PM/SO_x$

Bailey, D. L. R., and P. Clayton. The measurement of suspended particulate and carbon concentration in the atmosphere using standard smoke shade methods. Report LR 325 (AP), Warren Spring Laboratory, Stevenage, 1980.

Heindryckx, R. Significance of total suspended particulate matter, as determined by optical density measurements. BECEWA, 1974. (as cited by Kretzschmar, 1975).

Ledbetter, J. O., and B. P. Cerepeka. Obscuration versus aerosol concentration. J. Environ. Sci. Health A15(2):173-181, 1980.

Rosen, H., A. D. A. Hansen, R. L. Dod, T. Novakov. Soot in urban atmospheres: Determination by an optical absorption technique. Science 208:741-744, 1980.

Swinford, R. L., and D. J. Kolaz. Field correlation of TSP data from a continuous particulate monitor and high volume air samples. Paper 80-38.3, 73rd APCA, Montreal, Canada, 1980.

Wallin, S. C. Calibration of the D.S.I.R. Standard Smoke Filter for Diesel Smoke. Int. J. Air Wat. Poll. 9:351-356, 1965; and discussions by Lindsey, A. J., M. Corn, S. R. Craxfor, L. R. Reed, and S. C. Wallin, IBID, 10:73-76, 1966.

## 3.7 REFERENCES


Apling, A. J., A. W. C. Keddie, M-L. P. M. Weatherley, and M. L. Williams, The High Pollution Episode in London, December, 1975. LR263(AP), Warren Spring Laboratory, Stevenage, England, 1977.

Bailey, D. L. R., and H. L. Nicholson. Smoke Filter Calibration Curve: 1-cm Filter Holder. LR89(AP), Warren Spring Laboratory, Stevenage, England, October 1968.

Ball, D. J., and R. Hume. The relative importance of vehicular and domestic emissions of dark smoke in Greater London in the mid-1970's, the significance of smoke shade measurements, and an explanation of the relationship of smoke shade to gravimetric measurements of particulate. Atmos. Environ. 11:1065-1073, 1977.

Barnes, R. Duplicate measurements of low concentrations of smoke and sulphur dioxide using two "National Survey" samplers with a common inlet. Atmos. Environ. 7:901-904, 1973.

Bourbon, P. A Propos de la Mesure des Poussieres et de l'Anhydride Sulfureux, Etude Réalisée a la Demande de la C.E.E., 1980.

British Standards Institution. Methods for the Measurement of Air Pollution. Part 2: Determination of Concentration of Suspended Matter. B.S. 1747, British Standards Institution, London, England, 1963.

British Standards Institution. Methods for the Measurement of Air Pollution. Part 3: Determination of Concentration of Sulphur Dioxide. B.S. 1747, British Standards Institution, London, England, 1963.

Cohen, A. L. Dependence of Hi-Vol measurements on airflow rate. Environ. Sci. Technol. 7:60-61, 1973.

Clayton, P. The Filtration Efficiency of a Range of Filter Media for Sub-Micrometre Aerosols. LR280(AP), Warren Spring Laboratory, Stevenage, England, 1978.

Commins, B. T., and R. E. Waller. Observations from a ten year study of pollution at a site in the city of London. Atmos. Environ. 1:49-68, 1967.

Dalager, S. Correlations between methods for measuring suspended particulates in ambient air. Atmos. Environ. 9:687-691, 1975.

Dalager, S. Samenligning af metoder til maling af svaevestov og svovldioxid. In: Luft kvalitets undersogelese Aalborg. 1. Svaevestovmalinger Norresundby, April-Juli 1973. Environplan A/S, Copenhagen, Denmark, April 1974.

Dams, R., and R. Heindryckx. A high-volume air sampling system for use with cellulose filters. Atmos. Environ. 7:319-322, 1973.

Douglas, J. W. B., and R. E. Waller. Air pollution and respiratory infection in children. Br. J. Prev. Soc. Med. 20:1-8, 1966.

Eickelpasch, D., and R. Hotz. Comparison of various outer air measurements. Stahl und Eisen 98:469-475, 1978.

Ellison, J. McK. The estimation of particulate air pollution from the soiling of filter paper. Staub Reinhalt. Luft 28:28-36, 1968.

Ferris, B. G. Jr., J. R. Mahoney, R. M. Patterson, and M. W. First. Air quality, Berlin, New Hampshire, March 1966 to December 1967. Am. Rev. Respir. Dis. 108:77-84, 1973.

Firket, M. Bull. The cause of the symptoms found in the Meuse Valley during the fog of December, 1930. Bull. Acad. R. Med. Belg. 683-741, 1931.

Fry, J. D. Determination of Sulphur Dioxide in the Atmosphere by Absorption in Hydrogen Peroxide Solution--The Effect of Evaporation of the Solution During Sampling. SSD/SW/M.246 Central Electricity Generating Board, South Western Region, England, April 1970.

Hagen, L. J., and N. P. Woodruff. Air pollution from duststorms in the Great Plains. Atmos. Environ. 7:323-332, 1973.

Hale, W. E., and N. E. Waggoner. The overall variability of CoH unit values and methods for increasing the accuracy of readout. J. Air Pollut. Control Assoc. 12:322-323, 1962.

Harrison, W. K. Jr., J. S. Nader, and F. S. Fugman. Constant flow regulators for the high-volume air sampler. Am. Ind. Hyg. Assoc. J. 21:115-120, 1960.

Hemeon, W. C. L., G. F. Haines, Jr., and H. M. Ide. Determination of haze and smoke concentration by filter paper samplers. Air Repair 3:22-28, 1953.

Herpertz, E. A simple long-term measuring procedure for determining the dust concentration in the near-ground air layer (LIB Method). Staub Reinhalt. Luft 29:12-18, 1969.

Holland, W. W., A. E. Bennett, I. R. Cameron, C. du V. Florey, S. R. Leeder, R. S. F. Schilling, A. V. Swan, and R. E. Waller. Health effects of particulate pollution: reappraising the evidence. Am. J. Epidemiol. 110:527-659, 1979.

Horvath, H., and R. J. Charlson. The direct optical measurement of atmospheric air pollution. J. Am. Ind. Hyg. Assoc. 30:500-509, 1969.

Human Studies Laboratory. Health Consequences of Sulphur Oxides: A Report from CHESS, 1970-1971. EPA-650/1-74-004, U.S. Environmental Protection Agency, May 1974.

Ingram, W. T. Smoke Curve Calibration. APTD-0928, U.S. Department of Health, Education, and Welfare, Public Health Service, March, 1969.

Ingram, W. T., and J. Golden. Smoke curve calibration. J. Air Pollut. Control Assoc. 23:110-115, 1973.

Johnson, N. L. Systems of frequency curves generated by methods of translation. Biometrika 36:149-176, 1949.

Katz, M. Guide to the Selection of Methods for Measuring Air Pollutants. WHO/AP/67.29, World Health Organization, Geneva, 1967.

Katz, M., and H. P. Sanderson. Filtration methods for evaluation of aerosol contaminants. In: Symposium on Instrumentation in Atmospheric Analysis. Special Technical Publication No. 250, American Society for Testing and Materials, Philadelphia, PA, 1958. pp. 29-41.

Kretzschmar, J. G. Comparison between three different methods for the estimation of the total suspended matter in urban air. Atmos. Environ. 9:931-934, 1975.

Laskus, L. Untersuchung der Korngrössenverteilung des atmosphärischen Staubes in Bodennähe. Staub Reinhalt.Luft 37:299-306, 1977.

Laskus, L., and D. Bake. Erfahrungen bei der Korngrössenanalyse von Luftstäuben mit dem Andersen. Kaskadenimpaktor. Staub Reinhalt. Luft 36:102-106, 1976.

Lawther, P. J., A. G. F. Brooks, P. W. Lord, and R. E. Waller. Day-to-day changes in ventilatory function in relation to the environment. Part I. - Spirometric values. Part II. Peak expiratory flow values. Environ. Res. 7:27-53, 1974.

Lawther, P. J., A. G. F. Brooks, P. W. Lord, and R. E. Waller. Day-to-day changes in ventilatory function in relation to the environment. Part III. Frequent measurement of peak flow. Environ. Res. 8:119-130, 1974.

Lawther, P. J., P. W. Lord, A. G. F. Brooks, and R. E. Waller. Air pollution and pulmonary airway resistance: a six year study with three individuals. Environ. Res. 13:478-492, 1977.

Lee, R. E. Jr., J. S. Caldwell, and G. B. Morgan. The evaluation of methods for measuring suspended particulates in air. Atmos. Environ. 6:593-622, 1972.

Lee, R. E., Jr. Measuring particulate matter in air. In: Instrumentation for Monitoring Air Quality. Special Technical Publication No. 555, American Society for Testing and Materials, Philadelphia, PA, 1974. pp. 143-156.

Lippman, M. Review of cascade impactors for particle size analysis and a new calibration for the Casella Cascade Impactor. J. Am. Ind. Hyg. Assoc. 20:406, 1959.

Lisjack, G. J. Comparison of High Volume and Tape Sampler Data, 1976. Allegheny County Health Department, Bureau of Air Pollution Control, Pittsburgh, PA, May 1977.

Liu, B. Y. H., P. Y. H. Pui, K. L. Rubow, and G. A. Kuhlmey. Research in Air Sampling Filter Media. Progress Report EPA Grant 804600, University of Minnesota, Minneapolis, MN, May 1978.

Logan, W. P. D. Mortality in the London fog incident, 1952. Lancet 1 (6755): 336-338, 1953.

McFarland, A. R. Test Report -- Wind Tunnel Evaluation of British Smoke Shade Sampler. Air Quality Laboratory Report 3565/05/79/ARM, Texas A&M University, College Station, TX, May 1979.

Mage, D. T. An empirical model for the Kolmogorov - Smirnov Statistic. J. Environ. Sci. Health Part A. 15: 1980c.

Mage, D. T. An explicit solution for $S_B$ parameters using four percentile points. Technometrics 22:247, May 1980a.

Mage, D. T. Frequency distributions of hourly wind speed measurements. Atmos. Environ. 14:367-374, 1980b.

Martin, A., and F. R. Barber. Some measurements of loss of atmospheric sulphur dioxide near foliage. Atmos. Environ. 5:345-352, 1971.

McKee, H. C., R. E. Childers, and O. Saenz, Jr. Collaborative Study of Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method). APTD-0904, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1971.

Ministry of Pensions and National Insurance: Report on an Enquiry into the Incidence of Incapacity for Work. II. Incidence of Incapacity for Work in Different Areas and Occupations. Her Majesty's Stationery Office, London, England, 1965.

Moulds, W. Some instrumental variations arising in routine air pollution measurements. Int. J. Air Water Pollut. 6:201-203, 1962.

Muyulle, E., D. Hachez, and G. Verduyn. An evaluation of measuring methods for particulate matter. In: Air Pollution Reference Measurement Methods and Systems. T. Schneider, H. W. deKoning and L. J. Brasser, eds., Elsevier Scientific Publishing Co., Amsterdam, Netherlands, 1978. pp.113-125.

Natanson, G. Referenced by N. A. Fuchs in The Mechanics of Aerosols, MacMillan, New York, 1964. p. 112.

National Research Council. Airborne Particles. National Academy of Sciences. Washington, DC, 1978a, pp. 243-288.

National Research Council. Sulfur oxides. National Academy of Sciences. Washington, DC, 1978b. pp. 180-209.

Organization for Economic Co-operation and Development. Methods of Measuring Air Pollution. Paris, France, 1965.

Park, J. C., D. M. Keagy, and W. W. Stalker. Developments in the use of the AISI automatic smoke sampler. J. Air Pollut. Control Assoc. 10:303-306, 1960.

Pashel G. E., and D. R. Egner. A comparison of ambient suspended particulate matter concentrations as measured by the British Smoke Sampler and the High Volume Sampler at 16 sites in the United States. Atmos. Environ., in press, 1980.

Patterson, R. K. Aerosol contamination from High-Volume Sampler exhaust. J. Air Pollut. Control Assoc. 30:169-171, 1980.

Pedace, E. A., and E. B. Sansone. The relationship between "soiling index" and suspended particulate matter concentrations. J. Air Pollut. Control Assoc. 22:348-351, 1972.

Ruppersberg, G. Die anderung des maritimen Dunst - Streukoeffizienten mit der relativen Feuchte. Meteorol. Forschungsergeb. Reihe B, 4:37-60, 1971.

Saucier, J. Y., and E. B. Sansone. The relationship between transmittance and reflectance measurements of "soiling index". Atmos. Environ. 6:37-43, 1972.

Simon, M. J. Comparison of High Volume and Tape Sampler Data, 1973-75. Allegheny County Health Department, Bureau of Pollution Control, Pittsburgh, PA, 1976.

Stalker, W. W., Dickerson, R. C., and G. D. Kramer. Atmospheric sulfur dioxide and particulate matter: a comparison of methods of measurements. J. Am. Ind. Hyg. Assoc. 24:68-79, 1963.

Steel, R. G. D., and J. H. Torrie. Principles and Procedures of Statistics, McGraw Hill, Inc., New York, 1960. pp. 80-83.

Stöber, W. Sampling and evaluation of aerosols under biomedical aspects. Gesellschaft für Aerosolforschung, 1979.

Sullivan, J. L. The calibration of smoke density. J. Air Pollut. Control Assoc. 12:474-478, 1962.

U. S. Congress. House of Representatives. Committee on Science and Technology. The Environmental Protection Agency's Research Program with Primary Emphasis on the Community Health and Environmental Surveillance System (CHESS): An Investigative Report. U. S. Government Printing Office, Washington, DC, November 1976.

U. S. Environmental Protection Agency. Addendum to "The Health Consequences of Sulphur Oxides: A Report from CHESS, 1970-1971," May 1974. EPA-600/1-80-021, U.S. Environmental Protection Agency, Cincinnati, OH, April 1980.

Waller, R. E. Experiments on the calibration of smoke filters. J. Air Pollut. Control Assoc. 14:323-325, 1964.

Waller, R. E., A. G. F. Brooks, and J. Cartwright. An electron microscope study of particles in town air. Int. J. Air Water Pollut. 7:779-786, 1963.

Waller, R. E., and P. J. Lawther. Some observations on London fog. Br. Med. J. 2:1356-1358, 1955.

Warren Spring Laboratory. Measurement of Atmospheric Smoke and Sulphur Dioxide: Reproducibility of Results. RR/AP/70, Warren Spring Laboratory, Stevenage, England, August 1962.

Warren Spring Laboratory. National Survey of Smoke and Sulphur Dioxide: Instruction Manual. Warren Spring Laboratory, Stevenage, England, 1966.

Warren Spring Laboratory. Accuracy and representativeness of the National Survey data. In: National Survey of Air Pollution, 1961-1971. Volume 5. Scotland, Northern Ireland, Accuracy of data, Index. Warren Spring Labotory, Stevenage, England, January 1975. pp. 111-119.

Warren Spring Laboratory. The National Survey of Air Pollution. The Use of the Daily Instrument for Measuring Smoke and Sulphur Dioxide. Warren Spring Laboratory, Stevenage, England, December 1961.

Warren Spring Laboratory. The Investigation of Atmospheric Pollution 1958-1966. Thirty-second Report. Her Majesty's Stationary Office, London, England, 1967.

Warren Spring Laboratory. The National Survey of Smoke and Sulphur Dioxide-Quality Control Tests on Analyses of Samples, October 1975 to February 1977. Warren Spring Laboratory, Stevenage, England, 1977b.

Wedding, J. B., A. R. McFarland, and J. E. Cermak. Large particle collection characteristics of ambient aerosol samplers. Environ. Sci. Technol. 11:387-390, 1977.

World Health Organization. Selected Methods of Measuring Air Pollutants. WHO Offset Publication No. 24, World Health Organization. Geneva, Switzerland, 1976.

Dams, R., and R. Heindryckx. A high-volume air sampler for use with cellulose filters. Atmos. Environ. 7:319-322, 1973.

Eickelpasch, D., and R. Hotz. Comparison of various outer air measurements. Stahl Eisen 98:479-485, 1978.

Ferris, B. G. Jr., J. R. Mahoney, R. M. Patterson, and M. First. Air quality, Berlin, New Hampshire, March 1966 to December 1967. Am. Rev. Respir. Dis. 108:77-84, 1973.

Firket, M. Bull. The cause of the symptoms found in the Meuse Valley during the fog of December 1930. Acad. R. Med. Belg. II (ser.5):683-741, 1931.

Fry, J. D. Determination of Sulphur Dioxide in the Atmosphere by Absorption in Hydrogen Peroxide Solution--the Effect of Evaporation of the Solution During Sampling. Central Electricity Generating Board, South West Region, England, April 1970.

Hagen, L. J., and N. P. Woodruff. Air pollution from duststorms in the Great Plains. Atmos. Environ. 7:323-332, 1973.

Hale, W., and N. Waggoner. The overall variability of CoH unit values and methods for increasing the accuracy of readout. J. Air Pollut. Control Assoc. 12:322-323, 1962.

Harrison, W., J. Nader, and F. Fugman. Constant flow regulators for high-volume air sampler. J. Am. Ind. Hyg. Assoc. 11:114-120, 1960.

Health Consequences of Sulfur Oxides: A report from CHESS, 1970-71. EPA-650/1-74-004 U.S. Environmental Protection Agency, Human Studies Laboratory. Research Triangle Park, NC, May 1974.

Hemeon, W., G. Haines, Jr., and H. Icle. Determination of haze and smoke concentration by filter paper samplers. Air Repair 3:22-28, 1953.

Herpertz, E. (1969) Ein einfaches Langzeitmessverfahren zur Bestimmung der Staubkonzentration in der bodennahen Atmosphare (LIB-Verfahren). Staub Reinhalt. Luft 29:408-413, 1969.

Holland, W., A. Bennett, I. Cameron, C. Florey, S. Leeder, R. Schilling, A. Swan, and R. Waller. Health effects of particulate pollution: reappraising the evidence. Am. J. Epidemiol. 110:527, 1979.

Horvath, M., and R. Charlson. The direct optical measurement of atmospheric air pollution. J. Am. Ind. Hyg. Assoc. 30:500-509, 1969.

Ingram, W. Smoke Curve Calibration. PHS Contract PH-86-68-66, New York University, New York, NY, 1969.

Ingram, W., and J. Golden. Smoke curve calibration. J. Air Pollut. Control Assoc. 23:110-115, 1973.

Johnson, N. L. Systems of frequency curves generated by methods of translation. Biometrika 36:149-176, 1949.

Katz, M. Guide to the Selection of Methods for Measuring Air Pollutants. WHO/AP/67.29, World Health Organization, Geneva, 1967.

Katz, M., and H. P. Sanderson. Filtration methods for evaluation of aerosol contaminants. In: Symposium on Instrumentation in Atmospheric Analysis. Special Technical Publication No. 250, American Society for Testing and Materials, Philadelphia, PA, 1958.

Kretzschmar, K. Comparison between three different methods for the estimation of the total suspended matter in urban air. Atmos. Environ. 9:931-935, 1975.

Laskus, Von L. Untersuchung der Korngrössen-verteilung des atmospharischeu Staubes in Bodeunahe. Staub Reinhalt. Luft 37:299, 1977.

Laskus, Von L. and D. Bake. Erfahrungen bei der Karngrössenanalyse von Luflstäuben mit dem andersne. Kaskadenimpaktor. Staub Reinhalt. Luft 36:102, 1976.

Lawther, P. J., A. G. F. Brooks, P. W. Lord, and R. E. Waller. Day-to-day changes in ventilatory function in relation to the environment. Part I. - Spirometric values. Part II. - Peak expiratory flow values. Environ. Res. 7:27-53, 1974.

Lawther, P. J., A. G. F. Brooks, P. W. Lord, and R. E. Waller. Day-to-day changes in ventilatory function in relation to the environment. Part III. Frequent measurement of peak flow. Environ. Res. 8:119-130, 1974.

Lawther, P., P. Lord, A. Brooks, and R. Waller. Air pollution and pulmonary airways resistance: a six year study with three individuals. Environ. Res. 13:478-492, 1977.

Lee, R. E. Jr., J. S. Caldwell, and G. B. Morgan. The evaluation of methods for measuring suspended particulates in air. Atmos. Environ. 6:593-622, 1972.

Lee, R. E., Jr. Measuring particulate matter in air. In: Instrumentation for Monitoring Air Quality. ASTM STP 555, American Society for Testing and Materials, Philadelphia, PA, 1974. pp. 143-156.

Lippman, M. Review of cascade impactors for particle size analysis and a new calibration for the Casella Cascade Impactor. J. Am. Ind. Hyg. Assoc. 20:406, 1959.

Lisjack, G. J. Comparison of High Volume and Tape Sampler Data, 1976. Allegheny County Health Department, Pittsburgh, PA, 1977.

Liu, B. Y. H., P. Y. H. Pui, K. L. Rubow, and G. A. Kuhlmey. Research in Air Sampling Filter Media. Progress Report EPA Grant 804600, University of Minnesota, Minneapolis, MN, May 1978.

Logan, W. P. D. Mortality in the London Fog Incident. Lancet. (6755): 336-338, 1953.

MacFarland, A. Test report. Wind Turned Evaluation of British Smoke Shade Sampler. Air Quality Laboratory Report 3565/05/79/ARM, Texas A&M, College Station, TX, 1979.

Mage, D. T. An empirical model for the Kolmogorov - Smirnov Statistic. J. Environ. Sci. Health Part A. 15: 1980c.

Mage, D. T. An explicit solution for $S_B$ parameters using four percentile points. Technometrics 22 May 1980a.

Mage, D. T. Frequency distributions of hourly wind speed measurements. Atmos. Environ. 14:367, 1980b.

Martin, A., and F. R. Barber. Some measurements of loss of atmospheric sulphur dioxide near foliage. Atmos. Environ. 5:345-352, 1971.

McK. Ellison, J. The estimation of particulate air pollution from the soiling of filter paper. Staub Reinhalt. Luft 28:28, 1968.

McKee, H. C., R. E. Childers, and O. Saenz, Jr. Collaborative Study of Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method). APTD-0904, U.S. Environmental Protection Agency, Research Triangle Park, NC, June, 1971.

Ministry of Pensions and National Insurance: Report on an enquiry into the incidence of incapacity for work. II. Incidence of incapacity for work in different areas and occupations. London, HMSO, 1965.

Moulds, W. Some instrumental variations arising in routine air pollution measurements. Int. J. Air Water Pollut. 6:201-203, 1962.

Muyulle, E., D. Hachez, and G. Verduyn. An evaluation of measuring methods for particulate matter. In: Air Pollution Reference Measurement Methods and Systems. T. Schneider, H. W. deKoning and L. J. Brassea, eds., Elsevier Science Publ. Co., Amsterdam, 1978.

Natanson, G. Referenced by N. A. Fuchs in The Mechanics of Aerosols, p. 112, MacMillan, New York, 1964.

Organization for Economic Co-operation and Development. Methods of Measuring Air Pollution. Paris, 1964.

Park, J. D., Keagy, D. M., and W. W. Stalker. Developments in the use of the AISI automatic smoke sampler. J. Air Pollut. Control Assoc. 10:303-306, 1960.

Pashel G. E., and D. R. Egner. A comparison of ambient suspended particulate matter concentrations as measured by the British Smoke Sampler and the High Volume Sampler at 16 sites in the United States. Atmos. Environ., in press, 1980.

Patterson, R. K. Aerosol Contamination from High-volume Sampler Exhaust. J. Air Pollut. Control Assoc. 30:169-171, 1980.

Pedace, E., and E. Sansone. The relationship between "soiling index" and suspended particulate matter concentrations. J. Air Pollut. Control Assoc. 22:348-351, 1972.

Ruppersberg, G. Die anderung des maritimen Dunst - Streukoeffizienten mit der relativen Feuchte. Meteorol. Forschungsergeb. Reihe B, 4:37-60, 1971.

Saucier, J., and E. Sansone. The relationship between transmittance and reflectance measurements of soiling index. Atmos. Environ. 6:37-43, 1972.

Simon, M. J. Comparison of High Volume and Tape Sampler Data, 1973-75. Allegheny County Health Department, Pittsburgh, PA, 1976.

Stalker, W. W., Dickerson, R. C., and G. D. Kramer. Atmospheric sulfur dioxide and particulate matter: A comparison of methods of measurements. J. Am. Ind. Hyg. Assoc. 24:68-79, 1963.

Steel, R. G. D., and J. H. Torrie. Principles and Procedures of Statistics, McGraw Hill, Inc., New York, 1960. pp. 81-82.

Stöber, W. Sampling and evaluation of aerosols under biomedical aspects. Gesellschaft für Aerosolforschung, 1979.

Sullivan, J. The calibration of smoke density. J. Air Pollut. Control Assoc. 12:10-474, 1962.

U. S. Congress. House of Representatives. Committee on Science and Technology. The Environmental Protection Agency's Research Program with Primary Emphasis on the Community Health and Environmental Surveillance System (CHESS): An Investigative Report. U. S. Government Printing Office, Washington, DC, 1976.

U. S. Environmental Protection Agency. CHESS Addendum, 1980.

Waller, R. E. Experiments on the calibration of smoke filters. J. Air Pollut. Control Assoc. 14:323-335, 1964.

Waller, R., A. Brooks, and J. Cartwright. An electron microscope study of particles in town air. Int. J. Air Water Pollut. 7:779-784, 1963.

Waller, R., and P. Lawther. Some observations on London fog. Br. Med. J. 2:1356-1358, 1955.

Warren Spring Laboratory. Measurement of Atmospheric Smoke and Sulphur Dioxide, Reproducibility of Results. RR/AP/70, Warren Spring Laboratory, Stevenage, England, August, 1962.

Warren Spring Laboratory. National Survey of Smoke and Sulphur Dioxide, Instruction Manual. Warren Spring Laboratory, Stevenage, England, 1966.

Warren Spring Laboratory. National Survey of Air Pollution, 1961 - 1971. Volume 5 Scotland - Ireland. Chapter 15: Accuracy of Data and Representativeness of National Survey Data. Warren Spring Laboratory, Stevenage, England, January 1975. pp. 111-118.

Warren Spring Laboratory. Stevenage. The National Survey of Air Pollution. Methods of Measurement, Warren Spring Laboratory, Stevenage, England, December 1961.

Warren Spring Laboratory. The Investigation of Atmospheric Pollution 1958-1966. Thirty-second Report. Her Majesty's Stationary Office, London, 1967.

Warren Spring Laboratory. The National Survey of Smoke and Sulphur Dioxide-Quality Control Tests on Analyses of Samples, October 1975 to February 1977. Warren Spring Laboratory, Stevenage, England, 1977b.

Wedding, J. B., A. R. McFarland, and J. E. Cermak. Large particle collection characteristics of ambient aerosol samplers. Environ. Sci. Technol. 11:387-390, 1977.

# APPENDIX 3A

## APPENDIX 3A

## EFFECT OF FLOW RATE VARIATION WITH CONSTANT AMBIENT CONCENTRATION

Assuming 100 percent collection efficiency for sampling a mixture of only black smoke particles, we can model the Hi-vol sampler collection rate as

$$\frac{dm}{dt} = X_o \, v \qquad (1)$$

where

$m$ = mass collected on filter, μg

$X_o$ = True mass concentration, $\mu g/m^3$, assumed constant

$v$ = Hi-vol flow rate, $m^3$/time

The flow rate (v) will be a function of the total collected mass (m). If we assume a simple relationship similar to Darcy's law for the decrease in flow rate as mass is collected on the filter, then

$$v = \frac{v_o \quad M_o}{M_o + m} \qquad (2)$$

where $v_o$ = initial flow rate with a clean filter

$M_o$ = a filter constant scaled into a pseudo-mass

Substituting into equation (1) and rearranging

$$(M_o + m) \, dm = v_o \, M_o \, X_o \, dt \qquad (3)$$

Integrating equation (3) we obtain

$$(M_o + M)^2 - M_o{}^2 = 2 \, v_o \, M_o \, T \, X_o \qquad (4)$$

where M μgm are collected in time T.

Rearranging

$$X_o = \frac{M^2 + 2 \, M \, M_o}{2 \, v_o \, M_o \, T} \qquad (5)$$

The average $\bar{X}$ TSP computed by averaging the initial and final flow rates is

$$\bar{X}_{TSP} = \frac{2\,M}{T\left(V_o + \frac{V_o\,M_o}{M + M_o}\right)} \qquad (6)$$

*

Taking the ratios of equation 5 to equation 6,

$$\frac{X_o}{\bar{X}_{TSP}} = \frac{\left(2 + \frac{M}{M_o}\right)^2}{4\left(1 + \frac{M}{M_o}\right)} \qquad (7)$$

For the case where flow rate drops by a factor of 2 during period T, M/Mo = 1 and $X_o/\bar{X}_{TSP}$ = 9/8. This implies that the Hi-vol measuring only black smoke particles as TSP will register (8/9) of the true value measured by the BS method.

Harrison, Nader, and Fugman (1960) also provided an analysis of the effect of variable flow rates with time. They modeled the Hi-vol in a different manner as follows:

$$\frac{dm}{dt} = X_o v \qquad (1)$$

and

$$\frac{dv}{dt} = -K\frac{dm}{dt} \qquad (2a)$$

where "K is a characteristic of the filter." Equation 2 is relatable to equation (2a) by differentiation which provides

$$\frac{dv}{dt} = -\frac{v_o M_o}{(M_o + m)^2}\frac{dm}{dt} \qquad (2b)$$

Equation (2b) is equivalent to (2a) only at t = o, where m = o and $K = v_o/M_o$. Substituting (2a) into equation (1) we obtain a first order linear model which provides that the log of v is linear with time.

$$v = v_o \, e^{-\int_o^t K X_o \, dt} \tag{8a}$$

The integration of equation (2a) predicts that there is a maximum mass, $M_{max}$ which can be sampled where v will equal zero; $M_{max} = v_o/K$. However, the integration of equations 1 and 2 predicts that the longer we sample, the more mass we will collect.

These relations can be tested by examination of the measured variations in flow rate with time. Table 3A-1 lists typical variations of Hi-vol flow rate on days with similar pollution levels observed at MRC (Waller, personal communication) as part of the series of special measurements over the 8:30 a.m. - 10:30 a.m. period reported by Lawther et al. (1974, 1977).

TABLE 3A-1. HI-VOL FLOW -- CFM

| Time | Day 1 | | | Day 2 | | |
|---|---|---|---|---|---|---|
| | Filter # 3112 | | | Filter # - Not recorded | | |
| | v | $v/v_o$ | $(v_o/v)^2$ | v | $v/v_o$ | $(v_o/v)^2$ |
| 0830 | 52 | 1.000 | 1.000 | 54 | 1.000 | 1.000 |
| 0850 | 44 | 0.846 | 1.397 | 46 | 0.852 | 1.378 |
| 0900 | -- | -- | -- | 44 | 0.815 | 1.506 |
| 0910 | 37 | 0.685 | 1.974 | -- | -- | -- |
| 0920 | -- | -- | -- | 37 | 0.685 | 2.130 |
| 0930 | -- | -- | -- | 34 | 0.630 | 2.522 |
| 0940 | 32 | 0.615 | 2.641 | -- | -- | -- |
| 0950 | -- | -- | -- | 32 | 0.593 | 2.848 |
| 1010 | 28 | 0.538 | 3.450 | -- | -- | -- |
| 1030 | 27 | 0.519 | 3.709 | 29 | 0.537 | 3.467 |

Substituting equation 4 into equation 2, we obtain:

$$\left(\frac{v}{v_o}\right) = \frac{M_o}{(M_o^2 + 2\, v_o\, M_o\, t\, X_o)^{\frac{1}{2}}} \qquad (8)$$

To obtain an equation to simplify the plotting of v and t the equation is inverted and squared,

$$\left(\frac{v_o}{v}\right)^2 = 1 + 2\, v_o\, t\, X_o / M_o \qquad (9)$$

The data $(v_o/v)^2$ should be linear with t if the assumption of Darcy's law for flow variation is reasonable. If the product $(v_o\ X_o/M_o)$ is constant, the data from both days 1 and 2 should fall about the same line. The results shown in Figure 3A-1 demonstrate the linear behavior of these results. It can be shown in Figure 3A-1 that the exponential relation of flow with time is not reasonable and the nonlinear model will be used to demonstrate effects of flow and concentration variations for British Smoke comparisons.

Calculation of the Effect of Simultaneous Flow and Concentration Variation

In the previous example, the TSP concentration was assumed to be a constant value $X_o$ which was composed entirely of the black smoke particles used to calibrate the BS reflectometric measurements. The two measurements of TSP and BS would be identical if the total flow volume was computed by integration. When the concentration is changing with time the two measurements will diverge even if the total flow is computed correctly by integration of the varying flow rates. To demonstrate this effect, the previous computation is repeated but the concentration of black smoke particles is allowed an (n + 1) fold linear increase with time from $X_o$ ($X_o \neq 0$) to $(n + 1)\ X_o$ over the sampling period T. During this same period, the flow rate will again be assumed to fall so that the mass M collected in time T will be related to decrease in flow rate by an equation similar to Darcy's law:

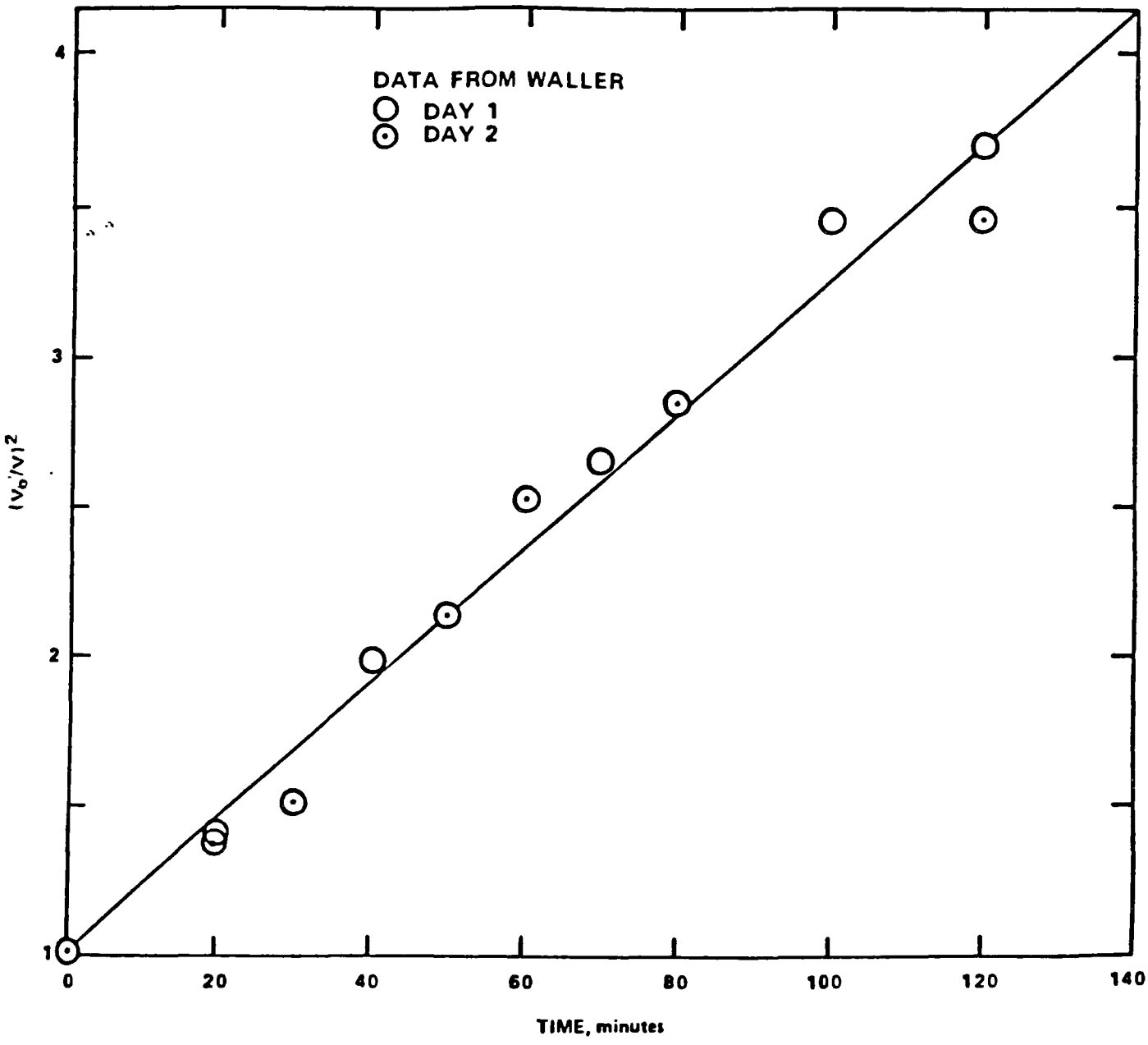



Figure 3A-1. $1/v^2$ variation of Hi-vol flow with time showing flow pattern predicted by Darcy's Law. Data from Waller by personal communication (1978).

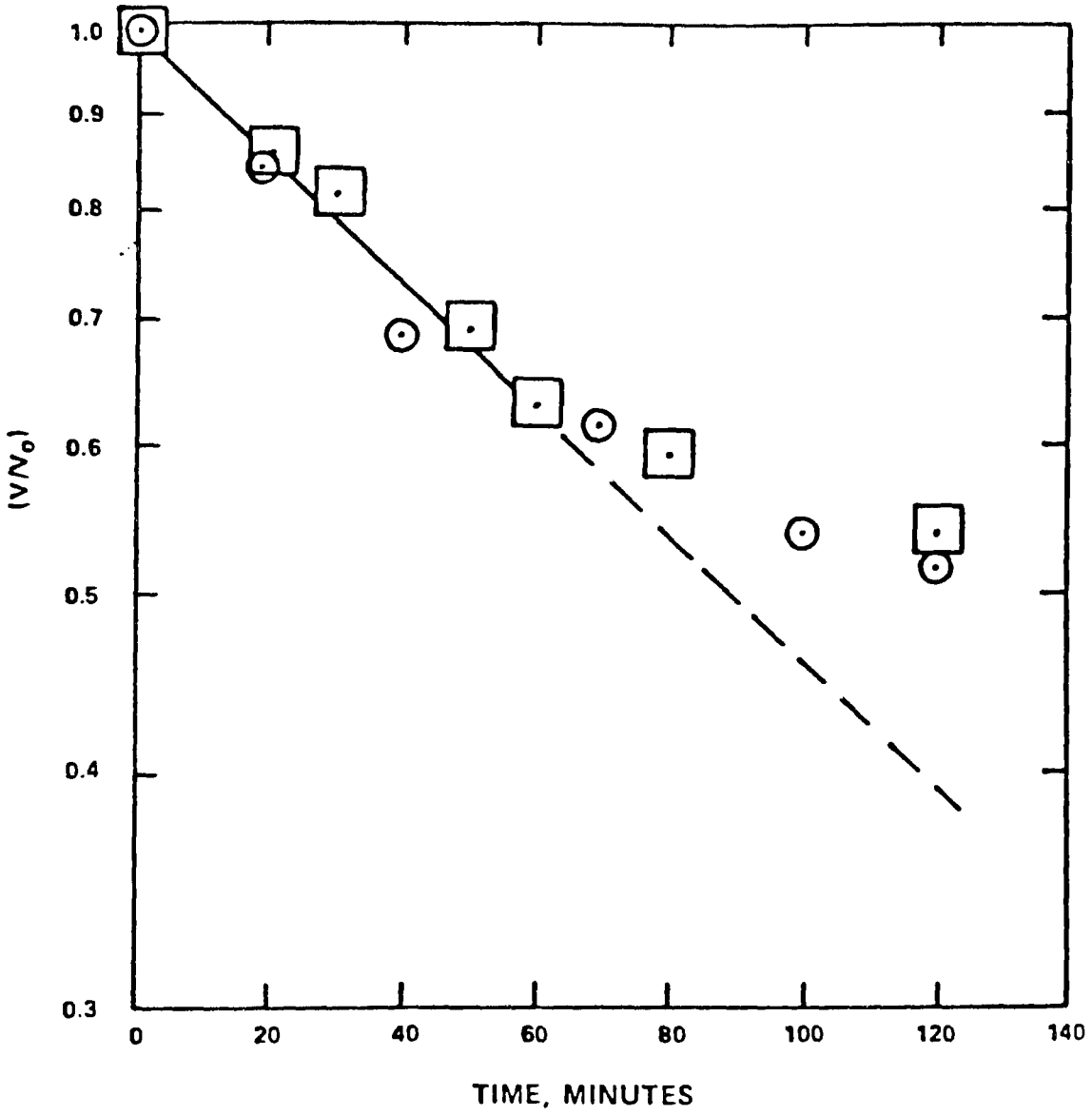



Figure 3A-2. Test for decrease in flow rate proportional to mass collected showing deviation from the expected exponential relationship.

Figure 3A-2 is a semilogarithmic plot of flow in CFM versus time. If the exponential relation holds a linear relationship will exist between log V and t. As expected the relation is linear at small values of m, in the first hour, but as m builds up the data appear to diverge as $(M_o + m)^2 >> M_o^2$.

The original equations (1) and (2) will still hold for this case:

$$\frac{dm}{dt} = X \quad v \tag{1}$$

and

$$v = \frac{v_o \quad M_o}{M_o + m} \tag{2}$$

If X varies linearly with time as stated above, then

$$X = X_o \ (1+ \ n \ t/T) \tag{10}$$

The true value of $\bar{X}$ which will be measured by the BS method is the average value of $(1 + n/2)X_o$. However, the TSP measure using flow integration will be,

$$\bar{X} = M/\int_o^T v \ dt \tag{11}$$

The ratio of TSP to BS defined as $\phi$ will be computed as,

$$\phi = \frac{M}{(1 + .5n) \ X_o \ \bar{V}T} \tag{12}$$

where $$\bar{V} = \frac{1}{T} \int_o^T \frac{v_o M_o}{M_o + m} \ dt \tag{13}$$

The value of m as a function of time must be evaluated by integrating as follows; substituting equations (2) and (10) in equation (1) we obtain:

$$\frac{dm}{dt} = Xo \ (1 + nt/T) \ \frac{v_o \quad M_o}{M_o + m} \tag{14}$$

Rearranging equation 14,

$$\int_o^{M(t)} (M_o + m)\, dm = \frac{X_o\, v_o\, M_o}{T} \int_o^t (T + nt)\, dt \qquad (15)$$

Performing the integration to the intermediate time t, where o < t < T, we obtain

$$(M(t) + M_o)^2 - M_o^{\,2} = \frac{X_o v_o M_o}{nT} \left[(T + nt)^2 - T^2\right] \qquad (16)$$

Solving for M (t),

$$M(t) = M_o \left[(1 + X_o v_o \left[(T + nt)^2 - T^2\right] / nM_o T)^{\frac{1}{2}} - 1\right] \qquad (17)$$

Substituting equation (17) into equation 13,

$$\bar{V} = \frac{1}{T} \int_o^T \frac{v_o\, dt}{(1 + X_o\, v_o \left[(T + nt)^2 - T^2\right]/nM_o\, T)^{\frac{1}{2}}} \qquad (18)$$

Defining a new variable of integration, y = 1 + n t/T, the equation 18 is simplified to,

$$\bar{v} = \frac{V_o}{n} \left(\frac{n\, M_o}{X_o V_o T}\right)^{\frac{1}{2}} \int_1^{n+1} \frac{dy}{\left[y^2 + n\, M_o/X_o V_o T - 1\right]^{\frac{1}{2}}} \qquad (19)$$

We can now define a parameter $\theta^2 = n\, M_o/X_o V_o T$, and

$$\bar{v} = \frac{v_o\, \theta}{n} \int_1^{n+1} \frac{dy}{y^2 + \left[\theta^2 - 1\right]^{\frac{1}{2}}} \qquad (20)$$

Integrating equation 20 we obtain

$$\bar{v} = \frac{v_o \theta}{n} \log\left(\frac{n + 1 + \left[(n + 1)^2 + \theta^2 - 1\right]^{\frac{1}{2}}}{1 + \theta}\right) \qquad (21)$$

Substituting into equation (12) the ratio of the Hi-vol to BS method becomes

$$\Phi = \frac{(M/M_o)\ \theta}{(1+0.5n) \log\left(\frac{n + 1 + \left[(n + 1)^2 + \theta^2 - 1\right]^{\frac{1}{2}}}{1 + \theta}\right)} \qquad (22)$$

In the limit as $n \to 0$ corresponding to the first example of constant concentration, $\phi \to 1$ (using L'Hopital's rule). For a situation where the flowrate is reduced by a factor of 2, M = Mo. If we allow the concentration being sampled to increase by a factor of 2 during the sampling period, n = 1 and equation 22 is reduced to a function of $\theta$ only,

$$\phi = \frac{(1)\ \theta}{(1.5)\ \log\left(\dfrac{2 + (3 + \theta^2)^{\frac{1}{2}}}{1 + \theta}\right)} \tag{23}$$

To scale $\theta$, let $v_o = 1.4\ m^3/min$

$T = 1$ day or 1440 min

$X_o = 100\ \mu g/m^3$

$X_o v_o T = 0.2016$ gm

$n = 1.0$ since X doubles

assume $M_o \simeq X_o v_o T$

$\theta \cong (nM_o/X_o V_o T)^{\frac{1}{2}} \cong 1$

Scaled to these levels, $\phi = \dfrac{1}{1.5\ \ln 2} = 0.962$, that is the Hi vol will measure ~ 96 percent of the BS material. If the same type of filter is assumed so that $M_o = X_o v_o T$ and $\theta = \sqrt{n}$, $M(T)/M_o$ can be determined from equation 17 as

$$M(T)/M_o = \sqrt{[n + (1 + n)^2 - 1]/n} - 1 \tag{24}$$

substituting into equation 22

$$\phi = \frac{\sqrt{(n + 1)_o^2 + (n - 1)} - \sqrt{n}}{(1 + 0.5n)\ \log\left(\dfrac{n + 1 + [(n + 1)^2 + (n - 1)]^{\frac{1}{2}}}{1 + \sqrt{n}}\right)} \tag{25}$$

The use of equation 25 gives $\phi$ as a function of n corresponding to a linear rise from 100 $\mu g/m^3$ to 100 (1 + n) $\mu g/m^3$ over the full day. The results are tabulated below in Table 3A-2.

TABLE 3A-2. $X_o$ = 100, T = 1 DAY, $\Phi$ = TSP/BS

| $\phi$ | n | X(T) |
|---|---|---|
| 1.000 | 0 | 100 |
| 0.962 | 1 | 200 |
| 0.933 | 2 | 300 |
| 0.909 | 3 | 400 |
| 0.890 | 4 | 500 |
| 0.853 | 6.5 | 750 |
| 0.825 | 9 | 1000 |
| 0.758 | 19 | 2000 |

APPENDIX 3B

APPENDIX 3B

Dimensional Analysis of BNLM Model.

The parameter C in the BNLM model has dimensions of $Mass^1$ $Length^{-3}$. It may, therefore, be a function of several variables which can be arranged into dimensionless groups. Table 3B-1 lists some of the parameters which can have an influence on the ratio BS/TSP. These parameters can be arranged in dimensionless groups corresponding to ratios of variables such as a Reynolds number (Re), a Richardson number (Ri), and a Froude number (Fr), such as:

$$Re = \frac{\lambda\ u\ p}{\mu}$$

$$Fr = \frac{u^2}{gZ}$$

and $$Ri = \lambda(\frac{\partial T}{\partial Z} + \Gamma)/(21-T).$$

We might try various combinations of these dimensionless groups, one of which is shown below;

$$C = 200\ k\ Ri^l\ Fr^m\ Re^n\ \rho$$

where k, l, m, and r are dimensionless constants and $\rho$ is the air density ($\mu g/m^3$). Since C is proportional to wind speed raised to the n+2m power, as wind speed goes to zero, C goes to zero. When wind speed becomes large, u>>0, then C becomes large forcing the BS/TSP ratio to become small as characteristically found in dust storm conditions (Hagen and Woodruff, 1975).

TABLE 3B-1. PARTIAL LISTING OF PARAMETERS WHICH CAN INFLUENCE THE MEASURE OF BS AND TSP

Dimensions M mass, L length, θ temperature, t time

| Parameter | Dimension |
|---|---|
| Stability, $\partial T/\partial Z$ | $\theta^1 L^{-1}$ |
| Δ Temperature, Heating Degrees (21-T°C) | $\theta^1$ |
| Monin-Obukhov Length, λ | $L^1$ |
| Wind Speed, u | $L^1 t^{-1}$ |
| Local Gravitation, g | $L^1 t^{-2}$ |
| Elevation above ground, Z | $L^1$ |
| Distance Between BS and TSP | $L^1$ |
| Distance to Nearest Street, X | $L^1$ |
| Wet adiabatic Gradient, Γ | $\theta$, $L^{-1}$ |
| Relative Humidity, % | -- |
| Air Viscosity, μ | $M^1 L^{-1} t^{-1}$ |
| Air Density, ρ | $M^1 L^{-3}$ |
| Start TSP flow | $L^3 t^{-1}$ |
| Stop TSP flow | $L^3 t^{-1}$ |
| Start BS flow | $L^3 t^{-1}$ |
| Stop BS flow | $L^3 t^{-1}$ |

APPENDIX 3C

APPENDIX 3C

In order to make a qualitative estimate of the effect of flow variation reference is made to a report by McFarland (1979) which describes a wind tunnel evaluation of the British Smoke Shade Sampler. In that study a theoretical model of Natanson (1964) was used to estimate the deposition of particulate matter in horizontal flow tubes by gravitational sedimentation with a zero windspeed. The penetration, P, is computed as:

$$P = 1 - 2\left(2\Phi\sqrt{1 - \Phi^{2/3}} + \sin^{-1}\Phi^{1/3} - \Phi^{1/3}\sqrt{1 - \Phi^{2/3}}\right)/\Pi \qquad (1)$$

where $\Phi = 2\,V_t L/4D\bar{u}$

$V_t$ = particle terminal velocity, cm/sec

$L$ = tube length, cm

$\bar{u}$ = Average flow velocity in tube, cm/sec

The terminal volocity of particles obeying a Stokes-Cunningham sedimentation relation is

$$V_t = \frac{C\rho_p \; D_p^{\,2} g}{18\mu} \qquad (2)$$

where $C = 1 + 2.46\,\lambda/D_p$

$\lambda = 1.7 \times 10^{-5}\,T/P$, mean free path, cm

$T$ = Temperature °K

$P$ = Gas pressure, torr

$\rho_p$ = Particle Density, $gm/cm^3$

$D_p$ = Particle diameter

$g$ = gravitational acceleration, $cm/s^2$

$\mu$ = gas viscosity, poise

McFarland (1979) computes the penetration as a function of the BS parameters

| | | |
|---|---|---|
| Tube length | = | 183 cm |
| Flow rate | = | 1.5 liter/min |
| Diameter | = | 0.635 cm |
| Viscosity | = | $1.85 \times 10^{-4}$ poise |
| Particle Density | = | 1 $gm/cm^3$ |
| $\lambda$ | = | $0.0675 \times 10^{-4}$ cm |
| $\bar{u}$ | = | 79 cm/sec |

We compute the air Reynolds number, $N_R$, to assure laminar flow

$$N_R = \frac{D\bar{u}\,\rho_{air}}{\mu} = \frac{0.635 \text{ cm} \; \frac{79 \text{ cm}}{\text{sec}} \; \frac{29 \text{ gm}}{24 \text{ liters}}}{1.85 \quad 10^{-4} \text{ poise}} = 327$$

Since $N_R$ <2100 we have laminar flow.

Solutions of equations 1 and 2 give penetration as a function of diameter D as shown in Table 3C-1.

TABLE 3C-1. PENETRATION OF AEROSOL TO THE BS FILTER AT 1.5 LITER/MINUTE

| Particle Diameter μm | Penetration P, % | $S_B$ Function Dp/(11-Dp) |
|---|---|---|
| 1.4 | 98 | 0.146 |
| 2.7 | 90 | 0.325 |
| 6.5 | 50 | 1.444 |
| 9.7 | 10 | 7.462 |
| 11.0 | 0 | ∞ |

Penetration is bounded by a physical upper limit because no particle with a terminal velocity greater than 79 cm/sec, corresponding to 11 μm, can enter into the inlet tube. The logical choice to model the penetration curve is by use of an $S_B$ model defined by Johnson (1949). This model requires that the logarithm of $D_p/(11-D_p)$ is normally distributed. The values of $D_p/(11-D_p)$ are listed in Table 3C-1 and are plotted on log-probability paper as Figure 3C-1. The use of the Johnson $S_B$ model for aerometric variables is described by Mage (1980 a,b). The line drawn on Figure 3C-1 was drawn by the technique of minimizing the Kolmogorov-Smirnov, KS, statistic for the fit. (Mage, paper in preparation). This KS statistic is related to the goodness of fit of the model (Mage, 1980c). In this case the KS statistic is about 0.01 with 2 degree of freedom which indicates the $S_B$ model cannot be rejected as providing a good fit to these data. The equation of the line is $Z = -0.343 + 0.845 \ln[D_p/(11 - D_p)]$ where Z is a standard normal variable.

With a BS sampler running at 0.72 liter per minute, the new penetration curve can be determined by a rescaling of Φ in equations 1 and 2 using $V_t = \frac{0.72}{1.5} 79 = 38$ cm/sec. Performing these computation we obtain the new penetration curve shown in Table 3C-2.

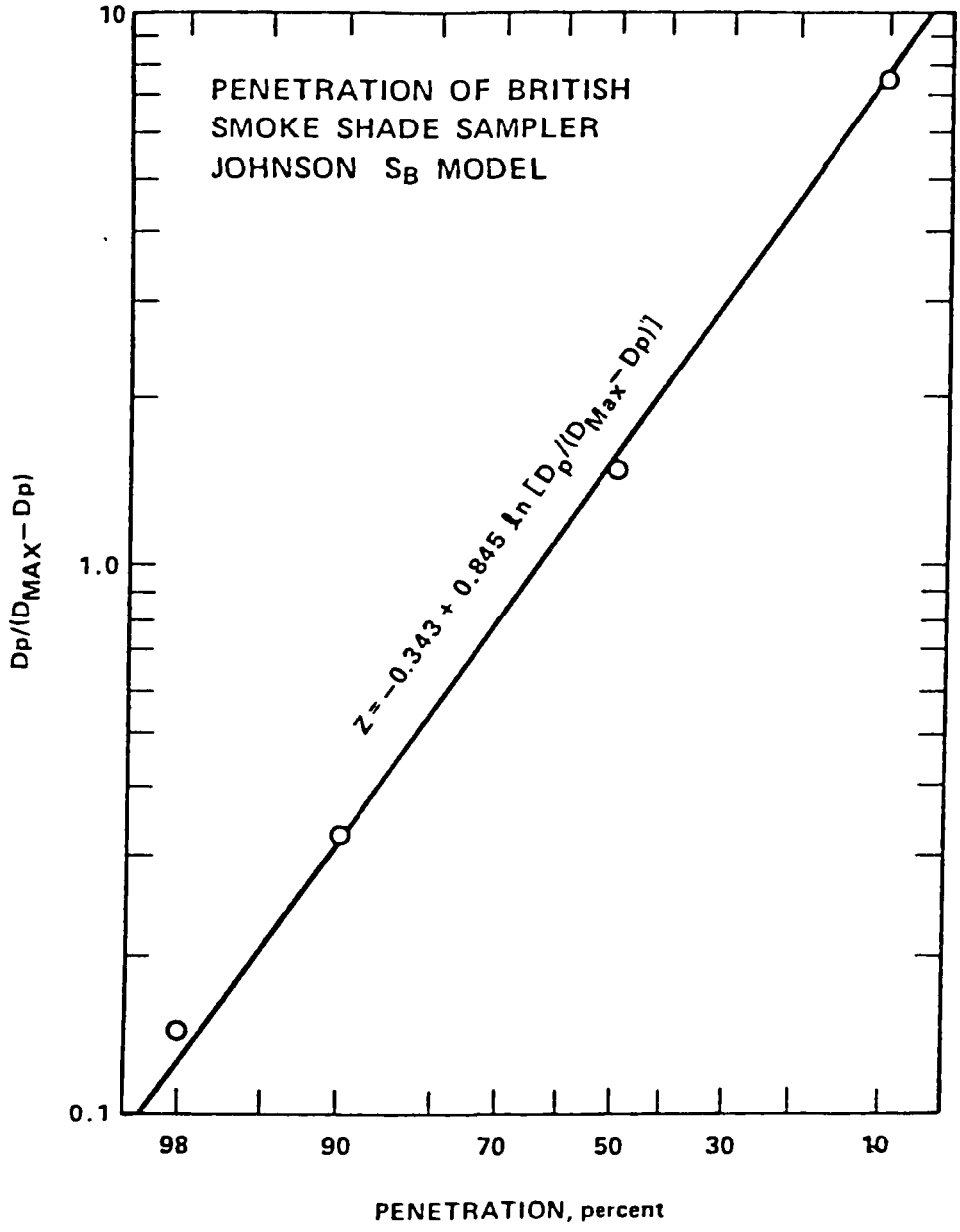



Figure 3C-1. Penetration of British Smoke sampler showing fit to the Johnson $S_B$ distribution.

TABLE 3C-2. PENETRATION OF AEROSOL TO THE BS FILTER AT 0.72 liter/minute

| Particle Diameter μm | Penetration P, % | $S_B$ Function Dp/(11-Dp) |
|---|---|---|
| 0.95 | 98 | 0.143 |
| 1.85 | 90 | 0.322 |
| 4.5 | 50 | 1.452 |
| 6.7 | 10 | 7.44 |
| 7.6 | 0 | ∞ |

Comparison of Tables 3C-1 and 3C-2 shows the $S_B$ penetration function is almost identical at both flowrates. We, therefore, can use Figure 3C-1 as a model for penetration of the BS at 0.72 liters per minute. The effect rate is to shift the penetration curve to a lower recovery of material.

# 4. SOURCES AND EMISSIONS

## 4.1 INTRODUCTION

Sulfur oxides and particulate matter are among the most pervasive pollutants emitted into the environment. Although particles and sulfur oxides occur naturally, their presence has also been linked with human activities for centuries. In the early 1600's, legislation was introduced in British Parliament to remove noxious materials from the air of London. Much later, these pollutants were identified as sulfur oxides and particulate matter.

The relation between emissions and ambient air concentrations is complex. Several issues surrounding the nature of this relation remain unresolved. Among these issues are the chemical composition of pollutants, their secondary formation, and long-range transport from sources. Some sources and emissions are evident, and their contribution to the national air pollution problem is apparent.

The purpose of this chapter is to provide background information in order to discuss, in later chapters, the health and welfare effects of ambient concentrations of particles and sulfur oxides. Accordingly, this chapter highlights the magnitude of emissions from the many diverse, manmade (anthropogenic) sources of particulate matter and sulfur oxides throughout the United States. Additionally, it places anthropogenic emissions in perspective with natural emissions of the substances. The chapter demonstrates that emissions from anthropogenic sources are of considerably more concern than those from natural sources. Moreover, while emissions from natural sources tend to be distributed uniformly, those from anthropogenic sources tend to concentrate, thereby greatly elevating pollutant levels in specific areas.

## 4.2 NATURAL SOURCES

Knowledge of natural sources of particulate matter and sulfur oxides is important for understanding air pollution. Baseline concentrations in continental and marine air represent natural exposure levels, and they also provide a reference for comparing concentrations in polluted air. Thus, the concentrations and biological effects of air pollutants can be compared with those of natural atmospheric components.

### 4.2.1 Terrestrial Dust

Terrestrial dust is transferred to the atmosphere by the action of wind on soils. Theoretical and experimental studies (Gillette, 1974) indicate that sand grains, produced by the weathering of rocks and soils and moved by wind, cause the pulverization of soil minerals, as in sandblasting, to produce fine particles. These particles may become airborne, and the resulting aerosol may be transported through the atmosphere for considerable distances. Loose soils in China and Argentina have accumulated from dust carried by wind (Holmes, 1971); airborne particles make up a significant fraction of some deep ocean sediments (Broecker, 1974). Dust from the Sahara Desert may be carried by air currents across the Atlantic Ocean as far as Florida and Barbados (Delaney et al., 1967; Junge, 1957).

Terrestrial dust in the atmosphere is derived from earth crustal material. Al, Si, Fe, and other major elements in rock-forming minerals are present in aerosol samples to nearly the same extent as in average earth crustal material (Lawson and Winchester, 1979). For crustal matter like calcite, which disaggregates relatively quickly, greater enrichment of its components, such as Ca, will occur (Johannson et al., 1976).

Atmospheric concentrations of many trace elements, including transition metals and semimetals, are 10- to 1000-fold higher than would be expected from physical dispersion of soil minerals. These anomalous trace element enrichments have been observed in many parts of the world, including northern Canada (Rahn, 1974), the South Pole (Zoller et al., 1974), and South America (Adams et al., 1977). Table 4-1 summarizes geometric mean enrichment factors, relative to Al, for 29 anomalous and 40 other elements according to Rahn's compilation of all published data up to 1976 (Rahn, 1976).

The atmospheric enrichment sources of these elements are unknown, but transport from polluting industries (Rahn, 1974), natural rock volatility (Goldberg, 1976), and biosphere emanations (Barringer, 1977) have all been suggested. In general, not enough is known about element ratios in the natural atmosphere to detect a pollution component.

The major elemental constituents of terrestrial dust occur principally in coarse particles with aerodynamic diameters (i.e., with inertial properties in aerosol sampling devices equivalent to those of unit density spheres) greater than approximately 1 μm. Figure 4-1 shows median particle size distributions of Si and Fe measured at ground level in New Mexico, Colorado, and New Hampshire during April 1976 (Winchester et al., 1979). The data indicate that more than 90 percent of the mass occurs on the first three impactor stages, >4, 4 to 2, and 2 to 1 μm aerodynamic diameter. The low relative abundance of submicron Si, Fe, and other major dust constituents reflects the greater amount of energy needed in order for fine particles to be generated from soils by the wind-driven sandblasting mechanism, normally not provided by the atmosphere near the ground.

In urban St. Louis and west suburban sampling sites, Si and Fe occur predominantly in coarse particles, with higher relative proportions in the >4-μm

TABLE 4-1. AEROSOL ENRICHMENT FACTORS RELATIVE TO Al

| EF[a] | Elements |
|---|---|
| 0.7-7 | Li, Na, K, Rb |
| | Be, Mg, Ca, Sr, Ba |
| | Sc, Y, lanthanides |
| | Al, Ga, Tl |
| | Si, Ti, Zr, Hf, Th, U |
| | Mn, Fe, Co, Nb |
| | F, P |
| 7-70[b] | Cr, Cs, V, W, B, Ni, Ge |
| 70-400[b] | H, In, Cu, Mo, Bi, Zn, As |
| 400-4000[b] | I, Hg, S, Cl, Au, Ag, Sn, Sb, |
| | Pb, Br, Cd, Te, Se, C, N |

[a]Geometric means of element ratios to Al, relative to geochemical average earth crustal material.

$$EF = \frac{(\text{element/Al})_{\text{aerosol}}}{(\text{element/Al})_{\text{crust}}}$$

[b]Anomalously enriched elements arranged in order of increasing EF.

Source: Based on Rahn (1976).

fraction, impactor stage 1 (Figure 4-1; Winchester et al., 1979). This situation probably reflects physical dust-raising forces in the urban area qualitatively similar to those in nonurban areas, although with a relatively stronger tendency in the city for the largest particles to become airborne by human activities. The concentrations of Si and Fe in the next-smaller coarse-particle size fractions appear to be less strongly enhanced in St. Louis than in nonurban locations.

The results in Figure 4-1 for Si and Fe indicate that total suspended particulate concentrations may be strongly affected by urban dust-generating activites. The coarsest particle sizes are affected to the greatest degree, while particles of aerodynamic diameters below about 2 μm are affected to a lesser extent. If the smaller particles are more significant in terms of health effects (U.S. Environmental Protection Agency, 1975), then it is essential to monitor concentrations in this size range without interference from coarser particles.

Figure 4-1 also presents median concentrations of Zn as a function of particle size. Zn is one of the atmospherically enriched elements listed in Table 4-1, and much of its mass occurs in the smallest particle size ranges. The fine-particle Zn concentrations are substantially higher in St. Louis than in the nonurban locations, suggesting that urban and nonurban processes lead to atmospheric release of submicron particles containing Zn. Total suspended Zn concentrations contain particles in the 1-10 μm particle size range.

The concentrations and elemental composition of terrestrial dust measured in remote continental areas of the Northern and Southern Hemispheres are similar. Table 4-2 compares measurements from Bolivia (Adams et al., 1977), northwestern Canada (Rahn, 1974), Switzerland (Dams and De Jonge, 1976),

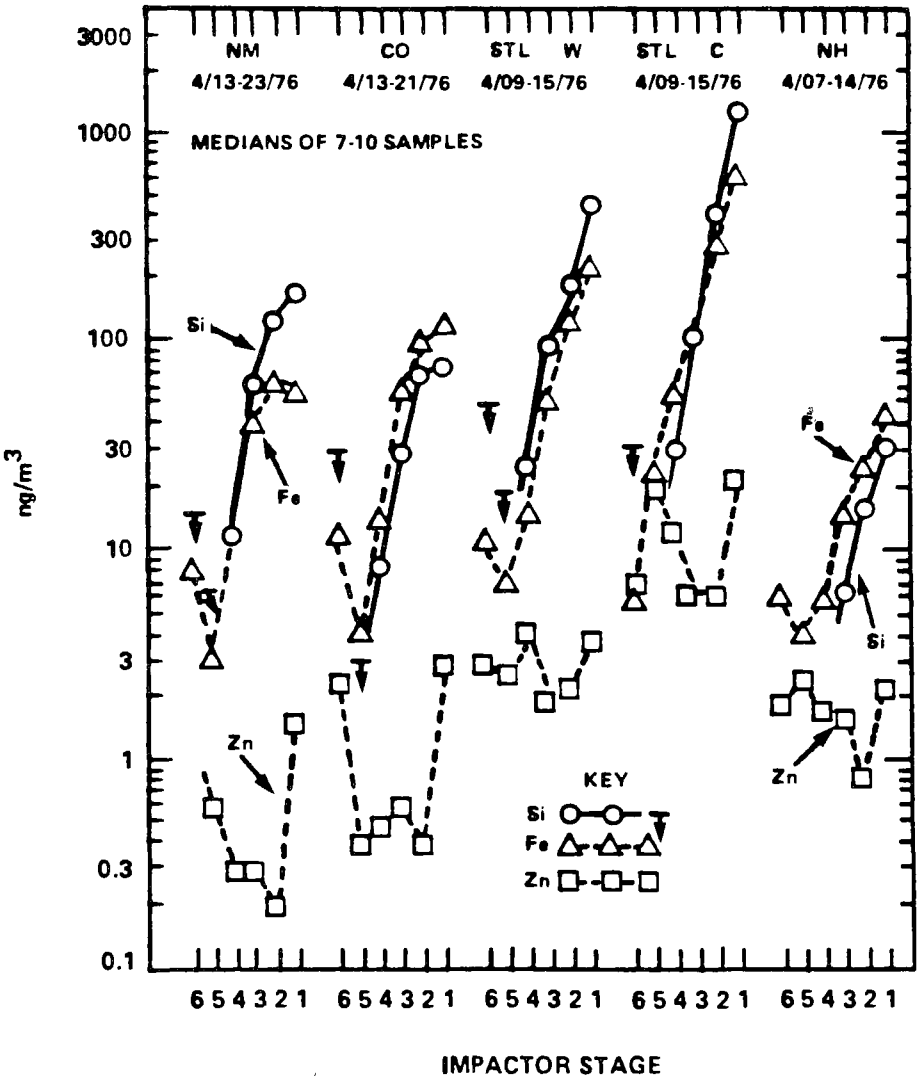



Figure 4-1. Median concentrations of Si, Fe, and Zn are plotted as a function of particle size. Samples were obtained during April 1976 at five sites: near Los Alamos, NM; Squaw Mountain, CO; west suburban St. Louis, MO; urban St. Louis, MO; and Hubbard Brook watershed NH.

Source: Winchester et al. (1979).

TABLE 4-2. COMPARISON OF AEROSOL COMPOSITION IN REMOTE REGIONS

| Determination | Location and reference | | | | |
|---|---|---|---|---|---|
| | Bolivia (10) | NW. territory, Canada (8) | Switzerland | North Cape, Norway (17) | South Pole (9, 18)[a] |
| Fe concn, $ng/m^3$ | 181 | 71 | 36 | 51 | 0.84 |
| Weight ratio to Fe[b] | | | | | |
| Na | 0.33 | 0.25 | 0.61 | 8.6 | 5.3 |
| K | 0.44 | 0.76 | 0.56 | 0.94 | 1.1 |
| Mg | 0.16 | 0.23 | 0.28 | 1.4 | 1.2 |
| Ca | 0.46 | 0.56 | 1.4 | 0.90 | 0.8 |
| Sc | 0.00024 | 0.0006 | 0.00021 | 0.00014 | 0.00026 |
| La | 0.0009 | 0.0013 | 0.0011 | 0.0008 | 0.0007 |
| Sm | 0.00015 | 0.0002 | 0.0002 | 0.0001 | 0.00015 |
| Al | 1.4 | 0.93 | 1.4 | 0.84 | 1.3 |
| Si | - | - | 2.8 | 2.8 | - |
| Ti | 0.086 | 0.070 | 0.068 | 0.061 | 0.16 |
| Th | 0.0003 | 0.0007 | 0.0003 | 0.0002 | 0.0002 |
| Mn | 0.014 | 0.021 | 0.042 | 0.049 | 0.021 |
| Co | 0.005 | 0.0006 | 0.0013 | - | 0.0008 |
| Cr | 0.0033 | 0.0083 | 0.010 | 0.013 | <0.06 |
| Cs | 0.0004 | - | 0.0004 | 0.0004 | 0.0002 |
| V | 0.002 | 0.003 | 0.008 | 0.033 | 0.0021 |
| W | 0.004 | 0.0002 | 0.0008 | - | 0.0024 |
| Ni | 0.003 | <0.01 | - | - | - |
| In | 0.00007 | 0.00002 | 0.00003 | 0.00008 | 0.00009 |
| Cu | 0.0075 | 0.013 | 0.024 | 0.045 | 0.047 |
| Zn | 0.024 | 0.053 | 0.275 | 0.17 | 0.053 |
| As | 0.0089 | 0.0044 | 0.0064 | 0.037 | 0.01 (0.05N) |
| I | 0.0014 | 0.0028 | 0.0075 | 0.012 | 0.13 (1.2N) |
| S | 0.095 | - | - | - | 80. |
| Cl | 0.37 | 0.13 | 0.20 | 5.8 | 4.2 |
| Sb | 0.0048 | 0.0018 | 0.0056 | 0.0075 | 0.0013 |
| Pb | 0.029 | - | 0.12 | 0.11 | 0.75 |
| Br | 0.0058 | 0.0076 | 0.036 | 0.092 | 2.1 (4.2N) |
| Cd | 0.006 | - | 0.014 | - | <0.02 |
| Se | 0.0010 | 0.0006 | 0.0012 | 0.005 | 0.01 |

[a]Pb values are from reference 9; all others are from reference 18. "N" denotes value from Nuclepore filter sample when different from Whatman cellulose filter value.
[b]Elements grouped according to enrichment factors as in Table 4-1.

northern Norway (Rahn, as quoted in Dams and De Jonge, 1976), and the South Pole (Zoller et al., 1974; Maenhaut et al., 1979). The concentrations of Fe, an element respresentative of terrestrial dust in these locations, ranges over a factor of 5 from South and North America and Europe. Concentrations are similar to those found in the Western United States (Figure 4-2; Winchester and Duce, 1977). Because of the paucity of land areas not covered by snow, concentrations at the South Pole are 100 times lower than the average of the other four locations. In general, all five locations have similar elemental iron ratios. Exceptions may be attributed to the relatively strong influence of sea salt (high Na, Mg, Cl, Br, and I concentrations at the sites in northern Norway and the South Pole) and certain pollutants (high V, Cu, Zn, and Pb concentrations at the sites in Switzerland and Norway).

The terrestrial dust component of atmospheric aerosols appears to be generally uniform worldwide in relative elemental composition, representing soil dispersion processes and anomalous enrichments of some elements. Certain excess elemental concentrations may be due to special processes, such as transport of sea salt and industrial pollutants, the raising of surface dust by human activity, or generation of fly ash and other dusts of earth crustal composition. Judicious comparison of both concentrations and relative elemental composition in the natural atmospheric aerosol and in more polluted air reveals the presence of these excess elemental concentrations.

### 4.2.2 Radioactive Aerosols

The fine fraction of aerosols of terrestrial origin contains radioactive daughter products of radon. Uranium and thorium in soils support radioactive Rn-222 (half-life, 3.823 days) and Rn-220 (half-life, 55 sec), which can diffuse into the atmosphere and subsequently decay to $\alpha$ and $\beta$ radioactive isotopes of

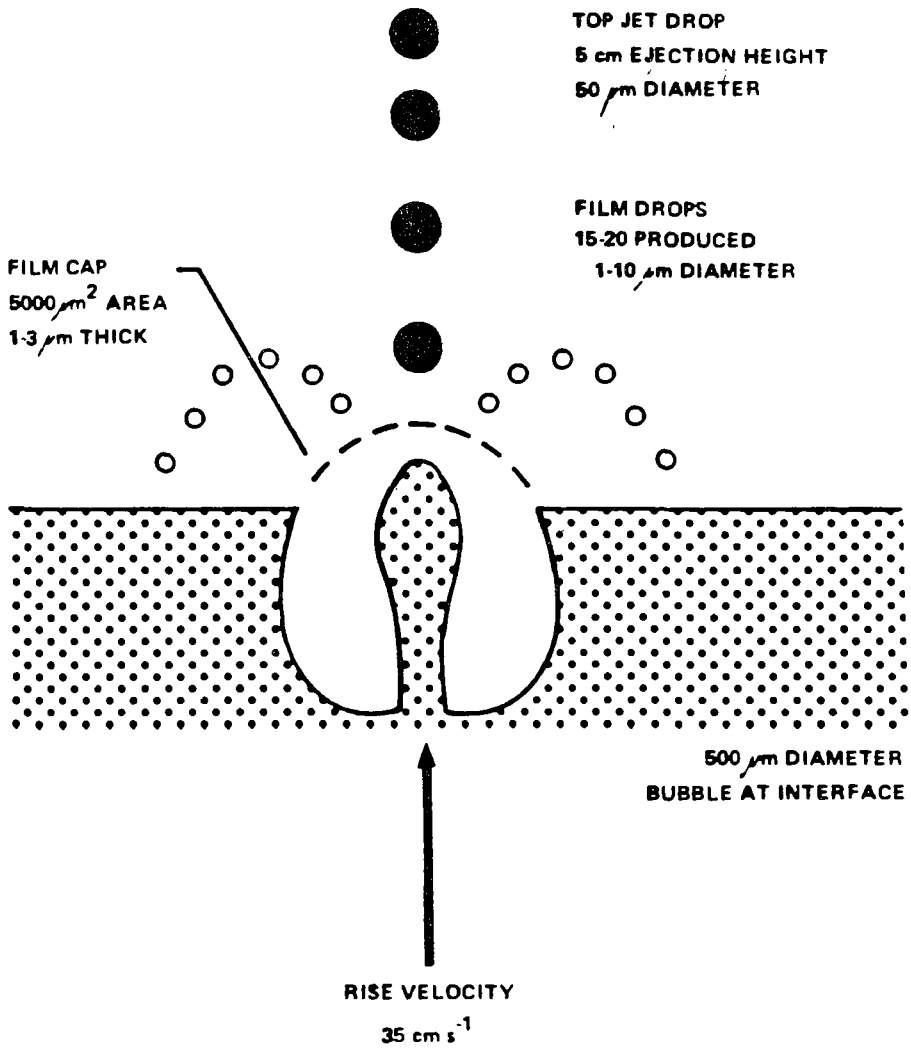



Figure 4-2. Bursting of a bubble, 500 $\mu$m in diameter, at the sea-air interface produces atmospheric particles.

Source: Blanchard (1963).

Po, Bi, and Pb. These daughter products attach themselves to fine aerosol particles which settle on surfaces near the ground.

### 4.2.3 Sea Spray

Aerosol droplets are generated at the ocean surface by the action of wind, principally through a process whereby air bubbles become entrained and rise to burst at the surface. Figure 4-2 illustrates how the collapsing bubble cavity ejects a central jet, which breaks into approximately four jet drops, each about 1/10 the diameter of the original bubble (Blanchard, 1963). The jet drops are composed of seawater and organic and other surface-active materials which may be concentrated into the 0.05- to 0.5-μm thickness of bubble surface (MacIntyre, 1974). Bubbles with diameters of 100 to 1000 μm occur abundantly in the sea surface and produce jet droplets of 10 to 100 μm in diameter, small enough to become airborne in moderate winds. Additional fine droplets are produced by rupture of the film cap from bubbles with diameters of >300 μm, and a 2000-μm bubble may produce up to 100 film drops of <10-μm diameter from a cap ∿.2 μm thick.

Both film and jet drops are enriched in surface-active material, but because of differences in the mechanics of droplet formation, there may be differences in chemical composition of the two kinds of drops (Berg and Winchester, 1978). For example, jet drops may be formed from thinner bubble layers than are film drops, and they may contain surface-active particulate matter scavenged from the water column by the rising bubbles.

The surface-active material enriched in jet and film drops may be of natural or pollutant origin and may include organic molecular films, organic and inorganic particulate matter suspended in near-surface waters, and viable

particles including viruses, bacteria, and larger living forms (Blanchard and Parker, 1977; Duce and Hoffman, 1976). Such materials, by becoming components of sea spray aerosol droplets, may be carried through the atmosphere far from the point of origin. The potential for virus transfer from coastal waters to the atmosphere and transport by winds inland to inhabited areas has been demonstrated (Baylor et al., 1977). Once the processes of formation and transport of natural sea spray droplets are understood, the potential sea-to-air transport of viable and nonviable water pollutants may be predicted.

Sea salt droplets are produced by dispersion of a condensed phase and tend to be most abundant in large particle sizes. Particles tend to be large because their formation requires less energy than does that of small particles.

Figure 4-3 shows size distributions of Cl and Br particles in the clean marine atmosphere of Hawaii (Moyers and Duce, 1972). Both elements occur predominantly in the 1- to 8-μm aerodynamic diameter range (impactor stages D, C, B), with lower concentrations in the <1-μm and >8-μm ranges. The droplets may originate primarily from film cap rupture, with a contribution of jet drops to the fraction collected by impactor stage A. The size distributions are similar, and the elements are in proportions approximating the composition of seawater, indicating that they are mainly constituents of the dispersed water rather than surface film material. Lower Br/Cl ratios in the smallest particle size ranges, however, suggest surface chemical fractionation during droplet formation or atmospheric chemical reactivity and gas-particle interactions, leading to changes in aerosol composition prior to sampling.

Figure 4-4 compares the particle size distributions of iodine and chlorine aerosols in the Hawaiian marine atmosphere (Moyers and Duce, 1972). Unlike Br,

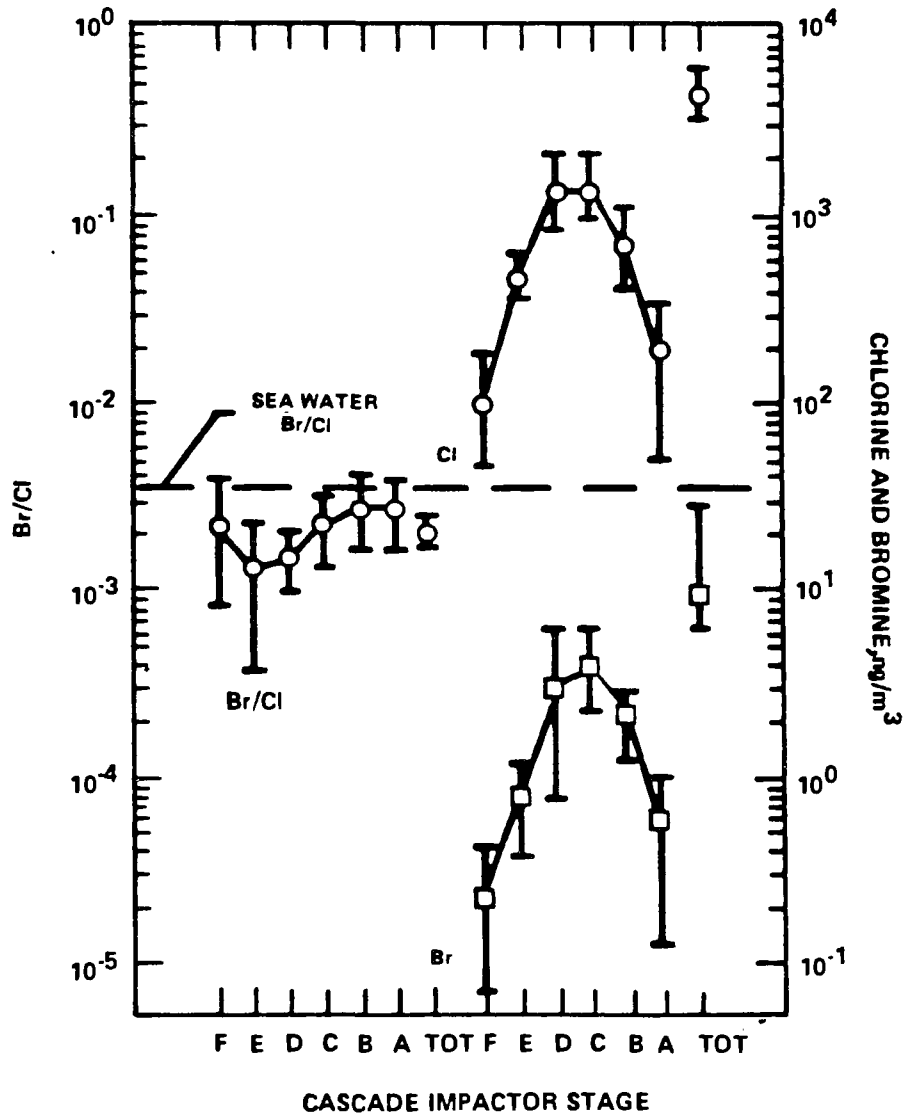



Figure 4-3. Average particle-size spectra for chloride concentration, bromide concentration, and bromide/chloride ratio were obtained with an Andersen impactor with a minimum stage E cutoff diameter of 0.5 $\mu$m.

Source: Moyers and Duce (1972).

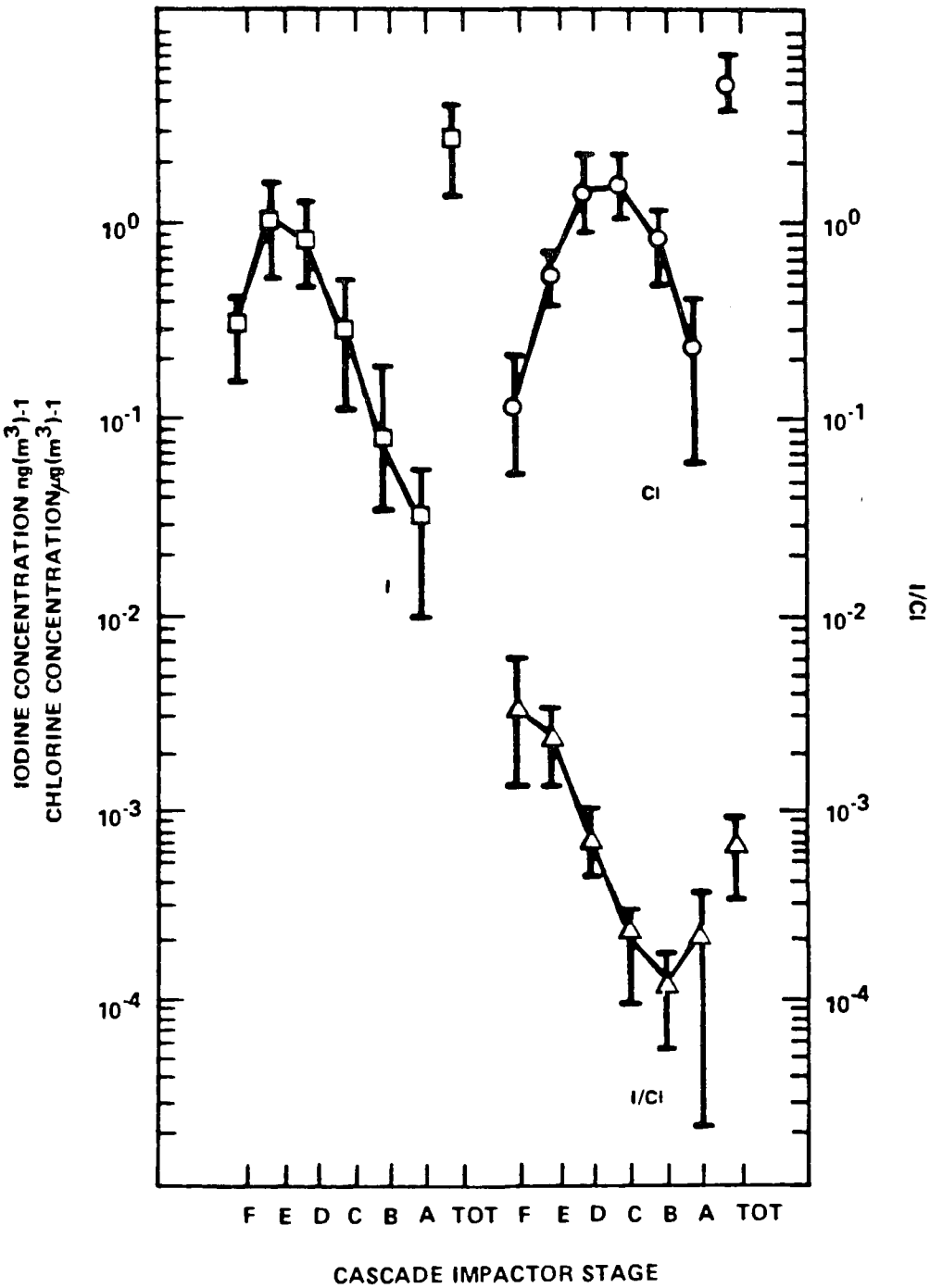



Figure 4-4. Average particle size spectra of particulate chloride concentration, particulate iodine concentration, and particulate iodide/chloride ratio were obtained with an Andersen impactor.

Source: Moyers and Duce (1972).

I is found mostly in the smallest particle fractions, stages F, E, D; the I/Cl ratio in particles is much higher than in seawater ($3 \times 10^{-6}$). Rainwater shows a similar degree of I enrichment (Duce et al., 1965). Volatility of iodine-containing vapors from the sea surface and reaction with fine aerosol particles may account for the enrichment; primary injection of iodine-rich surface films into the atmosphere may also contribute. The mechanisms of element fractionation at the surface of the sea are still poorly understood and are the object of intense research (Working Symposium, 1972; International Symposium, 1974).

### 4.2.4 Volcanic Emissions

Emissions from volcanic eruptions and fumaroles may contribute to the global aerosol and atmospheric sulfur background and have climatic significance. Materials injected into the stratosphere may persist for many months but then be rapidly removed in the troposphere. The famous eruption of Krakatoa in 1883 injected enough dust into the stratosphere to cause brilliant sunsets thousands of kilometers away and a global reduction of incoming solar radiation (Wexler, 1951a,b). In most industrialized continental areas, the contribution of volcanic emissions is negligible in comparison with regional-scale anthropogenic emissions.

The average global emission rates of sulfur and several of its compounds have been estimated by a number of investigators (Koyama et al., 1965; Holser and Kaplan, 1966; Kellogg et al., 1972; Storber and Jepson, 1973; Friend, 1973; Cadle, 1975). Table 4-3 (Granat et al., 1976) shows that the median of four estimates of elemental sulfur emitted to the atmosphere is 3 Tg of sulfur per year. Anthropogenic emissions to the atmosphere are estimated at 65 Tg of sulfur per year, of which 98 percent is $SO_2$ and some 2 percent is sulfate (Friend, 1973).

TABLE 4-3. SULFUR EMITTED BY VOLCANOES AND FUMAROLES (Tg/year)[a]

| Reference | To air | To river runoff | To air and river runoff |
|---|---|---|---|
| (Koyama et al., 1965) | | | 7 |
| (Holser et al., 1966) | | | 12 |
| (Kellogg et al., 1972) | 0.75 | | |
| (Stoiber, 1973) | 3.5 | 4 | |
| (Friend, 1973) | 2 | 5 | 7 |
| (Cadle, 1975) | 3.75 | | |

[a]1 Tg = $10^{12}$ g.

Source: Granat et al. (1976).

The Agung eruption of 1963 injected into the stratosphere about 0.3 Tg of sulfur, 0.2 Tg in the Northern Hemisphere and 0.1 Tg in the Southern Hemisphere (Granat et al., 1976). This injection led to the formation of submicron sulfate aerosol with an estimated residence time of 6 months (Junge et al. 1961) to a year or longer (Castleman et al., 1974). This global burden is 30 times greater than the estimated pre-Agung stratospheric sulfur inventory of 0.01 Tg of sulfur (Granat et al., 1976). Explosive volcanic eruptions have injected substantial, although smaller, amounts of sulfur into the stratosphere several times since 1963 (Castleman et al., 1974).

Volcanic emissions of heavy metals into the lower atmosphere can be comparable to industrial pollution emissions on a regional basis. Metallic constituents of particulate matter emitted from Mount Etna, Sicily, in June 1976 (Buat-Menard and Arnold, 1978) were compared with estimated pollution emissions from bordering countries of the Mediterranean basin. Mount Etna was

found to be the predominant source of Se, a source comparable in strength to anthropogenic sources of Cd, Hg, Cu, and Zn, but insignificant in comparison with automotive emissions of Pb. Consequently, in regions with active volcanism, natural emissions of heavy metals must be considered in estimating total metals emissions inventories. In other regions, volcanism has little influence on atmospheric chemical composition.

4.2.5 Biosphere Emanations

A significant natural source of sulfur, organic matter, and elemental constituents of aerosols is the terrestrial and marine biosphere. Volatile, reduced sulfur compounds are released to the atmosphere by microbiological processes and may become oxidized to $SO_2$ and sulfate. The compounds released include hydrogen sulfide ($H_2S$), methyl mercaptan, dimethyl sulfide (DMS), dimethyl disulfide, and carbon disulfide (Lovelock et al., 1972; Rasmussen, 1974; Lovelock, 1974). The releases of $H_2S$ and DMS may have the greatest impact on the global sulfur cycle (Granat et al., 1976). The greatest $H_2S$ concentrations occur where anaerobic surface conditions prevail, such as tidal flats and shallow oceanic and freshwater bodies with reduced bottom conditions. For DMS, natural soil sources may be predominant, with secondary releases from senescent leaves, marine algae, and fresh leaves (Granat et al., 1976; Hitchcock, 1975). Terrestrial $H_2S$ and DMS releases on a global basis are estimated at 5 Tg of sulfur per year, and oceanic releases may be as high as 27 Tg of sulfur per year (Granat et al., 1976), constituting a major component of the current total of natural and anthropogenic sulfur releases to the atmosphere (Kellogg et al., 1972). Low aerosol sulfur concentrations in the Southern Hemisphere suggest that little sulfate is formed as a result of these emissions (Lawson and Winchester, 1979a).

Volatile organic compounds released from plants have been estimated at 200 Tg/year (Went, 1960). Isoprene derivatives such as terpenes, carotenoids, and other compounds are believed to predominate. They are likely to be partially oxidized to form aerosol particles rather than completely oxidized to $CO_2$ and $H_2O$, resulting in blue haze and submicron condensation nuclei (Went, 1960; Went et al., 1967; Rasmussen and Went, 1965; Schnell and Vali, 1972, 1973). In cities, anthropogenic emissions form the bulk of the organic content of the atmosphere; in the countryside, natural organic emissions may dominate.

Aerosol particles, including organic material and trace metals and nutrient elements such as S, K, and P, are released from plants. Trace metals have long been known to occur in fluids secreted by plants (Curtis, 1944). Radiotracer Sr is transferred from plant foliage to the atmosphere, presumably in wax particles (Moorby and Squire, 1963) which may be affected by electric fields (Fish, 1972). Transpiration causes the transfer of both cations and anions to the atmosphere (Nemeryuk, 1970). Twenty-seven trace elements have been identified in exudates from coniferous trees (Curtin et al., 1974). Zn and Pb radiotracer experiments show that particles greater than 5 μm in diameter contain most of the metals released (Beauford et al. 1975, 1977). S, K, and P have also been shown to be associated with tropical forests and to occur in large aerosol particles (Lawson and Winchester, 1979b). The metal content of plant-derived aerosols is so high that it has been suggested as an indicator for geochemical prospecting (Barringer, 1977; Curtin et al., 1974).

### 4.2.6 Biomass Burning

The worldwide burning of biomass, especially in the clearing of tropical forests for agriculture, contributes substantially to the global release of trace gases and carbonaceous particulate matter. The gaseous flux of carbon

to the atmosphere has been the focus of recent research because the release of $CO_2$ from burning natural vegetation may be comparable in magnitude to that from fossil fuels (Woodwell et al., 1978). Other estimates of $CO_2$ release from forest burning are lower (Bolin, 1977; Baes et al., 1976). The range of estimates is 0.5 Pg of C to more than Pg of C per year (Pg = $10^{15}$ g) as compared with 5-6 Pg of C from fossil fuels (Seiler and Crutzen, 1979). The role of forests and grasslands in the global $CO_2$ balance, whether forested land areas are decreasing through clearing, and whether the terrestrial biomass is a net source or a net sink of $CO_2$ are unresolved questions (Bolin, 1979).

Biomass burning results in the formation of charcoal, which cannot be utilized by microorganisms and consequently persists in the environment, perhaps for longer than 1000 years (Seiler and Crutzen, 1979). Because of its low density, much of the charcoal is transported by flowing water and also becomes airborne and transported by winds to the oceans. Carbon particles account for some 0.02 to 0.1 percent of the dry weight of Pacific and Atlantic Ocean sediments (Smith et al., 1973; Griffin and Goldberg, 1975), providing evidence for long-range atmospheric transport, fallout, and settling of these particles through the water column.

Chemical analysis of particulate matter from temperate forest burning indicates approximately 50 percent benzene-soluble organic matter, 40 percent elemental carbon, and only 10 percent mineral matter (Ryan and McMahon, 1976). The estimated extent of biomass burning worldwide suggests an annual release of roughly 200 to 450 Tg of particulate matter containing 90 to 200 Tg of elemental carbon (Seiler and Crutzen, 1979). With a mean residence time of up to a week for fine particulate matter generated near the earth's surface

(Junge, 1963; Martell and Moore, 1974) and uniform mixing up to 1000 m in altitude, carbon particle concentrations would average 4 $\mu g/m^3$. The estimated average particulate carbon concentration attributed to biomass burning indicates that soot carbon constitutes a significant fraction of the aerosol loading in the atmosphere.

The fluxes of gaseous and particulate sulfur to the atmosphere may also be due in part to biomass burning. Carbonyl sulfide (COS) has been detected by gas sampling in a forest fire (Crutzen et al., 1979). Moreover, enhanced regional concentrations of fine particulate S and K have been found in central Brazil during the agricultural burning season (Lawson and Winchester, 1978). As a consequence, estimates of pollution sources in such areas should include an evaluation of biomass burning near the sampling sites.

## 4.3 MANMADE SOURCES OF SULFUR OXIDES AND PARTICULATE MATTER

### 4.3.1 Sulfur Oxide Emissions

4.3.1.1 National and Regional Overview--In 1977, stationary fuel combustion and industrial processes accounted for about 97 percent of the anthropogenic emission of sulfur oxides in the United States. The remaining 3 percent was emitted primarily by motor vehicles (U.S. Environmental Protection Agency, 1978a). Table 4-4 and Figure 4-5 (U.S. Environmental Protection Agency, 1978a) indicate that in 1975, combustion of fossil fuels by electric utilities and industrial facilities produced three-quarters of the total stationary source emissions of sulfur oxides. Industrial processes such as smelting accounted for the remaining one-quarter. This section discusses both national and regional sulfur oxide emission trends.

4.3.1.1.2 National sulfur oxide emissions and fuel use: Historical trends. Figure 4-6 (U.S. Environmental Protection Agency, 1978a; U.S. Department of

TABLE 4-4. NATIONAL SULFUR OXIDES EMISSIONS INVENTORY SUMMARY[a]

| Emissions source | Sulfur oxides, $10^6$ metric tons/yr | % of Total |
|---|---|---|
| Utility fuel combustion | | |
| Coal | 16.59 | 57.0 |
| Oil | 1.90 | 6.5 |
| Other | 0.11 | 0.4 |
| Total | 18.60 | 63.4 |
| Industrial fuel combustion | | |
| Coal | 2.04 | 7.0 |
| Oil | 1.35 | 4.6 |
| Other | 0.25 | 0.9 |
| Total | 3.64 | 12.5 |
| Industrial processes | | |
| Primary | | |
| Metal | 3.47 | 11.9 |
| Petroleum and chemical | 1.70 | 5.9 |
| Other | 0.80 | 2.7 |
| Total | 5.97 | 20.5 |
| Commercial, residential, and miscellaneous fuel use | | |
| Coal | 0.22 | 0.7 |
| Oil | 0.61 | 2.1 |
| Other | 0.01 | <0.1 |
| Total | 0.84 | 2.9 |
| Miscellaneous | 0.06 | 0.2 |
| Total | 29.09 | 100 |

[a]Transportation emissions are not included.

Source: U.S. Environmental Protection Agency (1978a).

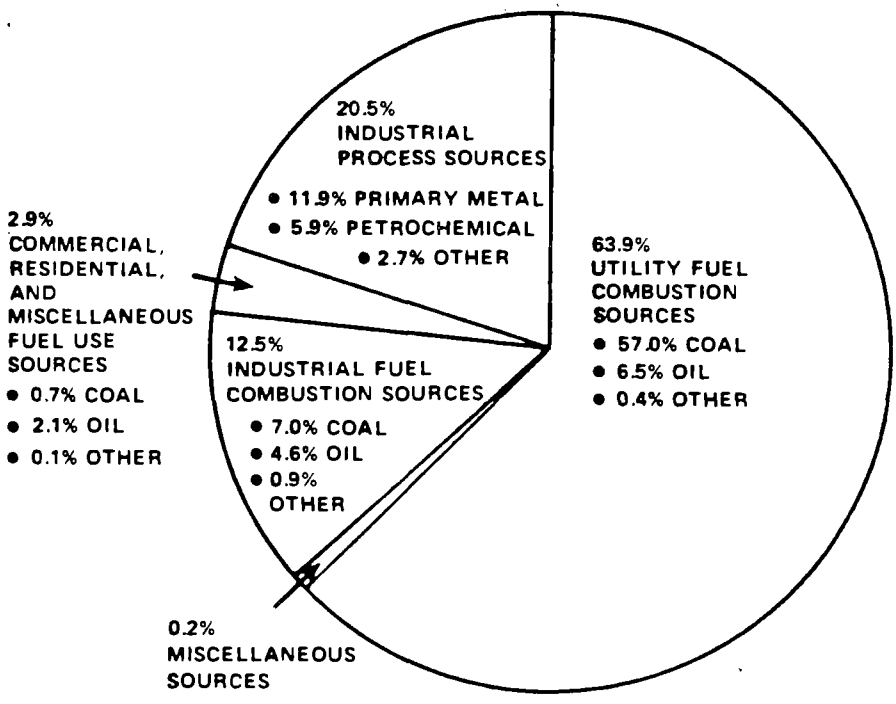



Figure 4-5. Percentage of 1975 national sulfur oxide emissions is shown by source category. Transportation emissions are not included.

Source. U.S. Environmental Protection Agency (1978a).

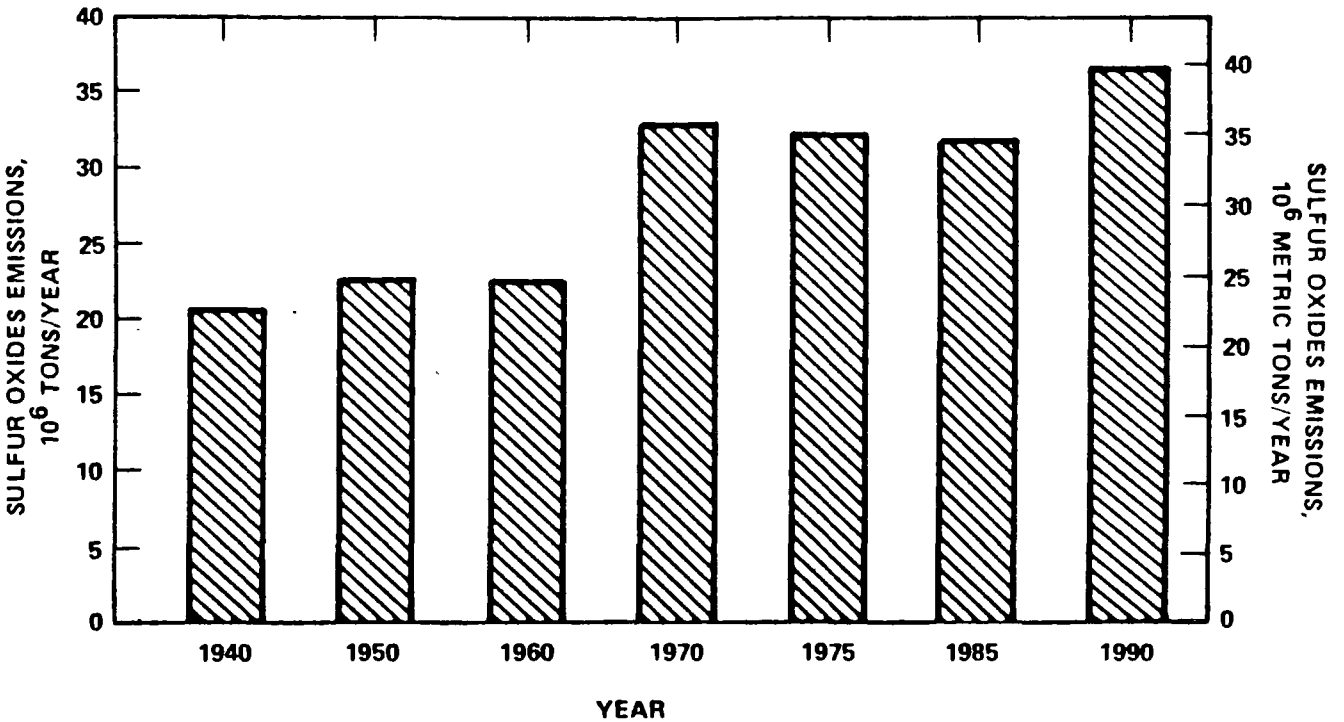



Figure 4-6. Bar chart represents nationwide estimates of sulfur oxide emissions are shown for 1940-90. For 1940-75, transportation sources are not included.

Sources: U.S. Environmental Protection Agency (1978a).
U.S. Department of Energy (1979a).

Energy, 1979a) illustrates the growth of $SO_x$ emissions from 1940 through 1975. Similarly, Table 4-5 and Figure 4-7 indicate the growth in the use of fossil fuels. These trends are discussed below with respect to the three primary types of fuel-using stationary sources: electric utilities, industrial facilities and residential and commercial establishments.

4.3.1.1.2.1 Utilities. Electric utilities account for almost two-thirds of the $SO_x$ emissions in the United States. These emissions result from the use of coal, oil, or gas to fire steam electric boilers. Table 4-5 shows that the proportion of low-sulfur fuels (oil and gas) used in electric power plants increased during the 1960's and then began to decrease; by 1977, coal accounted for almost 60 percent of the fossil fuels used by electric utilities. The increase in oil and gas use in the 1960's reflects the increased availability and relatively low prices of oil and gas, the lower capital costs of oil- and gas-fired boilers, and the environmental advantages of using oil and gas rather than coal. However, the oil embargo of 1973-74 coupled with the sudden fourfold increase in world oil prices reversed this trend.

The substitution of cleaner fuels and the imposition of environmental controls on coal-fired power plants account, in part, for the slight reduction in $SO_x$ emissions in 1970-75 (Figure 4-6).

4.3.1.1.2.2 Industrial facilities. Table 4-4 and Figure 4-5 (U.S. Environmental Protection Agency, 1978a) show that industrial facilities account for about one-third of total $SO_x$ emissions. Most of these emissions result from specific industrial processes, such as ore smelting.

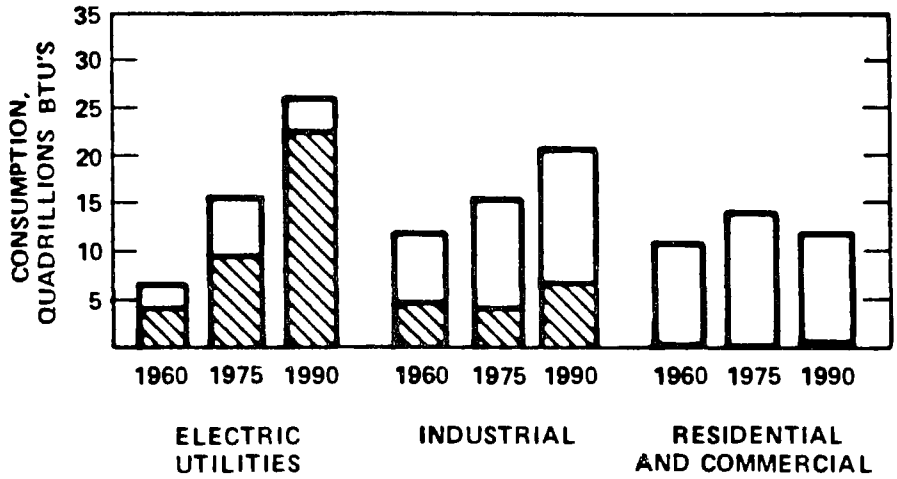
Over one-third of the industrial $SO_x$ emissions (and one-eighth of the total national $SO_x$ emissions) result from the combustion of fossil fuels to produce process heat and steam for industrial facilities. Table 4-5 shows

TABLE 4-5. U.S. FOSSIL FUEL CONSUMPTION FOR STATIONARY SOURCES BY YEAR BY CONSUMING SECTOR[a]
(quadrillion btu)

| Year | Electric utility | Industry | Residential and commercial | Total stationary sources |
|---|---|---|---|---|
| 1960 | | | | |
| Oil | 0.56 | 2.32 | 5.14 | 8.02 |
| Gas | 1.78 | 4.48 | 4.25 | 10.51 |
| Coal | 4.22 | 4.68 | 1.05 | 9.95 |
| Total | 6.56 | 11.48 | 10.44 | 28.48 |
| 1970 | | | | |
| Oil | 2.11 | 2.33 | 6.71 | 11.15 |
| Gas | 4.02 | 9.58 | 7.47 | 21.07 |
| Coal | 7.45 | 5.05 | 0.49 | 12.99 |
| Total | 13.58 | 16.96 | 14.67 | 45.21 |
| 1975 | | | | |
| Oil | 3.23 | 2.47 | 5.95 | 11.65 |
| Gas | 3.25 | 8.64 | 7.67 | 19.56 |
| Coal | 9.28 | 3.65 | 0.17 | 13.10 |
| Total | 15.76 | 14.76 | 13.79 | 44.31 |
| 1977 | | | | |
| Oil | 4.03 | 2.71 | 5.19 | 11.93 |
| Gas | 3.29 | 8.24 | 7.56 | 19.09 |
| Coal | 10.27 | 3.82 | 0.13 | 14.22 |
| Total | 17.59 | 14.77 | 12.88 | 45.24 |
| 1990 | | | | |
| Oil | 3.17 | 3.73 | 3.78 | 10.68 |
| Gas | 0.51 | 9.98 | 7.79 | 18.28 |
| Coal | 22.05 | 6.64 | 0.05 | 28.74 |
| Total | 25.73 | 20.35 | 11.62 | 57.70 |

[a]Historical fuel consumption data (1960-77) taken from Federal Energy Data System (FEDS) (DOE/EIA-0192), July 1979. The 1990 fuel use is based on the Series C projections of the Department of Energy (it assumes moderate supply and demand). There are minor discrepancies in the data based used to compile the 1960, 1970, and 1975 data and the 1977 and 1990 data due to differences in the definitions of fuel categories (such as inclusion or exclusion of natural gas liquids in the use of natural gas).

Source: U.S. Department of Energy, (1979a). (The model utilized in these air emission projections is the Regional Emission Projection Systems. REPS is documented in "An Air Emissions Analysis of Energy Projections for the Annual Report to Congress," a memorandum by Edward Pechan dated September 1978).
U.S. Department of Energy (1979b).



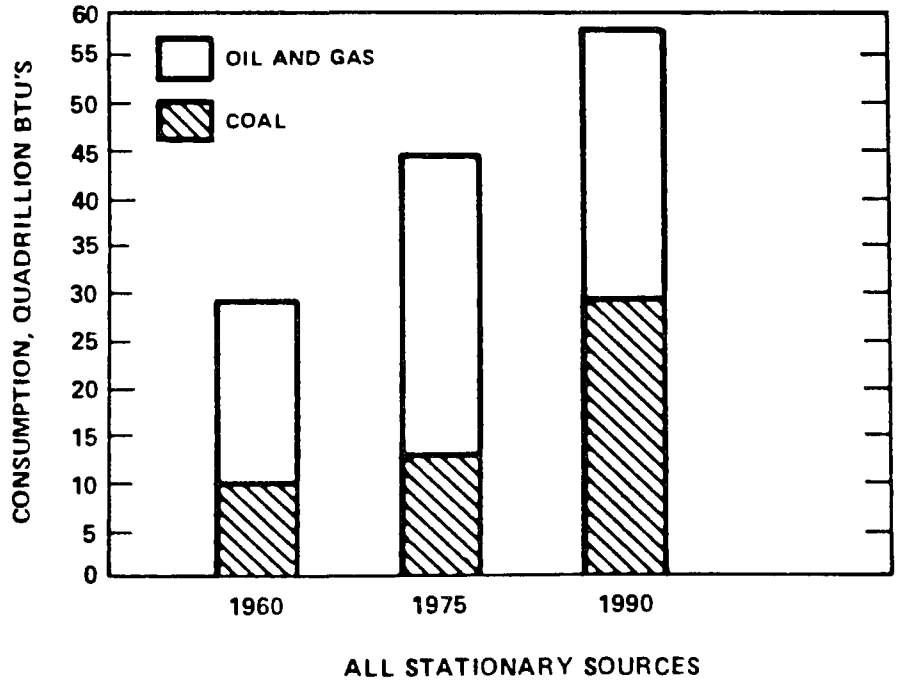




Figure 4-7. Bar chart represents stationary-source fossil fuel consumption by consuming sector for 1960, 1975, and 1990 illustrates data presented in Table 4-5.

that use of fossil fuels by industry grew less rapidly than utility fossil fuel use in the 1960's and declined between 1970 and 1975. This decline appears to be the result of two factors: massive conservation efforts by industry in response to sharply higher oil and gas prices, and the effects of the 1974 recession on large fuel-using industries.

Table 4-5 and Figure 4-7 show that although in 1975 total fuel consumption by industry and utilities was about the same, industry burned much less coal. This difference accounts for the relatively smaller share of total $SO_x$ emissions from industrial fuel use.

4.3.1.1.2.3 Residential and commercial establishments. The residential and commercial fuel-using sector accounts for only about 3 percent of total $SO_x$ emissions. But unlike utility and industrial $SO_x$ emissions, residential and commercial emissions are released near the ground and thus can significantly affect the air quality in the immediate area. Also, most of the $SO_2$ emissions from residential and commercial space heating occur in areas of high population density. Finally, these emissions are highest during the winter heating season.

On the other hand, low-sulfur oil and natural gas are burned for space heating by the commercial sector. The $SO_2$ emissions are usually much lower from this sector than from the other $SO_2$ sources. Assuming trends continue, Table 4-5 shows that coal use in this sector may be almost eliminated by 1990. Government policies affecting the pricing and allocation of heating oil and natural gas have promoted the use of these low-sulfur fuels.

4.3.1.1.3 Future trends. Based on data from the National Environmental Data System (NEDS) and projections of fuel use by the Energy Information Administration (EIA), national total $SO_x$ emissions are expected to decline through 1985 and increase thereafter. This forecast is illustrated in Figure 4-6.

The EIA fuel use projections generally assume reduced overall energy growth rates, greater use of coal, reduced dependence on oil imports, continued increases in energy prices, and more energy use by electric utilities. Rising oil costs will tend to increase coal use and, hence, $SO_x$ emissions. The predicted decline in $SO_x$ emissions until 1985 assumes stricter New Source Performance Standards (NSPS) for new power plants and some industrial facilities and retirement of older facilities. According to DOE projections, this trend may be counteracted by the use of fossil fuel, especially coal, which is expected to increase total $SO_x$ emissions after 1985 (Figure 4-6).

4.3.1.1.3.1 Utilities. The projected increased coal use by electric utilities is expected to be the result of reduced availability of oil and gas and sharply higher prices after 1974. In late 1978, Congress enacted the Powerplant and Industrial Fuel Use Act, which prohibits new oil- and gas-fired boilers and requires existing utilities to phase out gas use by 1990. This legislation is expected to further restrict oil and gas use by utilities. Thus, coal, which accounted for 60 percent of all utility fossil fuel use in 1977, is forecasted by the Department of Energy to increase over 85 percent by 1990, as shown in Table 4-5.

In 1960, electric utilities accounted for only about 23 percent of the fossil fuel used by stationary sources; by 1990 this share is estimated to increase to about 49 percent.

4.3.1.1.3.2 Industrial facilities. Because of environmental constraints and increased availability of natural gas, industrial coal use is projected by DOE to decline during the 1960's. By 1990, a resurgence of coal use for industrial boilers and process heat is expected. The Fuel Use Act prohibits large new industrial boilers from using oil or gas and provides the Department

of Energy with the authority to extend this prohibition to existing coal-capable units of future nonboiler combustors. Nevertheless, coal is not anticipated to account for more than one-third of the fossil fuel use in industrial facilities by 1990.

4.3.1.1.3.3 Residential and commercial establishments. Conservation, use of solar power, and electrification are expected to cause decrease in fossil fuel use in this sector. Coal use by residences and businesses is expected to diminish by 1990. Therefore, $SO_x$ emissions from this sector are not expected to increase over the 1980's.

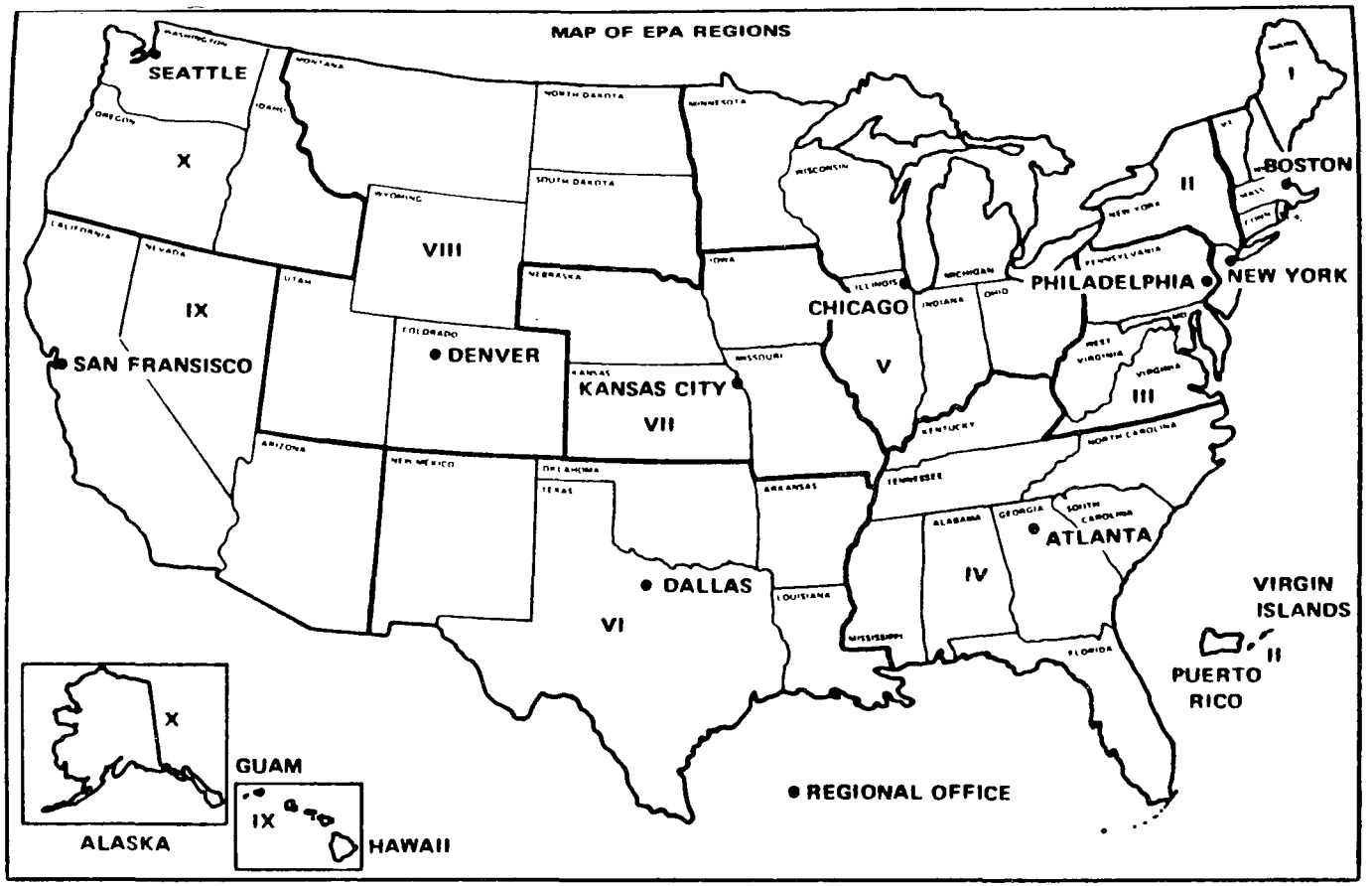
4.3.1.1.4 Regional $SO_x$ emissions.

4.3.1.1.4.1 Current emissions distribution. $SO_x$ emissions vary greatly throughout the country. As is evident in Figure 4-8, (U.S. Environmental Protection Agency, 1978a), two of the nine EPA regions--the South Atlantic and Midwest regions--accounted for more than half of all $SO_x$ emissions nationwide in 1975. Figure 4-9 (U.S. Environmental Protection Agency, 1979) indicates the density of $SO_x$ emissions on a county basis. This variation is the result of three factors.

(1) The variation in energy consumption, which is primarily a function of population density and industrial energy use.

(2) The type of fuel used. Areas with a large portion of hydroelectric, nuclear, or low-sulfur fossil fuel use have lower emissions than areas more dependent on coal or high-sulfur oil.

(3) The presence of large $SO_x$-emitting industrial facilities, such as primary metal processors.




| | I | II | III | IV | V | VI | VII | VIII | IX | X |
|---|---|---|---|---|---|---|---|---|---|---|
| $SO_x$ emissions | | | | | | | | | | |
| ($10^6$ metric tons) | 0.59 | 1.40 | 4.04 | 5.92 | 9.64 | 2.28 | 1.59 | 0.72 | 2.63 | 0.31 |
| Percent of U.S. total | 2.0 | 4.8 | 13.9 | 20.3 | 33.1 | 7.8 | 5.5 | 2.5 | 9.0 | 1.1 |

Figure 4-8. Distribution of 1975 sulfur oxide emissions and percentages of U.S. total sulfur oxide emissions are shown for the EPA regions.

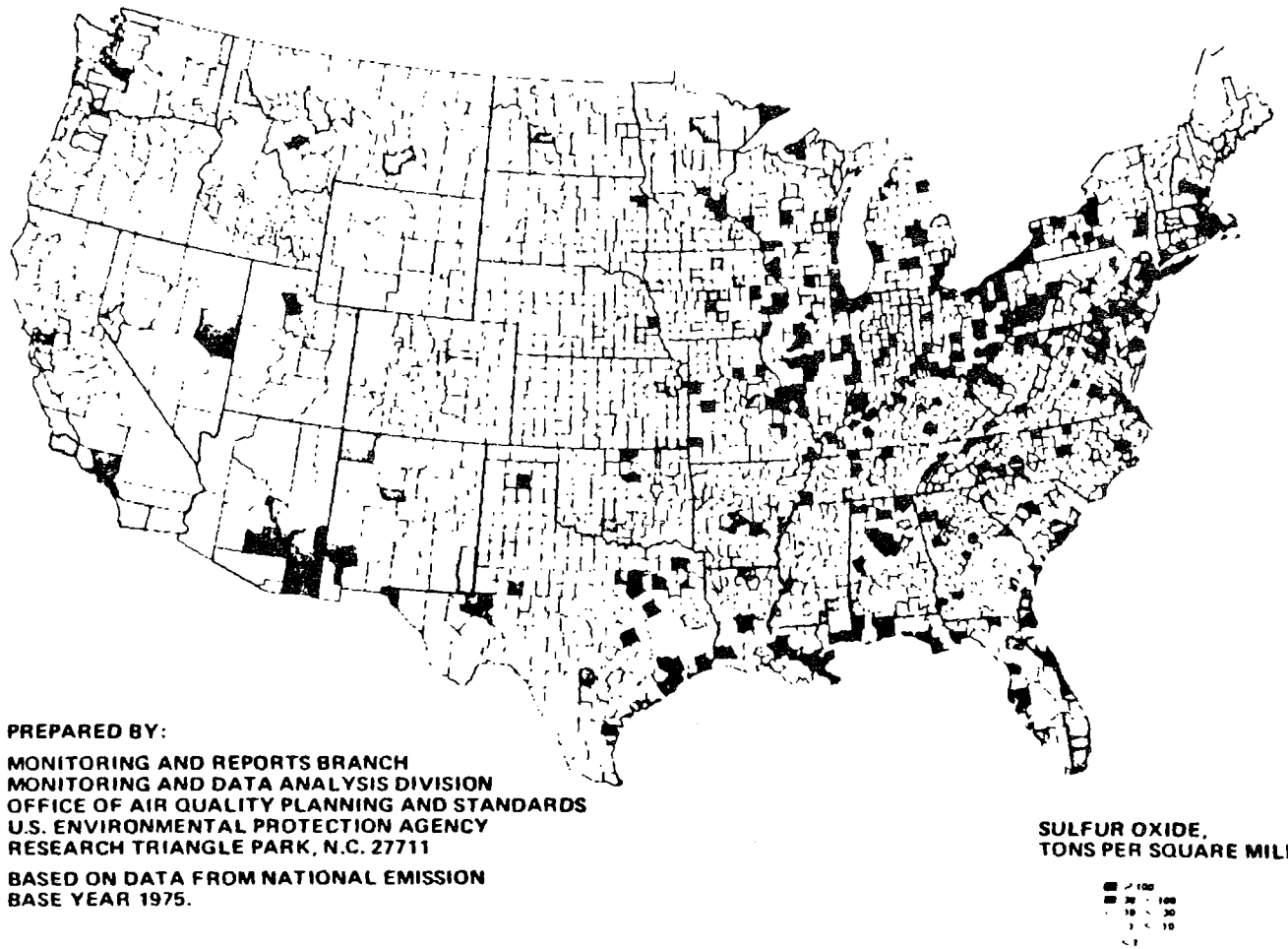



Figure 4-9. Sulfur oxide emission density by county.

Electric utility fuel combustion accounted for about 64 percent of total $SO_x$ emissions nationwide in 1974. On a regional basis, $SO_x$ emissions from power plants vary from 5.2 percent in Region X (Northwest) to more than 80 percent in Regions IV and V. These variations, illustrated in Table 4-6, are also affected by the presence of industrial process sources.

4.3.1.1.4.2 Industrial process sources. In 1975, industrial process sources account for about one-fifth of the national $SO_x$ emissions from stationary sources. Specifically, the primary metals industry contributes nearly 12 percent, and the petroleum and chemical industries together contribute about 6 percent of the national $SO_x$ emissions. Most $SO_x$ emissions in EPA Regions VI, IX, and X (61.5, 86.6, and 56.1 percent, respectively) are from industrial process sources. Industrial process sources account for less than 7 percent of the $SO_x$ emissions in Regions I, IV, and V.

As seen in Figure 4-10 (U.S. Environmental Protection Agency, 1974), most of the primary copper, lead, and zinc smelters are in EPA Regions VI, IX, and X. Smelters are large emitters of $SO_x$.

El Paso County in Texas, southeastern Arizona counties, and counties in western Montana have high $SO_x$ emissions from smelters.

Petroleum-refining capacity is greatest in EPA Regions V, VI, and IX, especially in Texas, Louisiana, California, and Illinois. Elemental sulfur production capacity is concentrated in Texas and Louisiana. Sulfuric acid plants are dispersed widely throughout the Nation, but the majority of larger plants are located in Florida. The literature does not address the location of other $SO_2$ sources of the chemical industry.

TABLE 4-6. PERCENTAGE OF EPA REGIONAL $SO_x$ EMISSIONS BY SOURCE CATEGORY[a]

| Emissions source | EPA region I | II | III | IV | V | VI | VII | VIII | IX | X |
|---|---|---|---|---|---|---|---|---|---|---|
| Utility fuel combustion | | | | | | | | | | |
| Coal | 7.6 | 24.9 | 61.7 | 75.0 | 79.6 | 11.6 | 69.0 | 28.0 | 2.1 | 4.2 |
| Oil | 37.5 | 32.8 | 8.1 | 7.0 | 1.0 | 6.2 | 1.6 | 0.7 | 6.5 | 0.8 |
| Other | <0.1 | 0.3 | 0.6 | 0.3 | <0.1 | 2.2 | 0.4 | 0.2 | <0.1 | 0.2 |
| Total | 45.1 | 58.1 | 70.5 | 82.3 | 80.6 | 20.0 | 71.0 | 28.9 | 8.6 | 5.2 |
| Industrial fuel combustion | | | | | | | | | | |
| Coal | 0.9 | 7.9 | 9.7 | 4.3 | 10.0 | 5.4 | 8.2 | 5.8 | 0.1 | 6.0 |
| Oil | 35.0 | 12.7 | 4.6 | 5.0 | 1.7 | 6.9 | 0.9 | 6.5 | 2.5 | 15.2 |
| Other | 0.2 | 0.2 | 0.5 | 0.4 | 0.8 | 3.5 | 0.3 | 1.5 | 0.7 | 3.7 |
| Total | 36.1 | 20.8 | 14.8 | 9.7 | 12.5 | 15.8 | 9.4 | 13.7 | 3.2 | 24.9 |
| Industrial processes | | | | | | | | | | |
| Primary metal | 0.0 | 0.3 | 4.4 | 0.5 | 1.5 | 20.7 | 9.0 | 37.1 | 80.5 | 39.1 |
| Petroleum and chemical | 0.5 | 4.3 | 4.6 | 3.5 | 1.7 | 34.7 | 2.9 | 13.2 | 5.0 | 8.4 |
| Other | 1.2 | 7.0 | 2.3 | 2.5 | 1.5 | 6.1 | 6.0 | 3.2 | 1.1 | 8.6 |
| Total | 1.7 | 11.6 | 11.3 | 6.5 | 4.7 | 61.5 | 17.9 | 53.5 | 86.6 | 56.1 |
| Commercial, residential and miscellaneous fuel use | | | | | | | | | | |
| Coal | 0.2 | 0.9 | 1.0 | 0.4 | 1.1 | <0.1 | 0.6 | 1.0 | <0.1 | 0.2 |
| Oil | 16.2 | 8.0 | 2.4 | 1.0 | 1.0 | 2.1 | 0.7 | 2.8 | 1.2 | 13.3 |
| Other | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | 0.1 | 0.1 |
| Total | 16.4 | 9.0 | 3.4 | 1.4 | 2.1 | 2.2 | 1.4 | 3.8 | 1.3 | 13.6 |
| Miscellaneous | 0.6 | 0.5 | 0.1 | 0.1 | 0.1 | 0.5 | 0.2 | 0.1 | 0.2 | 0.2 |

[a]Transportation sources are not included.

Source: U.S. Environmental Protection Agency (1978a).

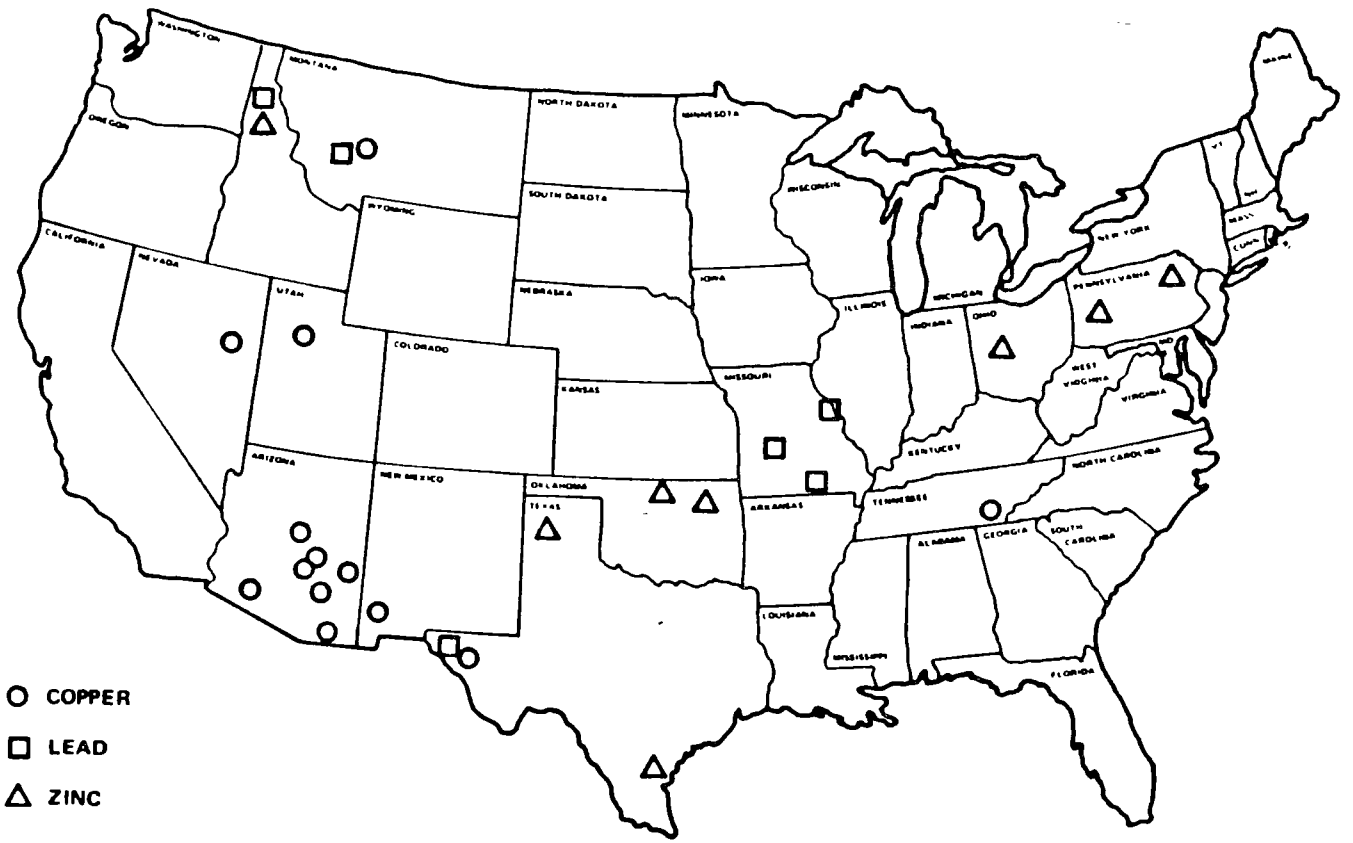



Figure 4-10. Locations are shown for existing primary metal smelters (midyear 1973).

Source: U.S. Environmental Protection Agency (1974).

4.3.1.1.4.3 Future regional emission patterns. In the 1980's, $SO_x$ emissions are expected to decline in Regions III, IV, and V and increase in other regions, particularly Region VI (see Table 4-7). Regional $SO_2$ emissions are expected to vary in the future because of differences in regional energy and economic growth rates. Furthermore, areas now relying on coal are expected to have lower $SO_x$ emissions as power plants and industrial facilities that emit large amounts of $SO_x$ are retired or fitted with high-efficiency emission controls. Finally, areas with little previous coal use are expected to convert from oil and gas to coal and therefore increase $SO_x$ emissions.

4.3.1.2 $SO_x$ Source Emissions Characteristics--Stationary sources may emit $SO_x$ in many forms. By volume, over 90 percent of total national $SO_x$ emissions are in the form of $SO_2$. The balance consists of primary sulfate, made up of gaseous sulfur trioxide ($SO_3$) and sulfuric acid ($H_2SO_4$), $H_2SO_4$ mist, and particulate sulfates, which include metallic sulfates ($MSO_4$, where M is a metal or ammonium ion) and $H_2SO_4$ that has been adsorbed onto particles.

Several factors affect the quantity and composition of $SO_x$ emissions from a particular source. Among these factors are the source type, operating conditions, fuel characteristics, and type of emissions control equipment.

Emissions of $SO_2$ from major $SO_x$ sources are documented in Compilation of Air Pollutant Emission Factors (U.S. Environmental Protection Agency, 1977). There is comparatively little information on primary sulfate emissions from major $SO_x$ sources. Research on the composition of primary sulfate emissions from utility and industrial boilers has only begun within the last few years. There is little information on the composition of $SO_x$ emissions from residential and commercial fuel combustion sources and industrial process sources.

TABLE 4-7. CURRENT AND PROJECTED SULFUR OXIDES EMISSIONS BY EPA REGION[a] ($10^6$ metric tons)

| | EPA region | 1975 | 1985 | 1990 |
|---|---|---|---|---|
| I | New England | 0.59 | 0.69 | 0.85 |
| II | New York/New Jersey | 1.40 | 1.66 | 2.23 |
| III | Mid-Atlantic | 4.04 | 3.68 | 3.92 |
| IV | South Atlantic | 5.92 | 5.04 | 5.80 |
| V | Midwest | 9.65 | 7.53 | 8.59 |
| VI | Southwest | 2.28 | 3.74 | 5.47 |
| VII | Central | 1.59 | 1.78 | 1.96 |
| VIII | North Central | 0.72 | 0.69 | 0.83 |
| IX | West | 2.63 | 2.97* | 3.02* |
| X | Northwest | 0.31 | 0.33 | 0.39 |

[a]Series C is based on moderate supply and demand assumptions. (The above estimates ignore potential decreases of emissions from smelters resulting from controls, e.g., NSPS, SIPs, etc.)

*The DOE model may not account for reductions in sulfur dioxide emissions expected within the next few years.

Sources: U.S. Environmental Protection Agency (1978a); U.S. Department of Energy (1979a).

4.3.1.2.1 Utility and industrial fuel combustion sources.

4.3.1.2.1.1 Coal. The amount of uncontrolled $SO_2$ emissions from a coal-fired utility or industrial boiler depends primarily on the amount of fuel burned, its sulfur content, and other characteristics of the fuel. Coal is a slow-burning fuel with a high ash content (Homolya and Cheney, 1978). Its low-flame temperatures lessen the production of $SO_3$ from $SO_2$ and atomic oxygen. Since coal ash is basic, some of the $H_2SO_4$ formed during combustion is neutralized by the ash (typically 5 to 15 percent by weight). Although the sulfur content of coal (ranging from 0.2 to 7 percent by weight) is high, some of the coal sulfur is trapped in the bottom ash and is not emitted to the atmosphere.

In the combustion of most coals (most commonly, bituminous), about 95 percent of the coal sulfur is emitted as gaseous $SO_2$ and $SO_3$; over 90 percent of the coal sulfur is converted to $SO_2$ (U.S. Environmental Protection Agency, 1977). The balance of the coal sulfur may be emitted as particulate sulfates or may combine with the slag or ash in the furnace and be disposed of as a solid waste. Most of the gaseous $SO_3$ is hydrated to gaseous or aerosol $H_2SO_4$ before exiting the boiler stack (Homolya and Cheney, 1979).

A study by Homolya and Cheney (1978) showed that 0.9 to 3.5 (average 2.1) percent by weight of $SO_x$ emissions from coal-fired boilers occurred as primary sulfate. The coals used in this study were 1.7 to 3.6 percent sulfur by weight.

Lignite is being used increasingly where it is plentiful at relatively low cost. The alkali content (especially sodium) of lignite ash has a major effect on the amount of coal sulfur retained in boiler ash deposits. A high-sodium lignite may retain over 50 percent of the available sulfur in the

boiler ash, while a low-sodium lignite may retain less than 10 percent of the available sulfur in the boiler ash (U.S. Environmental Protection Agency, 1977).

Other studies show that excess boiler oxygen enhances the emission of primary sulfate from coal-fired boilers (Homolya and Cheney, 1978; Bennett and Knapp, 1978). The excess oxygen increases oxidation of $SO_2$ to $SO_3$ and then $H_2SO_4$. Industrial boilers generally use higher excess oxygen levels than do utility boilers.

Dirty equipment may increase primary sulfate emissions from coal-fired boilers because boiler deposits catalyze the oxidation of $SO_2$ to sulfates. The frequency of soot-blowing operations can affect the emissions of primary sulfate from boilers with catalytically active deposits. During such operations, sulfate boiler deposits may be emitted to the atmosphere.

Emission control equipment may have a significant impact on the composition and concentration of $SO_x$ from coal-fired boilers. Electrostatic precipitators and flue gas desulfurization systems are used to abate particulate and $SO_x$ emissions.

Electrostatic precipitators provide a high degree of particulate control. They usually have little overall effect on $SO_2$ emissions but may reduce total sulfate emissions by 50 percent or more (Homolya and Cheney, 1978). Some tests have shown variability in $SO_2$ emissions from boilers equipped with "hot side" electrostatic precipitators. Conditions in these units may promote sulfate formation. Arcing can cause localized "hot spots" in which the high temperatures enhance sulfate formation, and corona discharges can produce ozone ($O_3$), which can oxidize $SO_2$ to $SO_3$ (McCurley and DeAngelis, 1978).

In the absence of particulate control devices, the mass median diameter of coal fly ashes is typically 8 to 30 μm (Natusch, 1978). Fly ashes emitted from electrostatic precipitators have a mass median diameter of 0.5 μm to 2 μm (Natusch, 1978). The collection efficiency for particulate sulfates is less than the collection efficiency for total particulate matter. Accordingly, the ratio of sulfate particles to total particles is higher in the electrostatic precipitator outlet stream than in the inlet stream (Homolya and Cheney, 1978; Bennett and Knapp, 1978; McCurley and DeAngelis, 1978). This phenomenon is referred to as sulfate enrichment of fine particulate matter.

Flue gas desulfurization systems may be designed to remove $SO_2$ with greater than 90 percent efficiency. Primary sulfate emissions removal from these systems appears to be highly dependent on design practices. Tests on a wet scrubber system showed a primary sulfate emissions removal efficiency of nearly 30 percent (Homolya and Cheney, 1979). However, several individual test results in the same study showed an increase of primary sulfate emissions across the wet scrubber. Two causes of these primary sulfate emissions increases may be penetration of the scrubber demisters by gaseous $H_2SO_4$, forming $H_2SO_4$ aerosol, and by scrubber liquor reentrainment. Like electrostatic precipitators, flue gas desulfurization systems are not generally efficient at collecting fine particulate matter.

Fuel modification can reduce $SO_x$ emissions. Coal may be modified by washing to reduce sulfur and ash content. Liquefaction and gasification of coal into new fuels can result in significant reduction of sulfur fuel content and therefore $SO_x$ emissions.

4.3.1.2.1.2 Oil. After coal, oil is the largest contributor to $SO_x$ emissions from fuel combustion sources. The amount of oil burned and its

characteristics are the primary factors affecting uncontrolled $SO_x$ emissions from oil-fired boilers.

In contrast to coal, oil is a fast-burning, low-ash fuel (typically 0.01 to 0.20 percent). Its high flame temperatures exacerbate the formation of $SO_3$, $H_2SO_4$, and particulate sulfates from $SO_2$ (Homolya and Cheney, 1978). Oil may contain metals, especially vanadium, which catalyze the formation of $SO_3$ in the combustion process. Studies show that increasing the vanadium content of oil increases the formation and emission of primary sulfate (Homolya and Cheney, 1978; Bennett and Knapp, 1978; Dietz et al., 1978). The mass mean diameter of uncontrolled particulate matter from oil is smaller than that from coal, ranging from 0.3 to 10 μm (Scinto, 1979).

Oil-fired boilers generally convert over 90 percent of available fuel sulfur to $SO_2$. Tests show that 2 to 12 (average 6.5) percent by weight of $SO_x$ emissions from oil combustion occur as primary sulfate (Homolya and Cheney, 1978). The tests were conducted with a variety of boilers and fuels with different amounts of sulfur and vanadium.

Excess oxygen enhances primary sulfate emissions from oil-fired boilers (Homolya and Cheney, 1978; Bennett and Knapp, 1978; Dietz et al., 1978). Fuel additives (usually containing magnesium oxide) are effective in reducing primary sulfate emissions from oil-fired boilers. Ideally, the fuel additives minimize the formation of $SO_3$ and can react with or adsorb $SO_3$ and $H_2SO_4$ and retain them in the bottom ash or combine them with particles to be collected by an electrostatic precipitator.

Oil-fired utility and industrial boilers can employ the same types of emissions control equipment as coal-fired boilers, although in many cases they may have only a mechanical particulate collector. Oil-fired $SO_x$ emissions are

affected by electrostatic precipitators and flue gas desulfurization systems in much the same way as coal-fired $SO_x$ emissions. Electrostatic precipitators have a lower particulate sulfate collection efficiency in oil-fired boilers than they do on coal-fired boilers (Leavitt et al., 1978). Particles from oil-fired boilers are smaller than those from coal-fired boilers and therefore collected less effectively. Factors affecting flue gas desulfurization systems on oil-fired boilers are similar to those affecting coal-fired boilers.

Tests of uncontrolled $SO_2$ emissions from coal- and oil-fired utility and industrial boilers compare favorably with U.S. EPA (1977) emission factors (McCurley and DeAngelis, 1978; Homolya et al., 1976). Primary sulfur emissions from oil-fired boilers may be 3 to 10 times greater than those from coal-fired boilers, given the same sulfur content (Homolya and Cheney, 1978). A recent study reported that power plants converted from coal to oil emitted more particulate sulfate and sulfur acid after conversion, even though the coal had a higher sulfur content and the same heating value as the oil (Homolya and Cheney, 1979).

4.3.1.2.2 Residential and commercial space heating. Residential and commercial space heaters mainly use natural gas and oil. Coal and wood are fuels used to a lesser degree for space heating. The Portland Aerosol Characterization Study (PACS) found that home heating was a major contributor to total suspended particle levels in the Portland Airshed (Cooper and Watson, 1979). $SO_x$ emissions from home heating may have been accordingly high.

Equipment design, operating parameters, and fuel characteristics affect the characteristics of $SO_x$ emissions from space heating. Proper burner adjustment, combustion modifications, and fuel additives may all minimize $SO_x$ emissions. Space heaters do not usually have any emissions controls.

$SO_2$ emissions from gas-fired and oil-fired residential sources correlate well with $SO_2$ emission factors in AP-42 (U.S. Environmental Protection Agency, 1977). Some tests have indicated $SO_3$ emission rates from an oil-fired source of nearly three times the expected rate derived with AP-42 factors (Surprenant et al., 1979). Further study is needed to determine whether these values are typical $SO_3$ emissions rates from oil-fired space heaters. The existing data base appears to characterize $SO_2$ emissions from gas, oil, and coal residential combustion sources, but more information is needed to characterize primary sulfate emissions from oil-fired and coal-fired space heaters.

4.3.1.2.3 Industrial process sources. The primary metals industries and the petroleum and chemical industries are major industrial process sources of $SO_x$ emissions. Mineral products industries account for a smaller portion of these emissions.

4.3.1.2.3.1 Primary metals industries. In the primary metals industries, copper, lead, and zinc smelters are potentially the largest $SO_x$ emitters. Most of the sulfur in unprocessed ores is converted to $SO_2$ in the smelting processes (U.S. Environmental Protection Agency, 1977). A relatively small amount of the sulfur is emitted as particulate sulfate and sulfuric acid.

Factors affecting $SO_2$ emissions from smelters are the amount of raw ore processed, the sulfur content of the ore, the process configuration, the degree of sulfur removal for each process step, and the degree of $SO_2$ emission control used. The bulk of $SO_2$ is formed in the roasting, smelting, sintering, and converting processes of the smelter industry (U.S. Environmental Protection Agency, 1974).

Sources of fugitive $SO_2$ emissions include roaster transfer points, furnace feed and discharge areas, and converter rollout. In copper smelters, fugitive

$SO_2$ emissions of up to 12 percent of the total generated $SO_2$ have been reported (U.S. Environmental Protection Agency, 1974).

Weak $SO_2$ off-gases are usually vented to the atmosphere. Single-contact sulfuric acid plants are the primary method of treatment for strong $SO_2$ off-gases. They may recover up to 97 percent of the off-gas $SO_2$ as sulfuric acid. Other $SO_2$ control methods with potentially higher removal efficiencies than single-contact sulfuric acid plants are double-contact sulfuric acid plants and the dimethylaniline (DMA) absorption process.

In the past, strong $SO_2$ gas streams were controlled because of the marketability of the recovered sulfur products. To ensure compliance with local and national ambient air quality standards, new $SO_2$ control equipment has been installed or is being planned for many smelters (especially copper smelters) in the United States. New and planned $SO_2$ control strategies include the establishment of sulfuric acid and liquid $SO_2$ plants and the installation of ducting and hoods to minimize fugitive $SO_2$ emissions from transfer points (U.S. Environmental Protection Agency, 1974).

4.3.1.2.3.2 Petroleum industry. The major sources of $SO_x$ emissions in the petroleum industry are catalytic cracking and sulfur-recovery processes and off-gas flares (U.S. Environmental Protection Agency, 1977; Dickerman et al., 1977). $SO_2$ emissions from the catalytic cracking process occur during the catalyst-regeneration step.

Major sour-gas streams are usually treated in a sulfur plant. Most sulfur plants utilize a modified Claus process for multistage oxidation of hydrogen sulfide to elemental sulfur. The sulfur recovery efficiency of these plants ranges from 92 to 97 percent, depending on the number of catalytic

stages. Tail gas is usually incinerated, and most of the remaining sulfur species are oxidized to $SO_2$. Some plants have installed tail gas cleanup systems to further reduce $SO_2$ emissions. These units can recover sulfur with up to 99.8 percent efficiency.

Minor off-gas streams and recovered vapors are often burned in flares. Most of the sulfur species present in these vapors are oxidized to $SO_2$.

4.3.1.2.3.3 Chemical production industries. Chemical process industries which emit significant amounts of $SO_x$ are explosives manufacturing, sulfuric acid plants, and elemental sulfur plants.

The manufacture of TNT and nitrocellulose explosives produces emissions of $SO_2$ and sulfuric acid mist. A major raw material in the production of these explosives is sulfuric acid. Sulfuric acid concentrators, sellite exhaust, and incinerators are the major $SO_x$ sources in these processes. $SO_x$ emissions may vary considerably with the efficiency of the process and the operating conditions (U.S. Environmental Protection Agency, 1977).

Sulfuric acid is manufactured primarily by the contact process. The three types of raw materials used by sulfuric acid plants are elemental sulfur, spent acid and hydrogen sulfide, and sulfide ores and smelter gases.

The amount of $SO_2$ emissions in acid-plant gases is an inverse function of the sulfur conversion efficiency of the process (U.S. Environmental Protection Agency, 1977). Sulfuric acid mist is generated by $SO_2$ absorbers. The quantity and size distribution of the acid mist are dependent on the type of sulfur feedstock used, the strength of the acid produced, and the conditions in the absorber. Electrostatic precipitators and fiber mist eliminators can reduce sulfuric acid mist emissions by up to 99 percent.

4.3.2 Particulate Matter Emissions

4.3.2.1 Major Manmade Sources of Particulate Matter--The 1975 National Emissions Data System (NEDS) data base (Table 4-8) shows a nationwide particulate emissions total of about 12.5 x $10^6$ metric tons. As shown in Table 4-9, the major source categories are stationary fuel combustion, mineral products, primary metals, and land vehicles, which together account for just over 80 percent of the national total. Table 4-10 summarizes data on the characteristics of particles from certain major sources.

4.3.2.1.1 Geographic distribution. The following discussion, tables, and figures are directed at characterizing the nature and extent of particulate emissions on the basis of region, State, major source category, and population exposure. Table 4-11 summarizes total emission data geographically and includes additional parameters such as population, land area, and emission densities. Population and emission densities are also illustrated in Figures 4-11 and 4-12, respectively. Several important points are worth noting with respect to Table 4-11 and Figures 4-11 and 4-12:

(1) EPA Regions IV and V account for nearly 50 percent of total U.S. particulate emissions; Regions III, IV, V, and VI total about 72 percent.

(2) Region V is the single greatest contributor (28.1 percent), and Ohio accounts for just under 40 percent of the Region's total and about 11 percent of the U.S. total.

(3) Except in Regions I, II, and IX, emissions appear to correlate with population.

TABLE 4-8. COMPARISON OF CALCULATED AND INVENTORIED EMISSIONS FOR THE UNITED STATES, 1975 ($10^3$ metric tons/year)[a]

| Source category | Calculated by EPA | 1975 NEDS |
|---|---|---|
| Fuel combustion (point and area) | 5,262 | 5,033 |
| Residential | 91 | 182 |
| Electric generation | 3,901 | 2,784 |
| Industrial | 1,089 | 1,861 |
| Commercial and institutional | 181 | 193 |
| Other | 0 | 13 |
| Industrial processes (point) | 6,985 | 5,647 |
| Chemical manufacturing | 181 | 207 |
| Food and agriculture | 1,361 | 593 |
| Primary metals | 1,270 | 989 |
| Secondary metals | 91 | 126 |
| Mineral products | 3,720 | 3,055 |
| Petroleum industry | 91 | 119 |
| Wood products | 272 | 271 |
| Evaporation | 0 | 17 |
| Other processes | 0 | 271 |
| Solid waste disposal (point and area) | 454 | 446 |
| Municipal incineration | 91 | 54 |
| Residential | 181 | 227 |
| Commercial and institutional | 91 | 49 |
| Industrial | 91 | 81 |
| Other | 0 | 34 |
| Transportation (area) | 1,179 | 1,058 |
| Gasoline vehicles | 774 | 677 |
| Diesel vehicles | 272 | 262 |
| Aircraft | 91 | 99 |
| Vessels | 45 | 20 |
| Miscellaneous (area) | 454 | 299 |
| Forest fires | 272 | 159 |
| Structural fires | 91 | 1 |
| Slash burning | 91 | 140 |
| Grand total (point and area) | 14,334 | 12,489 |

[a]Section 4.3.2.2 contains more recent data on emissions from transportation sources.

Source: U.S. Environmental Protection Agency (1978a).

TABLE 4-9a. MAJOR NATIONAL SOURCES OF PARTICULATE MATTER (SOURCE: 1975 NEDS INVENTORY)

| | Source category | Emissions ($10^3$ metric tons/yr) | Percent of U.S. total | Cumulative percent of U.S. total |
|---|---|---|---|---|
| 1. | Stationary fuel combustion | 5033 | 40.3 | 40 |
| 2. | Mineral products | 3055 | 25 | 65 |
| 3. | Primary metals | 989 | 7.9 | 72.9 |
| 4. | Land vehicles | 939 | 7.5 | 80.4 |
| 5. | Food and agriculture | 593 | 4.7 | 85.1 |
| 6. | Solid waste disposal | 446 | 3.6 | 88.7 |
| 7. | Wood products | 271 | 2.2 | 90.9 |
| 8. | Chemical manufacturing | 207 | 1.7 | 92.6 |
| 9. | Forest fires | 159 | 1.3 | 93.9 |
| 10. | Slash burning | 140 | 1.1 | 95 |

TABLE 4-9b. MAJOR NATIONAL SOURCES OF PARTICULATE MATTER (SOURCE: 1977 SURE INVENTORY)

| | Source category | Emissions ($10^3$ metric tons/yr) | Percent of U.S. total | Cumulative percent of U.S. total |
|---|---|---|---|---|
| 1. | Stationary fuel combustion | 3007 | 39 | 39 |
| 2. | Mineral products | 2211 | 29 | 68 |
| 3. | Food and agriculture | 608 | 7.9 | 75.9 |
| 4. | Primary metals | 585 | 7.6 | 83.5 |
| 5. | Chemical manufacturing | 203 | 2.6 | 86.1 |
| 6. | Wood products | 180 | 2.3 | 88.4 |
| 7. | Solid waste disposal | 128 | 1.7 | 90.1 |
| 8. | Secondary metals | 108 | 1.4 | 91.5 |

TABLE 4-10. SUMMARY OF MAJOR SOURCE CATEGORIES AND PARTICLE CHARACTERIZATION DATA

| Source category | Particulate emissions ($10^3$ metric tons) 1975 NEDS | 1977 SURE | Particle size data* | Trace element components† |
|---|---|---|---|---|
| Industrial Processes | 5,647 | 4,347 | | |
| - Mineral Products | 3,055 | 2,211 | | |
| Cement | ~900 | 312 | 25% I, 75% C (before control)‡<br>40% F (after control) | Similar to parent material, i.e., limestone, clay, shale, gypsum, sand, etc. |
| Stone | ~642 | 837 | --- | |
| Asphalt concrete | ~150 | 157 | 100% C (before control)‡<br>30-60% F (after control) | |
| - Primary Metals | 989 | 585 | | |
| Iron | ~247 | 191 | 100% I, 75% F‡ | Fe, Si, Al, Ca, Mg, Zn, Mn, Pb, P |
| Aluminum | ~198 | 54 | 100% I, 60% F‡ | Fe, Si, Al, Ca, Mg, Mn, Zn, Pb, Ni, Cr, P |
| Steel | ~188 | 59 | 100% I‡ | F, Cl, Al |
| Coke | ~76 | - | 100% I, 75% F‡ | As, Be, Cd, Cr, Co, Pb, Ni, Se, POM |
| Copper | ~37 | 60 | 100% I, 50% F‡ | As, Pb, Cd, Se, Ag |
| - Food/Agriculture | 593 | 608 | 25% I, 75% C‡ | Grain dust |
| Fuel Combustion | 5,033 | 3,007 | | |
| - Electric Generation | 2,784 | 1,670 | 50% I, 50% C | |
| - Industrial | 1,861 | 1,274 | 50% F, 50% C | Cl, Fe, Ti, F, V, Ni, B, Mn, As |
| - Commercial/Institutional | 193 | 63 | 100% F | |
| - Residential | 182 | - | 100% F | |

*F = Fine (<2 μm)
I = Inhalable (<15 μm)
C = Coarse (>15 μm)

†See detailed breakdown for fuel combustion in Section 3

‡Data obtained from FPEIS

TABLE 4-11. STATE-BY-STATE LISTING OF TOTAL PARTICULATE EMISSIONS, POPULATION, AND DENSITY FACTORS

| Region and State | Population 1000's | Total area, $mi^2$ | Total emissions, $10^3$ metric tons | Population density, people/$mi^2$ | Emission density, tons/$mi^2$ | State emissions, percent of U.S. |
|---|---|---|---|---|---|---|
| Region 1 | | | | | | |
| Connecticut | 3,117 | 5,009 | 32.7 | 622 | 6.5 | 0.26 |
| Maine | 1,070 | 33,215 | 50.9 | 32 | 1.5 | 0.41 |
| Massachusetts | 5,809 | 8,257 | 87.1 | 704 | 10.5 | 0.70 |
| New Hampshire | 822 | 9,304 | 13.8 | 88 | 1.5 | 0.11 |
| Rhode Island | 927 | 1,214 | 8.7 | 764 | 7.2 | 0.07 |
| Vermont | 476 | 9,609 | 6.3 | 50 | 0.66 | 0.05 |
| Total | 12,221 | 66,608 | 199.5 | 183 | 3.0 | |
| Percent of U.S. | 5.6 | 1.8 | 1.6 | | | |
| Region II | | | | | | |
| New Jersey | 7,336 | 7,836 | 118.3 | 936 | 15.1 | 0.95 |
| New York | 18,084 | 49,576 | 366.2 | 365 | 7.4 | 2.93 |
| Puerto Rico | 2,712 | 3,435 | 106.2 | 790 | 30.9 | 0.85 |
| Virgin Islands | 62 | 133 | 4.1 | 466 | 30.8 | 0.03 |
| Total | 28,194 | 60,980 | 594.8 | 462 | 9.75 | |
| Percent of U.S. | 12.9 | 1.7 | 4.8 | | | |
| Region III | | | | | | |
| Delaware | 582 | 2,057 | 27.2 | 283 | 13.2 | 0.22 |
| District of Columbia | 702 | 67 | 6.4 | 10,478 | 95.5 | 0.05 |
| Maryland | 4,144 | 10,577 | 119.2 | 392 | 11.3 | 0.95 |

TABLE 4-11 (continued)

| Region and State | Population 1000's | Total area, $mi^2$ | Total emissions, $10^3$ metric tons | Population density, people/$mi^2$ | Emission density, tons/$mi^2$ | State emissions, percent of U.S. |
|---|---|---|---|---|---|---|
| Pennsylvania | 11,862 | 45,333 | 655.3 | 262 | 14.5 | 5.25 |
| Virginia | 5,032 | 40,817 | 395.7 | 123 | 9.7 | 3.17 |
| West Virginia | 1,821 | 24,181 | 325.5 | 75 | 13.5 | 2.61 |
| Total | 24,143 | 123,032 | 1,529.3 | 196 | 12.4 | |
| Percent of U.S. | 11.1 | 3.4 | 12.2 | | | |
| Region IV | | | | | | |
| Alabama | 3,665 | 51,609 | 482.2 | 71 | 8.3 | 3.43 |
| Florida | 8,421 | 58,560 | 252.2 | 144 | 4.3 | 2.02 |
| Georgia | 4,970 | 58,876 | 172.7 | 84 | 2.9 | 1.38 |
| Kentucky | 3,428 | 40,395 | 655.4 | 85 | 16.2 | 5.25 |
| Mississippi | 2,354 | 47,716 | 167.7 | 49 | 3.5 | 1.34 |
| North Carolina | 5,469 | 52,586 | 241.0 | 104 | 4.6 | 1.93 |
| South Carolina | 2,848 | 31,055 | 177.5 | 92 | 5.7 | 1.42 |
| Tennessee | 4,214 | 42,244 | 347.8 | 100 | 8.2 | 2.78 |
| Total | 35,369 | 383,041 | 2,442.5 | 92 | 6.4 | |
| Percent of U.S. | 16.3 | 10.6 | 19.5 | | | |
| Region V | | | | | | |
| Illinois | 11,229 | 56,400 | 791.6 | 199 | 14.0 | 6.34 |
| Indiana | 5,302 | 36.291 | 530.7 | 146 | 14.6 | 4.25 |
| Minnesota | 3,965 | 84,068 | 264.0 | 47 | 3.1 | 2.11 |
| Michigan | 9,104 | 58,216 | 283.3 | 156 | 4.9 | 2.27 |
| Ohio | 10,690 | 41.222 | 1,367.3 | 259 | 33.2 | 10.95 |

TABLE 4-11 (continued)

| Region and State | Population 1000's | Total area, $mi^2$ | Total emissions, $10^3$ metric tons | Population density, people/$mi^2$ | Emission density, tons/$mi^2$ | State emissions, percent of U.S. |
|---|---|---|---|---|---|---|
| Wisconsin | 4,609 | 56,154 | 275.1 | 82 | 4.9 | 2.20 |
| Total | 44,899 | 332,351 | 3,512 | 135 | 10.6 | |
| Percent of U.S. | 20.6 | 9.2 | 28.1 | | | |
| Region VI | | | | | | |
| Arkansas | 2,109 | 53,104 | 132.5 | 40 | 2.5 | 1.06 |
| Louisiana | 3,841 | 48,523 | 376.9 | 79 | 7.8 | 3.02 |
| New Mexico | 1,168 | 121,666 | 201.6 | 10 | 1.7 | 1.61 |
| Oklahoma | 2,766 | 69,919 | 127.6 | 40 | 1.8 | 1.02 |
| Texas | 12,487 | 267,338 | 686.2 | 47 | 2.6 | 5.57 |
| Total | 22,371 | 560,550 | 1,534.8 | 40 | 2.7 | |
| Percent of U.S. | 10.3 | 15.5 | 12.3 | | | |
| Region VII | | | | | | |
| Iowa | 2,870 | 56,290 | 262.0 | 51 | 4.7 | 2.10 |
| Kansas | 2,310 | 82,264 | 197.0 | 28 | 2.4 | 1.58 |
| Missouri | 4.778 | 69.686 | 346.3 | 69 | 5.0 | 2.77 |
| Nebraska | 1,553 | 77,227 | 215.2 | 20 | 2.8 | 1.72 |
| Total | 11,511 | 285,467 | 1,020.5 | 40 | 3.6 | |
| Percent of U.S. | 5.3 | 7.4 | 8.2 | | | |

TABLE 4-11 (continued)

| Region and State | Population 1000's | Total area, $mi^2$ | Total emissions, $10^3$ metric tons | Population density, people/$mi^2$ | Emission density, tons/$mi^2$ | State emissions, percent of U.S. |
|---|---|---|---|---|---|---|
| Region VIII | | | | | | |
| Colorado | 2,583 | 104,247 | 52.6 | 25 | 0.5 | 0.42 |
| Montana | 753 | 147,138 | 83.5 | 5 | 0.6 | 0.67 |
| North Dakota | 643 | 70,665 | 79.1 | 9 | 1.1 | 0.63 |
| South Dakota | 686 | 77,047 | 53.4 | 9 | 0.7 | 0.43 |
| Utah | 1,228 | 84,916 | 94.5 | 14 | 1.1 | 0.76 |
| Wyoming | 390 | 97,914 | 133.4 | 4 | 1.4 | 1.07 |
| Total | 6,283 | 581,927 | 496.5 | 11 | 1.0 | |
| Percent of U.S. | 2.9 | 16.1 | | | | |
| Region IX | | | | | | |
| Arizona | 2,270 | 113,909 | 113.4 | 20 | 1.0 | 0.91 |
| California | 21,520 | 158,693 | 506.2 | 136 | 3.2 | 4.05 |
| Hawaii | 887 | 6,450 | 59.4 | 138 | 9.2 | 0.48 |
| Nevada | 610 | 110,540 | 91.1 | 6 | 0.8 | 0.73 |
| Guam | 85 | 212 | 2.5 | 401 | 11.8 | 0.02 |
| American Samoa | 27 | 76 | 0.02 | 355 | 0.3 | - |
| Total | 25,399 | 389,880 | 772.6 | 65 | 2.0 | |
| Percent of U.S. | 11.7 | 10.8 | 6.2 | | | |

TABLE 4-11 (continued)

| Region and State | Population 1000's | Total area, $mi^2$ | Total emissions, $10^3$ metric tons | Population density, people/$mi^2$ | Emission density, tons/$mi^2$ | State emissions, percent of U.S. |
|---|---|---|---|---|---|---|
| Region X | | | | | | |
| Alaska | 382 | 586,412 | 51.7 | 1 | 0.09 | 0.41 |
| Idaho | 831 | 83,557 | 73.5 | 10 | 0.9 | 0.59 |
| Oregon | 2,329 | 96,981 | 107.1 | 24 | 1.1 | 0.86 |
| Washington | 3,612 | 68,192 | 154.6 | 53 | 2.3 | 1.24 |
| Total | 7,154 | 835,142 | 386.9 | 9 | 0.5 | |
| Percent of U.S. | 3.3 | 23.0 | 3.1 | | | |
| U.S. Totals | 217,546 | $3.62 \times 10^6$ | 12,492 | 60 | 3.45 | |

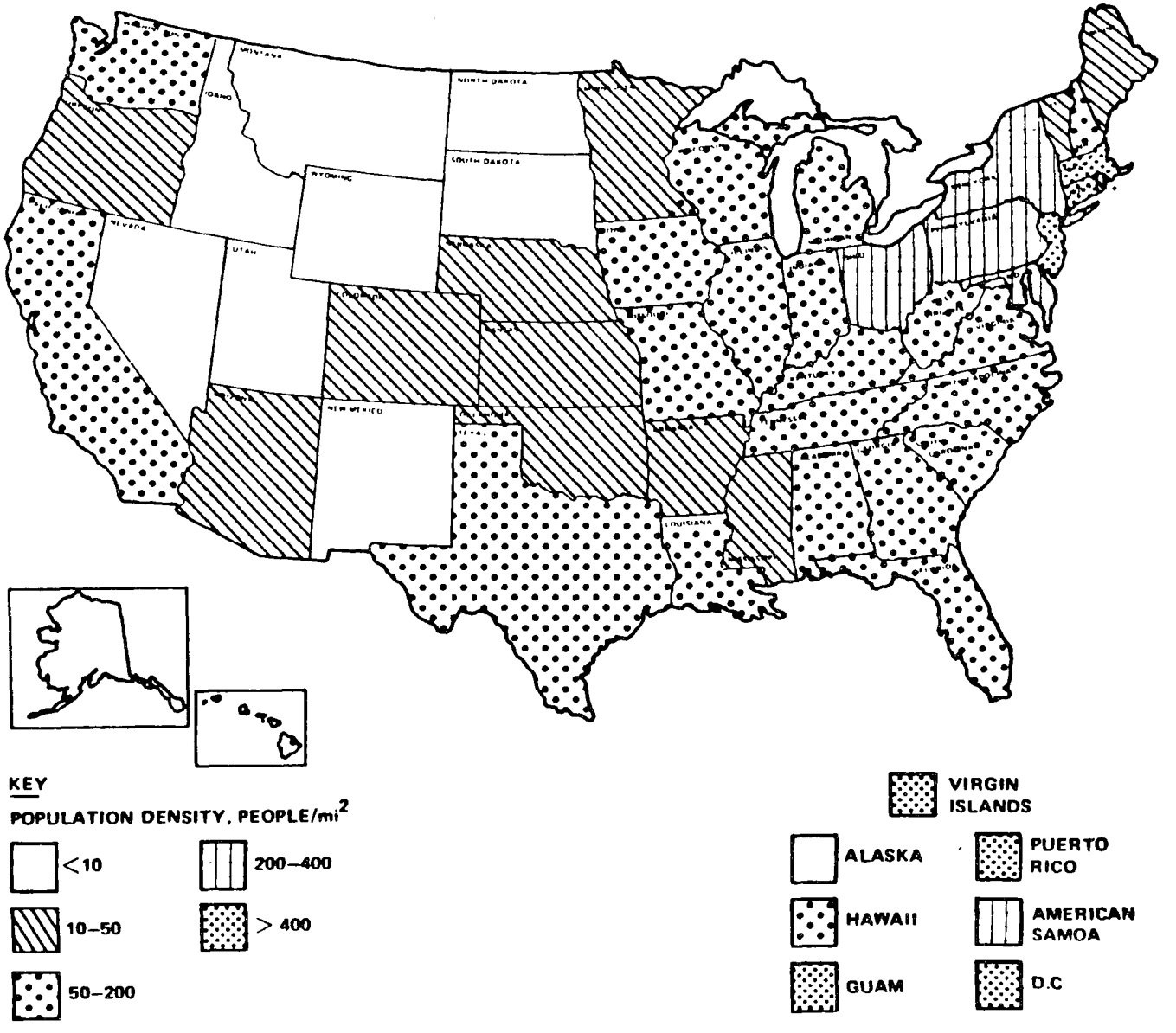



Figure 4-11. Characterization of U.S. population density is shown by State.

Source: U.S. Department of Commerce (1977).

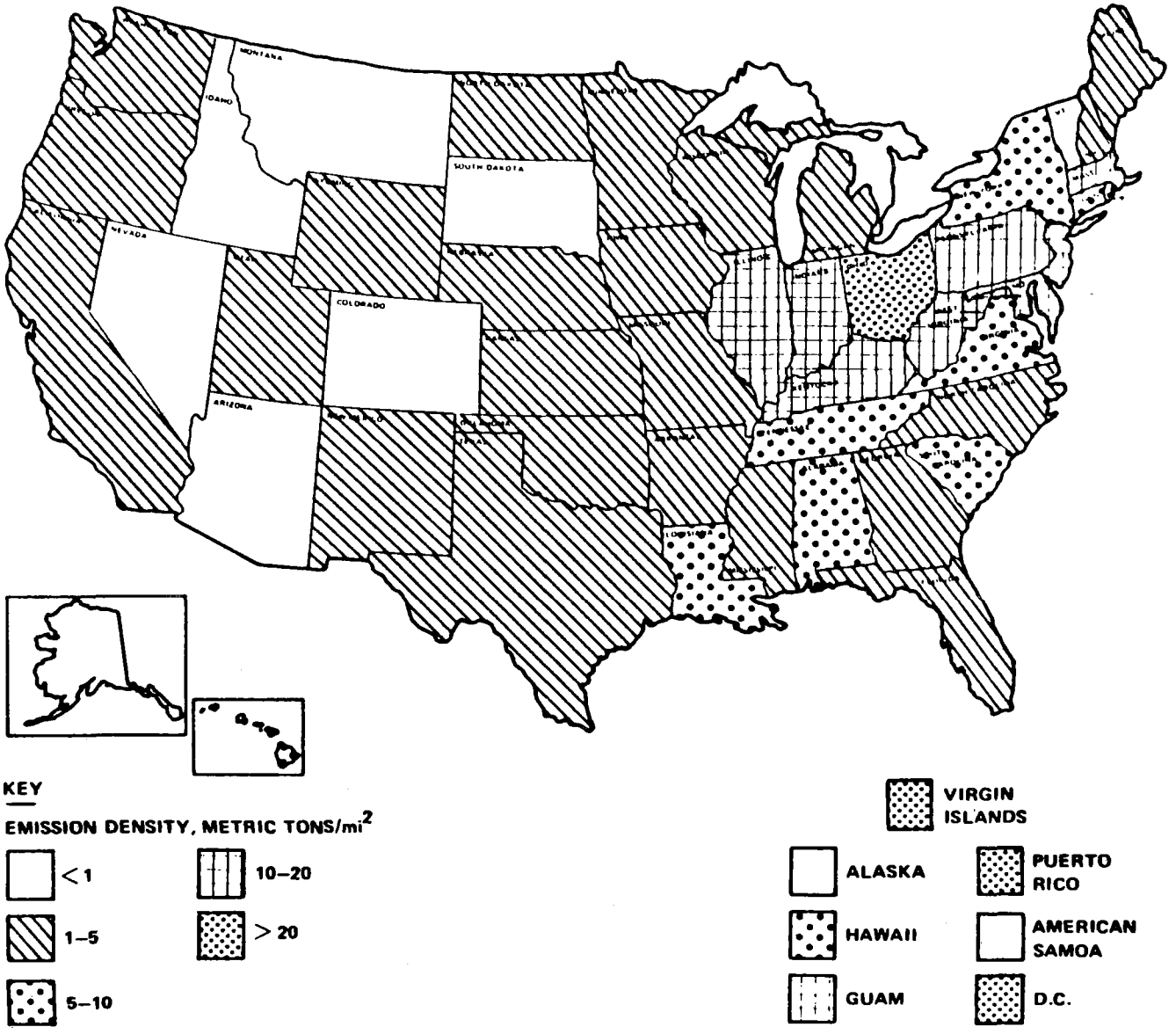



Figure 4-12. Characterization of U.S. particulate emission density is shown by State.

Source: U.S. Environmental Protection Agency (1978a).

4.3.2.1.2 Source identification and attribution. The geographic distribution of stationary source emissions usually coincides with ambient air quality concentrations, but more sophisticated techniques are generally used to link specific sources to levels measured by ambient samplers. Filters from particulate high-volume samplers can be subjected to detailed analyses to determine the types of materials being collected. Two studies conducted in recent years serve as examples of this types of approach.

In Worcester, MA, high total suspended particulate levels were consistently recorded during the winter months. A study was performed to determine what portion of the collected particles was re-entrained road dust, specifically road salt. The results of this study showed that road salt contributed 40 to 60 percent of the material collected on the filter.

The chemical mass balance method was used to assess the impact of major particulate sources in Portland and Eugene, OR. The results of this study showed that on high-impact days, carbon from vegetative burn sources, such as field-burning, slash burning, and space heating with wood contributed between 26 to 51 percent of the fine particulate mass and up to 35 percent of the total suspended particulate mass. These and other methods used for source attribution are discussed extensively elsewhere in this document.

4.3.2.1.3 Particulate matter emission trends. Nationwide emissions of particulate matter have been documented since 1940. After a peak in 1950, there has since been a downward trend in total emissions (U.S. Environmental Protection Agency, 1978b, c). Table 4-12 summarizes emissions from the major source categories for these years, and Figure 4-13 depicts the same information in a bar graph. Transportation and miscellaneous categories are included to indicate their estimated magnitude.

TABLE 4-12. TRENDS IN NATIONAL PARTICULATE EMISSIONS 1940-1977 ($10^6$ METRIC TONS/YEAR)

| Source category | 1940 | 1950 | 1960 | 1970 | 1971 | 1972 | 1973 | 1974 | 1975 | 1976 | 1977 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Transportation | 0.5 | 1.1 | 0.6 | 1.2 | 1.1 | 1.2 | 1.2 | 1.2 | 1.1 | 1.1 | 1.1 |
| Highway vehicles | 0.2 | 0.4 | 0.4 | 0.7 | 0.7 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| Nonhighway Vehicles | 0.3 | 0.7 | 0.2 | 0.5 | 0.4 | 0.4 | 0.4 | 0.4 | 0.3 | 0.3 | 0.3 |
| Stationary fuel combustion | 8.7 | 8.1 | 6.7 | 7.1 | 6.6 | 6.4 | 6.5 | 5.6 | 5.0 | 4.6 | 4.8 |
| Electric utilities | 1.8 | 2.7 | 4.0 | 4.1 | 4.0 | 4.1 | 4.4 | 3.8 | 3.7 | 3.3 | 3.4 |
| Industrial | 5.6 | 4.1 | 2.2 | 2.6 | 2.2 | 2.2 | 2.0 | 1.8 | 1.5 | 1.1 | 1.2 |
| Other | 1.3 | 1.3 | 0.5 | 0.4 | 0.4 | 0.3 | 0.3 | 0.3 | 0.2 | 0.2 | 0.2 |
| Industrial processes | 9.9 | 12.6 | 14.1 | 11.9 | 11.3 | 10.6 | 10.3 | 8.9 | 6.5 | 6.2 | 5.4 |
| Chemicals | 0.4 | 0.6 | 0.4 | 0.3 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Petroleum refining | 0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Metals | 3.3 | 3.8 | 2.6 | 2.1 | 1.9 | 1.9 | 2.1 | 1.9 | 1.4 | 1.5 | 1.3 |
| Mineral products | 4.0 | 5.5 | 8.0 | 7.8 | 7.4 | 6.9 | 6.4 | 5.5 | 3.7 | 3.2 | 2.7 |
| Other processes | 2.2 | 2.6 | 3.0 | 1.6 | 1.7 | 1.5 | 1.5 | 1.2 | 1.1 | 1.2 | 1.1 |
| Solid waste | 0.5 | 0.7 | 0.9 | 1.1 | 0.8 | 0.7 | 0.6 | 0.6 | 0.5 | 0.5 | 0.4 |
| Miscellaneous | 5.2 | 3.7 | 3.3 | 0.9 | 1.1 | 0.7 | 0.6 | 0.7 | 0.6 | 0.8 | 0.7 |
| Forest wildfires and Managed burning | 3.4 | 1.7 | 1.0 | 0.5 | 0.7 | 0.5 | 0.4 | 0.5 | 0.4 | 0.6 | 0.5 |
| Agricultural burning | 1.4 | 1.6 | 1.9 | 0.3 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Coal refuse burning | 0.4 | 0.4 | 0.4 | 0.1 | 0.1 | 0 | 0 | 0 | 0 | 0 | 0 |
| Structural fires | 0 | 0 | 0 | 0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Total | 24.8 | 26.2 | 25.6 | 22.2 | 20.9 | 19.6 | 19.2 | 17.0 | 13.7 | 13.2 | 12.4 |

Note: A zero indicates <50,000 metric tons per year. Section 4.3.2.2 updates transportation sources.

Source: U.S. Environmental Protection Agency (1978b, c).

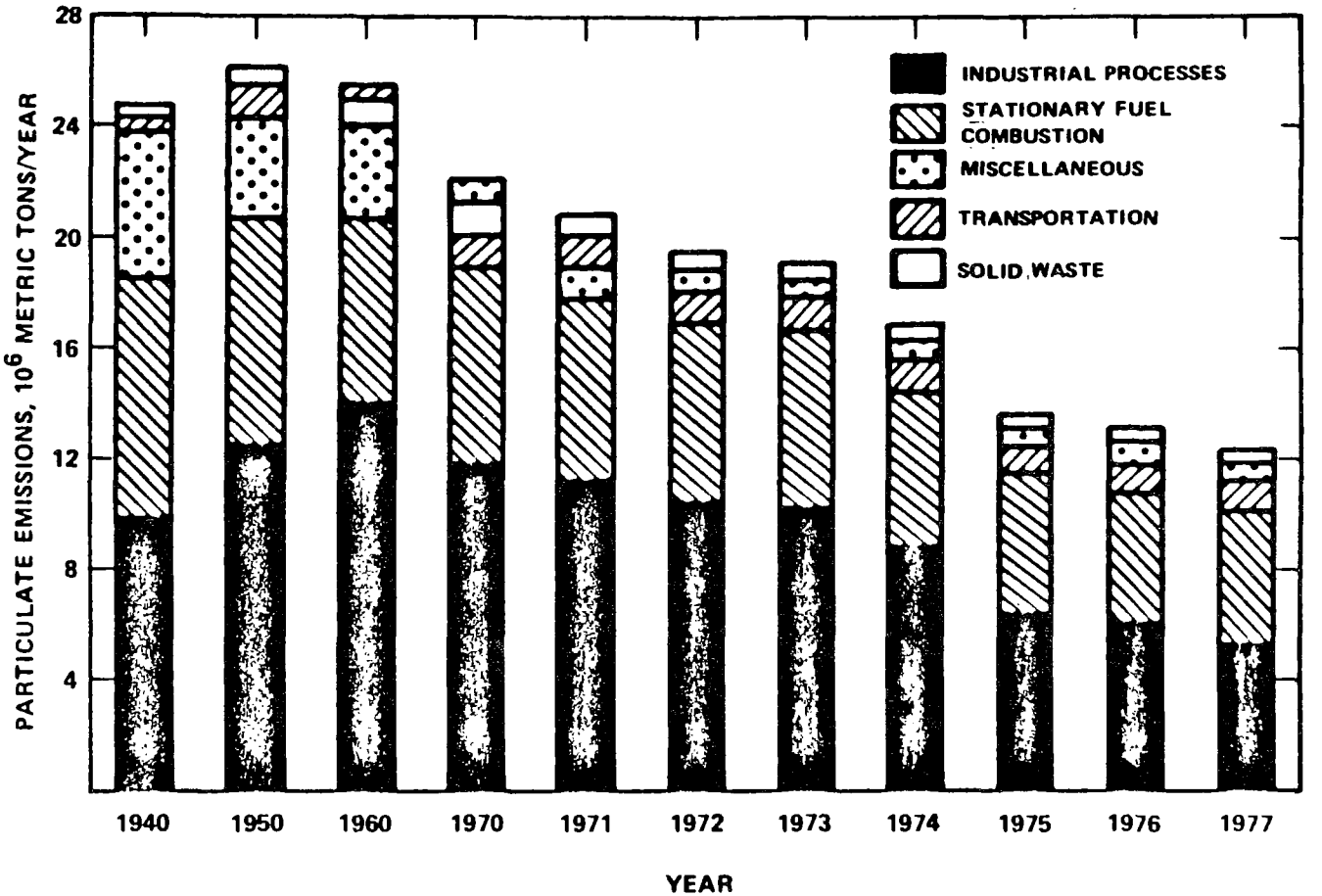



Figure 4-13. Bar chart depicts the trend in national particulate emissions since 1940.

Source: U.S. Environmental Protection Agency (1978b,c).

It may be noted that although stationary fuel combustion emissions have declined since 1940, industrial process emissions increased until 1960 and solid waste emissions increased until 1970 before starting to decline. From 1970 to 1977, major sources of emissions declined by the following percentages: stationary fuel combustion, 32 percent; industrial processes, 55 percent; solid waste, 64 percent; and total emissions, 44 percent.

The downward trend in emissions particularly since 1970 may be related to increased regulatory activity at both the State and national levels. The Clean Air Act Amendments of 1970 encouraged State governments to focus on their suplementation plans. In addition, EPA initiated Federal regulation of new and significantly modified air pollution sources in 1971 through the promulgation of New Source Performance Standards (NSPS). Between 1970 and 1977, these standards were developed for 27 source categories; those which were regulated for particulate matter are listed below along with their effective dates (Federal Register, 1979):

Fossil fuel-fired steam generators - 1971
Incinerators - 1971
Portland cement plants - 1971
Asphalt concrete plants - 1973
Petroleum refineries - 1973
Secondary lead smelting - 1973
Secondary brass and bronze plants - 1973
Iron and steel plants - 1973
Sewage treatment plants - 1973
Primary copper smelters - 1974
Primary zinc smelters - 1974
Coal preparation plants - 1974
Ferroalloy production facilities - 1974
Iron and steel plants: electric arc furnaces - 1974
Kraft pulp mills - 1976
Grain elevators - 1978
Lime manufacturing plants - 1977

There is now a program to promulgate NSPS for 59 additional industries by August 7, 1982. Those for which particulate standards are likely to be adopted are listed below in order of priority (Federal Register, 1979):

Petroleum refineries: Fugitive sources
Acrylic resins
Mineral wool
Stationary internal combustion engines
Industrial boilers
Nonmunicipal incineration
Nonmetallic mineral processing
Metallic mineral processing
Secondary copper
Phosphate rock preparation
Steel and gray iron foundries
Polyethylene resins
Charcoal production
Synthetic rubber
Byproduct coke ovens
Synthetic fibers
Plywood manufacture
Potash
Clay and fly ash sintering
Glass
Gypsum
Sodium carbonate
Secondary zinc
Phenolic resins
Urea - melamine resins
Polystyrene resins
ABS-SAN resins
Fiberglass
Polypropylene resins
Asphalt roofing plants
Brick and related clay products
Ceramic clay manufacturing
Ammonium nitrate fertilizer
Castable refractories
Borax and boric acid
Polyester resins
Ammonium sulfate
Starch
Perlite
Detergent

Another factor in future particulate emission levels is the program dealing with National Emission Standards for Hazardous Air Pollutants (NESHAPS) Emissions of asbestos, beryllium, and mercury, currently regulated under NESHAPS, are expected to decrease in future years (Council on Environmental Quality, 1978).

Other regulatory mechanisms which will likely result in declines in particulate emission levels are the Prevention of Significant Deterioration (PSD) regulation for attainment areas and the Emission Offset Policy for nonattainment areas.

4.3.2.1.4 Discussion of major source categories

4.3.2.1.4.1 Stationary fuel combustion. Total emissions of particulate matter from stationary fuel combustion sources were estimated at just over 5 x $10^6$ metric tons in 1975, about 40 percent of the total U.S. figure for all categories. The breakdown (in $10^6$ metric tons) within this source category was as follows:

Electric generation - 2.8 (55 percent)

Industrial - 1.9 (37 percent)

Commercial/institutional - 0.19 (3.8 percent)

Residential - 0.18 (3.6 percent)

Internal combustion/miscellaneous 0.01 (0.2 percent)

As noted, electric generation and industrial fuel consumption accounted for over 90 percent of total category emissions. The geographic distribution of these emissions in primarily centered in the "power plant" corridor which runs from Missouri, Tennessee, and Kentucky, through Illinois, Indiana, Ohio, West Virginia, and Pennsylvania, into New York. (Figure 4-14). All States contributing $\geq$1 percent of U.S. total combustion emissions are indicated by shaded areas. These areas also correspond to the most populated portions of the country. Table 4-13 shows the quantities emitted by electric generation and industrial, commercial and institutional, and residential fuel use. Table 4-14 provides a ranking of States contributing $\geq$1.0 percent of the total U.S. combustion-related emissions. As noted in this table, Ohio emits more than twice that of any other State and accounts for just over 16 percent of the

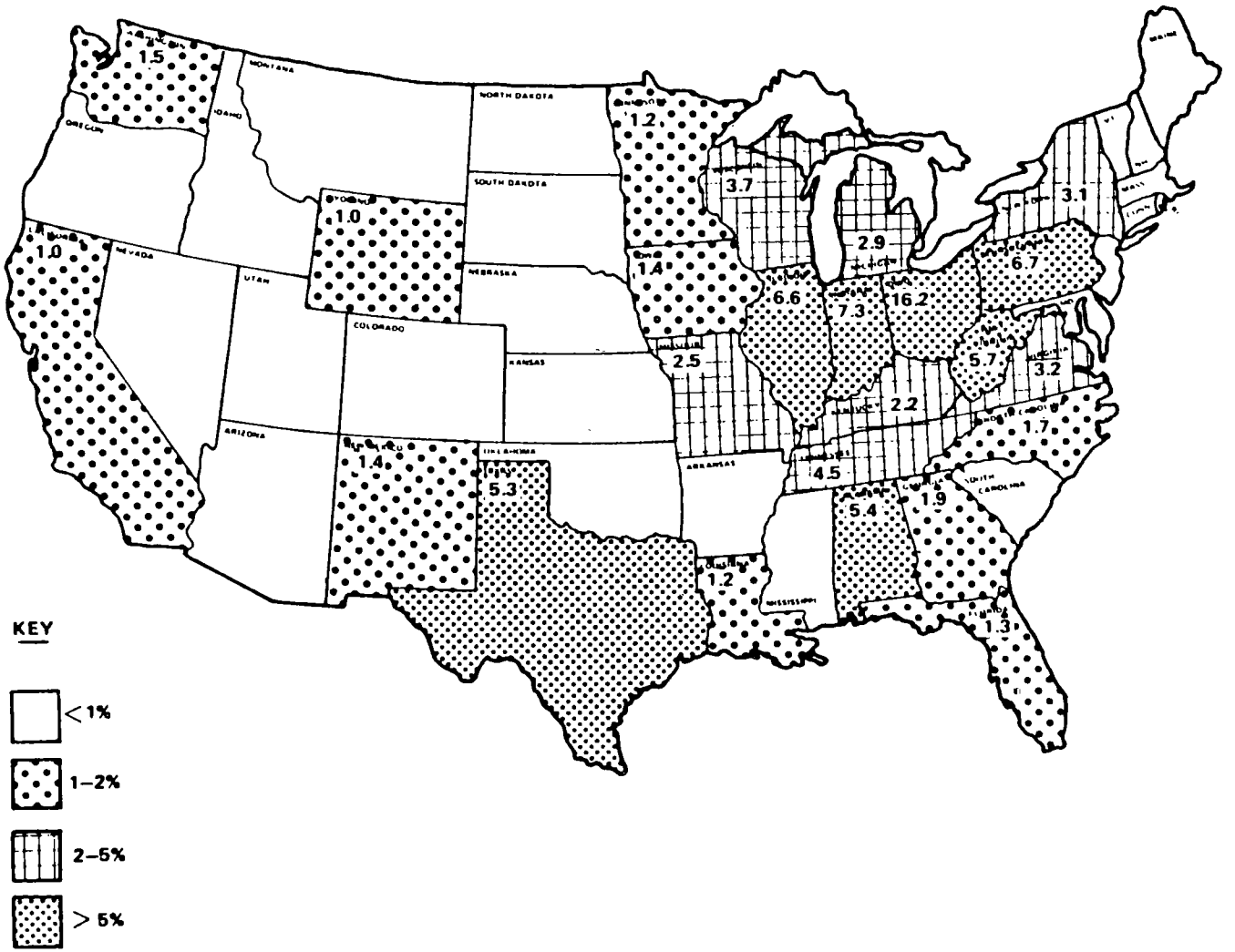



Figure 4-14. Percent fractionation of stationary fuel combustion particulate emissions is shown for States emitting ⩾ 1.0 percent of U.S. mineral products total.

Source: U.S. Environmental Protection Agency (1978c).

TABLE 4-13. STATIONARY FUEL COMBUSTION PARTICULATE EMISSIONS
($10^3$ metric tons/year)

| State | Total fuel combustion | % of U.S. | Electric generation | Industrial | Commercial/ institutional | Residential |
|---|---|---|---|---|---|---|
| Alabama | 272 | 5.4 | 184 | 82 | 2 | 4 |
| Alaska | 27 | 0.5 | 6 | 19 | 1 | 1 |
| Arizona | 11 | 0.2 | 2 | 7 | 1 | 1 |
| Arkansas | 21 | 0.4 | 1 | 15 | 1 | 4 |
| California | 53 | 1.0 | 16 | 26 | 5 | 6 |
| Colorado | 17 | 0.3 | 5 | 9 | 2 | 1 |
| Connecticut | 14 | 0.3 | 2 | 6 | 2 | 4 |
| Delaware | 5 | 0.1 | 2 | 3 | 0 | 0 |
| District of Columbia | 4 | 0.1 | 1 | 1 | 2 | 0 |
| Florida | 64 | 1.3 | 44 | 17 | 2 | 1 |
| Georgia | 94 | 1.9 | 48 | 42 | 1 | 3 |
| Hawaii | 15 | 0.3 | 2 | 13 | 0 | 0 |
| Idaho | 10 | 0.2 | 0 | 8 | 1 | 1 |
| Illinois | 332 | 6.6 | 213 | 93 | 17 | 9 |
| Indiana | 366 | 7.3 | 236 | 118 | 7 | 5 |
| Iowa | 69 | 1.4 | 40 | 24 | 2 | 3 |
| Kansas | 23 | 0.5 | 10 | 11 | 1 | 1 |
| Kentucky | 109 | 2.2 | 83 | 20 | 2 | 4 |
| Louisiana | 63 | 1.2 | 21 | 39 | 2 | 1 |
| Maine | 18 | 0.4 | 2 | 13 | 1 | 2 |
| Maryland | 40 | 0.8 | 30 | 4 | 2 | 4 |
| Massachusetts | 42 | 0.8 | 8 | 16 | 11 | 7 |
| Michigan | 144 | 2.9 | 110 | 25 | 3 | 6 |
| Minnesota | 63 | 1.2 | 18 | 35 | 5 | 5 |
| Mississippi | 24 | 0.5 | 5 | 15 | 1 | 3 |
| Missouri | 124 | 2.5 | 32 | 83 | 4 | 5 |
| Montana | 15 | 0.3 | 7 | 6 | 1 | 1 |
| Nebraska | 27 | 0.5 | 14 | 11 | 1 | 1 |
| Nevada | 5 | 0.1 | 4 | 0.5 | -- | 0.5 |

TABLE 4-13. STATIONARY FUEL COMBUSTION PARTICULATE EMISSIONS
($10^3$ metric tons/year)

| State | Total fuel combustion | % of U.S. | Electric generation | Industrial | Commercial/ institutional | Residential |
|---|---|---|---|---|---|---|
| New Hampshire | 5 | 0.1 | 1 | 2 | 1 | 1 |
| New Jersey | 39 | 0.8 | 12 | 15 | 6 | 6 |
| New Mexico | 68 | 1.4 | 65 | 1 | 1 | 1 |
| New York | 156 | 3.1 | 84 | 25 | 33 | 14 |
| North Carolina | 85 | 1.7 | 48 | 24 | 3 | 10 |
| North Dakota | 46 | 0.9 | 6 | 33 | 6 | 1 |
| Ohio | 816 | 16.2 | 643 | 147 | 18 | 8 |
| Oklahoma | 0.5 | 0.01 | -- | -- | -- | 0.5 |
| Oregon | 34 | 0.7 | -- | 29 | 1 | 4 |
| Pennsylvania | 336 | 6.7 | 208 | 93 | 16 | 19 |
| Puerto Rico | 26 | 0.5 | 1 | 24 | -- | -- |
| Rhode Island | 4 | 0.07 | -- | 2 | 1 | 1 |
| South Carolina | 44 | 0.9 | 13 | 24 | 3 | 4 |
| South Dakota | 9 | 0.2 | 4 | 3 | 1 | 1 |
| Tennessee | 229 | 4.5 | 165 | 59 | 1 | 4 |
| Texas | 267 | 5.3 | 42 | 219 | 5 | 1 |
| Utah | 33 | 0.7 | 7 | 24 | 1 | 1 |
| Vermont | 2 | 0.04 | -- | 1 | -- | 1 |
| Virginia | 161 | 3.2 | 87 | 62 | 4 | 8 |
| Washington | 73 | 1.5 | -- | 67 | 2 | 4 |
| West Virginia | 286 | 5.7 | 96 | 184 | 3 | 3 |
| Wisconsin | 188 | 3.7 | 126 | 45 | 10 | 7 |
| Wyoming | 50 | 1.0 | 32 | 16 | 1 | 1 |
| American Samoa | -- | -- | -- | -- | -- | -- |
| Guam | 1 | 0.02 | 1 | -- | -- | -- |
| U.S. Virgin Islands | -- | -- | -- | -- | -- | -- |

TABLE 4-14. TOTAL FUEL COMBUSTION PARTICULATE EMISSIONS: RANK BY STATE AND CUMULATIVE PERCENT OF U.S. TOTAL (FOR STATES EMITTING ≥1.0 PERCENT OF U.S. TOTAL)

| State | Percent of U.S. | Cumulative percent |
|---|---|---|
| Ohio | 16.2 | 16.2 |
| Indiana | 7.3 | 23.5 |
| Pennsylvania | 6.7 | 30.2 |
| Illinois | 6.6 | 36.8 |
| West Virginia | 5.7 | 42.5 |
| Alabama | 5.4 | 47.9 |
| Texas | 5.3 | 53.2 |
| Tennessee | 4.5 | 57.7 |
| Wisconsin | 3.7 | 61.4 |
| Virginia | 3.2 | 64.6 |
| New York | 3.1 | 67.7 |
| Michigan | 2.9 | 70.6 |
| Missouri | 2.5 | 73.1 |
| Kentucky | 2.2 | 75.3 |
| Georgia | 1.9 | 77.2 |
| North Carolina | 1.7 | 78.9 |
| Washington | 1.5 | 80.4 |
| Iowa | 1.4 | 81.8 |
| New Mexico | 1.4 | 83.2 |
| Florida | 1.3 | 84.5 |
| Louisiana | 1.2 | 85.7 |
| Minnesota | 1.2 | 86.9 |
| California | 1.0 | 87.9 |
| Wyoming | 1.0 | 88.9 |

U.S. total. The highest ranked six states account for almost 50 percent of U.S. emissions; 14 States, 75 percent; and all 24 States contributing $\geq$1.0 percent, about 90 percent of the total in the U.S. Combustion of coal is the primary reason for high emissions in Ohio, Indiana, Pennsylvania, Illinois, West Virginia, Alabama, Texas, and Tennessee, which are among the leading coal-producing States.

A review of the 1976 NEDS file (unpublished data, U.S. Environmental Protection Agency, 1976) shows total stationary fuel combustion emissions equal to $3.2 \times 10^6$ metric tons, but this figure does not include area estimates for residential fuel or portions of commercial and institutional and industrial fuel use. The total breakdown for 1976 was as follows ($10^6$ metric tons):

Electric generation - 2.2 (68 percent)

Industrial - 1.0 (29 percent)

Commercial/institutional - 0.09 (2.5 percent)

Internal combustion - 0.01 (0.5 percent)

The detailed information available from the 1976 NEDS inventory also gives an idea of the emissions breakdown by fuel type within each category as shown:

Electric generation

- bituminous coal - 91 percent
- residual oil - 5 percent

Industrial -

- bituminous coal - 57 percent
- wood/bark waste - 19 percent
- residual oil - 10 percent
- bagasse - 5 percent

Commercial/institutional -

- o bituminous coal - 67 percent
- o anthracite coal - 17 percent
- o residual oil - 10 percent

The size of particles from combustion-related emissions depends primarily on the fuel and firing method. For example, cyclone and pulverized-coal furnaces, typically used in electric generation, discharge predominantly fine material; stoker-fired boilers, used mainly in industrial boilers, emit coarser material. Table 4-15 shows that oil- and gas-fired units emit mostly fine-sized particles (Surprenant et al., 1976). Air emissions of various trace elements, based on 1974 emissions data, are shown in Table 4-16 and Table 4-17. As noted, electric generation is the prime contributor for all of these chemical constituents.

Forecasts concerning anticipated fuel consumption in 1985 are available in a published report by the Department of Energy (1977). Coal usage is expected to increase from 590 x $10^6$ metric tons (1976) to about 934 x $10^6$ metric tons (1985), a 58 percent increase. Total energy consumption of petroleum liquids is expected to show a modest increase from about 37 x $10^6$ bbls/day (1977) to about 44 x $10^6$ bbl/day in 1985, (a 19 percent increase). Consumption of natural gas is expected to decline by about 7 percent from 20 trillion $ft^3$/year (1977) to 18.7 trillion $ft^3$/year in 1985. As noted earlier, increased coal burning will result in three noteworthy effects:

(1) an unchanged magnitude of overall particulate emissions, since well-controlled coal-burning plants emit about the same amounts as uncontrolled oil-fired plants

(2) a redistribution of these overall emissions because of construction of new plants, and

(3) an increase in trace element emissions.

TABLE 4-15. FUEL COMBUSTION: PERCENT OF EMISSIONS LESS THAN 3 μm FOR FOUR SOURCE CATEGORIES AND BY FUEL TYPE[a]

| Source category/fuel | % < 3 μm |
|---|---|
| Electric generation | |
| Coal | 34 |
| Residual Oil | 91 |
| Distillate Oil | 88 |
| Natural Gas | 92 |
| Industrial | |
| Coal | 3 |
| Residual Oil | 90 |
| Distillate Oil | 90 |
| Natural Gas | 92 |
| Commercial/Institutional | |
| Coal | 3 |
| Residual Oil | 90 |
| Distillate Oil | 90 |
| Natural Gas | 90 |
| Residential | |
| Coal | 2 |
| Residual Oil | -- |
| Distillate Oil | 90 |
| Natural Gas | 90 |

[a]Based on total mass emission data from 1974, typical fuel firing methods used within each category, and the degree and extent of emission reduction normally achieved.

Source: Surprenant et al. (1976).

TABLE 4-16. TRACE ELEMENT AIR EMISSIONS: PERCENT OF TOTAL FROM CONVENTIONAL STATIONARY COMBUSTION SYSTEM CATEGORIES

| Source | As | Ba | Be | B | Br | Cd | Cl |
|---|---|---|---|---|---|---|---|
| Electric generation | 90 | 88 | 89 | 90 | 84 | 61 | 83 |
| Industrial | 8 | 9 | 9 | 9 | 13 | 21 | 13 |
| Commercial/institutional | 2 | 3 | 2 | 1 | 2 | 18 | 2 |
| Residential | 0.06 | 0.1 | 0.06 | 0.05 | 1 | 0.007 | 2 |
| Total, metric tons/year | 2,994 | 2,767 | 236 | 4,990 | 6,078 | 299 | 644,112 |

| | Cr | Co | Cu | F | Fe | Pb | Mn | Hg |
|---|---|---|---|---|---|---|---|---|
| Electric generation | 84 | 63 | 72 | 83 | 77 | 92 | 89 | 81 |
| Industrial | 11 | 23 | 16 | 13 | 20 | 7 | 10 | 14 |
| Commercial/institutional | 5 | 14 | 12 | 2 | 3 | 1 | 1 | 3 |
| Residential | 0.1 | 0.3 | 0.07 | 2 | 0.2 | 0.05 | 0.5 | 2 |
| Total, metric tons/year | 1,633 | 463 | 2,540 | 33,566 | 154,224 | 1,179 | 4,627 | 54 |

| | Ni | Se | Ti | U | V | Zn | Zr |
|---|---|---|---|---|---|---|---|
| Electric generation | 60 | 85 | 89 | 86 | 63 | 89 | 78 |
| Industrial | 21 | 13 | 9 | 10 | 20 | 10 | 20 |
| Commercial/institutional | 19 | 2 | 2 | 4 | 17 | 1 | 2 |
| Residential | 0.02 | 1 | 0.06 | 0.05 | 0.02 | 0.1 | 0.2 |
| Total, metric tons/year | 7,348 | 789 | 56,246 | 1,542 | 9,979 | 2,087 | 2,087 |

Source: Surprenant et al. (1976).

TABLE 4-17. TRACE ELEMENTS IN SOLID WASTE (ASH): PERCENT OF TOTAL GENERATED BY CONVENTIONAL STATIONARY COMBUSTION SYSTEM CATEGORIES

| Source | As | Ba | Be | B | Br | Cd | Cl | Cr |
|---|---|---|---|---|---|---|---|---|
| Electric generation | 88.9 | 83.2 | 83.1 | 84.6 | 0 | 82.6 | 0 | 75.1 |
| Industrial | 8.9 | 13.2 | 12.5 | 12.8 | 0 | 14.1 | 0 | 11.7 |
| Commercial/institutional | 0.9 | 1.4 | 1.8 | 1.1 | 0 | 1.4 | 0 | 5.4 |
| Residential | 1.6 | 2.2 | 2.6 | 1.6 | 0 | 1.9 | 0 | 7.8 |
| Total, metric tons/year | 12,247 | 15,967 | 737 | 16,239 | 0 | 110 | 0 | 5,035 |

| | Co | Cu | F | Fe | Pb | Mn | Hg | Ni |
|---|---|---|---|---|---|---|---|---|
| Electric generation | 69.3 | 77.6 | 0 | 86.9 | 80.9 | 97.7 | 77.9 | 80.8 |
| Industrial | 8.9 | 12.1 | 0 | 8.8 | 14.6 | 1.2 | 20.2 | 12.0 |
| Commercial/institutional | 8.2 | 4.1 | 0 | 1.8 | 1.8 | 0.6 | 1.8 | 2.9 |
| Residential | 13.7 | 6.2 | 0 | 2.5 | 2.6 | 0.4 | 0.1 | 4.3 |
| Total, metric tons/year | 1,923 | 4,282 | 0 | 1,369,872 | 2,531 | 12,519 | 6 | 4,699 |

| | Se | Ti | U | V | Zn | Zr |
|---|---|---|---|---|---|---|
| Electric generation | 76.0 | 83.1 | 84.5 | 83.6 | 82.6 | 85.5 |
| Industrial | 22.1 | 12.8 | 12.9 | 12.1 | 12.8 | 11.1 |
| Commercial/institutional | 1.0 | 1.7 | 1.1 | 1.3 | 1.8 | 1.4 |
| Residential | 1.0 | 2.4 | 1.6 | 2.0 | 2.8 | 2.1 |
| Total, metric tons/year | 370 | 178,718 | 4,509 | 8,455 | 6,895 | 17,237 |

Source: Surprenant et al. (1976).

In 1978, EPA estimated that of 623 large coal- and oil-fired power plants, only 62 percent were in compliance with particulate emission standards. (Council on Environmental Quality, 1978).

4.3.2.1.4.2 Mineral products industries. Particulate emissions from the mineral industries were $3.1 \times 10^6$ metric tons in 1975, which represented 25 percent of the U.S. total. The 1970 total was $7.8 \times 10^6$ metric tons, which represented 35 percent of the U.S. total at that time (U.S. Environmental Protection Agency, 1978c). States accounting for the largest percentage of emissions are Kentucky (15 percent), Illinois (10 percent), Pennsylvania (6 percent), Virginia (6 percent), Texas (6 percent), Calfornia (6 percent), and Ohio (5 percent) as shown in Figure 4-15 and Figure 4-16 (U.S. Environmental Protection Agency, 1978c).

Mineral industries incorporated in the above emission estimated include the production of asphalt concrete, brick, castable refractory, Portand cement, fiberglass, glass, gypsum, lime, mineral wool, cleaned coal, phosphate rock, potash, crushed and broken stone, sand and gravel, and other similar products. Production data for some of the larger categories are presented in Table 4-18. Production facilities for crushed and broken stone, sand and gravel, and asphalt concrete are located in virtually every States. In contrast, phosphate rock is produced primarily in Florida, while potash is produced mostly in New Mexico.

Emissions sources vary with the type of mineral industry but usually occur in several specific categories. Typical point source emissions occur from crushing, screening, grinding, conveyor transfer points, loading, and drying or calcining. Drying and calcining are potentially the largest emission source. Fugitive dust sources such as blasting, hauling, haul roads, stockpiles, plant

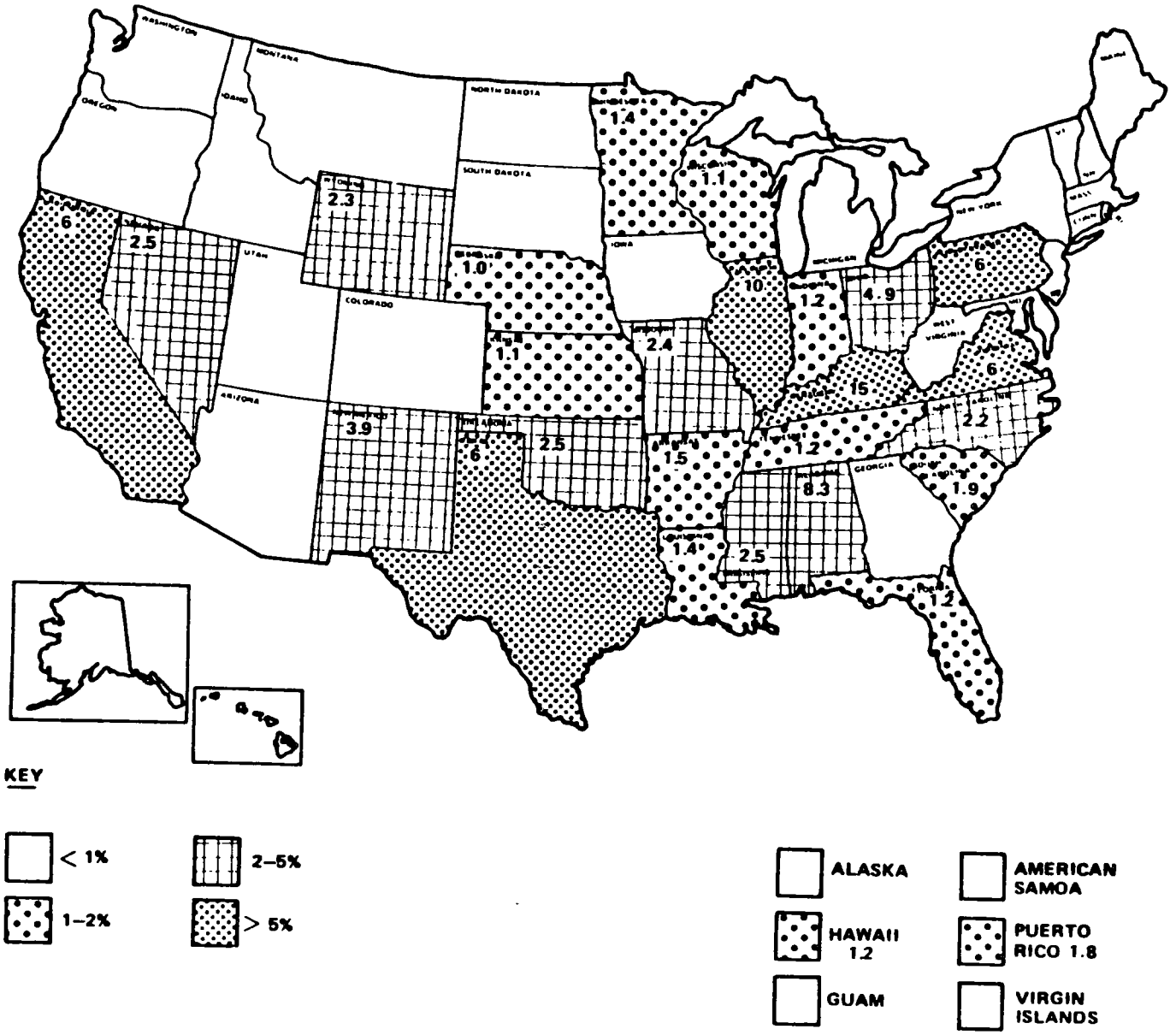



Figure 4-15. Percentage fractionation of mineral products industry particulate emissions is shown for State emitting ≥ 1.0 percent of U.S. mineral products total.

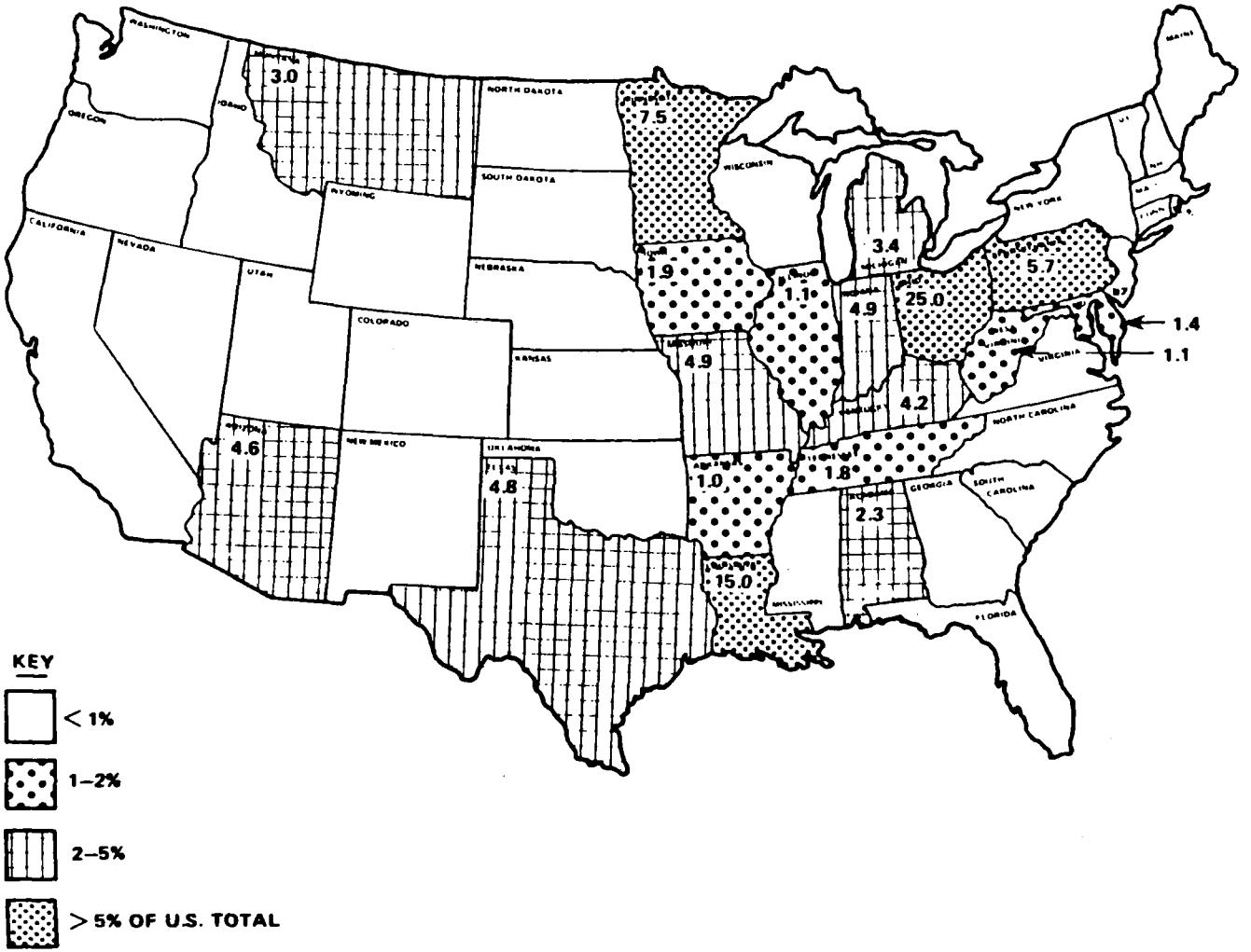



**Figure 4-16. Map shows geographic distribution (as percent of total) of particulate emissions from primary metal production by State.**

**Source: Based on unpublished data from 1976 NEDS file.**

TABLE 4-18. PRODUCTION SUMMARY FOR MAJOR MINERAL PRODUCTS INDUSTRIES

| Mineral | 1975 production quantity ($10^3$ metric tons) | Production value ($\$10^6$) | Number of active operations | Major producing states |
|---|---|---|---|---|
| Crushed and broken stone | 820,000 | 2,100 | 4,800 | PA, IL, TX, FL, OH |
| Sand and gravel | 720,000 | 1,300 | 5,500 | AK, CA, MI, IL, TX, OH |
| Asphalt concrete | 300,000 | 5,300 | 4,300 | CA, IL, OH, PA, NY |
| Cement | 68,000 | 2,100 | 160 | CA, PA, TX, MI, MO |
| Phosphate rock | 45,000 | 1,100 | <50 | FL, NC, TN |
| Gypsum | 17,000 | 230 | 130 | CA, MI, IA, TX |
| Lime | 17,000 | 530 | 170 | OH, PA, TX, MO, MI |
| Potash | 4,200 | 220 | 11 | NM |

Source: U.S. Department of the Interior (1977) and Khan et al. (1977).

yards, and uncovered conveyors are significant but have not been quantified. Fugitive emissions and some point-source emissions (conveyor transfer points and loading) tend to produce particles larger than 15 μm. Significant fractions of the fugitive emissions may even settle out on the plant property. Drying and calcining tend to produce relatively finer particles. Composition of the emissions is similar to that of the mineral being processed.

(1) Portland cement production. The production of Portland cement encompasses most operations that are typical of the mineral industry and is one of the largest sources of emissions. Estimated 1975 emissions are 900,000 metric tons, or one-quarter of the mineral industry total. U.S. production of Portland cement is expected to increase by 60 percent in the next 25 years (Hall and Ela, 1978).

Portland cement manufacture accounts for about 98 percent of the cement production in the United States (U.S. Environmental Protection Agency, 1979). The more than 30 raw materials used to make cement may be divided into four basic components: lime (calcareous), silica (siliceous), alumina (argillaceous), and iron (ferriferous). The raw materials undergo separate crushing after the quarrying operation, and, when needed for processing, are proportioned, ground, and blended using either the wet or dry process.

In the dry process, the moisture content of the raw materials is reduced to less than 1 percent either before or during the grinding operation. The dried materials are then pulverized into a powder and fed directly into a rotary kiln. Drying, decarbonating, and calcining are accomplished as the material travels through the heated kiln, finally burning to incipient fusion and forming the clinker. The clinker is cooled, mixed with about 5 percent gypsum by weight, and ground to the final product fineness. The cement is then stored for later packaging and shipment.

With the wet process, a slurry is made by adding water to the initial grinding operation. After the materials are mixed, the excess water is removed, and final adjustments are made to obtain a desired composition. This final homogeneous mixture is fed to the kilns as a slurry of 30 to 40 percent moisture or as a wet filtrate of about 20 percent moisture. The burning, cooling, addition of gypsum, and storage are carried out as in the dry process.

Operation of the kiln and associated clinker cooler are potentially the largest source of emissions, as indicated by the emission factor of 71-76 kg per metric ton of feed (U.S. Environmental Protection Agency, 1977). Emissions after control vary widely from site to site, depending on the applicable regulation (Federal NSPS, State or local); enforcement practices; and the type, design and reliability of the control device. The Federal NSPS (promulgated in 1971) limits emissions to 0.15 kg/metric ton of feed, an emission reduction of 99.8 percent.

Very limited data on the particle size and chemical composition of cement kiln emissions are available. About 10 percent of the emissions before control are less than 3 μm and 40 percent are less than 3 μm after control as an industry average (Weart et al., 1974). When an electrostatic precipitator is used to meet NSPS, the mean size of the emitted particles is 1 μm (Barrett, 1979). The particulate emissions result from raw material attrition, volatilization of components in the feed, and the fuel (when coal or oil is used). Chemical composition of the emission is probably similar to the collected dust, as shown in Table 4-19.

(2) Crushed and broken stone. In 1975, U.S. output of crushed stone was $820 \times 10^6$ metric tons, consisting of limestone (74 percent), granite (11 percent), trap rock (8 percent), sandstone (8 percent), and other (4 percent). Production is expected to double by the year 2000. Crushed stone was produced

TABLE 4-19. TYPICAL COMPOSITION OF CEMENT KILN DUST

| Component | | Weight % |
|---|---|---|
| Clay (HCl insoluble, fired at 800°C) | | 4.61 |
| Organic substance | | 2.06 |
| Cations | | |
| Lithium | $Li^+$ | 0.0064 |
| Sodium | $Na^+$ | 12.25 |
| Potassium | $K^+$ | 24.50 |
| Rubidium | $Rb^+$ | 0.475 |
| Cesium | $Cs^+$ | 0.0074 |
| Magnesium | $Mg^{++}$ | Trace |
| Calcium | $Ca^{++}$ | 9.26 |
| Strontium | $Sr^{++}$ | 0.015 |
| Anions | | |
| Fluoride | $F^-$ | 0.46 |
| Chloride | $Cl^-$ | 1.43 |
| Bromide | $Br^-$ | 0.040 |
| Iodide | $I^-$ | 0.0552 |
| Carbonate | $CO_3^{--}$ | 29.59 |
| Sulfate | $SO_4^{--}$ | 9.06 |
| Sulfide | $S^{--}$ | Trace |
| Borate | $BO_3^{---}$ | 0.152 |
| Phosphate | $PO_4^{---}$ | Not detectable |

| Heavy metals (weight %) | | | Heavy metal oxides (weight %) | |
|---|---|---|---|---|
| Chromium | Cr | 0.011 | $Cr_2O_3$ | 0.016 |
| Manganese | Mn | 0.013 | $MnO_2$ | 0.021 |
| Iron | Fe | 0.84 | $Fe_2O_3$ | 1.19 |
| Zinc | Zn | 1.62 | ZnO | 2.02 |
| Lead | Pb | 0.562 | PbO | 0.607 |

| | |
|---|---|
| Sum of all determinations | 97.825 |
| Oxygen (from CaO not bound in carbonate) | 2.98 |
| Sum of all constituents | 100.805 |

Source: Barrett (1979).

in every State except Delaware and North Dakota. The leading producers, accounting for 30 percent of production, were Pennsylvania, Illinois, Texas, Missouri, and Ohio. The most important end uses of crushed stone are road base (55 percent), concrete (13 percent), cement (11 percent), and many other smaller uses totaling 21 percent (Reed, 1978). Emission sources include all those typical of the mineral industry except kiln and dryer. EPA emission factors for plant process facilities (i.e., excluding fugitive dust sources) indicate potential emissions of 5.5 kg/metric ton, of which 3.1 kg/metric ton will settle out on the plant property and 2.4 kg/metric ton will remain suspended (U.S. Environmental Protection Agency, 1977). Potential suspended particulate emissions based on 1975 production of 820 x $10^6$ metric tons are 1 million metric tons per year. Suspended particulate emissions after control are 200,000 tO 400,000 metric tons per year.

Chemical composition of emissions is similar to that of the material processed. Table 4-20 presents chemical composition data for limestone, which is the primary product of the crushed and broken stone industry.

(3) Asphalt concrete production. Asphalt concrete is a mixture of aggregate asphalt cement, and occasionally mineral fillter. Production in 1975 was 300 x $10^6$ metric tons, and is expected to increase to 375 x $10^6$ metric tons by 1985 (U.S. Department of the Interior, 1975). Asphalt concrete is used for highways and streets (67 percent), commercial uses (28 percent), and airports and private uses (5 percent). Most plants are located in urban areas where there is a constant market for the product. California, Illinois, Ohio, Pennsylvania, and New York each contain over 5 percent of the U.S. asphalt concrete plants. An asphalt concrete plant may include: dryers; systems for screening, handling, storing, and weighing hot aggregate; systems

TABLE 4-20. TYPICAL VALUES OF TRACE ELEMENTS IN PARTICULATE EMISSIONS FROM CRUSHED AND BROKEN STONE PROCESSES[a] (ppm)

| Element | Limestone |
|---|---|
| As | <10 |
| Ba | 30-300 |
| Be | <1 |
| Br | <0.3 |
| Cd | <0.3 |
| Cu | 0.5-4 |
| Cr | <10 |
| Fe | 200-2000 |
| K | 100-1000 |
| Mn | 6-60 |
| Ni | <6 |
| Pb | <3 |
| Sb | <0.3 |
| Se | <3 |
| Sr | 100-1000 |
| Zn | <30 |
| U | 0.1-1 |
| V | 1-2 |

[a]Data are typical analyses of limestone which are assumed to adequately represent the crushed and broken stone industry.

for loading and unloading; and transfer and storage systems associated with emission control systems. The rotary dryer typically used to dry and heat the aggregate is potentially the largest emission source, as shown by the emission factor of 22.5 kg/metric ton (U.S. Environmental Protection Agency, 1977). However, essentially all plants have at least primary control equipment capable of reducing emissions to below 7.5 kg/metric tons. The best controlled plants achieve emissions rates of 0.01 kg/metric ton. Total emissions are 100,000 to 150,000 metric tons per year, which is equivalent to 0.33 to 0.50 kg/metric tons. Fine particles probably represent 30 to 60 percent of the controlled emissions.

4.3.2.1.4.3 Primary metals. Particulate emissions from the primary metal industries were $1.0 \times 10^6$ metric tons in 1975, or 11 percent of the U.S. total. In contrast, emissions in 1970 were $2.1 \times 10^6$ metric tons, or 10 percent of the U.S. total (U.S. Department of Interior, 1977). Eight States (Ohio, Minnesota, Pennsylvania, Indiana, Missouri, Texas, New Mexico, and Louisiana) account for 73 percent of the total, with Ohio alone accounting for 25 percent and Louisiana 15 percent as shown in Figure 4-16 (unpublished data, U.S. Environmental Protection Agency, 1976).

The most important primary metal industries included in the above emission estimates are aluminum, integrated iron and steel (including coke, pig iron, and steel production), ferroalloys, lead, copper, and zinc. Table 4-21 shows that the aluminum and integrated iron and steel industries account for 72 percent of the particulate emissions from the primary metal industries.

The iron and steel industry is the largest primary metal industry in terms of material produced and value of production, as shown in Table 4-22. Iron, steel, and coke production had a value of $50 billion in 1975, compared with $5-6 billion for aluminum, ferroalloys, lead, copper, and zinc combined. Pennsylvania, Indiana, and Ohio are the largest producers of iron and steel.

TABLE 4-21. DISTRIBUTION OF EMISSIONS AMONG PRIMARY METAL INDUSTRIES[a]

| Industry or operation | Percent of total emissions |
|---|---|
| Iron production | 25 |
| Steel production | 19 |
| Byproduct coke | 7.7 |
| Aluminum | 20 |
| Ferroalloy | 11 |
| Copper | 3.8 |
| Lead | 1.8 |
| Zinc | 0.6 |
| Miscellaneous | 11 |
| Other | Each less than 0.03 |

Source: Unpublished data, U.S. Environmental Protection Agency (1976).

TABLE 4-22. PRODUCTION OF PRIMARY METALS, 1975

| Product | Production, $10^6$ metric tons | Value, $\$10^6$ | Principal producing states |
|---|---|---|---|
| Steel | 106 | 30,700 | PA, OH, IN |
| Pig iron | 73 | 13,700 | PA, OH, IN |
| Coke | 52 | 4,950 | PA, OH, IN, AL |
| Aluminum | 3.5 | 2,976 | Northwestern & South Central U.S. |
| Ferroalloys | 1.7 | 988 | Eastern U.S. |
| Copper | 1.3 | 1,814 | AZ, NM, UT, MT |
| Lead | 0.5 | 274 | MO, ID, CO |
| Zinc | 0.4 | 366 | PA, TX, ID |

Source: Desy (1978).

The types of particles emitted include heavy metals found on impurities in the ores, particles of the material being processed, fluorides and fluxes, and polynuclear aromatic compounds from coke ovens. Most of the emissions discussed in this report result from high-temperature processing equipment such as coke ovens, calcining of aluminum hydroxide in reverberatory furnaces, open and semicovered electric arc furnaces, blast furnaces, basic osygen furnaces, and sintering operations. Stack and fugitive process emissions from the above high-temperature operations are predominantly fine particles. Fugitive dust sources such as coal and ore handling, truck traffic on unpaved roads, and storage piles may produce larger particles.

(a) Byproduct coke ovens. In 1975, 52 x $10^6$ metric tons of coke were produced at 62 plants located in 19 states. The largest producers were Pennsylvania (27 percent), Indiana (16 percent), Ohio (15 percent), and Alabama (8 percent). Production of coke will probably keep pace with the increase in steel production, which is expected to be 1.6 percent per year to the year 2000 (Desy,1978).

Coking is the process of heating coal in an atmosphere of low oxygen to remove volatile components. In the byproduct process, which represents over 98 percent of the industry, these volatile organic compounds are recovered. Particulate emissions result from charging of coal to the hot ovens, door and topside leaks, underfiring, pushing (removal of hot coke), and quenching. Estimated U.S. particulate emissions from coke ovens were 74 x $10^3$ metric tons in 1976.

Door and topside leaks and underfiring produce primarily fine particles, including particulate organic compounds. Charging, pushing, and quenching produce large particles of coal or coke particles and fine particles that consist, at least partly, of condensed organic components.

(b) Iron production. Pig iron was produced at about 200 blast furnaces in 1975. Total production was 73 x $10^6$ metric tons. The largest producing states were Pennsylvania (22 percent), Indiana (20 percent), and Ohio (18 percent). Pig iron production will keep pace with the expected increase in steel production of 1.6 percent per year to the year 2000.

A blast furnace consists of a refractory-lined steel shaft in which the charge is continuously added to the top, and preheated air is blown in through the bottom and emitted as combustible gas. The charge consists of iron ore, sinter or pellets, coke, limestone or dolomite, and possibly small amounts of iron or steel scrap. The combustible gases are cleaned and burned in the steel plant. Particulate emission sources include the combustion gases, tapping operations, and blast furnace slips (operations that require bypassing the control device). Estimated 1976 emissions were 82 x $10^3$ metric tons.

The emitted particles are probably all fine particles that either escape the control device or result from tapping. Composition of the blast furnace flue dust is iron (36 to 50 percent), silicon dioxide (9 to 13 percent), aluminum oxide (2 to 5 percent), calcium oxide (4 percent), carbon (4 to 14 percent), and other components. Data on heavy metals are scarce; one source reports 0.0014 percent cadmium, 0.083 percent lead, and 0.93 percent zinc (Katari and Gerstle, 1977).

(c) Steel production. During 1975, the United States produced 106 x $10^6$ metric tons of steel. The largest producers were Pennsylvania (22 percent), Ohio (17 percent), and Indiana (17 percent). Steel production is expected to increase 1.6 percent per year to the year 2000.

Steel is produced by a refining process that lowers the carbon and silicon content of the charge and removes impurities, mainly phosphorous and sulfur. Excess oxygen in the molten steel is removed by deoxidizing elements such as

manganese, silicon, or aluminum. Pig iron represents about 55 percent of the iron feed, and scrap represents the majority of the remainder. Steel is currently produced by three types of furnaces, as shown in Figure 4-17 (Desy, 1978).

The basic oxygen furnace produces steel from a furnace charge composed of about 70 percent molten pig iron and 30 percent scrap. The tremendous agitation produced by the oxygen lancing produces high dust loadings (11 to 18 $g/m^3$) of iron and small amounts of fluorides. Most of the particles are less than 5 μm. One source reports that the particulate material contained 80 ppm cadmium, 4600 ppm lead, and 45,000 ppm zinc. Estimated 1976 emissions were $91 \times 10^3$ metric tons.

From 1960 to 1975, steel production in open hearth furnaces delcined from 90 percent of the U.S. total to 20 percent. Open hearth furnaces are being replaced by basic oxygen furnaces. The composition of particulate emissions is similar to that of the basic oxygen furnace. About 50 to 60 percent of the emissions before control are less than 5 μm, and probably 90 percent are fine particles after control. Total open hearth particulate emissions were about $30 \times 10^3$ metric tons in 1976.

Two types of electric furnaces, the arc furnace and the induction furnace, are used to produce steel. The arc furnace is used to produce high-alloy steels, as well as a considerable amount of mild steel. The induction furnace produces primarily specialty and high alloy steels with no real emission problems and therefore is omitted in the remainder of this report. Particulate emissions from arc furnaces consist primarily of oxides of iron, manganese, aluminum, calcium, magnesium, and silicon. Particulate fluorides are also emitted. Emissions are primarily fine particles.

(d) Aluminum production. Almost 4 million metric tons of aluminum were produced at 31 U.S. plants in 1975. The production of aluminum consumes large amounts of electric energy, and plants are therefore often located where energy is inexpensive. The Northwest (Washington and Oregon) and South Central states (Tennessee, Arkansas, Louisiana,) are large producers. U.S. production, despite increased imports, is expected to increase 11 percent per year, reaching 18 million tons by the year 2000.

Aluminum is produced from bauxite, a hydrated oxide of aluminum associated with silicon, titanium, and iron. Most bauxite ore is purified by the Bayer process, in which the ore is dried, ground in ball mills, and mixed with sodium hydroxide. Iron oxide, silica, and other impurities are removed by settling, dilution, and filtration. The aluminum hydroxide is precipitated from this diluted, cooled solution and calcined to produce pure alumina ($Al_2O_3$).

Aluminum metal is manufactured by the Hall-Heroult process, which involves the electrolytic reduction of alumina dissolved in a molten salt bath of cryolite (a complex of $NaF \cdot AlF_3$) and various salt additives.

The largest potential sources of emission are bauxite calcining with an emission factor of 100 kg/metric tons, and the reduction process, which has an emission factor of 40 to 50 kg/metric tons. Reported U.S. emissions after control are 87,000 metric tons for the calcining operation and $105 \times 10^3$ metric for the elctrolytic reduction process.

Particulate emissions are primarily alumina, with about 25 percent particulate fluorides (U.S. Environmental Protection Agency, 1977). Some 35 to 44 percent of the particles are less than 1 μm before control.

4.3.2.1.4.4 Industrial process fugitive particulate emissions (IPFPE). It appears that three broad categories account for nearly all of the potential

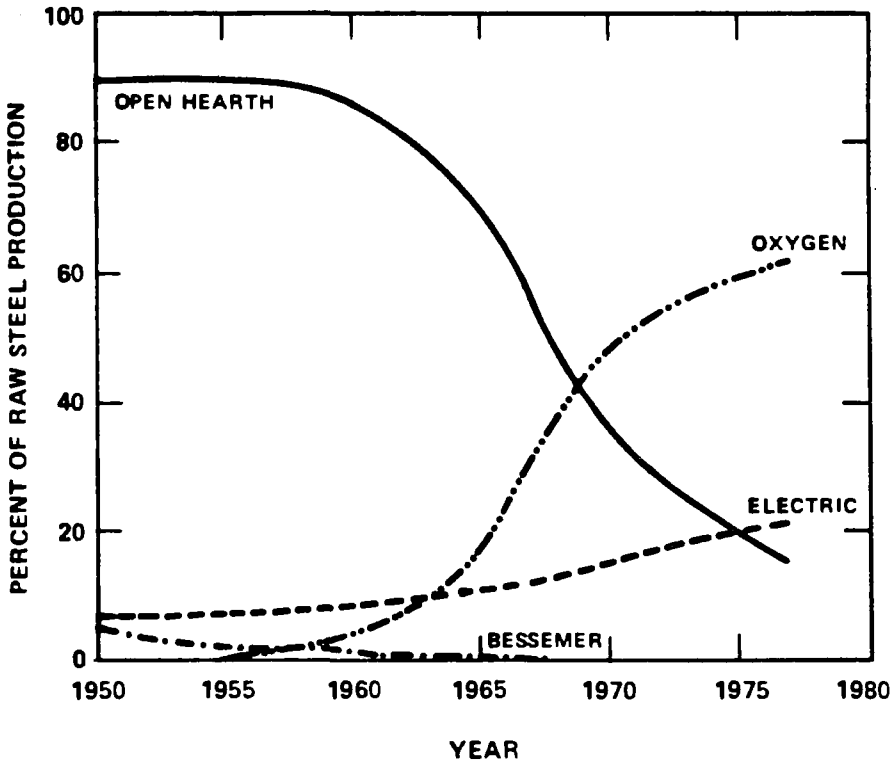



Figure 4-17. U.S. raw steel production is characterized by process, 1950-77.

Source: Desy (1978).

industrial process fugitive particulate emissions in the United States. These three categores are mineral products (48.1 percent), food and agriculture (37.2 percent), and primary metals (14.3 percent) (See Table 4-23).

In the mineral products industries, particulate emissions tend to reflect the composition of their parent materials. While some of these emissions are in the fine and inhalable range, most of the emissions are not well characterized. For mineral extraction and beneficiation (crushed and broken stone, surface coal mining, and sand and gravel operations), which by itself accounts for greater than 20 percent of nationwide emissions, no reliable particle size data are available.

Grain elevator operations account for the particulate emissions in the food and agriculture category. These emissions consist almost entirely of grain dust generated by abrasion of the individual kernels of grain. Few of these particles are in the inhalable category.

Primary metal production encompasses six separate industies. Fugitive particulate emissions in this category result both from the handling and transporting of raw materials and from the smelting and refining of these raw materials into their finished metal products. While emissions of the first type are not well characterized, emissions of the second type often consist of fine and inhalable metal fumes, including toxic trace metals. Some of these toxic components of particulate emissions are listed in Table 4-24. This characterization should apply not only to fugitive emissions but to the stack emissions from these industries as well.

The remaining two categories, secondary metals and wood products, account for less than 1 percent of the national total of industrial process fugitive particulate emissions. Metal fume fugitive particles from secondary metal melting operations also include toxic components, which are presented in Table 4-24.

TABLE 4-23. INDUSTRIAL PROCESS FUGITIVE PARTICULATE EMISSIONS

| Category percent of U.S. total | Industry | Annual uncontrolled emission $10^3$ metric tons | Estimated % of total plant uncontrolled emissions | Fraction emissions represented | Size characteristics | Major components |
|---|---|---|---|---|---|---|
| Mineral products (48.1%) | Mineral extraction and beneficiation | 730[a] | 100.0 | L | No data | Same as parent material (important for toxic minerals such as asbestos, beryllium, silica[b]) |
| | Portland cement | 698 | 5.7 | M | 10 to 15% <10 μm[c] | Limestone, clay, shale, gypsum, iron-bearing and siliceous materials |
| | Asphaltic concrete | 95 | 1.4 | L | 50 to 70% <4 μm[b] | Sand, crushed stone, limestone, hydrated lime |
| | Lime manufacturing | 47 | 1.4 | H | 45 to 70% <5 μm[b] | Limestone, lime |
| | Crecrete batching | 31 | 100.0 | H | 10 to 20% <5 μm[b] | Cement dust (see Portland cement above) |
| | Total | 1,601 | | | | |
| Food and agriculture (37.2%) | Grain elevators | 1,239 | 100.0 | H | 10 to 100 μm[d] | Grain dust |

TABLE 4-23 (continued)

| Category percent of U.S. total | Industry | Annual uncontrolled emission $10^3$ metric tons | Estimated % of total plant uncontrolled emissions | Fraction emissions represented | Size characteristics | Major components |
|---|---|---|---|---|---|---|
| Primary metals (14.3%) | Coke/iron/steel | 234 | 10.6 | H | 50% inhalable[e] | Polycyclic organic matter, coal dust, coke dust, iron oxide dust, kish, (graphitic material), metal fume (primarily iron oxide)[b,f,g] |
| | Foundries | 122 | 53.5 | H | 100% inhalable, 26% fine[b] | Metal oxide fume (primarily oxides of silicon and iron) fine carbonaceous fume[b,f] |
| | Aluminum | 57 | 26.0 | M | 80% inhalable, 55% fine[b] | Particulate fluorides, alumina ($Al_2O_3$), carbon dust, condensed hydrocarbons, tars |
| | Copper | 43 | 37.7 | H | 67% inhalable,[e] at least 25% fine[h,i] | Cu, Fe, S, $SiO_2$ from ore concentrate; metal fume consisting of oxides of As, Pb, Zn, Cu, Cd[b,j] |
| | Zinc | 5 | 5.7 | L | 100% inhalable;[b,k] 50% fine[k] | Ore concentrate dust; metal fume consisting of oxides of Zn, Pb, Cd Fe[b] |
| | Total | 475 | | | | |
| Secondary metals | Lead | 4 | 6.2 | H | 100% inhalable, 67% fine[b,k] | Metal fume consisting of oxides of Zn, Pb, Sn |
| (0.2%) | Aluminum | 2 | 5.6 | H | 99% inhalable, 94% fine[b,h] | $Al_2O_3$, $AlCl_3$, fluorides, NaCl, oxides of alkali metals[l] |

TABLE 4-23 (continued)

| Category percent of U.S. total | Industry | Annual uncontrolled emission $10^3$ metric tons | Estimated % of total plant uncontrolled emissions | Fraction emissions represented | Size characteristics | Major components |
|---|---|---|---|---|---|---|
| | Copper (brass/bronze) | 1 | 10.9 | M | 100% <5 μm[h] | Metal fume consisting primarily of oxides of Zn, Pb[l] |
| | Zinc | 1 | 6.9 | M | 100% <5 μm,[b,h] 702 < 1 μm[h] | Metal fumes consisting of oxides of Zn, Al, Cu; $NH_6Cl$, $ZnCl_2$, carbonaceous materials[b,l] |
| | Total | 8 | | | | |
| Wood products (0.2%) | Lumber and furniture | 9 | 52.9 | L | No Data | Sawdust |
| All categories (100.0%) | | 3,331 | | | | |

*L = Low, <40 percent.
M = Moderate, 40 to 70 percent.
H = High >70 to 100 percent.

[a]Total includes surface coal mining and crushed stone extraction only
[b]Jutz et al. (1977).
[c]Sussman (1977).
[d]Thimsen and Aften (1968).
[e]Industry total estimated from data presented in Drehmel et al. (1979)
[f]Steiner (1977).
[g]Bohn et al. (1978).
[h]Drehmel et al. (1979).
[i]Daugherty and Coy (1979).
[j]Nelson et al. (1977).
[k]Zoller et al. (1978).
[l]Vandergrift et al. (1971).

TABLE 4-24. TOXIC COMPONENTS OF FUGITIVE (AND STACK) PARTICULATE EMISSIONS

| Industry | POM[a] | As | Be | Pb | Cr | Cd | Hg | Se | Ag | Co | Ni | Fluorides | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Primary metals | | | | | | | | | | | | | |
| 1. Coke | ++ | + | + | + | + | + | | + | | + | + | | 1 |
| 2. Iron | | | | + | | | | | | | | + | 2,3 |
| 3. Steel | | | | + | + | | | | | | | + | 2,3,4 |
| 4. Foundries | | | | + | + | | | | + | + | + | | 5 |
| 5. Aluminum | + | | | | | | | | | | | ++ | 5,6 |
| 6. Copper | | ++ | | ++ | | + | | + | + | | | | 5,6 |
| 7. Lead | | + | | ++ | | + | | + | + | | | | 3,5,6,7 |
| 8. Zinc | | | | ++ | | + | + | | | | | | 5 |
| Secondary Metals | | | | | | | | | | | | | |
| 1. Lead | | | | ++ | | | | | | | | | 3 |
| 2. Aluminum | | | | | | | | | | | | ++ | 3 |
| 3. Copper (brass/bronze) | | | | ++ | | + | | | | | | | 3 |
| 4. Zinc | | | | + | + | + | | | | | + | | 3,5 |

[a]Polycyclic organic matter. The symbol (+) is used to indicate the presence of trace or minute quantities of a toxic component in the particulate emissions from an industry.
[b]If large quantities (>5 percent by weight) of the toxic component are present in the emission, the symbol (++) is used.
1, U.S. Environmental Protection Agency (1978).
2, Steiner (1977).
3, Vandegrift et al. (1971).
4, Bahn et al. (1978).
5, Jutze et al. (1977).
6, Nelson et al. (1977).
7, Daugherty and Coy (1979).

Fugitive particulate emissions, by definition, are difficult to collect and control. For a given industry, there are generally a large number of fugitive emission sources; e.g., 20 separate sources have been identified for foundaries (Jutze et al., 1977). In terms of total emissions, one or two of these sources may predominate. Fugitive particulate emissions on the plant site may result from open sources, such as wind erosion of storage piles and vehicular traffic over plant roads; from loading, unloading, transfer, and handling operations; from incompletely controlled point sources, such as furnace charging and tapping; and from poorly maintained equipment, such as leaking furnaces or coke oven doors.

Even though fugitive particulate emission totals may appear small when compared with large point sources, they may take on added importance because of the concentration of control efforts on point source emissions. In situations where point sources are well controlled or emissions are released from high stacks, fugitive particulate emissions will exert the primary effect on local air quality. Extremely high particulate levels have been measured in areas with a predominant industrial-process fugitive particulate influence (Lynn et al., 1976; Lebowitz, 1975).

Measurement and characterization of IPFPE. Many of the emission factors currently used for IPFPE are based on engineering judgment or extrapolation from similar processes. There is often little test data available to support these estimates. This is partially because of the inherent difficulties in the measurement of fugitive particulate emissions. If a pollutant is not easily collected and controlled, it follows that it will not be easy to measure.

The measurement techniques that have been used for fugitive particulate emissions are of three general types. The quasi-stack method is considered to be the most accurate. This technique involves hooding a source of emissions and sampling from the captured air stream. This method is not feasible for many sources. For sources that are enclosed in a building with a limited number of openings to the ambient atmosphere, the roof monitor method can be used. Pollutant concentrations in the air flowing to the ambient atmosphere are measured, along with the airflow rate through the opening. For sources which are not enclosed, an upwind-downwind sampling technique can be used. From pollutant concentrations measured upwind and downwind from the source, windspeed, and diffusion equations, the source strength can be estimated. With the exception of the quasi-stack method, the measurement techniques are indirect, and the accuracy of the results can vary considerably (Kolnsberg, 1976).

Characterization of fugitive particulate emissions according to size and composition presents some problems. When information on particle size is required, all of the difficulties described previously for emission rate sampling would seem to apply. One indirect appraoch which has been used is the application of stack emission size measurements to fugitive particulates from the same source. While this approach may be valid in some cases, it must be carefully applied. Often stack emission size measurements are made at the inlet to an air pollution control device. In some cases, there may have been a preferential removal of large particles prior to this point by gravitational settling or passage through a mechanical collector.

Composition of fugitive particulate emissions is easier to characterize. In the absence of direct measurements, indirect methods may be sufficient. For a process which is a source of both ducted and fugitive emissions, it is not unreasonable to assume that both types will be similar in composition (although the relative proportions of the components may be different). For open sources and for handling, conveying, transfer, and unloading operations, emissions should be of the same composition as the parent material. For sources which do not fit into either of these categories, direct measurement is necessary.

Derivation of estimated uncontrolled IPFPE inventory. The most complete reference on industrial process fugitive particulate emissions is a detailed literature review compiled by Jutze et al. (1977). Nineteen industries which are major emitters of fugitive particulates were identified. Within each industry, the processes and operations with fugitive emission potential were evaluated. For each process, a fugitive emission factor was developed. A later report applied some of these emission factors to nationwide production data for each industry in an attempt to estimate national totals for uncontrolled fugitive particulate emissions. This later report included only process emissions, omitting such plant-site open sources as storage pile erosion, vehicular traffic, unloading, and some handling and transfer operations.

The estimates in Table 4-23 attempted to include these omitted sources. For each source which had been neglected, the appropriate emission factor was applied to nationwide production data (Jutze et al. 1977). The uncontrolled emissions estimates derived in this matter were added to the nationwide totals described above (Zoller et al., 1978).

The only exception to this procedure was in the integrated iron and steel industry. Fugitive particulate emissions from this industry have been extensively measured (Cusino, 1979), and more up-to-date estimates of annual uncontrolled emissions were readily available (Spawn, 1979). Since these estimates were based on emission factors derived from extensive testing, they were considered more reliable and were used in place of the earlier totals (Zoller et al., 1978). Since the integrated iron and steel industry includes coke, iron, and steel production, all of which had previously been reported as separate industries (Jutze et al, 1977), the number of industrial categories was reduced from 19 to 17.

In addition to estimates of annual uncontrolled fugitive particulate emissions from each industrial category, Table 4-23 contains some information on size and composition characteristics of the emissions. As previously noted, there are often numerous fugitive particulate emission sources within an industry. Because size distribution data are lacking for many of these sources, it is not possible to characterize all emissions within an industry. In particular, industries which have a large open source contribution tend to be poorly characterized.

4.3.2.1.4.5 Nonindustrial fugitive particulate emissions. This section addresses the fugitive particulate emissions related to traffic entrainment of dust from public paved and unpaved roads, agriculture operations, construction activities, surface mining operations, and fires. With the exception of fires, all of these sources may be classified as open-dust sources; i.e., they entail dust entrainment by the interaction of machinery with aggregate materials and by the forces of wind on exposed materials.

Table 4-25 gives estimates of nationwide annual emissions of suspended particulate matter from these sources (Cooper et al., 1979). Off-road motor vehicles and inactive tailings piles are also potentially significant open dust sources (TRW, Inc., 1977). It is estimated that fugitive dust emissions exceed particulate emissions from traditional point sources in 90 percent of the Air Quality Control Regions that are not meeting the standards for total suspended particles (Carpenter and Weant, 1978).

Emissions from the interaction of machinery with aggregate materials vary strongly from one case to the next. The parameters which cause these variations may be grouped into threee categories: (1) measures of source activity or energy expended (for example, the speed and weight of a vehicle traveling on an unpaed road); (2) properties of the material being disturbed (for example, the content of silt in the surface material on an unpaved road); (3) Climatic parameters (for example, number of precipitation-free days per year on which emissions tend to be at a maximum.

Cowherd et al. (1974) have advanced the concept that open-dust source emission factors be considered in mathematical equations with multiplicative correction terms containing the above parameters as appropraite, so that the factors are applicable to a wide range of source conditions. For example, measured emissions factors for unpaved roads, which span two orders of magnitude, are predicted by an emission factor equation with a precision factor of 1.46; the 95 percent confidence interval for a predicted emission value, P, was found to extend from P/1.46 to 1.46 P (Cowherd et al., 1979).

Table 4-26 groups nonindustrial fugitive emission source categories by dust generation mechanism. Also shown are the emission-related properties of

TABLE 4-25. ESTIMATED ANNUAL SUSPENDED PARTICULATE EMISSION RATES FROM OPEN-DUST SOURCES IN THE UNITED STATES

| Source category | Estimated emission rate, $10^6$ tons/year |
|---|---|
| Unpaved roads | 320.0 |
| Wind erosion of cropland | 44 |
| construction activities | 27 |
| Paved roads | 7.9 |
| Wild fires | 3.4 |
| Agricultural tilling | 3.2 |
| Minerals | |
| Suface mining - other | 2.8 |
| Tailings | 0.8 |
| Surface mining - coal | 0.4 |
| Prescribed fires | 0.43 |
| Total | 409.0 |
| Total, nonroad | 81.0 |

Source: Cooper et al. (1979).

TABLE 4-26. PARAMETERS AFFECTING EMISSIONS FACTORS FOR OPEN DUST SOURCES

| Generic source category | Material | Equipment | Climate |
|---|---|---|---|
| Vehicular traffic on unpaved surfaces | Surface silt content | Vehicle speed<br>Vehicle weight | |
| Vehicular traffic on paved surfaces | Surface silt content<br>Surface loading | Vehicle weight | |
| Batch-drop operations | Silt content<br>Moisture content | Loader capacity | Wind speed |
| Continuous-drop operations | Silt content<br>Moisture content | | Wind speed |
| Wind erosion of storage piles and exposed areas | Surface erodibility<br>Surface silt content<br>Surface moisture content | | Wind speed |
| Blasting | Silt content<br>Moisture content<br>Hardness | Quantity and distribution of blasting agent | |

Source: Cowherd et al. (1979).

the materials being disturbed, the equipment which effects the disturbance (except in the case of wind erosion), and the prevailing climate where the source operation occurs. The use of the silt content as a measure of the dust-generation potential of a material acted on by the forces of wind or machinery was an important step in extending the applicability of the emission factor equations to the wide variety of aggregate materials of industrial importance. The upper size limit of silt particles (75 μm in diameter) is the smallest for which size analysis by dry seiving is practical, and this size is also a reasonable upper limit for particles which can become airborne. The wind erosion parameters given in Table 4-26 were taken largely from the Wind Erosion Equation developed by Woodruff and Siddoway (1965).

Construction activities and surface mining operations may entail emissions from all of the generic source categories given in Table 4-26. Emissions during building and road construction are generated by land clearing, blasting, ground excavation, cut and fill operations, and wind erosion of disturbed land. Dust-producing operations in surface mining include: topsoil and overburden removal; drilling and blasting; ore loading, transport, and dumping; and land reclamation and wind erosion of disturbed areas.

Open-dust sources produce emissions which span a wide range of particle sizes. In developing emission factors which relate to total suspended particles, it is necessary to consider the particle capture efficiency of the standard high-volume sampler. In the past, the 30-μm Stokes diameter, based on a typical dust particle density of 2 to 2.5 g/cm$^3$, has been used to approximate the effective cutoff diameter for the high-volume sampler (Cowherd et al., 1974 and Chapter 3 of this document). Recent wind tunnel experiments have provided more definitive data on particle capture efficient (McFarland et al., 1979).

Table 4-27 presents data on fractions of inhalable particles (IP) in measured particle emissions from open-dust sources. These data were obtained with a high-volume parallel-slot cascade impactor with a cyclone preseparator and directional sampling intake. The reliability of these data is weakened by the need to correct for residual particle bounce and to extrapolate the measured size distributions from the cyclone cutpoint of about 10 μm (Cowherd, et al., 1979).

4.3.2.2. Mobile Source Particulate Matter--Mobile sources, excluding off-road vehicles, account for about 2.5 percent of the nationwide total particulate emissions from all sources. Mobile-source emissions may be divided into two general categories: engine-related particles emitted in vehicle exhaust and vehicle-related particles including tire wear debris and asbestos from clutch and brake lining wear (Bradow et al., 1979; U.S. Environmental Protection Agency, 1978c; Dennis, 1974; Jacko and DuCharme, 1973). Less than 10 percent of the annual vehicle-related particulate material (~22 thousand metric tons/year in 1977) is airborne (Pierson and Brachaczek, 1974). Engine-related particles were emitted at a rate of about 325 thousand metric tons/year in 1977. Because of their size, 0.01-10 μm (Khatri and Johnson, 1978), they may be deposited in the lung. Engine-related particles are mostly under 1 μm in diameter and have relatively low settling velocities in the atmosphere. Therefore, they tend to be transported in the ambient air in a manner similar to gaseous pollutants (Whitby and Cantrell, 1976). Such particles become widely dispersed and can penetrate and deposit in the human respiratory system (Lee et al., 1976).

Engine-related particulate emissions from mobile sources may be divided into three types of aerosols: those dominated by lead halides, by sulfate,

TABLE 4-27 SUMMARY OF INHALABLE PARTICULATE (IP) FRACTIONS FOR OPEN-DUST SOURCES

| Source/control method | No. of tests | Avg. IP fraction in TSP emissions | Standard deviation |
|---|---|---|---|
| Unpaved roads/surface material | | | |
| Uncontrolled | | | |
| Dirt | 9 | 0.45 | 0.17 |
| Dirt and slag | 2 | 0.72 | 0.01 |
| Crushed slag | 17 | 0.54 | 0.14 |
| Gravel | 5 | 0.38 | 0.13 |
| Sand and gravel | 6 | 0.35 | 0.08 |
| Controlled | | | |
| Dirt and slag treated with Coherex | 2 | 0.88 | 0.12 |
| Crush rock treated with Trex | 3 | 0.57 | 0.22 |
| Paved roads (uncontrolled) | 11 | 0.77 | 0.16 |
| Aggregate storage pile stacking | | | |
| Iron ore pellets | 3 | 0.49 | 0.26 |
| Coal | 2 | 0.55 | 0.31 |

Source: Relder and Cowherd (1979).

and by carbonaceous matter with associated absorbed organics. Emission rates of these particles are classified according to engine type--either gasoline (spark ignition) or diesel (compression ignition).

Spark ignition vehicles may be subdivided further by fuel type:

- Leaded gasoline--pre-1975 domestic passenger cars, some imported passenger cars, and some heavy-duty trucks.
- Unleaded gasoline--almost all 1975-to-present domestic passenger cars and all 1980-to-present domestic and imported passenger cars.

Compression ignition vehicles may be subdivided into three classes by engine type:

- Four-stroke light-duty engines--domestic and imported diesel-powered passenger cars.
- Four-stroke heavy-duty engines--domestic and imported trucks and buses.
- Two-stroke heavy-duty engines--domestic trucks and buses.

Table 4-28 lists total particulate emissions and major aerosol components by the various vehicle categories. All of the particulate emission rates are derived from results of laboratory tests which simulate actual urban driving patterns. The lowest particulate emitter is an unleaded gasoline vehicle, catalyst-equipped without an air pump; and the highest emitter is a two-stroke heavy-duty diesel truck. The particulate emission rate of an average two-stroke heavy-duty diesel truck is over 2000 times that of a gasoline vehicle with catalyst and no air pumps.

Particulate matter from vehicles using leaded gasoline consists mostly of the inorganic compounds of lead, bromine, and chlorine and substantial quantities of carbonaceous material (Springer, 1978). The dominant lead compound present

TABLE 4-28. MOTOR VEHICLE ENGINE PARTICULATE EMISSIONS
(simulated urban driving conditions)

| Engine type | Vehicle type | Total particulate emission rate, (g/mi) | Fuel specific Exhaust particle emission rate, g/kg fuel | Major component emission rates, g/km (g/mi) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Lead[a] | Carbon[b] | Organic | Sulfate[c] |
| Gasoline | Leaded gasoline pre-1970 | 0.18(0.29) | 1.6[d] | 0.067 (0.108) | 0.059(.095) | 0.061(0.098) | 0.002(003) |
| | 1970-later | 0.08(0.13) | 0.69[d] | 0.048 (0.077) | 0.026(.042) | 0.008(.013) | 0.01 (.002) |
| | Unleaded gasoline | | | | | | |
| | Catalyst, no air | 0.009(0.01) | 0.078[d] | - | 0.003(.005) | 0.001(.002) | 0.003(.005) |
| | Catalyst, air | 0.031(0.05) | 0.26[d] | - | 0.006(.010) | 0.001(.002) | 0.010(.016) |
| | Light-duty diesel | 0.31 (0.49 | 4.7 | 0.001(0.002) | 0.23(.37) | 0.047(.076) | 0.007(.011) |
| | Heavy-duty diesel | 1.0(1.6) | 2.6 | 0.004(0.006) | 0.75(1.21) | 0.12(0.19) | 0.059(.093) |
| | 2-stroke truck | 1.8(2.8) | 4.3 | 0.001(0.002) | 1.33(2.14) | 0.90(1.45) | 0.091(.130) |

[a]As PbBrCl for gasoline; as Pb for diesel.

[b]Including both elemental carbon and organic carbon.

[c]Based on 0.03 with sulfur gasoline and 0.23 with sulfur diesel fuel.

[d]Assumes 15 miles per gallon.

[e]No. 1 fuel, low-speed driving conditions.

Source: Emissions summarized from Bradow et al. (1979).

is PbBrCl and is due to the presence of the scavengers ethylene dichloride and ethylene dibromide in leaded fuel. Table 4-28 shows that pre-1970 vehicles (0.18 g/km) emit about twice the total particulate mass of 1970 and later vehicles (0.08 g/km). Data on major particulate components for 1970 and later are limited. When compared to date from the pre-1970 grouping, there are indications of increased percentages (but decreased masses) of lead compounds and a decreased percentage of carbon and organic compounds. This shift is probably a result of the leaner engine combustion of the later model years. Lead emissions are directly related to fuel lead content, and all the leaded particulate data presented in Table 4-28 have been normalized to a lead content of 1.8 g/gal. As a result of gasoline lead phaseout (Federal Register, 1973), the increased relative abundance of catalyst-equipped cars (1975-present), and the certification of all 1980 domestic and imported vehicles on unleaded fuel only, annual mobile source lead particulate emissions are decreasing (U.S. Department of the Interior, 1977). The available data on particle size indicate a mass median diameter less than 0.54 μm, probably about 0.25 μm (Moran, et al., 1971). The introduction of catalyst-equipped vehicles requiring unleaded gasoline has substantially decreased engine particulate emissions since 1975.

The particulate matter from catalyst vehicles using unleaded gasoline is dominated by sulfate and carbonaceous material. Sulfate emissions vary directly with fuel sulfur level and are greater from air-pump-equipped catalyst cars (0.010 g/km) than from catalyst cars without air (0.003 g/km) (Kawecki, 1978). The particles emitted from catalyst vehicles burning unleaded gasoline have aerodynamic diameters smaller than those from vehicles burning leaded gasoline or diesel fuel these smaller particles have a mass median diameter of about

0.05 μm (Groblicki, 1976). The smaller percentages of trace metals and soluble organics from catalyst vehicles are due to the predominance of sulfate and the efficiency of the catalyst systems for the reduction of organic emissions.

Diesel particulate matter is appropriately described by examining three engine groups: light duty, four-stroke heavy duty, and two-stroke heavy duty (includes both trucks and buses). All of these engine groups emit carbon particles together with an oily mixture of organic compounds, some minor amounts of sulfates, and traces of metallic constituents such as iron, copper, calcium, and zinc (Lee and Duffield, 1979). Sulfate emissions from diesel passenger cars can be substantial (about 7mg/km) and are typically comparable with many in-use catalyst cars with air pumps (10mg/Km).

Carbon-containing species dominate the composition of diesel particles. Elemental carbon is usually the major component. The amount of associated organic material varies substantially among engine types and is greatest with two-stroke engines (Hare and Bradow, 1979). Particulate emission rates for all diesel groups are sensitive to many parameters, including vehicle size and operating conditions (speed, load) and fuel (aromatics and sulfur content). Table 4-28 presents estimates of particulate emission rates and characteristics for the various engine groups under urban driving conditions. Most of these data were developed with dynamometer simulations of normal driving with a typical No. 2 diesel fuel. The total particulate emission rate (0.31 g/km) reported for light duty diesels is a population-weighted value for vehicles on the road in 1977. The emission rates of the two-stroke bus (1.1 g/km) are lower than those of the two-stroke truck (1.8 g/km). The reduced emission rates of the bus probably are caused by the use of No. 1 fuel and by lower driving speeds.

The two-stroke diesel has the highest emission rate of particulate organic matter, typically about 50 percent of the total particulate mass (Hare and Bradow, 1979). A major portion of this material is similar to lubricating oil (Black and High, 1978). A smaller fraction of organic matter is associated with four-stroke diesel particles.

This oily matter contains a great number of organic chemicals, all with rather low volatility. For example, the substance with the lowest molecular weight conventionally measured in these mixtures contains 15 carbon atoms, and the most abundant group of chemicals contains 21 to 25 carbon atoms (Black and High, 1978). These substances have rather low vapor pressures and, partially because of their association with the carbon in diesel soot, they exist primarily as particles rather than gases under ambient conditions (Black and High, 1978).

Because of the large number of compounds, their molecular complexity, identification, and measurement of individual species in the oily component of diesel soot have been a challenging analytical problem. Recently, attempts have been made to limit the problem by studying the biological activity of various chemical fractions of the mixture (Huisingh et al., 1978). Ames bioassay results have suggested that the major mutagenic activity in such mixtures is located in oxygenated subfractions (Huisingh et al., 1978). The size distribution of diesel particulate matter suggests a mass median diameter of about 0.2 μm (Dolan and Kittelson, 1979). These particles have low settling velocities and thus remain suspended in the ambient air for long periods of time. Their size permits respiratory system penetration and deposition (Schreck, 1978).

Figure 4-18 illustrates the relative emissions of specific particulate components by vehicle type. Approximately 90 average unleaded gasoline passenger

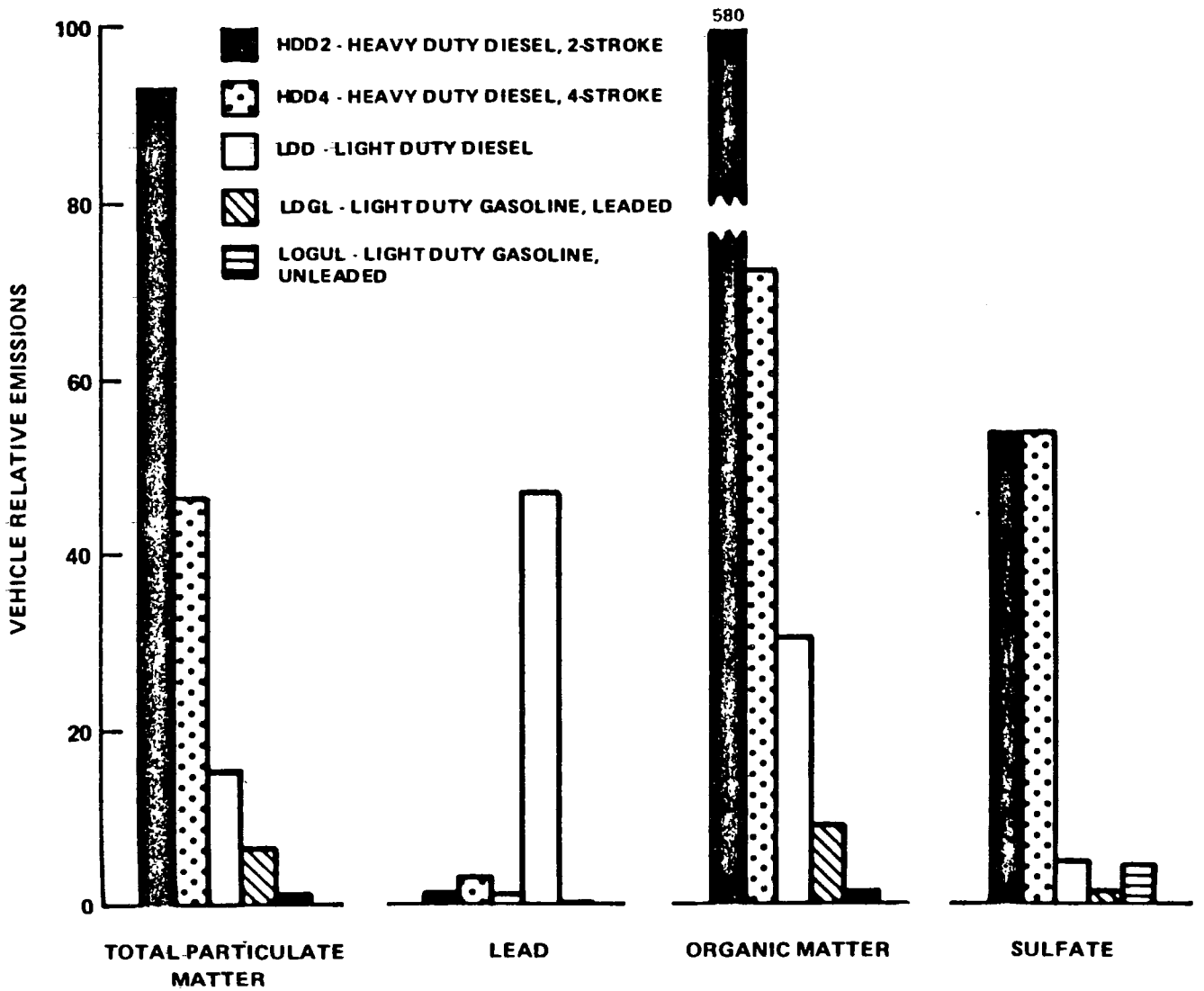



Figure 4-18. Relative particulate emissions are shown for vehicle categories (total and major components).

cars would be required to emit total particulate mass per mile comparable to a single two-stroke heavy-duty diesel truck under urban driving conditions. Similarly, about 580 unleaded gasoline passenger cars would be required to emit particulate organic mass per mile comparable to that of a two-stroke heavy-duty diesel truck. About 10 catalyst-equipped passenger cars would be required for sulfate emissions comparable to a single heavy-duty diesel. Light-duty diesels and catalyst gasoline cars emit similar amounts of sulfate. The heavy-duty and light-duty relative emission rates are important for estimation of ambient particulate burden, but the work functions of the various vehicle categories differ dramaticaly. On a per-passenger mile basis or per-ton mile basis, the emission rates are not nearly so different in magnitude. Examination of the fuel-specific emissions (i.e. mass of total particulate matter emitted per unit of fuel combusted) indicates somewhat lower particle emissions from heavy-duty diesels than from light-duty diesels.

Estimation of the atmospheric particulate loading from highway vehicles requires specific factors detailing the emission rate per vehicle (in grams/mile), the vehicle population, and the distance traveled. Based on these factors, a scenario for the estimation of the national vehicle particulate emission in thousands of metric tons per year has been developed (see Figure 4-19). This scenario assumes that light-duty diesel-powered passenger vehicles will reach a 25 percent penetration of total U.S. sales by 1995 with no stricter governmental regulation of particulate emissions. Figure 4-19 indicates that for 1977, the total vehicular suspended particulate level is 345,000 metric tons/year (engine and vehicle related) and is composed of 190,300 metric tons/year of elemental carbon; 67,900 metric tons/year of soluble organic compounds; 77,022 metric tons/ year of lead salts; and 9,600 metric tons/year

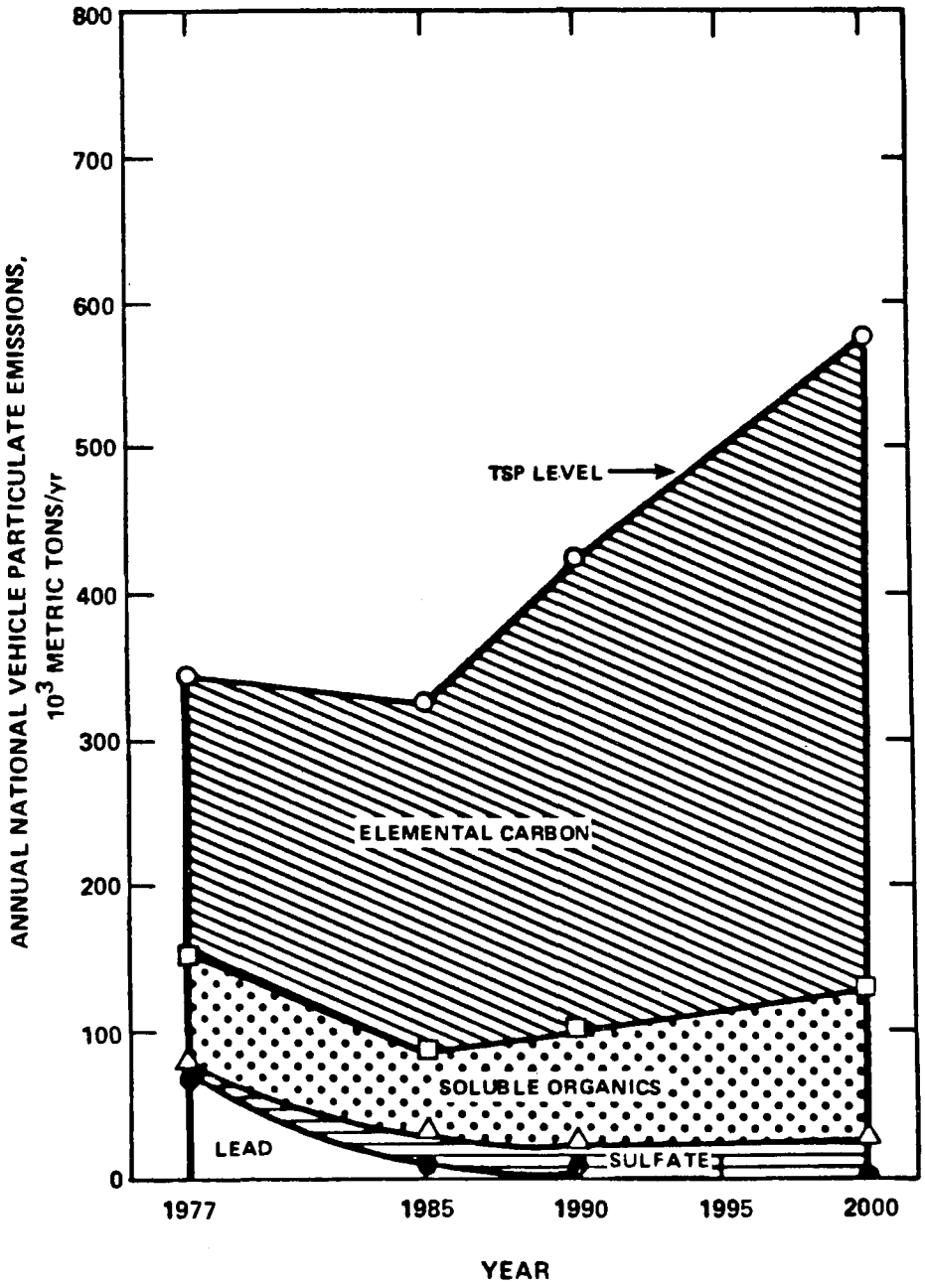



Figure 4-19. Total suspended particulate composition is projected, based on best diesel estimate without particulate regulation.

of sulfate. In this scenario, the total suspended particulate level declines from 1977 to 1985 and after reaching a mimimum in 1985, increased markedly as the proportion of diesels in the vehicle population increases. By the year 2000, diesel particulate emissions (i.e., elemental carbon and soluble organics) dominate the total suspended particulate composition, representing greater than 90 percent of the total emitted particulate matter. Scenarios utilizing different assumptions (e.g., estimates of diesel populations, future governmental particulate regulations, relaxing of emissions standard) would indicate different projected total suspended particulate levels. However, the overall trend of diesel-powered vehicles dominating total suspended particulate composition would remain unchanged.

## 4.4 SUMMARY

Sulfur oxides and particulate matter are emitted into the atmosphere from a variety of sources, both natural and man-made. Natural souces of these pollutants include terrestrial dust (windblown soil and rock particles), radioactive aerosols, sea spray, volcanic emissions, biosphere emanations (products of biological processes), and biomass burning. Although natural contributions of sulfur oxides and particulate matter to the atmosphere greatly exceed the total man-made contributions, natural emissions are globally distributed whereas man-made emissions tend to be much more concentrated.

Over 90 percent of the national sulfur oxides emsisions are in the form of sulfur dioxide; the balance consists of sulfates in various forms. The quantity and composition of these emissions vary from source to source and depend upon several factors, including fuel characteristics, operating conditions, and types of emissions-control equipment in use.

Total man-made emissions of sulfur oxides in the United States are currently calculated to be approximately 29 million metric tons per year from stationary sources. Transportation sources contribute less than 1 million metric tons of sulfur oxides, or not quite 3 percent of the total emissions. Of the total stationary sources, utility plant combustion of coal and oil is the primary contributor (62 percent), while other industrial processes account for about 32 percent, and residential and commercial use of coal and oil amounts to less than 3 percent of the total sulfur oxide emissions. These patterns vary considerably from one region to another, with over 75 percent of the total national emissions coming from the eastern half of the United States. Historically, overall emissions of sulfur oxides have increased from about 23 million metric tons per year in 1940 to as high as 35 million metric tons per year in 1973. Although the past few years have seen a slight decline in emissions, an increase to nearly 40 million metric tons is expected by 1990.

As with sulfur oxides, the characteristics of particulate matter vary according to type of source, emissions-control equipment, and other factors. Overall man-made emissions of particulate matter amounted to about 12.5 million metric tons per year in 1975 in the United States. The distribution of sources varies geographically but, again, the eastern half of the United States dominates by accounting for 66 percent of the national total. The nature of sources for particulate matter is also varied. Forty percent of these emissions come from stationary fuel combustion sources, principally electric generation and industrial fuel use, and 25 percent from mineral processing industries. The remainder is distributed among primary metal production, land vehicles, food and agricultural processes, solid waste disposal, and other sources. In addition, there are also considerable emissions of fugitive particulate matter from both industrial (3.3 million metric tons/yr) and non-industrial (409 million tons/yr) sources.

## 4.4 REFERENCES


Adams, F., R. Dams, L. Guzman, and J. W. Winchester, Background aerosol composition on Chacaltaya Mountain, Bolivia. Atmos. Environ. 11:629-634, 1977.

Baes, C. F., Jr., H. E. Goeller, J. S. Olson, and R. M. Rotty. The global carbon dioxide problem. Report ORNL-5194, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

Barrett, K. W. A Review of Standards of Performance for New Stationary Sources-Portland Cement Industry. Prepared by MITRE Corporation for the U.S. Environmental Protection Agency. EPA-450/3-79-012. March 1979.

Barringer, A. R., U.S. Geological Survey Professional Paper 1015, 1977. pp. 231-251. Airtrace--an airborne geochemical exploration technique.

Baylor, E. R., M. B. Baylor, D. C. Blanchard, L. D. Syzdek, and C. Appel, Virus transfer from surf to wind, Science 198:575-580, 1977.

Beauford, W., J. Barber, and A. R. Barringer. Heavy metal release from plants into the atmosphere. Nature 256:35-37, 1975.

Beauford, W., J. Barber, and A. R. Barringer, Release of particles containing metals from vegetation into the atmosphere. Science 195:571-573, 1977.

Benkoritz, Karmen M. Compiling a Multistate Emissions Inventory. In: Proceedings of a Specialty Conference on Emission Factors and Inventories. West Coast Section, APCA, Anaheim, CA, November 1978. pp. 122-139.

Bennett, L. and K. T. Knapp. Sulfur and trace metal particulate emissions from combustion sources. In: Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources. Volume 2, Characterization. EPA-600/9-78-020b. U.S. Environmental Protection Agency, ORD, Research Triangle Park, NC, August 1978. pp. 165-183.

Berg, W. W. Jr., and J. W. Winchester. Aerosol chemistry of the marine atmosphere. In: Chemical oceanography, 2nd ed., vol. 7. J. P. Riley and R. Chester, eds., Academic Press, London, 1978.

Black, F., and L. High. Diesel hydrocarbon emissions, particulate and gas phase. Presented at Symposium on Diesel Particulate Emissions Measurement and Characterization, Ann Arbor, MI, May 1978.

Blanchard, D. C., The electrification of the atmosphere by particles from bubbles in the sea. Prog. Oceanogr. 1:71-202, 1963.

Blanchard, D. C., and B. C. Parker. In: The Aquatic Microbial Community, vol. 15. J. Cairns, ed., Garland, New York, 1977. pp. 625-653.

Bohn, R., T. Cuscino, and C. Cowherd. Fugitive Emissions from Integrated Iron and Steel Plants. EPA-600/2-78-050. U.S. Environmental Protection Agency, March 1978.

Bolin, B. Changes of land biota and their importance for the carbon cycle. Science 196:613-615, 1977.

Bolin, B. On the role of the atmosphere in biogeochemical cycles. Q. J. Meteorol. Soc. 105:25-42, 1979.

Bradow, R. L., F. M. Black, J. N. Braddock, C. T. Hare, M. Ingalls, and J. M. Kawecki. Study of Particulate Emissions from Motor Vehicles. A Report to Congress. Draft report prepared by Southwest Research Institute, San Antonio, TX, under Contract No. 68-02-2951 and by Biospherics Inc., Rockville, MD, under Contract No. 68-02-2926 to the U.S. Environmental Protection Agency, Research Triangle Park, N.C., 1979.

Broecker, W. S. Chemical Oceanography. Harcourt Brace Jovanovitch, New York, 1974.

Buat-Menard, P., and M. Arnold. The heavy metal chemistry of atmospheric particulate matter emitted by Mount Etna volcano. Geophys. Res. Lett. 5:245-248, 1978.

Cadle, R. D. Volcanic emissions of halides and sulfur compounds to the troposphere and stratosphere. J. Geophys. Res. 80:1650-1652, 1975.

Carpenter, B. H., and G. E. Weant III. Particulate Control for Fugitive Dust. Report No. EPA-600/7-78-071. U.S. Environmental Protection Agency, Research Triangle Park, NC, April 1978.

Casteleman, A. W. Jr., H. R. Munklewitz, and B. Manowitz. Istopic studies of the sulfur component of the stratospheric aerosol layer. Tellus 26:222-234, 1974.

Curtis, L. C., The influence of guttation fluid on pesticides. Phytopathology 34:196-205, 1944.

Cooper, D. W., J. S. Sullivan, M. Quinn, R. C. Antonelli, and M. Schneider. Setting Priorities for Control of Fugitive Particulate Emissions from Open Sources. EPA-600/7-79-186. U.S. Environmental Protection Agency, Washington, DC, August 1979.

Cooper, J. A., and J. G. Watson. Portland Aerosol Characterization Study (PACS). Application of Chemical Mass Balance Methods to the Identification of Major Aerosol Sources in the Portland Airshed. Oregon Graduate Center, Beaverton, OR, April 1979.

Cowherd, C., Jr., et al., 1974

Cowherd, C., Jr., R. Bohn, and T. Cuscino, Jr. Iron and Steel Plant Open Source Fugitive Emission Evaluation. EPA-600/2-79-103. U.S. Environmental Protection Agency, Washington, DC, May 1979.

Council on Environmental Quality. Environmental Quality--9th Annual Report of the Council on Environmental Quality. December 1978.

Crutzen, P. J., L. E. Heidt, J. P. Krasnec, W. H. Pollack, and W. Seiler. Biomass burning as a source of the atmospheric gases CO, $H_2$, $N_2O$, NO, $CH_3Cl$, and COS. Nature in press, 1979.

Curtin, G. C., H. D. King, and E. L. Mosier. Movement of elements into the atmosphere from coniferous trees in subalpine forests of Colorado and Idaho, J. Geochem. Explor. 3:245-263, 1974.

Cuscino, T. A. Particulate Emission Factors Applicable to the Iron and Steel Industry. Midwest Research Institute Project No. 4468-L(23). EPA Contract No. 68-02-2814, Task 23. Final Report. August 7, 1979.

Dams, R., and J. De Jonge. Chemical composition of Swiss aerosols from the Jungfraujoch. Atmos. Environ. 10:1079-1084, 1976.

Dannis, M. L. Rubber dust from the normal wear of tires. Rubber Chem. Techno. 47:1011-1037, 1974.

Daugherty, D. P., and D. W. Coy. Assessment of the Use of Fugitive Emission Control Devices. EPA-600/7-79-045. U.S. Environmental Protection Agency, February 1979.

Delany, A. C., D. W. Parkin, J. J. Griffin, E. D. Goldberg, and B. E. F. Reinman. Airborne dust collected at Barbados. Geochim. Cosmochim. Acta 31:885-909, 1967.

Desy, D. H. Iron and Steel, Mineral Commodity Profile. Report No. MCP-15, U.S. Department of the Interior, Washington, D.C. July 1978.

Dickerman, J.D., et al. Industrial Process Profiles for Environmental Use Chapter 3, Petroleum Refinining Industry. EPA-600/2-77-023c. U.S. Environmental Protection Agency, IERL, Research Triangle Park, NC, January 1977.

Dietz, R. N., R. F. Wieser, and L. Newman. Operating Parameters Affecting Sulfate Emissions from an Oil-Fired Power Unit. In: Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources. Vol. 2, Characterization. EPA-600/9-78-020b. U.S. Environmental Protection Agency, ORD, Research Triangle Park, NC, August 1978. pp. 239-270.

Dolan, D. F., and D. B. Kittelson. Roadway measurements of diesel exhaust aerosols. SAE Paper No. 790492, Detroit, MI, March 1979.

Drehmel, D. C., D. P. Daugherty, and G. H. Gooding. State of control technology for industrial fugitive process particulate emissions. In: Symposium on the Transfer and Utilization of Particulate Control Technology. Vol. 4, Fugitive Dusts and Sampling, Analysis and Characterization of Aerosols. EPA-600/7-79-044d. U.S. Environmental Protection Agency, February 1979.

Duce, R. A., and E. J. Hoffman. Chemical tractionation at the air/sea interface. Annu. Rev. Earth Planet. Sci. 4:187-228, 1976.

Duce, R. A., J. W. Winchester, and I. W. Van Nahl. Iodine, bromine, and chlorine in the Hawaiian marine atmosphere. J. Geophys. Res. 70:1775-1799, 1965.

Eimutis, E. C., and R. P. Quill. Source Assessment: Overview Matrix for National Criteria Pollutant Emissions. EPA-600/2-77-107c. U.S. Environmental Protection Agency, Research Triangle Park, NC, 1977.

Federal Register, 44:49223, 49225-49226, 1979.

Federal Register, Regulation of fuels and fuel additives. 38:33, 734-33, 741, 1973.

Fish, B. R. Electrical generation of naturalaerosols from vegetation. Science 175:1239-1240, 1972.

Friend, J. P. The global sulfur cycle. In: Chemistry of the Lower Atmosphere. S. I. Rasool, ed., Plenum Press, New York, 1973. pp. 177-201.

Gillette, D. A. On the production of soil wind erosion aerosols having the potential for long range transport. J. Rech. Atmos. 8:735-744, 1974.

Goldberg, E. D. Rock volatility and aerosol composition. Nature 260:128-129, 1976.

Granat, L., H. Rodhe, and R. O. Hallberg. The global sulfur cycle. Ecol. Bull. (Stockholm) 22:89-134, 1976.

Griffin, J. J., and E. D. Goldberg. The fluexes of elemental carbon in coastal marine sediments. Limnol. Oceanogr. 20:456-463, 1975.

Groblicki, P. E. General Motors Sulfate Dispersion Experiment: Aerosol Sizing Measurements. Publication No. GMR-2127, EV-28. Prepared by General Motors Research Laboratories, Warren, MI to the Environmental Protection Agency Symposium on General Motors Sulfate Dispersion Experiment, Research Triangle Park, NC. April 1976.

Hall, W. B., and R. E. Ela. Cement and Mineral Commodity Profiles. Report No. MCP-26, U.S. Department of the Interior, Bureau of Mines, November 1978.

Hare, C. T., and R. L. Bradow. Characterization of Heavy-Duty Diesel Gaseous and Particulate Emissions, and Effects of Fuel Composition. See Paper No. 790490. Detroit, MI, February 26-March 2, 1979.

Hidy, G. M. et al. Design of the Sulfate Regional Experiment (Sure). Vol I: Supporting Data and Analysis. Electric Power Research Institute, Palo Alto, CA, February 1976.

Hitchcock, O. R. Biogenic contributions to atmospheric sulfate levels. Presented at the Second Annual Conference on Water Reuse, Chicago, 1975.

Holmes, 1971.

Holser, W. I. and I. R. Kaplan. Isotope geochemistry of sedimentary sulphates. Chem. Geol. 1:93-135, 1966.

Holser, et al., 1966.

Homolya, J. B., H. M. Barnes, and C. R. Fortune. A characterization of the gaseous sulfur emissions from coal and oil-fired boilers. In: Proceedings of the Fourth National Conference on Energy and the Environment. AICHE, New York, 1976. pp. 490-494.

Homolya, J. B., and J. L. Cheney. An assessment of sulfuric acid and sulfate emissions from the combustion of fossil fuels. In: Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources. Volume 2, Characterization. EPA-600/9-78-020b, U.S. Environmental Protection Agency, ORD, Research Triangle Park, NC, August 1978. pp. 3-11.

Homolya, J. B., and J. L. Cheney. A study of primary sulfate emissions from a coal-fired boiler with FGD. J. Air. Pollut. Control Assoc., vol. 29, September 1979.

Homolya, J. B., and J. L. Cheney. Primary Sulfate Emissions from Oil Combustion. U.S. Environmental Protection Agency, Research Triangle Park, NC 1978.

Husingh, J. et al. Application of bioassay to the characterization of diesel particle emissions. In: Symposium on Application of Short-Term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures. EPA 600/9-78-027. U.S. Environmental Protection Agency, Research Triangle Park, NC, 1978.

International Symposium on the Chemistry of Sea/Air Particulate Exchange Processes (collected papers). J. Rech. Atmos. 8:501-1007, 1974.

Jacko, M. G., and R. T. DuCharme. Brake emissions--emission measurements from brake and clutch linings from selected mobile sources. Report 68-04-0020, prepared by Bendix Research Laboratories, Southfield, MI. U.S. Environmental Protection Agency, Ann Arbor, MI. March 1973.

Johansson, I. B., R. E. Van Grieken, and J. W. Winchester. Elemental abundance variation with particle size in north Florida aerosols. J. Geophys. Res. 81:1039-1046, 1976.

Junge, C. E. Air Chemistry and Radioactivity, Academic Press, New York, 1963.

Junge, C. E. Chemical analysis of aerosol particles and of gas traces on the island of Hawaii. Tellus 9:528-537, 1957.

Junge, C. E., C. W. Chagnon, and J. E. Manson. Stratospheric aerosols. J. Meteorol. 18:81-108, 1961.

Jutze, G. A., et al. Technical Guidance for Control of Industrial Process Fugitive Particulate Emissions. EPA-450/3-77-0110. U.S. Environmental Protection Agency, March 1977.

Katari, V. S., and R. W. Gerstle. Industrial Process Profile for Environmental Use. Chapter 24, The Iron and Steel Industry. Prepared by Radian Corp. for the U.S. Environmental Protection Agency, EPA-600/2-77-023x, February 1977.

Kawecki, J. M. Emission of Sulfur-Bearing Compounds from Motor Vehicle and Aircraft Engines. A Report to Congress. Prepared by Biospherics, Inc., Rockville, MD, under Contract No. 68-02-2926 to the U.S. Environmental Protection Agency, Washington, DC. Publication No. EPA-600/9-78-028. August 1978.

Kellogg, W. W., R. D. Cadle, E. R. Allen, A. L. Lazrus, and E. A. Martell. The sulfur cycle. Science 175:587-596, 1972.

Khan, Z. S., et al. Source Assessment: Asphalt Hot Mix. Prepared by Monsanto Research Corp. for the U.S. Environmental Protection Agency. EPA-600/2-77-107n (PB-276-731). December 1977.

Khatri, N. J., and J. H. Johnson. Physical size distribution characterization of diesel particulate matter and the study of the coagulation process. SAE Paper No. 780788. September 1978.

Kolnsberg, H. J. A Guideline for the measurment of air-borne fugitive emissions from industrial sources. In: Symposium on Fugitive Emissions Measurement and Control. EPA-600/2-76-246. U.S. Environmental Protection Agency, September 1976.

Koyama, T. E., N. Nakai, and E. Kamata. Possible discharge rate of hydrogen sulfide from polluted coastal belts in Japan. J. Earth Sci. 13:1-11, 1965.

Lawson, D. R., and J. W. Winchester. A standard crustal aerosol as a reference for elemental enrichment factors. Atmos. Environ. 13:925-930, 1979.

Lawson, D. R., and J. W. Winchester. Atmospheric sulfur aerosol concentrations and characteristics from the Sourth American continent. Science 205:1267-1269, 1979a.

Lawson, D. R., and J. W. Winchester. Sulfur and trace element relationships in aerosols from the South American continent. Geophys. Res. Lett. 5:195-198, 1978.

Lawson, D. R., and J. W. Winchester. Sulfur, potassium, and phosphorus associations in aerosols from South American tropical rain forests. J. Geophys. Res. 84:3723-3727, 1979b.

Leavitt, C. et al. Environmental Assessment of Coal and Oil-Firing in a Controlled Boiler, Vol. II, Comparative Assessment. Prepared by TRW, Inc., for the U.S. Environmental Protection Agency. EPA-600/7-78-164b. U.S. Environmental Protection Agency, Research Triangle Park, NC August 1978.

Lee, Robert E., Jr., and F. V. Duffield. Sources of Environmentally Important Metals in the Atmosphere. In: Ultratrace Metal Analysis in Biological Sciences and Environment, A Symposium, 174th meeting, American Chemical Society, Chicago, Illinois, August 29-30, 1977. Advances in Chemistry Series, American Chemical Society, Washington, DC, 1979. pp. 146-171.

Lee, S. D., M. Malanchuk, and V. N. Finelli. Biologic effects of auto emissions. 1. Exhaust from engine with and without catalytic converter, J. Toxicol. Environ. Health 1:705-712, 1976.

Lebowitz, M. F. Short-term testing for fugitive dust effect. Presented at the 68th Air Pollution Control Association Meeting, Boston, MA. Paper No. 75-25.4. June 1975.

Littman, Fred E. Regional Air Pollution Study. Emission Inventory Summarization. EPA-600/4-79-004. U.S. Environmental Protection Agency, ORD, Research Triangle Park, NC, January 1979.

Lovelock, J. E. $CS_2$ and the natural sulfur cycle. Nature 248:625-626, 1974.

Lovelock, J. E., R. J. Maggs, and R. A. Rasmussen. Atmospheric dimethyl sulfide and the natural sulfur cycle. Nature 237:452-453, 1972.

Lynn, D. A., G. L. Deane, R. C. Galkiewicz, and R. M. Bradway. National Assessment of the Urban Particulate Problem. Volume 1, Summary of National Assessment. Report No. EPA-450/3-76-024. U.S. Environmental Protection Agency, Research Triangle Park, NC June 1976.

MacIntyre, F. Chemical fractionation and sea-surface microlayer processes. In: The Seas, vol. 5. E. D. Goldberg, ed., Wiley, New York, 1974.

Maenhaut, W., W. H. Zoller, R. A. Duce, and G. L. Hoffman. Concentration and size distribution of particulate trace elements in the South Polar atmosphere, J. Geophys. Res. 84:2421-2431, 1979.

Martell, E. A., and H. E. Moore. Tropospheric aerosol residence times: a critical review. J. Rech. Atmos. 8:903-910, 1974.

McCurley, W. R., and Daryl G. DeAngelis. Measurement of sulfur oxides from coal-fired utility and industrial boilers. In: Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources. Vol. 2, Characterization. EPA-600/9-78-020b. U.S. Environmental Protection Agency, ORD, Research Triangle Park, NC, August 1978. pp. 67-85.

McFarland, A. R., C. A. Ortiz, and C. E. Rodes. Characteristics of aerosol samplers used in ambient air monitoring. Presented at the 86th National Meeting of the American Institute of Chemical Engineers, Houston, TX April 1979.

Moorby, J., and H. M. Squire. The loss of radioactive isotopes from the leaves of plants in dry conditions. Radiat. Bot. 3:163-167, 1963.

Moran, J. B., O. Manary, R. Fay, and M. Baldwin. Development of Particulate Emission Control Techniques for Spark-Ignition Engines. Final Report prepared by Organic Chemicals Department, The Dow Chemical Co., Midland, MI, under Contract EHS70-101. U.S. Environmental Protection Agency, Ann Arbor, MI, July 1971.

Moyers, J. L., and R. A. Duce. Gaseous and particulate bromine in the marine atmosphere. J. Geophys. Res. 77:5330-5338, 1972a.

Moyers, J. L., and R. A. Duce. Gaseous and particulate iodine in the marine atmosphere. J. Geophys. Res. 77:5229-5238, 1972.

Natusch, D. F. S. Characterization of fly ash from coal combustion. In: Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources. Vol. 2, Characterization. EPA-600/9-78-020b. U.S. Environmental Protection Agency, ORD, Research Triangle Park, NC August 1978. pp. 149-163.

Nemeryuk, G. E. Migration of salts into the atmosphere during transpiration. Sov. Plant Physiol. 17:560-566, 1970.

Nelson, K. W., M. O. Varner, and T. J. Smith. Nonferrous metallurgical operations. In: Air Pollution, (3rd ed.) vol. IV, A. C. Stern, ed., Academic Press, New York, 1977.

Pierson, W. R., and W. W. Brachaczek. Airborne particulate debris from rubber tires. Rubber Chem. Technol. 27:1275-1299, 1974.

Rahn, K. A. The chemical composition of the marine aerosol. Technical Report, University of Rhode Island, Kingston, July 1976.

Rahn, K. A. Sources of trace elements in aerosols--an approach to clean air. Ph.D. Thesis, University of Michigan, Ann Arbor, 1974.

Rasmussen, R. A. Emission of biogenetic hydrogen sulfide. Tellus 26:254-260, 1974.

Rasmussen, R. A., and F. W. Went. Volatile organic material of plant origin in the atmosphere. Proc. Natl. Acad. Sci. U.S.A. 53:215-220, 1965.

Reed, A. H. Stone, Mineral Commodity Profiles. U.S. Department of the Interior, Bureau of Mines. Report No. MCP-17, July 1978.

Reider, J. P., and C. Cowherd, Jr. Inhalable Particulate Emission Factor Assessment and Development. Final Report, EPA Contract No. 68-02-2609, Assignment No. 11. U.S. Environmental Protection Agency, Research Triangle Park, NC April 1979.

Ryan, P. W., and McMahon. Some chemical and physical characteristics of emissions from forest fires. Paper 76-2.3, presented at the 69th Annual Meeting of the Air Pollution Control Association, Portland, OR, June 22-July 1, 1976.

Shcreck, R. M. Health Effects of Diesel Exhaust. Biomedical Sciences Dept., General Motors Research Laboratories, Warren, MI, 1978.

Schnell, R. C., and G. Vali. World-wide source of leaf-derived freezing nuclei. Nature 246:212-213, 1973.

Schnell, R. C., and G. Vali. Atmospheric ice nuclei from decomposing vegetation. Nature 236:163-165, 1972.

Scinto, L. L. Primary Sulfate Emissions from Coal and Oil Combustion-Rough Draft.. Prepared by TRW, Inc, for the U.S. Environmental Protection Agency, IERL, Research Triangle Park, NC, August 1979.

Seiler, W., and P. J. Crutzen. Estimates of gross and net fluexes of carbon between the biosphere and the atmosphere from biomass burning. Climatic Change, in press, 1979.

Smith, D. M., J. J. Griffin, and E. D. Goldberg. Elemental in marine sediments: a baseline for burning. Nature 241:268-270, 1973.

Spawn, P. Letter report submitted under Contract No. 68-02-2687, Technical Directive No. 007. September 20, 1979.

Springer, J. J. Current and future trends of exhaust emissions from HD highway vehicles. Presentation to Federally Coordinated Program of Highway Research and Development, Federal Highway Administration, College Park, MD. October 1978.

Steiner, B. A. Ferrous metallurgical operations. In: Air Pollution, (3rd ed.), vol. IV. A. C. Stern, ed., Academic Press, New York, 1977.

Stoiber, 1973.

Stoiber, R. E., and A. Jepson. Sulfur dioxide contributions to the atmosphere by volcanoes. Science 182:2577-578, 1973.

Suprenant, N. F. et al. Emissions Assessment of Conventional Stationary Combustion Systems. Volume 1, Gas and Oil-Fired Residential Heating Sources Prepared by TRW, Inc., for the U.S. Environmental Protection Agency. EPA-600/7-79-020b, U.S. Environmental Protection Agency, IERL, Research Triangle Park, NC, May 1979.

Surprenant, N. et al. Preliminary Emissions Assessment of Conventional Stationary Combustion Systems. Vol. II, Final Report. Prepared by TRW, Inc., for the U.S. Environmental Protection Agency. EPA-600/2-76-046b. U.S. Environmental Protection Agencies, Research Triangle Park, NC, March 1976.

Sussman, V. H. Mineral product industries. In: Air Pollution, 3rd. ed., vol. IV. A. C. Stern, ed., Academic Press, New York 1977.

Timsen, D. J., and P. W. Aften. A Proposed Design for Grain Elevator Dust Collection.. S. Air Pollut. Control Admin. 18:738, 1968.

TRW, Inc. Guideline for Development of Control Strategies in Areas with Fugitive Dust Problems. OAOPS Report No. 1.2-71. U.S. Environmental Protection Agency, Research Triangle Park, NC, October 1977.

U.S. Department of Commerce, Bureau of the Census. Statistical Abstract of the United States - 1977. U.S. Department of Commerce, Washington, DC.

U.S. Department of Energy. Annual Report to Congress, Vol. II. DOE/EIA-0036/2, U.S. Department of Energy, Washington, DC, 1977.

U.S. Department of Energy. Annual Report to Congress, 1978, Volume III. DOE/EIA-0173/3. U.S. Department of Energy, Energy Information Administration, Washington, D.C. 1979a. (The model utilized in these air emissions projections is the Regional Emission Projection Systems. REPS is documentated in "An Air Emissions Analysis of Energy Projections for the Annual Report to Congress," a memorandum by Edward Pechan dated September 1978).

U.S. Department of Energy, 1979b.

U.S. Department of Energy. 1985 Air Pollution Emissions. DOE/PE-0001. U.S. Department of Energy, Washington, DC, December 1977.

U.S. Department of the Interior, 1975.

U.S. Department of the Interior, Bureau of Mines, Division of Fuels Data. Carbon black in 1976. In Mineral Industry Surveys, 1977.

U.S. Department of the Interior. Minerals Yearbook 1975. Vol. I, Metals, Minerals, and Fuels. U.S. Department of the Interior, Washington, DC., 1977.

U.S. Environmental Protection Agency. An Assessment of the Health Effects of Coke Oven Emissions. External Review Draft. U.S. Environmental Protection Agency, Research Triangle Park, NC, April 1978.

U.S. Environmental Protection Agency. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Vol. 1, Proposed Standards. EPA-450/2-74-002a. U.S. Environmental Protection Agency, OAQPS, Research Triangle Park, NC, October 1974.

U.S. Environmental Protection Agency. Unpublished data, 1976.

U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors, 3rd ed. Publication AP-42. U.S. Environmental Protection Agency, OAQPS, Research Triangle Park, NC, August 1977.

U.S. Environmental Protection Agency. National Air Quality and Emissions Trends Report 1977. Publication No. 450/2-78-052. U.S. Environmental Protection Agency, Research Triangle Park, NC, December 1978a.

U.S. Environmental Protection Agency. National Air Data Branch, Monitoring and Data Analysis Division. 1975 Narional Emissions Report. EPA-450/2-78-020, U.S. Environmental Protection Agency, Research Triagnel Park, NC, May 1978b. pp. vii and 1.

U.S. Environmental Protection Agency. National Air Pollutant Emission Estimates, 1940-1976. EPA-450/1-78-003. U.S. Environmental Protection Agency, July 1978c.

U.S. Environmental Protection Agency, 1979.

U.S. Environmental Protection Agency. Position Paper on regulation of atmospheric sulfates. Report EPA-450/2-75-007. U.S. Environmental Protection Agency, Research Triangle Park, NC, 1975.

Vandegrift, A. E. et al. Particulate Pollutant System Study. Volume III, Handbook of Emission Properties. NTIS Report No. PB-203-522. May 1971.

Weart, T. E. et al. Fine Particulate Emission Inventory and Control Survey. Prepared by Midwest Research Institute for the U.S. Environmental Protection Agency. EPA-450/3-74-040. U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1974.

Went, F. W. Organic matter in the atmosphere, and its possible relation to petroleum formation. Proc. Natl. Acad. Sci. U.S.A. 46:212-221, 1960.

Went, F. W., D. E. Slemmons, and H. N. Mozingo. The organic nature of atmospheric condensation nuclei, Proc. Natl. Acad. Sci. U.S. 58:69-74, 1967.

Wexler, H. On the effects of volcanic dust on insolation and weather. Bull. Am. Meteorol. Soc. 32:10-15, 1951.

Wexler, H. Spread of the Krakotoa volcanic dust cloud as related to the high-level circulation. BUll. Am. Meteorol. Soc. 32:48-51, 1951.

Whitby, K. T., and B. Cantrell. Atmospheric aerosols--characteristics and measurements. Session 29, Fine Particles. In: International Conference on Environmental Sensing and Assessment, Las Vegas, NV, September 14-17, 1975. Institute of Electrical and Electronics Engineers, New York, 1976.

Winchester and Duce, 1977.

Winchester, J. W., R. J. Ferek, D. R. Lawson, J. O. pilotte, M. H. Thiemens, and L. E. Wangen. Comparison of aerosol sulfur and crustal element concentrations in particle size fractions from continental U.S. locations. Water Air Soil Pollut., in press, 1979.

Woodruff, N. P., and F. H. Siddoway. A wind erosion equation. Soil Sci. Soc. Am. Proc. 29:602-608, 1965.

Woodwell, G. M., R. H. Whittaker, W. A. Reiners, G. E. Likens, C. C. Delwiche, and D. B. Botkin. The biota and the world carbon budget. Science 199: 141-146, 1978.

Working Symposium on Sea-to-Air Chemistry (collected papers). J. Geophys. Res. 77:5059-5349, 1972.

Zoller, J., T. Bertke, and T. Janzen. Assessment of Fugitive Particulate Emission Factors for Industrial Processes. EPA-450/3-78-107. U.S. Environmental Protection Agency, Research Triangle Park, NC, September 1978.

Zoller, W. H. E. S. Gladney, and R. A. Duce. Atmospheric concentrations and sources of trace metals at the South Pole. Science 183:198-200, 1974.

# 5. ENVIRONMENTAL CONCENTRATION AND EXPOSURE

## 5.1 DIMENSION OF EXPOSURES TO PARTICLES AND SULFUR DIOXIDE

The impact of air pollution on health and welfare is a function of dose delivered to the receptor and the ability of the receptor to cope with the resultant stress. It is almost impossible to measure directly the air pollution dose to a population or even an individual except in the laboratory. Most often the dose is estimated. This is particularly true for sulfur dioxide and airborne particles. The stress experienced by a critical organ or receptor tissue from particle inhalation depends on particle size, composition, morphology, acidity or basicity, and other physical-chemical properties of the aerosol. The delivered dose is also a function of the anatomical features of the receptor as well as manner of breathing, breathing rate, and integrity of bodily defense systems.

Throughout their lifetime people inhale a complex mixture of gases and particles. Other segments of the environment such as vegetation, materials, ect. are also exposed to the same complex mixtures. Its composition varies with time at any given location because of changing atmospheric conditions. The mixture of particles and gases comes from a variety of sources (either directly or after partial reaction), and the composition is therefore quite different at different locations.

As an alternative to direct measurement of dose, exposure could be used as an approximation for studies on air pollution risk and effects. The exposure-response relationship for air pollution is most important for establishing standards Unfortunately, to extrapolate from measurements of ambient levels at a few locations to an individual or population exposure is a very difficult task at present. The outdoor air's contribution to indoor concentrations is still being

investigated. The additional exposures to gases and particles from nonoccupational indoor sources are not adequately quantified.

Indoor air quality and activity patterns complicate air pollution exposure estimates and are discussed later in this chapter. First, the ambient outdoor concentrations of particulate matter and sulfur dioxide are examined. The status of national air quality is presented for TSP (total suspended particulate matter) and $SO_2$. This first section discusses mass concentration measurements of TSP, including information by size fraction. Both particle size and composition are important characteristics of atmospheric aerosols. The relationships between ambient exposures to pollutants are presented in the concluding section after a discussion of the relationship between indoor and outdoor concentrations.

## 5.2 AMBIENT MEASUREMENTS

### 5.2.1 Ambient TSP Concentrations

The accuracy and precision of TSP monitoring are limited by three general considerations: (1) sampling methods, including instrumentation, analytical methods, and quality assurance; (2) sampling frequency; and (3) location of monitors.

Chapter 3 discusses the first of these considerations; the second and third are discussed in this chapter. Sampling frequency affects the confidence limits on mean TSP concentrations and annual or seasonal trends. It is appropriate to discuss this limitation at the beginning of this section before the 1978 national TSP data base is presented. The siting of TSP monitors influences significantly the levels measured, and hence the interpretation of data. These considerations are presented with examples in several sections of this chapter.

In 1978 there were 4105 TSP monitoring sites in the United States and its territories that reported data to the National Aerometric Data Bank (NADB) of

the U.S. Environmental Protection Agency. Of these, only 2882 had enough observations per quarter and per year for the data to be considered valid for estimating annual averages.

Table 5-1 lists a number of such sites for each State and territory. The number of sites reporting valid data range from zero in Delaware and American Samoa to 318 in Ohio. The most populous state, California, had 60 and New York had 236.

The U.S. Environmental Protection Agency has established a uniform sampling schedule to be followed by all State and local agencies. It requires a 24-hr sample (midnight to midnight) every 6th day. Hence, in 1 year there are 60 or 61 possible sampling days from which to derive the mean value and distribution, and to determine attainment of standards. In 1978 14 percent of all reporting sites had 60 or more observations.

Sampling days are missed and samples must be voided for a variety of reasons. Therefore, a minimum requirement has been established for considering the data from any site as valid in determining an annual average: there must be at least five observations during each quarter of a calender year and at least ~~23~~ 26 observations for the year. Of the Federal, State, and local TSP sites reporting data to NADB, 70 percent met this requirement.

The distribution of observations for the 2882 valid monitoring sites in 1978 is shown in Figure 5-1. Ten (10) percent of these sites had less than 47 observations; 50 percent had more than 56 observations. However, 80 percent of the monitoring sites collected fewer than 60 samples. Three percent of the monitors sampled at an equivalent frequency of 1 day in 3, and fewer than 2 percent collected samples at a frequency of 1 day in 2.

The NAAQS for TSP is expressed as an annual geometric mean and as a once-per-year daily value. Frequency of monitoring is a fundamental parameter of the air

TABLE 5-1. VALID MONITORING SITES OPERATING IN 1978

| State | Number of Valid Sites | Percent of total | Percent of U.S. population |
|---|---|---|---|
| Alabama | 76 | 3 | 1.70 |
| Alaska | 15 | 1 | 0.19 |
| Arizona | 9 | <1 | 1.05 |
| Arkansas | 37 | 1 | 0.99 |
| California | 60 | 2 | 10.03 |
| Colorado | 61 | 2 | 1.20 |
| Connecticut | 36 | 1 | 1.45 |
| Delaware | NA | NA | 0.27 |
| District of Columbia | 8 | <1 | 0.33 |
| Florida | 105 | 4 | 3.90 |
| Georgia | 37 | 1 | 2.32 |
| Hawaii | 9 | <1 | 0.41 |
| Idaho | 29 | 1 | 0.39 |
| Illinois | 131 | 5 | 5.21 |
| Indiana | 47 | 2 | 2.47 |
| Iowa | 50 | 2 | 1.34 |
| Kansas | 22 | 1 | 1.07 |
| Kentucky | 82 | 3 | 1.60 |
| Louisiana | 27 | 1 | 1.81 |
| Maine | 22 | 1 | 0.50 |
| Maryland | 52 | 2 | 1.92 |
| Massachusetts | 37 | 1 | 2.70 |
| Michigan | 124 | 4 | 4.25 |
| Minnesota | 54 | 2 | 1.84 |
| Mississippi | 15 | 1 | 1.10 |
| Missouri | 27 | 1 | 2.23 |
| Montana | 21 | 1 | 0.35 |
| Nebraska | 37 | 1 | 0.72 |
| Nevada | 20 | 1 | 0.29 |
| New Hampshire | 23 | 1 | 0.38 |
| New Jersey | 79 | 3 | 3.42 |
| New Mexico | 56 | 2 | 0.55 |
| New York | 236 | 8 | 8.41 |
| North Carolina | 83 | 3 | 2.54 |
| North Dakota | 18 | 1 | 0.30 |
| Ohio | 318 | 11 | 4.98 |
| Oklahoma | 26 | 1 | 1.29 |
| Oregon | 37 | 1 | 1.08 |
| Pennsylvana | 112 | 4 | 5.50 |
| Puerto Rico | 10 | <1 | NA |
| Rhode Island | 6 | <1 | 0.44 |
| South Carolina | 46 | 2 | 1.32 |
| South Dakota | 10 | <1 | 0.32 |

TABLE 5-1. (continued)

| State | Number of Valid Sites | Percent of total | Percent of U.S. population |
|---|---|---|---|
| Tennessee | 90 | 3 | 1.97 |
| Texas | 148 | 5 | 5.87 |
| Utah | 20 | 1 | 0.57 |
| Vermont | 4 | 1 | 0.22 |
| Virginia | 115 | 4 | 2.35 |
| Washington | 47 | 2 | 1.68 |
| West Virginia | 13 | 1 | 0.85 |
| Wisconsin | 107 | 4 | 2.15 |
| Wyoming | 22 | 1 | 0.18 |
| American Samoa | NA | NA | NA |
| Guam | 3 | <1 | NA |
| Virgin Islands | 3 | <1 | NA |

[a]NA, Not applicable.

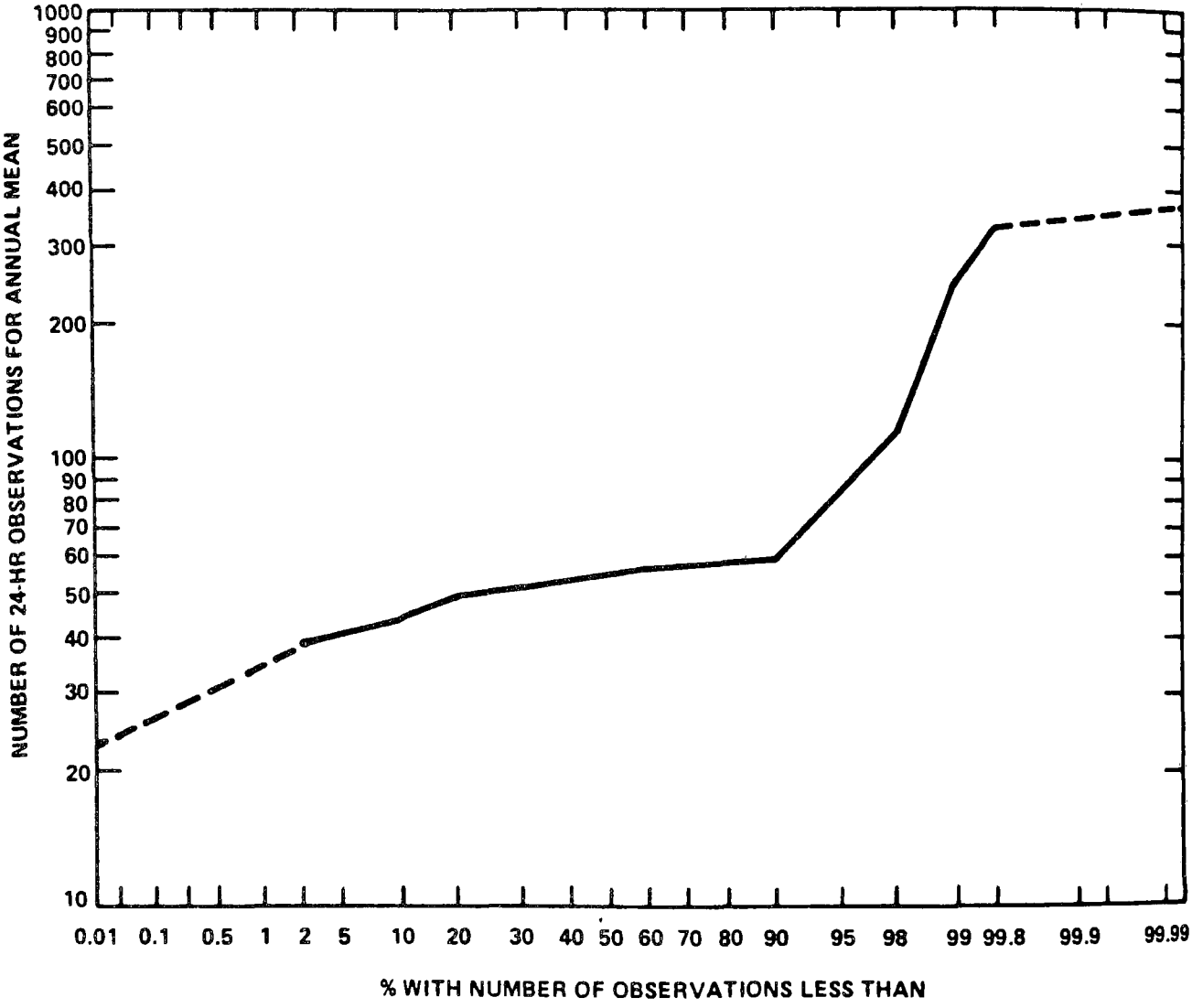



Figure 5-1. Distribution of the number of observations in 1978 per valid site is for a total of 2882 sites.

quality data used for comparison with the standards. The period of determining an annual average for comparison is a calendar year. If the number of 24-hr observations is less than 365, then the true mean concentration for the year can only be expressed as residing within a range of values. By assuming that the actual distribution of values is log normal, then confidence intervals can be calculated from the geometric mean and the standard deviation. Figure 5-2 shows the effect of sample size on the 95 percent confidence intervals for a hypothetical site whose true annual geometric mean is equivalent to the standard. From this example we can only conclude that the annual geometric mean is 75 $\pm$ 13 $\mu g/m^3$, if the mean for that year was determined from a sample size of 61. Increasing the sampling frequency to 1 day in 2 reduces the level of uncertainty so that the annual mean can be expressed as 75 $\pm$ 3 $\mu g/m^3$. Hunt (1972) demonstrated that the confidence intervals around the geometric annual mean were broadened as the sampling size decreased and as the standard geometric deviation increased.

A critical factor in evaluating compliance with once-a-year standards is the effect of sampling frequency. Figure 5-1 shows that in 1978 the majority of valid sites (80 percent) had fewer than 60 sampling days. The sites with more frequent sampling had a greater chance of sampling the higher concentrations. Table 5-2 illustrates this point. Assuming that there are a number of days on which the observations are above the standards, the probability of selecting 2 or more days on which standards are exceeded is a function of sampling frequency. If there are 10 days above the standards, there is only a slightly better than 50 percent chance of actually monitoring on 2 of those days given a sampling frequency of 61 out of 365 days. When the sampling frequency is doubled to 122 sampling days, the probability of capturing 2 days out of 10 that exceed the standards increases to 80 percent. This analysis serves to show the relative

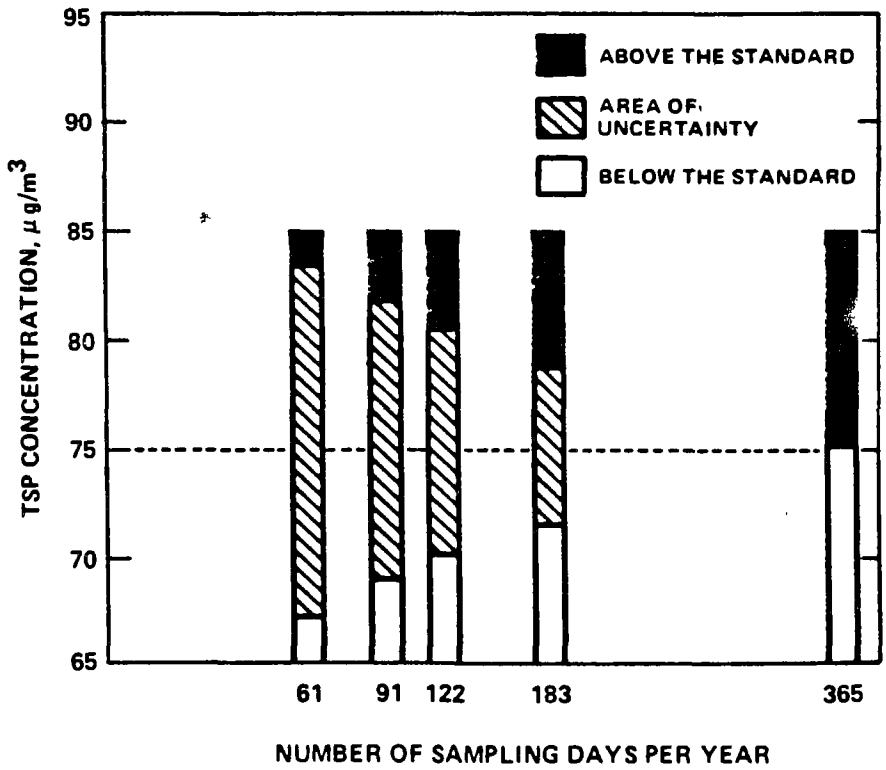



Figure 5-2. The 95 percent confidence intervals about the annual primary standard for TSP is shown for various sampling frequencies (assume the standard geometric deviation equals 1.6).

TABLE 5-2. PROBABILITY OF SELECTING TWO OR MORE DAYS WHEN SITE EXCEEDS STANDARD

| Actual number of excursions | Sampling frequency, days/year | | | |
|---|---|---|---|---|
| | 61 | 122 | 183 | 365 |
| 2 | 0.03 | 0.11 | 0.25 | 1.00 |
| 4 | 0.13 | 0.41 | 0.69 | 1.00 |
| 6 | 0.26 | 0.65 | 0.89 | 1.00 |
| 8 | 0.40 | 0.81 | 0.96 | 1.00 |
| 10 | 0.52 | 0.90 | 0.99 | 1.00 |
| 12 | 0.62 | 0.95 | 0.99 | 1.00 |
| 14 | 0.71 | 0.97 | 0.99 | 1.00 |
| 16 | 0.78 | 0.98 | 0.99 | 1.00 |
| 18 | 0.83 | 0.99 | 0.99 | 1.00 |
| 20 | 0.87 | 0.99 | 0.99 | 1.00 |
| 22 | 0.91 | 0.99 | 0.99 | 1.00 |
| 24 | 0.93 | 0.99 | 0.99 | 1.00 |
| 26 | 0.95 | 0.99 | 0.99 | 1.00 |

changes in the magnitude of the problem relating to sampling frequencies. In actuality, samples are not taken randomly; they are taken systematically, usually at a rate of once every 6 days. The problem is further complicated in that the log normal distribution of TSP concentrations does not apply uniformly to all sites.

The 1978 TSP data were examined to determine whether there was a relationship between the number of observations and the maximum concentration observed. Figure 5-3 is a plot of the maximum concentration versus the number of observations for 1448 sites. No relationship is apparent. For the 37 sites having maximum 24-hr values exceeding 450 $\mu g/m^3$, 21 are reported from sites with fewer than 60 observations. Where there were fewer than 35 observations, no high values were found. This comparison is not totally valid because each monitor is sampling from a different set of values. It does indicate that analyses using the aggregated data sets may not be adversely affected by differences in observations. However, comparing sites on the basis of their violating the once-per-year standard for TSP without regard to sampling frequency, is questionable.

An additional complication occurs when the meteorological regimes affecting the TSP concentrations are considered. Attainment of standards may depend on the number of "clean" sampling days versus the number of "dirty" sampling days. Watson (1979) exemplifies this problem with Portland, OR, TSP data. The annual geometric mean TSP data show a decreasing trend from 1973 through 1975, with a significant increase in 1976. If these data are reexamined and weighted by the meteorological regimes actually sampled in each year, the conclusions are changed. The stratified mean TSP values show a large drop in concentrations occurring between 1974 and 1975, with the levels being constant for the year before and after. Since these means are determined from a sample set varying from 49

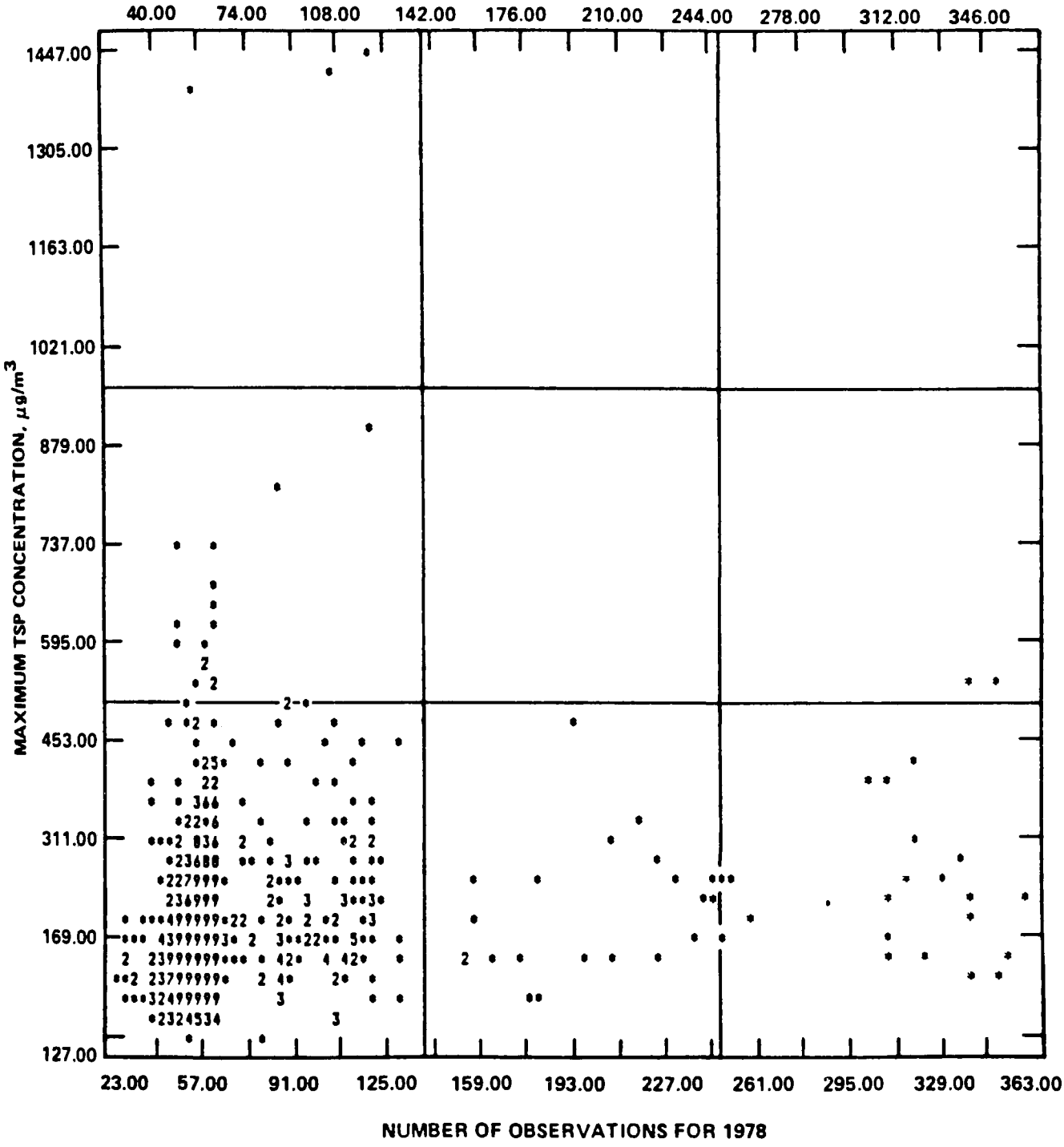



Figure 5-3. In this scattergram of maximum TSP concentration against number of observations in 1978, the total number of sites is 1448. The number 9 indicates nine or more; hence, the numbers do not sum to the total.

samples in 1974 to 79 samples in 1976, a statistical test is required to determine whether the means of any year are significantly different from those of any other year. The 95 percent confidence intervals for all stratified means do overlap. Watson concludes, then, that there is a reasonable chance that the true means do not really vary from year to year.

The choice of sampling location can obviously affect the concentrations measured. Remote sites are chosen specifically to gain understanding of background levels of either natural or transported suspended particulate matter. At a specific location, the height of the monitor above the ground influences concentrations. If the monitor is elevated above surface sources, lower concentrations might be expected. The elevations of the 1978 valid sites ranged from ground to 748 feet above surface, with a mean height of 23 feet. Only 5 percent of all monitors were higher than 40 feet above grade. Table 5-3 gives the height distribution of monitors.

A scattergram (Figure 5-4) of the site median value against the site elevation suggests that larger values might be associated with lower monitoring sites. However, careful inspection of the cross-tabulation of the median value by elevation (Table 5-4) and the cross-tabulation (Table 5-5) of the 90th percentiles by elevation fails to reveal any significant relationship. The cut points for the median and 90th percentiles were preselected. The intent was to group all the national TSP monitoring sites by, in percentages, first 5, next 20, next 25, next 25, next 20, and final 5. This approximate breakdown can be seen in the column on the right labeled "ROW TOTAL." To determine whether elevation might be affecting concentrations, inspect two rows, 70 to 97 $\mu g/m^3$ and >97 $\mu g/m^3$. If the monitors closer to the ground were actually systematically "seeing" a greater mass of suspended particles, then for both rows the column percent (third number in grid) would be higher in the first and second columns

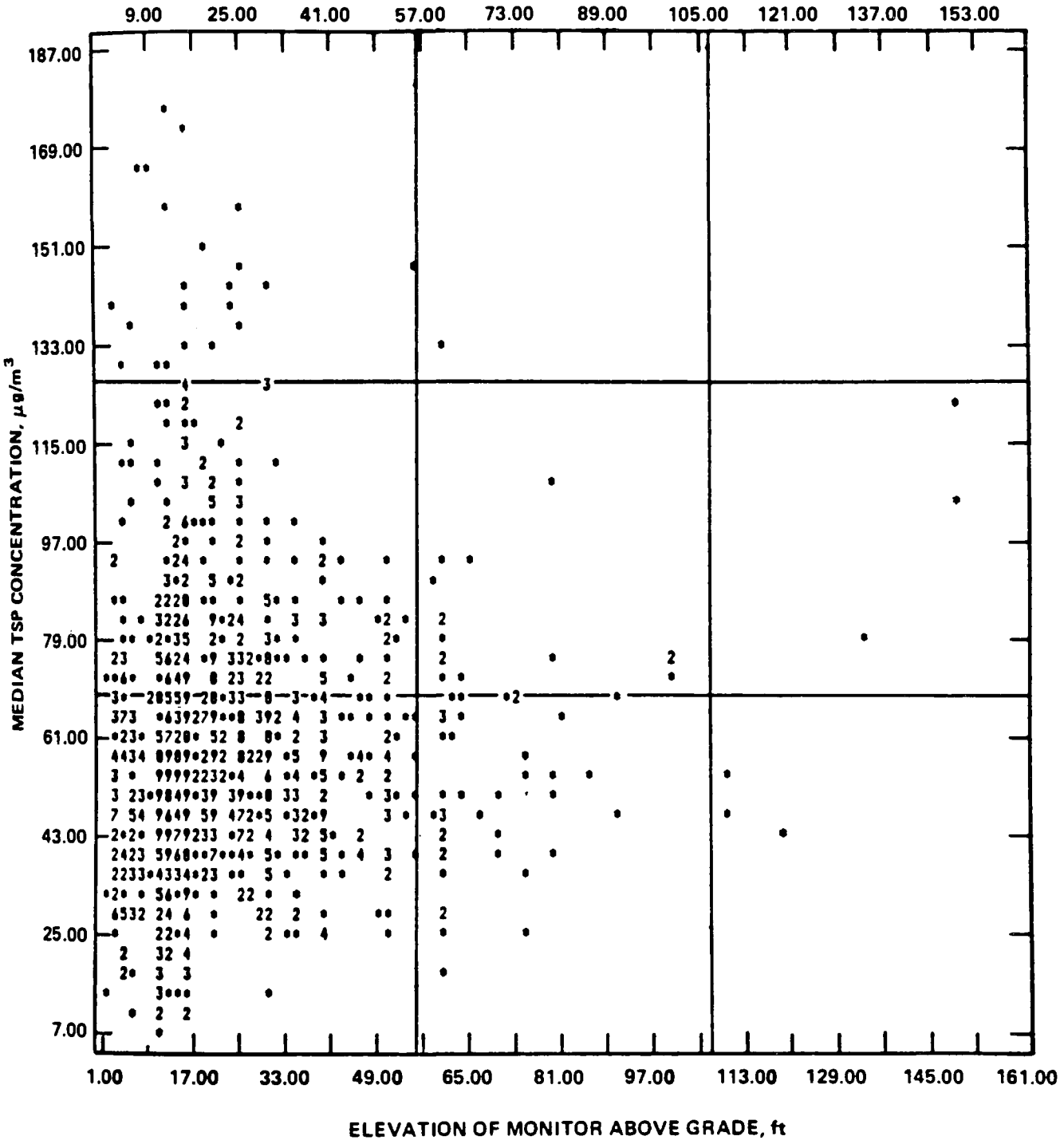



Figure 5-4. In this scattergram of median TSP concentration against elevation of monitor above grade, the total number of sites is 1448. The number 9 indicates nine or more; hence, the numbers do not sum to the total.

TABLE 5-3. HEIGHT ABOVE GRADE FOR 1978 TSP MONITORS

| Height, ft | Number | Percent of total | Cumulative number | Cumulative percent |
|---|---|---|---|---|
| 0-5 | 396 | 13.7 | 396 | 13.7 |
| 5-10 | 549 | 19 | 945 | 32.7 |
| 10-16 | 645 | 22.4 | 1590 | 55.1 |
| 16-20 | 474 | 16.4 | 2064 | 71.5 |
| 20-25 | 275 | 9.6 | 2339 | 81.1 |
| 25-35 | 160 | 5.6 | 2499 | 86.7 |
| 35-40 | 241 | 8.4 | 2740 | 95.1 |
| >40 | 142 | 4.9 | 2882 | 100.0 |

TABLE 5-4. CROSS-TABULATION OF MEDIAN CONCENTRATION OF TSP BY HEIGHT OF MONITOR ABOVE GRADE

| Median TSP concentration, $\mu g/m^3$ | Height above grade, ft | | | | | | Row total |
|---|---|---|---|---|---|---|---|
| | <4 | 4-10 | 10-16 | 16-25 | 25-40 | >40 | |
| <27 | | | | | | | |
| Number of sites | 6 | 39 | 29 | 16 | 10 | 12 | 112 |
| Percent of row | 5.4 | 34.8 | 25.9 | 14.3 | 8.9 | 10.7 | |
| Percent of column | 6.9 | 8.6 | 4.0 | 2.5 | 2.3 | 3.1 | |
| Percent of total | 0.2 | 1.4 | 1.1 | 0.6 | 0.4 | 0.4 | 4.1 |
| 27-44 | | | | | | | |
| Number of sites | 22 | 106 | 139 | 87 | 85 | 76 | 515 |
| Percent of row | 4.3 | 20.6 | 27.0 | 16.9 | 16.5 | 14.8 | |
| Percent of column | 25.3 | 23.5 | 19.1 | 13.4 | 19.5 | 19.8 | |
| Percent of total | 0.8 | 3.9 | 5.1 | 3.2 | 3.1 | 2.8 | 18.9 |
| 44-56 | | | | | | | |
| Number of sites | 27 | 118 | 184 | 157 | 104 | 93 | 683 |
| Percent of row | 4.0 | 17.3 | 26.9 | 23.0 | 15.2 | 13.6 | |
| Percent of column | 31.0 | 26.1 | 25.3 | 24.3 | 23.9 | 24.3 | |
| Percent of total | 1.0 | 4.3 | 6.7 | 5.7 | 3.8 | 3.4 | 25.0 |
| 56-70 | | | | | | | |
| Number of sites | 20 | 97 | 178 | 186 | 121 | 110 | 712 |
| Percent of row | 2.8 | 13.6 | 25.0 | 26.1 | 17.0 | 15.4 | |
| Percent of column | 23.0 | 21.5 | 24.5 | 28.7 | 27.8 | 28.7 | |
| Percent of total | 0.7 | 3.6 | 6.5 | 6.8 | 4.4 | 4.0 | 26.1 |
| 70-97 | | | | | | | |
| Number of sites | 11 | 68 | 144 | 148 | 96 | 81 | 548 |
| Percent of row | 2.0 | 12.4 | 26.3 | 27.0 | 17.5 | 14.8 | |
| Percent of column | 12.6 | 15.0 | 19.8 | 22.9 | 22.1 | 21.1 | |
| Percent of total | 0.4 | 2.5 | 5.3 | 5.4 | 3.5 | 3.0 | 20.1 |
| >97 | | | | | | | |
| Number of sites | 1 | 24 | 54 | 53 | 19 | 11 | 162 |
| Percent of row | 0.6 | 14.8 | 33.3 | 32.7 | 11.7 | 6.8 | |
| Percent of column | 1.1 | 5.3 | 7.4 | 8.2 | 4.4 | 2.9 | |
| Percent of total | 0.0 | 0.9 | 2.0 | 1.9 | 0.7 | 0.4 | 5.9 |
| Column total | | | | | | | |
| Number of sites | 87 | 452 | 728 | 647 | 435 | 383 | 2732 |
| Percent of total | 3.2 | 16.5 | 26.6 | 23.7 | 15.9 | 14.0 | 100.0 |

TABLE 5-5. CROSS-TABULATION OF 90TH PERCENTILE CONCENTRATION OF TSP BY HEIGHT OF MONITOR ABOVE GRADE

| 90th percentile TSP concentration, $\mu g/m^3$ | Height above grade, ft | | | | | | Row total |
|---|---|---|---|---|---|---|---|
| | >4 | 4-10 | 10-16 | 16-25 | 25-40 | >40 | |
| 54 | | | | | | | |
| Number of sites | 7 | 41 | 29 | 18 | 7 | 12 | 114 |
| Percent of row | 6.1 | 36.0 | 25.4 | 15.8 | 6.1 | 10.5 | |
| Percent of column | 8.0 | 9.1 | 4.0 | 2.8 | 1.6 | 3.1 | |
| Percent of total | 0.3 | 1.5 | 1.1 | 0.7 | 0.3 | 0.4 | 4.2 |
| 54-79 | | | | | | | |
| Number of sites | 20 | 119 | 131 | 88 | 99 | 81 | 538 |
| Percent of row | 3.7 | 22.1 | 24.3 | 16.4 | 18.4 | 15.1 | |
| Percent of column | 23.0 | 26.3 | 18.0 | 13.6 | 22.8 | 21.1 | |
| Percent of total | 0.7 | 4.4 | 4.8 | 3.2 | 3.6 | 3.0 | 19.7 |
| 79-99 | | | | | | | |
| Number of sites | 23 | 122 | 182 | 160 | 103 | 90 | 680 |
| Percent of row | 3.4 | 17.9 | 26.8 | 23.5 | 15.1 | 13.2 | |
| Percent of column | 26.4 | 27.0 | 25.0 | 24.7 | 23.7 | 23.5 | |
| Percent of total | 0.8 | 4.5 | 6.7 | 5.9 | 3.8 | 3.3 | 24.9 |
| 99-124 | | | | | | | |
| Number of sites | 16 | 95 | 167 | 178 | 113 | 106 | 673 |
| Percent of row | 2.4 | 14.1 | 24.7 | 26.4 | 16.7 | 15.7 | |
| Percent of column | 18.4 | 21.0 | 22.9 | 27.5 | 26.0 | 27.7 | |
| Percent of total | 0.6 | 3.5 | 6.1 | 6.5 | 4.1 | 3.9 | 24.7 |
| 124-188 | | | | | | | |
| Number of sites | 19 | 54 | 168 | 157 | 95 | 78 | 571 |
| Percent of row | 3.3 | 9.5 | 29.4 | 27.5 | 16.6 | 13.7 | |
| Percent of column | 21.8 | 11.9 | 23.1 | 24.3 | 21.8 | 20.4 | |
| Percent of total | 0.7 | 2.0 | 6.1 | 5.7 | 3.5 | 2.9 | 20.9 |
| 188 | | | | | | | |
| Number of sites | 2 | 21 | 51 | 46 | 18 | 16 | 154 |
| Percent of row | 1.3 | 13.6 | 33.1 | 29.9 | 11.7 | 10.4 | |
| Percent of column | 2.3 | 4.6 | 7.0 | 7.1 | 4.1 | 4.2 | |
| Percent of total | 0.1 | 0.8 | 1.9 | 1.7 | 0.7 | 0.6 | 5.6 |
| Column total | | | | | | | |
| Number of sites | 87 | 452 | 728 | 647 | 435 | 383 | 2732 |
| Percent of total | 3.2 | 16.5 | 26.6 | 23.7 | 15.9 | 14.0 | 100.0 |

than the others in that row. This is not the case. In fact, on a percentage basis there are more monitors at 16 to 25 feet above the ground experiencing higher levels.

Monitor elevation does not appear to be systematically biasing the national TSP data. The influence appears to be unimportant in the aggregate. However, there may be a correlation between moritor height and location with respect to pollution sources. Some studies in 5.2.1.24 indicate a relation of monitor elevation, distance from roadway, and TSP concentrations at specific locations. Other siting considerations are discussed later.

The inferences drawn about air quality levels, trends, and population exposures from the TSP data presented in this chapter are made in full knowledge of the following limitations of TSP monitoring: (1) sampling sites are not standardized; (2) frequency of sampling is quite varied; (3) the vast majority of sites reporting have fewer than 60 sampling days per year; (4) the frequency of sampling is not randomized with respect to meteorological conditions. (5) no spatial averaging is used in analyzing or reporting data; and (6) though the monitor is stationary, the population it is intended to represent is highly mobile, spending a portion of its time indoors.

5.2.1.1 Composition and Range of Concentrations--The particles that make up atmospheric aerosols, are solid or liquid, ranging in size from a few tenths of an Ångstrom to several hundred micrometers. They may be described by their size range, physical or chemical composition, origin, or effects. The actual classification of atmospheric aerosols is determined by the measurement technique. Suspended particulate matter is a subset of this larger class of aerosols, and is ubiquitous in man's environment. It includes primary particulate matter (pollen, dust, soot, fibers) emitted from natural or anthropogenic sources and suspended in ambient air, and secondary particulate matter (sulfates, nitrates,

condensed metal, and organic vapors) which is formed in the atmosphere by gaseous reactions involving sulfur dioxide, nitrogen dioxide, metal, and organic vapors. Aerosols can be formed by condensation of gases or vapors, by grinding and abrasion, or residues of evaporation of cloud droplets, ocean spray or biological fluids. These particulates, once in the atmosphere, can be transformed by coagulation and condensation at the same time that they are being transported and diluted by air movement. The mix of particulates to which a population is exposed contains both inert substances and biologically active substances. In addition, these aerosols may be transformed either on mixing with indoor air, on inhalation, or on deposition. Health effects from aerosol exposures may be induced or exacerbated by simultaneous exposures (or in some cases, prior exposures) to other air contaminants such as sulfur dioxide, nitrogen dioxide, and ozone. It is therefore important to know not only the properties of the particles, but also to what gases the population would be simultaneously exposed.

The standard method of measuring the particulate content of outdoor air has been to weigh the total amount of particulate matter retained on a filter paper through which ambient air has been drawn by a high-volume air pump for 24 hr. This measurement technique defines only the mass per unit volume of particles present in the air over the sampling period.

Figure 5-5 is drawn from the distribution of 1978 annual arithmetic means (Table 5-6). Also displayed in Figure 5-5 is the cumulative frequency of sites for which the 90th percentile value is equal to or less than given value. Half of all the Nation's sites had annual arithmetic mean values less than 60 $\mu g/m^3$. The overall mean value for the country is 64 $\mu g/m^3$. Annual mean values range from 9 to 288 $\mu g/m^3$. Only 14 valid sites had annual mean concentrations equal to or less than 16 $\mu g/m^3$. At the other end of the distribution, 25 percent of

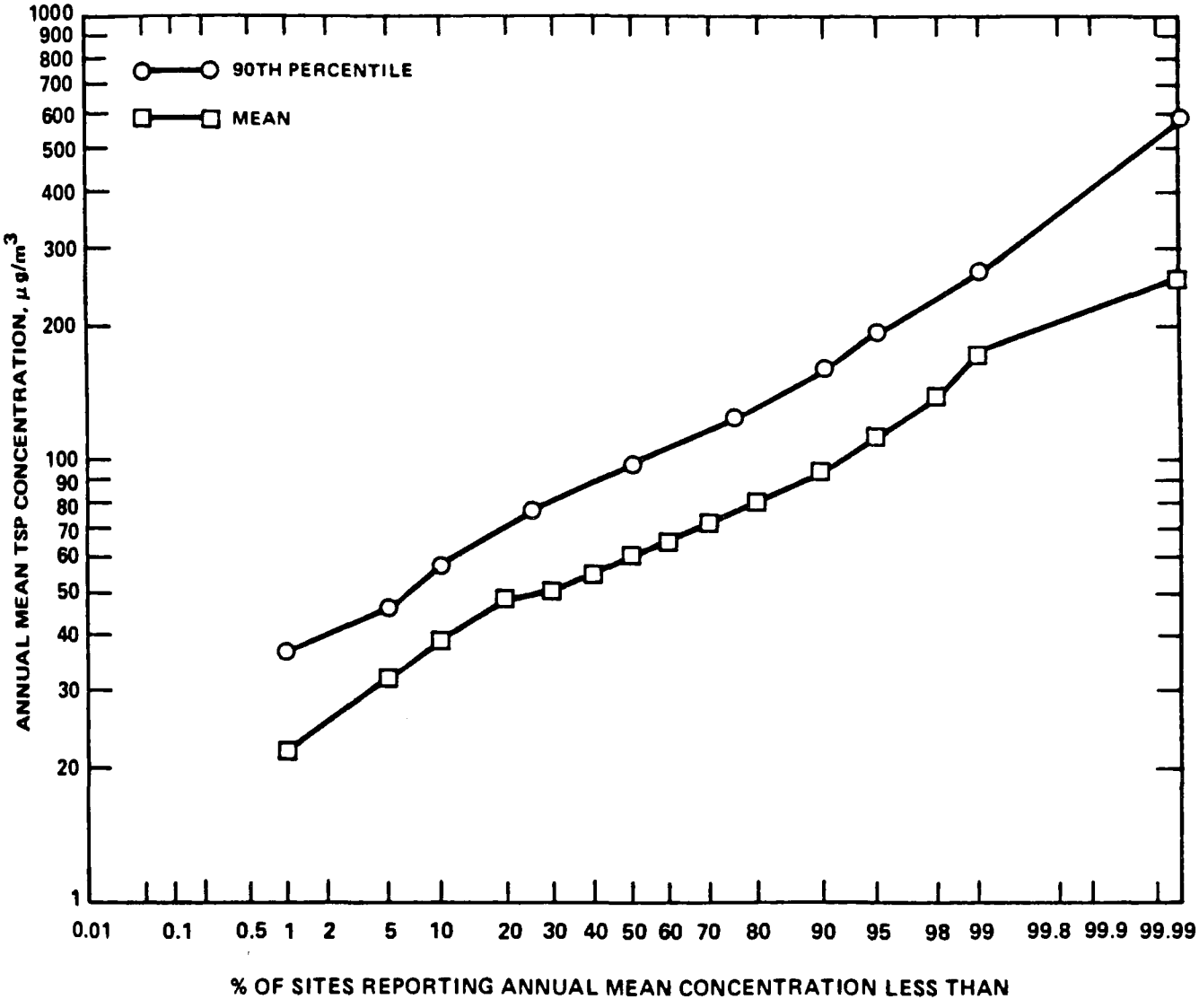



Figure 5-5. Distribution of mean and 90th percentile TSP concentrations is shown for valid 1978 sites.

TABLE 5-6. DISTRIBUTION OF VALID SITES BY 1978 ANNUAL AVERAGE TSP CONCENTRATIONS[a]

| 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 9 | 1 | 0 | 0 | 52 | 67 | 2 | 32 | 93 | 13 | 0 | 89 | 134 | 2 | 0 | 98 |
| 11 | 1 | 0 | 0 | 53 | 51 | 2 | 34 | 94 | 11 | 0 | 89 | 135 | 3 | 0 | 98 |
| 13 | 2 | 0 | 0 | 54 | 65 | 2 | 36 | 95 | 13 | 0 | 90 | 136 | 1 | 0 | 98 |
| 14 | 4 | 0 | 0 | 55 | 38 | 1 | 37 | 96 | 12 | 0 | 90 | 137 | 3 | 0 | 98 |
| 15 | 3 | 0 | 0 | 56 | 55 | 2 | 39 | 97 | 12 | 0 | 91 | 138 | 2 | 0 | 98 |
| 16 | 3 | 0 | 0 | 57 | 51 | 2 | 41 | 98 | 14 | 0 | 91 | 139 | 1 | 0 | 98 |
| 17 | 2 | 0 | 1 | 58 | 82 | 3 | 44 | 99 | 11 | 0 | 92 | 140 | 3 | 0 | 98 |
| 18 | 3 | 0 | 1 | 59 | 65 | 2 | 46 | 100 | 7 | 0 | 92 | 141 | 2 | 0 | 99 |
| 19 | 3 | 0 | 1 | 60 | 61 | 2 | 48 | 101 | 12 | 0 | 92 | 142 | 1 | 0 | 99 |
| 20 | 6 | 0 | 1 | 61 | 65 | 2 | 50 | 102 | 5 | 0 | 92 | 143 | 4 | 0 | 99 |
| 21 | 4 | 0 | 1 | 62 | 52 | 2 | 52 | 103 | 9 | 0 | 93 | 144 | 1 | 0 | 99 |
| 22 | 10 | 0 | 1 | 63 | 65 | 2 | 55 | 104 | 11 | 0 | 93 | 145 | 1 | 0 | 99 |
| 23 | 2 | 0 | 2 | 64 | 57 | 2 | 56 | 105 | 7 | 0 | 93 | 146 | 1 | 0 | 99 |
| 24 | 7 | 0 | 2 | 65 | 51 | 2 | 58 | 106 | 7 | 0 | 94 | 147 | 1 | 0 | 99 |
| 25 | 6 | 0 | 2 | 66 | 45 | 2 | 60 | 107 | 8 | 0 | 94 | 149 | 1 | 0 | 99 |
| 26 | 6 | 0 | 2 | 67 | 45 | 2 | 61 | 108 | 7 | 0 | 94 | 150 | 1 | 0 | 99 |
| 27 | 9 | 0 | 2 | 68 | 49 | 2 | 63 | 109 | 9 | 0 | 94 | 151 | 1 | 0 | 99 |
| 28 | 13 | 0 | 3 | 69 | 48 | 2 | 65 | 110 | 3 | 0 | 95 | 153 | 1 | 0 | 99 |
| 29 | 11 | 0 | 3 | 70 | 53 | 2 | 67 | 111 | 6 | 0 | 95 | 154 | 1 | 0 | 99 |
| 30 | 12 | 0 | 4 | 71 | 39 | 1 | 68 | 112 | 5 | 0 | 95 | 156 | 1 | 0 | 99 |
| 31 | 18 | 1 | 4 | 72 | 36 | 1 | 69 | 113 | 6 | 0 | 95 | 158 | 1 | 0 | 99 |
| 32 | 17 | 1 | 5 | 73 | 45 | 2 | 71 | 114 | 12 | 0 | 96 | 159 | 1 | 0 | 99 |
| 33 | 23 | 1 | 6 | 74 | 33 | 1 | 72 | 115 | 3 | 0 | 96 | 162 | 1 | 0 | 99 |
| 34 | 18 | 1 | 6 | 75 | 30 | 1 | 73 | 116 | 6 | 0 | 96 | 163 | 3 | 0 | 99 |
| 35 | 20 | 1 | 7 | 76 | 47 | 2 | 75 | 117 | 7 | 0 | 96 | 165 | 1 | 0 | 99 |
| 36 | 22 | 1 | 8 | 77 | 35 | 1 | 76 | 118 | 2 | 0 | 96 | 167 | 1 | 0 | 99 |
| 37 | 24 | 1 | 9 | 78 | 31 | 1 | 77 | 119 | 2 | 0 | 96 | 169 | 2 | 0 | 99 |
| 38 | 31 | 1 | 10 | 79 | 42 | 1 | 78 | 120 | 1 | 0 | 96 | 170 | 1 | 0 | 99 |
| 39 | 32 | 1 | 11 | 80 | 30 | 1 | 79 | 121 | 5 | 0 | 96 | 173 | 1 | 0 | 99 |
| 40 | 27 | 1 | 12 | 81 | 33 | 1 | 80 | 122 | 2 | 0 | 97 | 175 | 1 | 0 | 99 |
| 41 | 41 | 1 | 13 | 82 | 26 | 1 | 81 | 123 | 5 | 0 | 97 | 176 | 3 | 0 | 100 |
| 42 | 40 | 1 | 15 | 83 | 30 | 1 | 82 | 124 | 4 | 0 | 97 | 177 | 2 | 0 | 100 |
| 43 | 30 | 1 | 16 | 84 | 24 | 1 | 83 | 125 | 3 | 0 | 97 | 184 | 1 | 0 | 100 |
| 44 | 45 | 2 | 17 | 85 | 31 | 1 | 84 | 126 | 4 | 0 | 97 | 187 | 1 | 0 | 100 |
| 45 | 43 | 1 | 19 | 86 | 22 | 1 | 85 | 127 | 4 | 0 | 97 | 188 | 1 | 0 | 100 |
| 46 | 47 | 2 | 20 | 87 | 19 | 1 | 86 | 128 | 5 | 0 | 97 | 190 | 1 | 0 | 100 |
| 47 | 44 | 2 | 22 | 88 | 24 | 1 | 87 | 129 | 3 | 0 | 98 | 194 | 1 | 0 | 100 |
| 48 | 55 | 2 | 24 | 89 | 11 | 0 | 87 | 130 | 4 | 0 | 98 | 195 | 1 | 0 | 100 |
| 49 | 50 | 2 | 26 | 90 | 19 | 1 | 88 | 131 | 2 | 0 | 98 | 196 | 1 | 0 | 100 |
| 50 | 55 | 2 | 27 | 91 | 16 | 1 | 88 | 132 | 2 | 0 | 98 | 197 | 1 | 0 | 100 |
| 51 | 64 | 2 | 30 | 92 | 13 | 0 | 89 | 133 | 3 | 0 | 98 | 201 | 1 | 0 | 100 |
| | | | | | | | | | | | | 256 | 1 | 0 | 100 |

[a]Key to columns: 1, TSP concentration, ~~mg~~ μg/m$^3$; 2, number of sites; 3, adjusted percentage of sites; 4, cumulative percentage of sites.

sites had annual means greater than 76 $\mu g/m^3$ and 10 percent were greater than 96 $\mu g/m^3$. The histogram of sites against concentrations (Figure 5-6) shows that over a third of all monitoring sites had annual mean values between 40 and 60 $\mu g/m^3$. Slightly less than another third had annual averages between 60 and 80 $\mu g/m^3$.

The distribution of 90th percentile values is also plotted in Figure 5-5. To interpret this distribution, consider that half of all valid monitors had a 90th percentile value in excess of 97 $\mu g/m^3$. For 10 percent of the monitors, 10 percent of the observations exceeded 160 $\mu g/m^3$. For one monitor, 10 percent of the observations exceeded 600 $\mu g/m^3$.

The annual mean TSP concentrations range from approximately 10 to over 250 $\mu g/m^3$. The lower values are associated with remote monitoring sites. The background sites in the National Air Sampling Network (NASN) like Glacier National Park and Acadia National Park had annual averages of 11 and 21 $\mu g/m^3$ in 1977.

Higher annual concentrations are found in many populated and industrialized areas. Table 5-7 is a listing of the 30 highest sites by annual averages. Topping the list are four central-city sites in commercial, residential, or industrial settings. The Phoenix, AZ, site (0136) had the highest annual mean of 256 $\mu g/m^3$, followed by a site in Calexico, CA at 201 $\mu g/m^3$ and an industrial site in Granite City, IL, at 197 $\mu g/m^3$.

It is apparent that these extremely high annual TSP concentrations are associated with commercial and industrial locations. Of the top 30 sites, 15 are industrial. Many of the higher concentrations (19 of 30) were found at central-city locations. Only four were classified as rural sites, most of which are also residential areas.

It is also likely that arid climates and dusty conditions in the vicinity of some monitoring sites might lead to suspension of surface material. However,

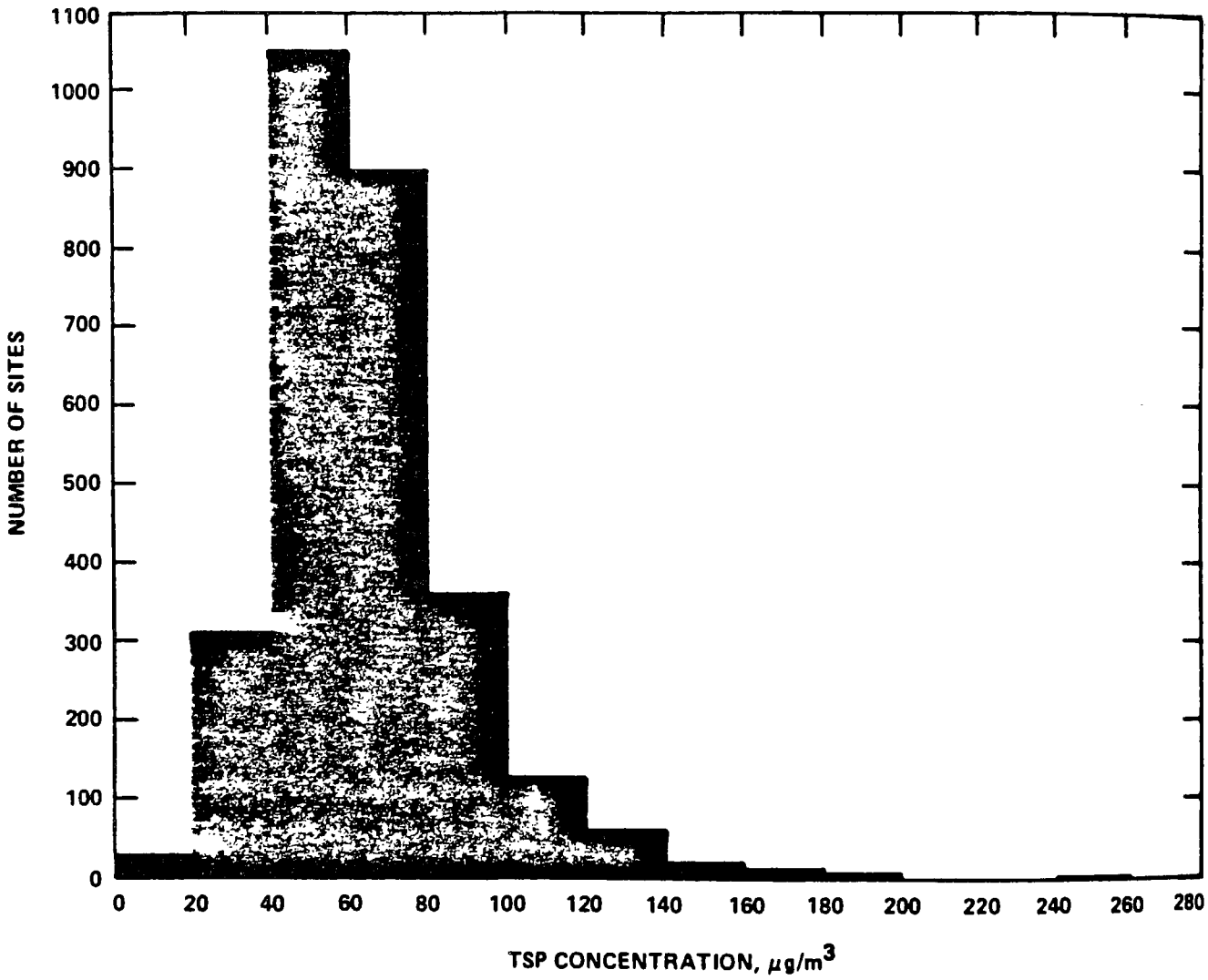



Figure 5-6. Histogram of number of sites against concentration shows that over one-third of the sites had annual mean concentrations between 40 and 60 $\mu g/m^3$.

TABLE 5-7. THIRTY SITES FOR HIGHEST TSP ANNUAL MEANS IN 1978

| Location | Site code | TSP concentration, $\mu g/m^3$ | Site type |
|---|---|---|---|
| 1. Phoenix, AZ | 013G | 256 | Center city<br>Commerical |
| 2. Calexico, CA | 001I | 201 | Center city<br>Residential |
| 3. Granite City, IL | 009F | 197 | Center city<br>Industrial |
| 4. Libby, MT | 010F | 196 | Center city<br>Residential |
| 5. Granite City, IL | 014F | 195 | Rural<br>Industrial |
| 6. Valencia Co., NM | 001F | 194 | Rural<br>Industrial |
| 7. Middletown, OH | 002H | 190 | Suburban<br>Industrial |
| 8. Routt Co., CO | 003F | 188 | Rural<br>Commercial |
| 9. Denver, CO | 002F | 187 | Center city<br>Commercial |
| 10. Brawley, CA | 001I | 184 | Center city<br>Commercial |
| 11. Kansas | 015F | 177 | |
| 12. Pittsburgh, PA | 017G | 177 | Center city<br>Commercial |
| 13. Caribou Co., ID | 015J | 176 | Center city<br>Industrial |
| 14. Dearborn, MI | 002G | 176 | Suburban<br>Industrial |
| 15. Houston, TX | 035H | 176 | Suburban<br>Industrial |
| 16. Lancaster Co., NE | 002G | 175 | Center city<br>Commercial |
| 17. Azusa, CA | 002I | 173 | Suburban<br>Industrial |
| 18. El Paso, TX | 022G | 170 | Suburban<br>Industrial |
| 19. Granite City, IL | 010F | 169 | Center city<br>Industrial |
| 20. Cleveland, OH | 013H | 169 | Center city<br>Residential |
| 21. Braddock, PA | 001G | 167 | Center city<br>Industrial |
| 22. Riverside, CA | 003F | 165 | Center city<br>Residential |

TABLE 5-7 (continued)

| Location | Site code | TSP concentration, $\mu g/m^3$ | Site type |
|---|---|---|---|
| 23. Bakersfield, CA | 003F | 163 | Center city<br>Commercial |
| 24. Lyon Co., NV | 002F | 163 | Rural<br>Industrial |
| 25. Cleveland, OH | 008H | 163 | Center city<br>Industrial |
| 26. Des Moines, IA | 046G | 162 | Center city<br>Industrial |
| 27. Stuttgart, AR | 005F | 159 | Center city<br>Residential |
| 28. San Benito, TX | 001F | 158 | Center city<br>Commercial |
| 29. East Chicago, IL | 004H | 156 | Center city<br>Industrial |
| 30. Detroit, MI | 023G | 154 | Suburban<br>Industrial |

it is impossible to ascertain the contribution of fugitive or resuspended dust to the concentrations measured at these 30 sites without more detailed analysis.

Daily, or 24-hr, TSP concentrations have a wide range. In remote areas such as the Pacific islands, daily values may be as low as a few micrograms per cubic meter. Over the continental United States, concentrations from 5 to 20 $\mu g/m^3$ are routinely reported. In other locations, daily TSP values can exceed 10 times the levels found in remote areas, on occasion exceeding 3000 $\mu g/m^3$. Values exceeding 1000 $\mu g/m^3$ are observed in remote arid regions as well as in populated urban areas. Daily TSP levels approaching these higher values, 500 to 1500 $\mu g/m^3$, are frequently associated with adverse meteorological conditions: low-level inversion, stagnation, or high winds resuspending surface material.

Table 5-8 lists the valid TSP monitoring sites with the highest 30 24-hr values. Only some of these sites are listed in the top 30 annual average list (Table 5-7). In cities like Topeka, KS, and Libby, MT, which are not densely populated or industrialized, these high concentrations may result from chance occurrences, such as fire or dust storm. In other cities like El Paso, TX, and Granite City, IL, which are industrialized, the maximum concentrations are more likely to be related to persistent sources of pollution.

5.2.1.2 TSP Concentrations by Location--Ambient TSP can be simply considered as arising from the particulate emission of three broad source categories: traditional sources (large and clearly recognized sources), nontraditional sources such as resuspension of surface dust, and natural sources. The relative contributions of these three sources are affected by meteorological conditions and location. Hence it is not surprising to see a wide variation in daily measurements at a single site, variation over an urban area, or variation among regions of the country. This section will, by illustration, examine these differences in TSP concentrations by location.

TABLE 5-8. THIRTY MONITORING SITES WITH THE HIGHEST 24-HR CONCENTRATIONS IN 1978

| | Location | Site code | TSP concentration, $\mu g/m^3$ | Site type |
|---|---|---|---|---|
| 1. | Soda Springs, ID | 004F | 1441 | Suburban<br>Residential |
| 2. | Lawrence Co., OH | 003H | 1433 | Rural<br>Commercial |
| 3. | Shoshone Co., ID | 021F | 1408 | Suburban<br>Industrial |
| 4. | Libby, MN | 010F | 1384 | Center city<br>Residential |
| 5. | Harris Co., TX | 018H | 1359 | Suburban<br>Industrial |
| 6. | Ohio | 004J | 1259 | |
| 7. | Phoenix, AZ | 013G | 1241 | Center city<br>Commercial |
| 8. | San Benito, TX | 001F | 1172 | Center city<br>Commercial |
| 9. | Tulsa, OK | 112F | 1061 | Center city<br>Commercial |
| 10. | Caribou Co., ID | 015J | 918 | Center city<br>Industrial |
| 11. | Granite City, IL | 014F | 837 | Rural<br>Industrial |
| 12. | Carey, OH | 002J | 835 | Suburban<br>Residential |
| 13. | Menominee, MI | 001F | 791 | Center city<br>Commercial |
| 14. | Weld Co., CO | 005F | 770 | Rural<br>Commercial |
| 15. | Storey, Co., NV | 001F | 744 | |
| 16. | Kennewick, WA | 001I | 728 | Center city<br>Residential |
| 17. | Charleston Co., SC | 038F | 719 | |
| 18. | Pasco, WA | 001F | 691 | Center city<br>Commercial |
| 19. | Topeka, KS | 002F | 672 | Center city<br>Residential |
| 20. | El Paso, TX | 019G | 671 | Suburban<br>Residential |
| 21. | Clarkston, WA | 001F | 663 | Center city<br>Commercial |
| 22. | Rochester, MN | 015G | 658 | Center city<br>Residential |

TABLE 5-8 (continued)

| Location | Site code | TSP concentration, $\mu g/m^3$ | Site type |
|---|---|---|---|
| 23. El Paso, TX | 022G | 647 | Suburban<br>Industrial |
| 24. Nampa, ID | 001F | 643 | Center city<br>Commercial |
| 25. Cook Co., IL | 002H | 630 | Suburban<br>Residential |
| 26. Denver, CO | 002F | 629 | Center city<br>Commercial |
| 27. Cedar Rapids, IA | 024G | 624 | Suburban<br>Industrial |
| 28. Valencia Co., NM | 001F | 619 | Rural<br>Industrial |
| 29. Big Spring, TX | 002F | 614 | Suburban<br>Commercial |
| 30. Turlock, CA | 001I | 606 | Suburban<br>Residential |

5.2.1.2.1 Industrial-commerical-residential. A study of TSP samples collected in 14 U.S. cities (EPA, 1976) has concluded that traditional sources, principally industrial, account for 15 $\mu g/m^3$ in residential areas and over 60 $\mu g/m^3$ at sites nearer industrial areas. Auto exhaust nontraditional emissions of road dust, fugitive dust, unducted emissions and a variety of widely dispersed sources can contribute 25 to 35 $\mu g/m^3$ to the citywide TSP levels. There is a background windborne particle level, both natural and manmade. Its contribution to annual TSP levels is estimated at 5 to 10 $\mu g/m^3$ and at times may be greater than 40 $\mu g/m^3$. This type of particle is found in higher concentrations in the East.

The general differences in annual TSP concentration among locations is seen in Figure 5-7. These differences reflect the character of the neighborhoods where the monitors are located. This figure summarizes the mean concentrations from 154 sites in 14 cities. Residential neighborhoods in and near cities have TSP levels between 50 and 70 $\mu g/m^3$. Commercial sites have a wider range of concentrations (60 to 110 $\mu g/m^3$). Industrial locations generally range between 80 to 150 $\mu g/m^3$.

The 1978 data base has been analyzed on the basis of a different set of descriptors. One description scheme classifies monitoring sites by their purpose: population exposures, source receptors, or background sites. Another scheme identifies sites by the amount of development: central city, suburban, rural, or remote. These classifications are not mutually exclusive.

When sites are distributed by descriptors, a distinct weighting becomes apparent. Almost 80 percent of the sites are population oriented; approximately 15 percent are source related, and less than 6 percent are background monitors. The distribution by development also reflects its population emphasis. Of the total monitors, 83 percent are at either central-city or suburban sites, 15

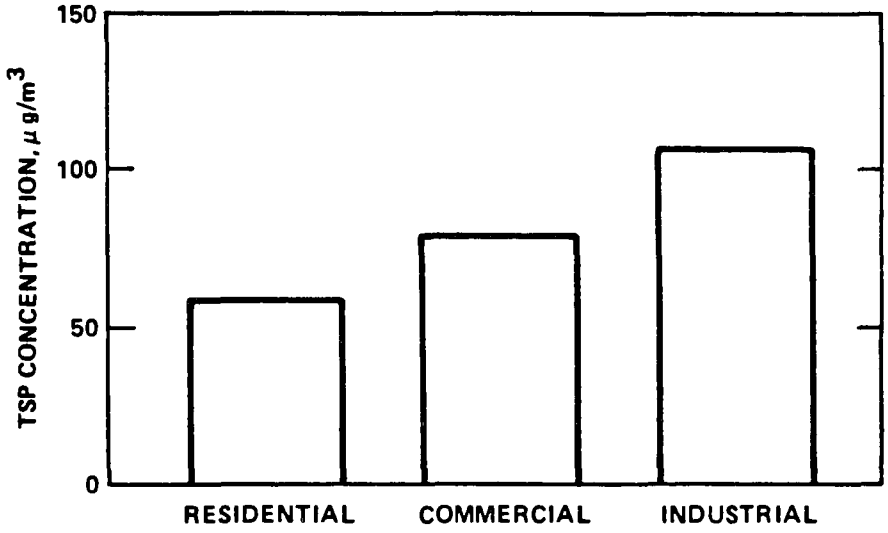



Figure 5-7. Histogram of mean TSP levels by neighborhood shows lowest levels in residential areas, higher levels in commercial areas, and highest levels in industrial areas.

Source: U.S. Environmental Protection Agency (1976).

percent are at rural sites, and 2 percent are at remote sites. More detail on how site location affects observed concentration is given in Tables 5-9 through 5-12, where sites are grouped by median values and the 90th percentile values in a cross-tabulation by site descriptors. It is informative to compare the common percentages in each grid and the row total. For instance, 38 percent of the background sites had median values less than or equal to 27 $\mu g/m^3$, whereas only 4.4 percent of all sites had these low values. Only 30 percent of the background sites had median values above 44 $\mu g/m^3$, and none had values above 97 $\mu g/m^3$, whereas 75.5 percent of source sites had median values above 44 $\mu g/m^3$. The pattern is consistent for the distribution of the 90th percentiles cross-tabulated by site purpose. Cross-tabulations of site median values and site 90th percentile values with the development-related site descriptors is further confirmation of the influences of siting on measured TSP concentrations. Rural and remote sites have lower median values and lower 90th percentile values. The suburban sites reflect the overall national distribution. The central-city sites have proportionately more sites in the higher concentration ranges.

5.2.1.2.2 Intracity comparisons. Because of the strong neighborhood influence on TSP concentrations, it is not unusual to find considerable variation in peak and mean concentrations across a community. It is instructive to examine intracity differences because it illustrates the difficulty in estimating population exposures to TSP.

Data on the nine cities having the highest annual TSP concentrations in 1977 are given in Table 5-13. Only sites having enough observations per quarter to report an annual mean are used. Although TSP concentrations in these cities were generally high, the less developed or less industrialized areas in each city had 1977 concentrations below the primary NAAQS, with the exception of Granite City, IL. The annual mean concentration for the highest sites can be two to four times higher than that for the cleanest sites within the same city.

TABLE 5-9. CROSS-TABULATION OF TSP SITES BY MEDIAN CONCENTRATION OF SITE DESCRIPTOR

| Median TSP concentration, $\mu g/m^3$ | Purpose of site | | | Row total |
|---|---|---|---|---|
| | Population | Source | Background | |
| <27 | | | | |
| Number of sites | 50 | 13 | 62 | 125 |
| Percent of row | 40.0 | 10.4 | 49.6 | |
| Percent of column | 2.2 | 3.1 | 38.0 | |
| Percent of total | 1.8 | 0.5 | 2.2 | 4.4 |
| 27-44 | | | | |
| Number of sites | 410 | 91 | 49 | 550 |
| Percent of row | 74.5 | 16.5 | 8.9 | |
| Percent of column | 18.1 | 21.7 | 30.1 | |
| Percent of total | 14.4 | 3.2 | 1.7 | 19.4 |
| 44-56 | | | | |
| Number of sites | 567 | 100 | 34 | 701 |
| Percent of row | 80.9 | 14.3 | 4.9 | |
| Percent of column | 25.1 | 23.9 | 20.9 | |
| Percent of total | 20.0 | 3.5 | 1.2 | 34.7 |
| 56-70 | | | | |
| Number of sites | 635 | 95 | 15 | 745 |
| Percent of row | 85.2 | 12.8 | 2.0 | |
| Percent of column | 28.1 | 22.7 | 9.2 | |
| Percent of total | 22.3 | 3.3 | 0.5 | 26.2 |
| 70-97 | | | | |
| Number of sites | 469 | 87 | 3 | 559 |
| Percent of row | 83.9 | 15.6 | 0.5 | |
| Percent of column | 20.8 | 20.8 | 1.8 | |
| Percent of total | 16.5 | 3.1 | 0.1 | 19.7 |
| >97 | | | | |
| Number of sites | 129 | 33 | 0 | 162 |
| Percent of row | 79.6 | 20.4 | 0.0 | |
| Percent of column | 5.7 | 7.9 | 0.0 | |
| Percent of total | 4.5 | 1.2 | 0.0 | 5.7 |
| Column total | | | | |
| Number of sites | 2260 | 419 | 163 | 2842 |
| Percent of total | 79.5 | 14.7 | 5.7 | 100.0 |

TABLE 5-10. CROSS-TABULATION OF TSP SITES BY 90TH PERCENTILE VALUES AND SITE DESCRIPTOR

| 90th percentile TSP concentration, $\mu g/m^3$ | Purpose of site | | | Row total |
|---|---|---|---|---|
| | Population | Source | Background | |
| <54 | | | | |
| Number of sites | 55 | 14 | 54 | 123 |
| Percent of row | 44.7 | 11.4 | 43.9 | |
| Percent of column | 2.4 | 3.3 | 33.1 | |
| Percent of total | 1.9 | 0.5 | 1.9 | 4.3 |
| 54-79 | | | | |
| Number of sites | 441 | 88 | 45 | 574 |
| Percent of row | 76.8 | 15.3 | 7.8 | |
| Percent of column | 19.5 | 21.0 | 27.6 | |
| Percent of total | 15.5 | 3.1 | 1.6 | 20.2 |
| 79-99 | | | | |
| Number of sites | 576 | 94 | 36 | 706 |
| Percent of row | 81.6 | 13.3 | 5.1 | |
| Percent of column | 25.5 | 22.4 | 22.1 | |
| Percent of total | 20.3 | 3.3 | 1.3 | 24.8 |
| 99-124 | | | | |
| Number of sites | 595 | 95 | 16 | 706 |
| Percent of row | 84.3 | 13.5 | 2.3 | |
| Percent of column | 26.3 | 22.7 | 9.8 | |
| Percent of total | 20.9 | 3.3 | 0.6 | 24.8 |
| 124-188 | | | | |
| Number of sites | 484 | 87 | 11 | 582 |
| Percent of row | 83.2 | 14.9 | 1.9 | |
| Percent of column | 21.4 | 20.8 | 6.7 | |
| Percent of total | 17.0 | 3.1 | 0.4 | 20.5 |
| >188 | | | | |
| Number of sites | 109 | 41 | 1 | 151 |
| Percent of row | 72.2 | 27.2 | 0.7 | |
| Percent of column | 4.8 | 9.8 | 0.6 | |
| Percent of total | 3.8 | 1.4 | 0.0 | 5.3 |
| Column total | | | | |
| Number of sites | 2260 | 419 | 163 | 2842 |
| Percent of total | 79.5 | 14.7 | 5.7 | 100.0 |

TABLE 5-11. CROSS-TABULATION OF TSP MEDIAN VALUE BY SITE DESCRIPTOR

| Median TSP concentration, $\mu g/m^3$ | Location of monitor | | | | Row total |
|---|---|---|---|---|---|
| | Central city | Suburban | Rural | Remote | |
| <27 | | | | | |
| Number of sites | 8 | 26 | 58 | 31 | 123 |
| Percent of row | 6.5 | 21.1 | 47.2 | 25.2 | |
| Percent of column | 0.7 | 2.3 | 14.0 | 55.4 | |
| Percent of total | 0.3 | 0.9 | 2.1 | 1.1 | 4.5 |
| 27-44 | | | | | |
| Number of sites | 149 | 204 | 159 | 20 | 532 |
| Percent of row | 28.0 | 38.3 | 29.9 | 3.8 | |
| Percent of column | 12.7 | 18.2 | 38.3 | 35.7 | |
| Percent of total | 5.4 | 7.4 | 5.8 | 0.7 | 19.3 |
| 44-56 | | | | | |
| Number of sites | 252 | 320 | 106 | 2 | 680 |
| Percent of row | 37.1 | 47.1 | 15.6 | 0.3 | |
| Percent of column | 21.5 | 28.6 | 25.5 | 3.6 | |
| Percent of total | 9.1 | 11.6 | 3.8 | 0.1 | 24.6 |
| 56-70 | | | | | |
| Number of sites | 346 | 310 | 55 | 1 | 712 |
| Percent of row | 48.6 | 43.5 | 7.7 | 0.1 | |
| Percent of column | 29.5 | 27.7 | 13.3 | 1.8 | |
| Percent of total | 12.5 | 11.2 | 2.0 | 0.0 | 25.8 |
| 70-97 | | | | | |
| Number of sites | 315 | 210 | 24 | 2 | 551 |
| Percent of row | 57.2 | 38.1 | 4.4 | 0.4 | |
| Percent of column | 26.9 | 18.8 | 5.8 | 3.6 | |
| Percent of total | 11.4 | 7.6 | .9 | 0.1 | 19.9 |
| >97 | | | | | |
| Number of sites | 103 | 49 | 13 | 0 | 165 |
| Percent of row | 62.4 | 29.7 | 7.9 | 0.0 | |
| Percent of column | 8.8 | 4.4 | 3.1 | 0.0 | |
| Percent of total | 3.7 | 1.8 | 0.5 | 0.0 | 6.0 |
| Column total | | | | | |
| Number of sites | 1173 | 1119 | 415 | 56 | 2763 |
| Percent of total | 42.5 | 40.5 | 15.0 | 2.0 | 100.0 |

TABLE 5-12. CROSS-TABULATION OF TSP 90TH PERCENTILE VALUES BY SITE DESCRIPTOR

| 90th percentile TSP concentration, $\mu g/m^3$ | Location of monitor: Central city | Suburban | Rural | Remote | Row total |
|---|---|---|---|---|---|
| <54 | | | | | |
| Number of sites | 8 | 31 | 56 | 27 | 122 |
| Percent of row | 6.6 | 25.4 | 45.4 | 22.1 | |
| Percent of column | 0.7 | 2.8 | 13.5 | 48.2 | |
| Percent of total | 0.3 | 1.1 | 2.0 | 1.0 | 4.4 |
| 54-79 | | | | | |
| Number of sites | 168 | 229 | 141 | 18 | 556 |
| Percent of row | 30.2 | 41.2 | 25.4 | 3.2 | |
| Percent of column | 14.3 | 20.5 | 34.0 | 32.1 | |
| Percent of total | 6.1 | 8.3 | 5.1 | 0.7 | 20.1 |
| 79-99 | | | | | |
| Number of sites | 253 | 315 | 109 | 8 | 685 |
| Percent of row | 36.9 | 46.0 | 15.9 | 1.2 | |
| Percent of column | 21.6 | 28.2 | 26.3 | 14.3 | |
| Percent of total | 9.2 | 11.4 | 3.9 | 0.3 | 24.8 |
| 99-124 | | | | | |
| Number of sites | 328 | 296 | 53 | 1 | 678 |
| Percent of row | 48.4 | 43.7 | 7.8 | 0.1 | |
| Percent of column | 28.0 | 26.5 | 12.8 | 1.8 | |
| Percent of total | 11.9 | 10.7 | 1.9 | 0.0 | 24.5 |
| 124-188 | | | | | |
| Number of sites | 328 | 197 | 38 | 2 | 565 |
| Percent of row | 58.1 | 34.9 | 6.7 | 0.4 | |
| Percent of column | 28.0 | 17.6 | 9.2 | 3.6 | |
| Percent of total | 11.9 | 7.1 | 1.4 | 0.1 | 20.4 |
| >188 | | | | | |
| Number of sites | 88 | 51 | 18 | 0.0 | 157 |
| Percent of row | 56.1 | 32.5 | 11.5 | 0.0 | |
| Percent of column | 7.5 | 4.6 | 4.3 | 0.0 | |
| Percent of total | 3.2 | 1.8 | 0.7 | 0.0 | 5.7 |
| Column total | | | | | |
| Number of sites | 1173 | 1119 | 415 | 56 | 2763 |
| Percent of total | 42.5 | 40.5 | 15.0 | 2.0 | 100.0 |

TABLE 5-13. RANGE OF ANNUAL GEOMETRIC MEAN CONCENTRATIONS IN AREAS WITH HIGH TSP CONCENTRATIONS IN 1977

| City | Number of sites | Number of sites with annual range >75 μg/ml | Annual range, μg/ml | Range of maximum 24-hr value, μg/ml |
|---|---|---|---|---|
| Tucson, AZ | 7 | 3 | 156-67 | 591-178 |
| Pocatello, ID | 4 | 3 | 218-65 | 1371-344 |
| Chicago, IL | 25 | 12 | 170-50 | 1106-152 |
| Granite City, IL | 8 | 8 | 185-85 | 485-227 |
| Taos County, NM | 1 | | 168 | 577 |
| Middletown, OH | 3 | 2 | 192-64 | 707-157 |
| Cleveland, OH | 23 | 13 | 152-48 | 705-128 |
| Youngstown, OH | 5 | 4 | 172-66 | 602-163 |
| El Paso, TX | 14 | 10 | 158-60 | 691-205 |

5.2.1.2.3 Regional differences in background concentrations. It has been demonstrated that TSP concentrations can vary across an urban area and among cities with different sources and meteorology. Superimposed on this intercity difference may be regional differences in the natural or transported fraction of TSP concentrations. Figure 5-8 shows the contribution of these sources to nonurban levels. It was assumed that the global and local contributions in the average would be similar. The greatest difference among regions is the contribution from "continental" and transported emissions. These two categories of particles contribute in such a way that nonurban sites in the West are typically 15 $\mu g/m^3$, in the Midwest, 25 $\mu g/m^3$, and in the East, 35 $\mu g/m^3$. Except for the Acadia National Park site (15 $\mu g/m^3$) and Millinocket (23 $\mu g/m^3$), all sites in Maine had 1977 annual averages above 30 $\mu g/m^3$. Nonurban sites in Wisconsin typically had TSP levels less than 25 $\mu g/m^3$. Nonurban sites in Montana had levels less than 20 $\mu g/m^3$ in 1977. The individual values were: Big Horn County, 17 $\mu g/m^3$; Custer County, 15 $\mu g/m^3$; Powder River County, 14 $\mu g/m^3$.

5.2.1.2.4 Special local problems with TSP. Neighborhood and regional influences on TSP measurements have already been highlighted. However, the influence of roadside sampling deserves special mention. Several studies have demonstrated that TSP measurements are very sensitive to vehicular traffic, road conditions, and distance from and above a nearby roadway. Measurements at sampling locations are dominated by open-area sources and mechanically resuspended dust from vehicular traffic within a 1-km radius around the site. It has been demonstrated in a few studies that the distance from the roadway and the level of traffic dramatically influence the concentrations measured. Figures 5-9 and 5-10 are monthly-average hourly particle data for a site in Fall River, MA. The concentration of the fine fraction (< 2.5 $\mu m$) varies only slightly over the day, whereas the coarse fraction, and hence TSP concentrations, vary with the traffic volume

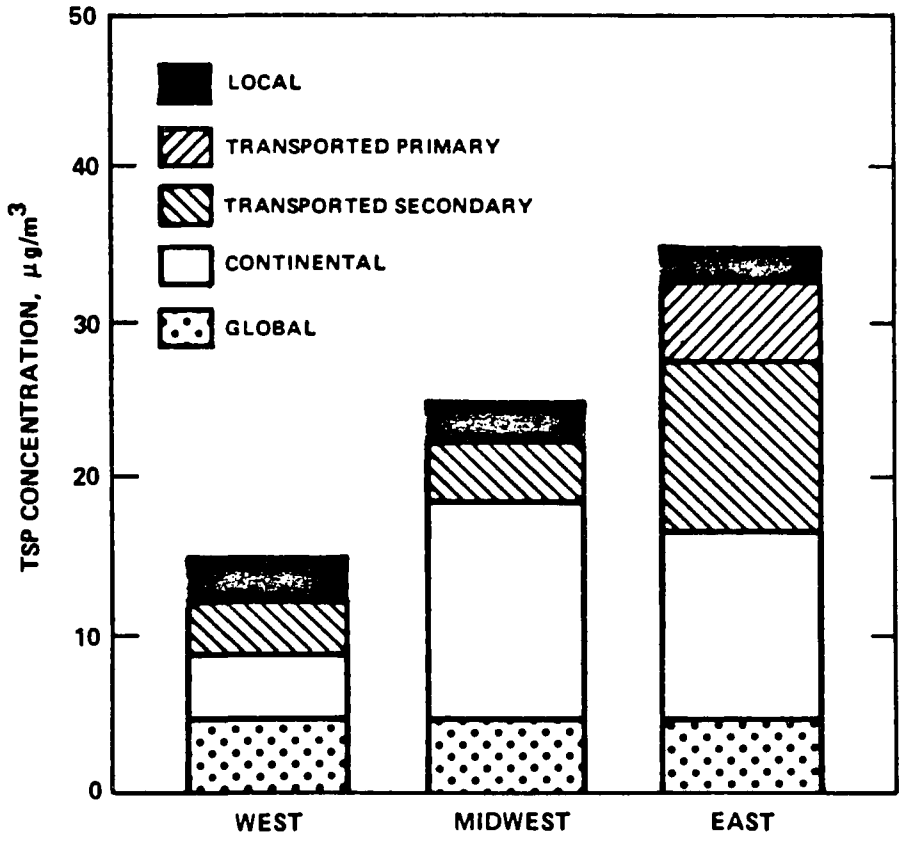



Figure 5-8. Average estimated contributions to nonurban levels in the East, Midwest, and West are most variable for transported secondary and continental sources.

Source: GCA.

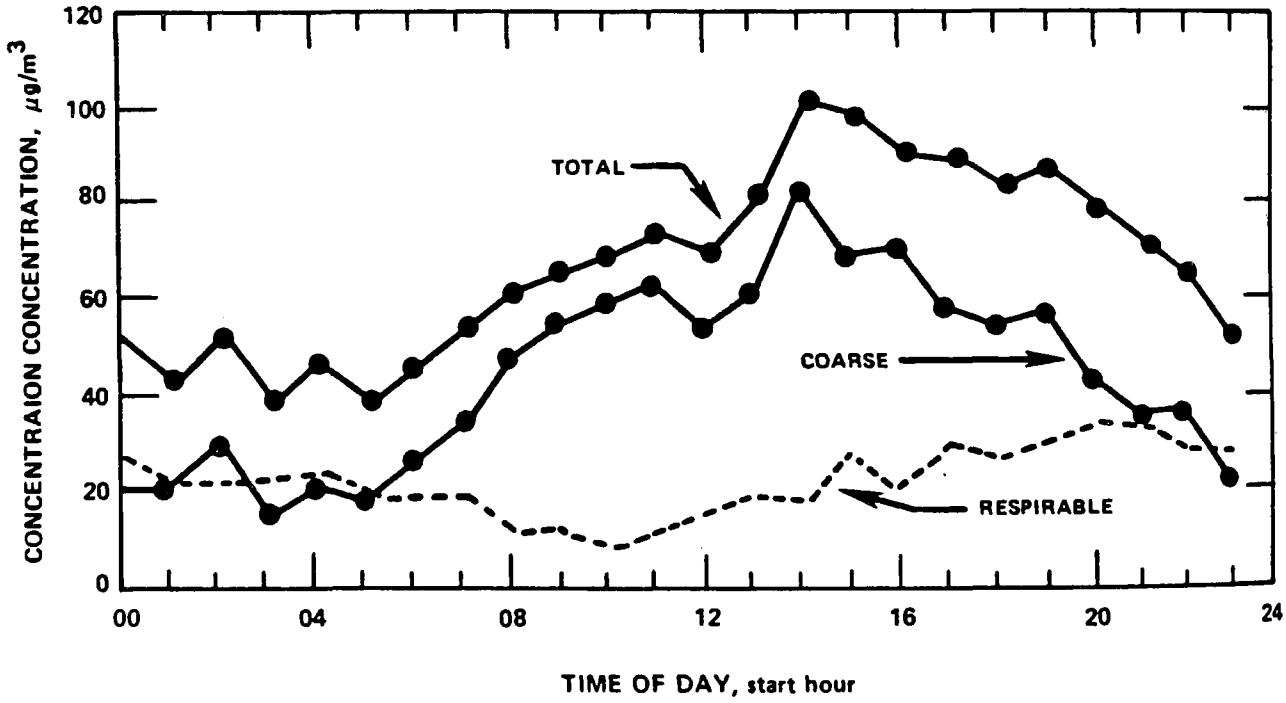



Figure 5-9. Average diurnal variation of coarse particles and Plymouth Avenue traffic in Fall River during April shows large contributions from suspended particles.

Source: Record et al. (1978).

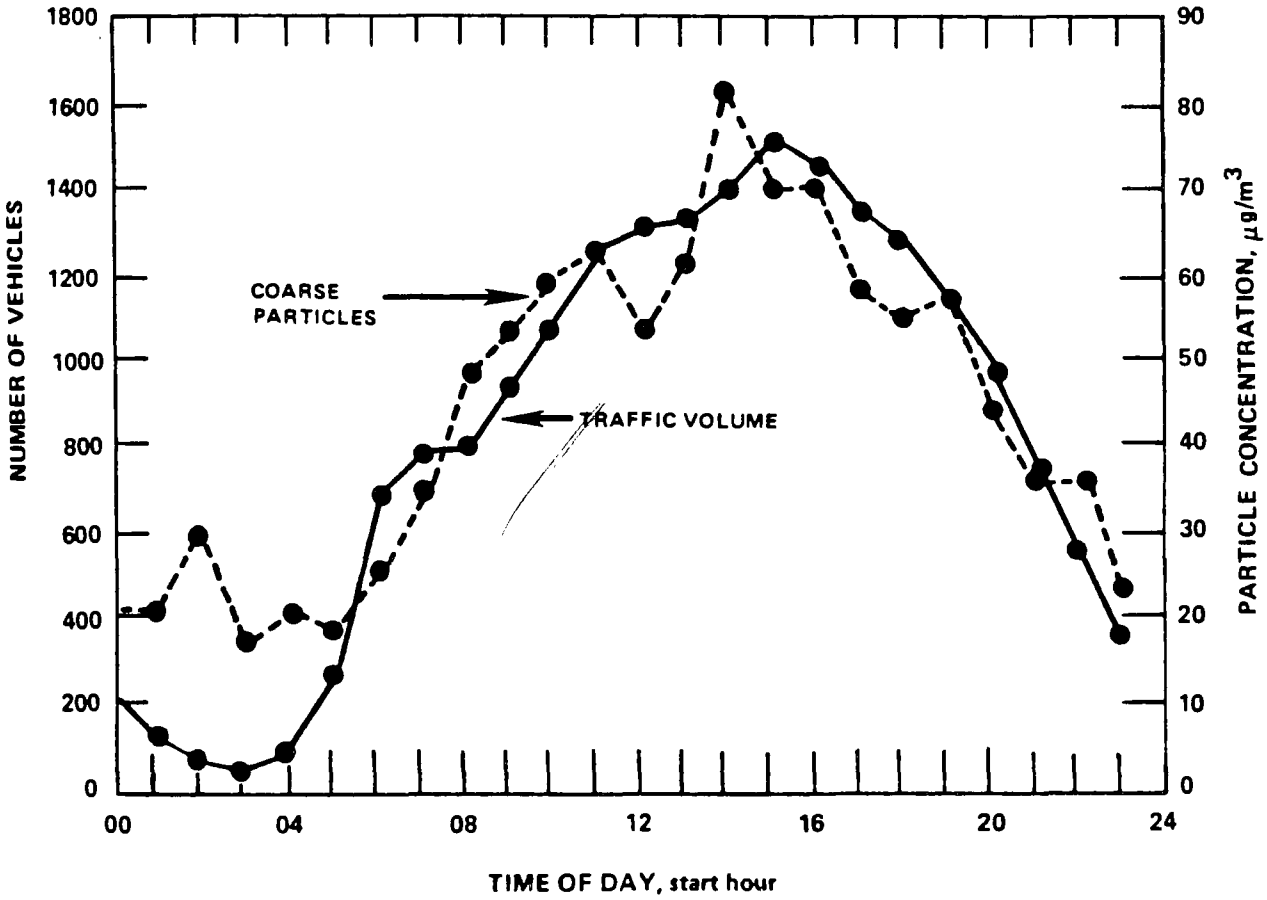



Figure 5-10. Average diurnal variation of APM concentrations at Fall River trailer during April is less for coarse particles than near road. The respirable particles were those recorded with a GCA ambient particle monitor.

Source: Record et al. (1978).

on a nearby road. Thus the population exposure to fine particles is poorly approximated by TSP measurements when the latter are dominated by local sources.

Variations in TSP concentrations have been considered in some detail. When reviewing the national status for TSP standards, it will be difficult to ascertain the severity, extent, or primary cause of higher concentrations without detailed site specification. In some instances, peak concentrations are the result of emissions from local industries; in other cases, some specific source is responsible. However, higher concentrations are also noted in areas where resuspended dust from vehicular traffic or wind erosion is the most likely source.

There are cases where high concentrations would be expected but are not recorded as such because the monitor location or frequency of sampling biases the sample.

5.2.1.3 Diurnal and Seasonal Variation in TSP Concentrations

5.2.1.3.1 Diurnal. TSP concentrations vary with local emissions strength, meteorological conditions, and the changes in the contributions from background particles. The TSP mass loadings to the atmosphere in general increase during the day and decrease at night (Figure 5-10). The atmosphere undergoes greater vertical mixing during the day, and wind speeds near the surface increase as a result. Greater vertical mixing coupled with increased source emissions causes particles mass loadings to increase. At night, decreased mixing and the resultant decreased surface winds permit settling of larger particles. With increased atmospheric stability, local elevated sources are not as likely to mix to the ground. There may be exceptions to this. Low-level sources such as automobiles, unducted industrial emissions, and residential furnaces and fireplaces emitting into an intense ground-level inversion at night can result in extremely high night concentrations. This situation does occur in many valley communities. Unfortunately, diurnal cycles are not well established because the standard sampling procedure for TSP measurements is a 24-hr sample, midnight to midnight.

5.2.1.3.2 Weekly patterns. Since human activity follows distinct weekly cycles, it is likely that anthropogenic sources of particles will also have weekly patterns. The most distinct weekly patterns are weekdays versus weekends. Trijonis et al. (1979) have examined the RAMS TSP and dichotomous data base for weekend-weekday differences in particle loadings. They concluded that there was only a slight (-9 percent) difference between weekend TSP values and weekday values for the average of five urban sites in St. Louis. For three suburban sites the difference was -5 percent and for two rural sites the difference was -12 percent. The urban difference was dominated by readings from one monitor in a heavily industrial and commercial area.

Greater differences were found for the dichotomous samples and for their elemental constituents. The TSP measurements are dominated by the larger particles, which are more affected by meteorological factors. Hence the weekly cycles in human activities would be masked more in the TSP measurements than in the weekly TSP dichotomous samples.

5.2.1.3.3 Seasonal. Analyzing temporal patterns can frequently provide insight into the nature and source of particulate matter. Meteorological parameters affect the generation and dispersion of particles. These parameters include, among others, degree-days, mixing height, ventilation factors, frequency of calms and stagnations, and precipitation. These are also seasonal patterns to sources. Many industries are seasonal in nature. Vacation periods in urban areas are accompanied by reduced automobile traffic.

Because meteorological parameters are so important, it is likely that seasonal patterns in one area cannot be generalized to other areas. Trijonis (1979) found a modest annual pattern of higher TSP concentrations in the summer months in St. Louis. Figure 5-11 supports this observation. It is a comparison between the TSP monthly mean values and the data from dichotomous sampling.

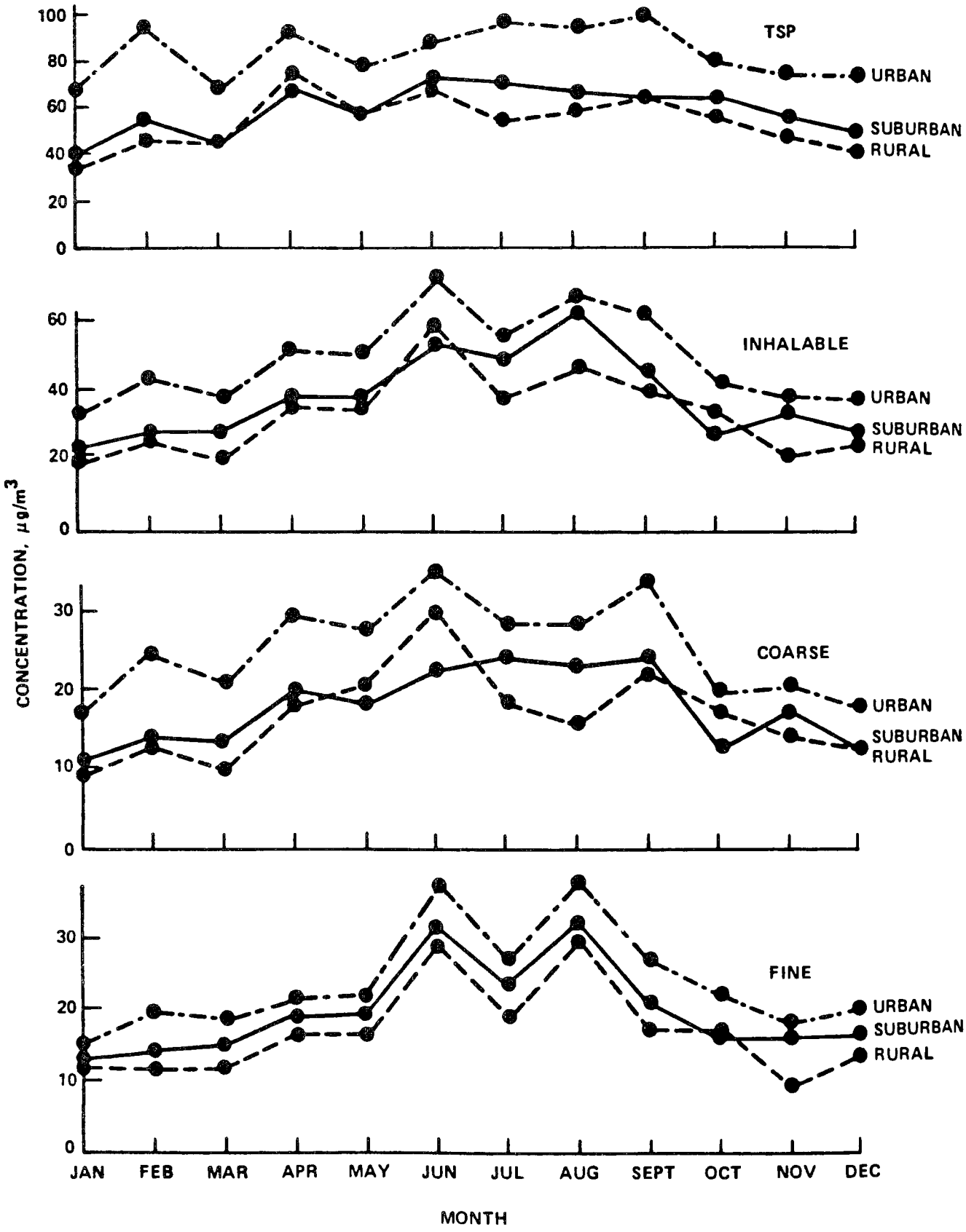



Figure 5-11. Seasonal variations in urban, suburban, and rural areas are shown for four size ranges of particles.

| Particle Type | Size, μm |
|---|---|
| Inhalable particles (IP) | <15 |
| Coarse particles | 2.5 - 15 |
| Fine particles | <2.5 |

The really distinct seasonal pattern is in the fine aerosol fraction. Summer fine-particle concentrations are twice as great as winter values. As discussed later, sulfates aerosol makes up most of the fine-fraction particles and shows a distinct seasonal pattern.

To illustrate the geographic specificity of these seasonal cycles, 3 years of monthly averaged TSP data are presented in Figure 5-12. The data are from Steubenville, OH, an industrialized site in the upper Ohio River Valley. Each monthly mean is derived from 20 or more sampling days. The TSP concentrations are considerably higher than the St. Louis values. The months with the highest TSP in Steubenville were March, April, and May in 1977, July, August, September, and November in 1978, and February and June in 1979. No clear seasonal pattern emerges from this 3-year period.

5.2.1.4 Trends in TSP concentrations--In 1957, a National Air Sampling Network (NASN) began to operate routinely on a national basis. The U.S. Public Health Service, with cooperation from State health departments, operated 231 urban and 37 nonurban stations. Some of these stations operated every other year, so in a given year there were 143 urban and 37 nonurban TSP high-volume monitoring sites in operation. These sites collected one 24-hr sample every other week for a total of 26 samples per year. In 1977, over 4000 stations reported TSP values to the National Aerometric Data Bank of the U.S. EPA. Not only has the number of sites greatly increased, but the sampling frequency has been 1 day in 6 since 1971. For some cities there are now data for more than 20 years of TSP monitoring. Although the sites may not be in exactly the same locations for

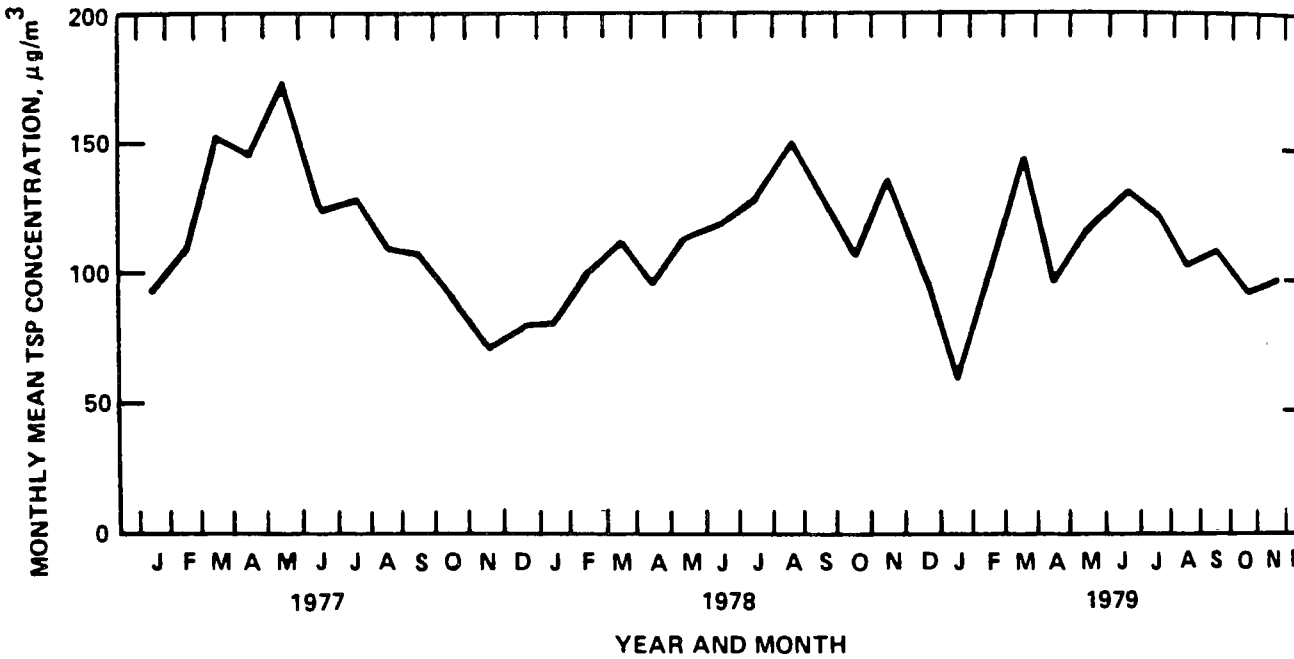



Figure 5-12. Monthly mean TSP concentrations are shown for the Northern Ohio Valley Air Monitoring Headquarters, Steubenville, OH. No clear seasonal pattern is apparent.

every city, general trends in TSP concentrations can be obtained. Figure 5-13 plots the annual geometric mean TSP concentrations for three groups of cities. In 1958, these five cities, classified as industrial, had annual mean TSP concentrations between 140 and 170 $\mu g/m^3$. By 1974 the annual mean concentrations had dropped to between 80 and 110 $\mu g/m^3$. Similarly, three of four cities classified as moderately industrialized showed substantial decreases. Only Denver increased. The four cities classified as lightly industrialized showed less overall change.

Examining the expanded data set for TSP from high-volume samplers shows that for 2707 sites, the composite median concentration has remained about 60 $\mu g/m^3$ between 1972 and 1977. The geometric mean over this period has decreased by approximately 8 percent. The decrease in the 90th percentile of the annual average concentrations is most pronounced over this period (see Figure 5-14). Lowering the TSP concentrations in locations with very high levels has been a target of State air pollution control strategies. In addition, displacing sources to rural regions, building new sources with taller stacks, converting to cleaner fuels, and restricting open burning have decreased the number of locations experiencing annual concentrations of over 100 $\mu g/m^3$.

For the period 1970-77 EPA reported an almost 50 percent reduction in TSP emissions. Most of this reduction occurred in the early 1970's as State air pollution control programs started many major emitters on compliance schedules. The rather modest composite overall reduction of 8 percent in annual TSP levels is difficult to interpret. The later part of this record follows an earlier period of substantial reduction in emissions. In many areas during this period, emphasis shifted from compliance to air quality maintenance. One partial explanation that must be considered is the fact that direct emissions from

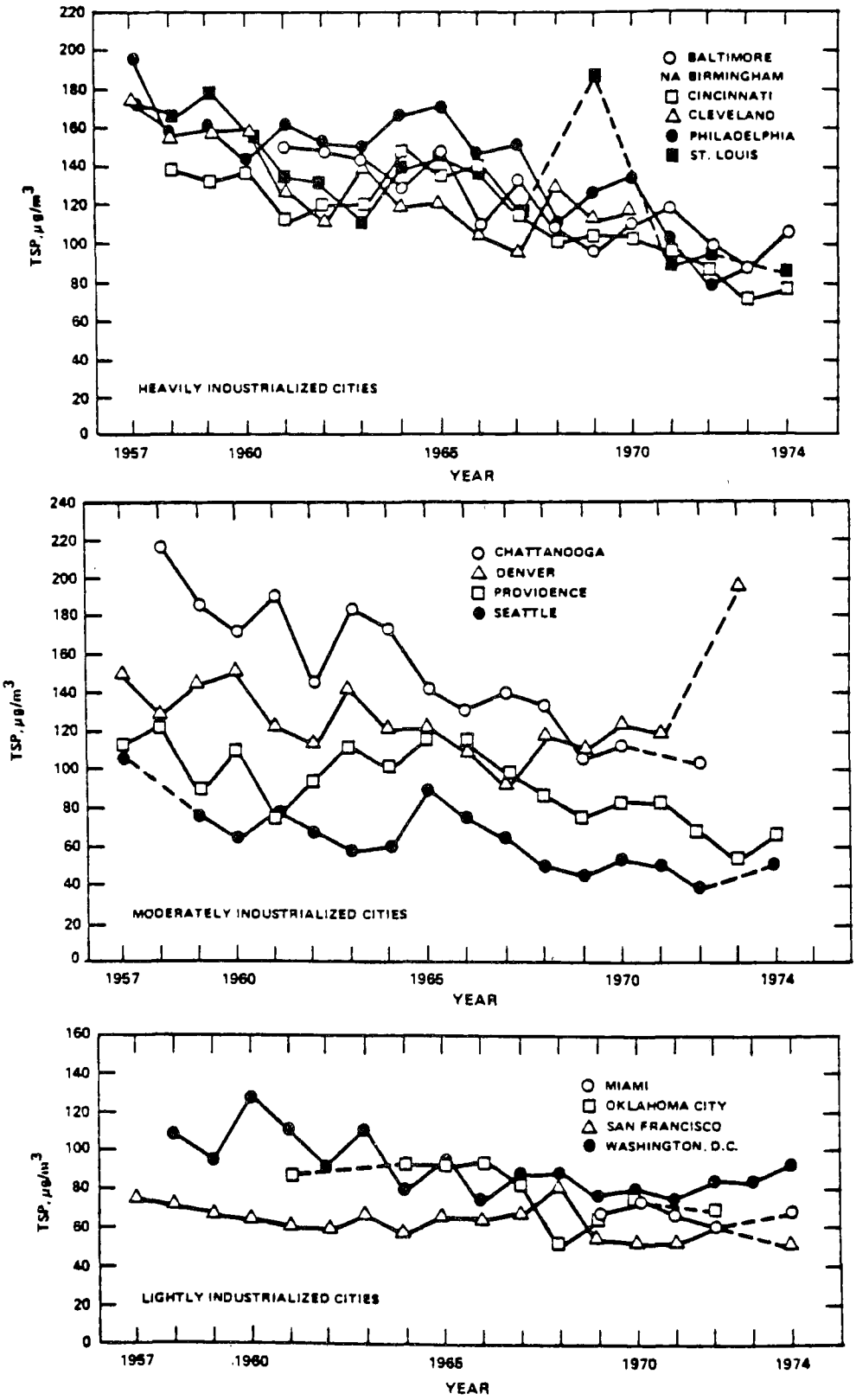



Figure 5-13. Annual geometric mean TSP trends are shown for NASN sites.

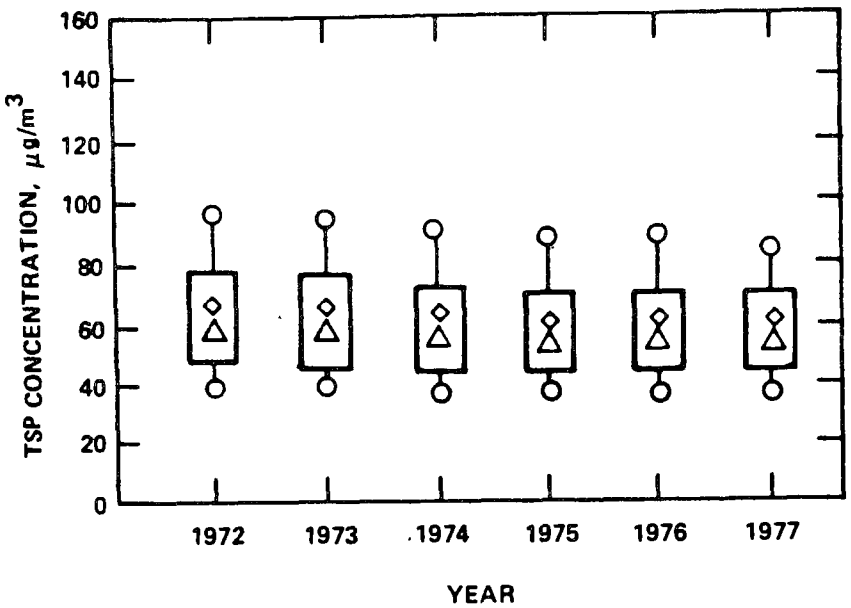
stationary sources contribute only a fraction to the TSP loadings of the atmosphere. As mentioned before, transported particles and particles from nontraditional sources also contribute to the mix of TSP.

Another perspective on regional differences is gained from observations of the 1978 data. Table 5-14 provides a summary statistic on the 50th and the 90th percentiles for valid monitors. Region IX ranks first for the mean 50th and 90th percentiles, followed by Region VII, Region VI and Region V. Regions I and II had consistently lower values.

The column presenting the standard deviations of the mean values for the 50th and 90th percentiles is also of interest. Smaller standard deviations suggest that there is more uniformity in reported concentrations among monitoring sites. Regions I, II, and IV have less variance among sites than other regions. This could be interpreted as either more uniform distribution of pollution levels or more uniformity and consistency in placing monitoring sites. The larger standard deviations in other regions, particularly in the West, probably mean that there is greater variation in pollution levels.

There are distinct regional differences in the trends of TSP concentrations. The distribution of site means and the actual rate of change in TSP levels differ among regions of the country. These trends are shown in Figures 5-15 and 5-16; it should be realized that the differences between years and even over the entire period have not been tested for significance. Therefore, intraregion and interregion comparisons are presented qualitatively.

In the Eastern United States, in EPA Regions I and II, the composite average across sites has decreased from 60 $\mu g/m^3$ to approximately 55 $\mu g/m^3$. The distribution of concentrations is much narrower in Regions I and II than it is in the more industrialized Regions III, IV, and V.



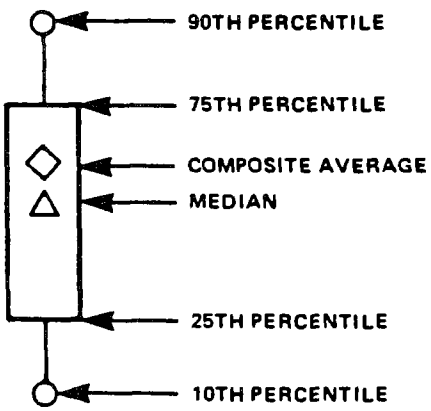
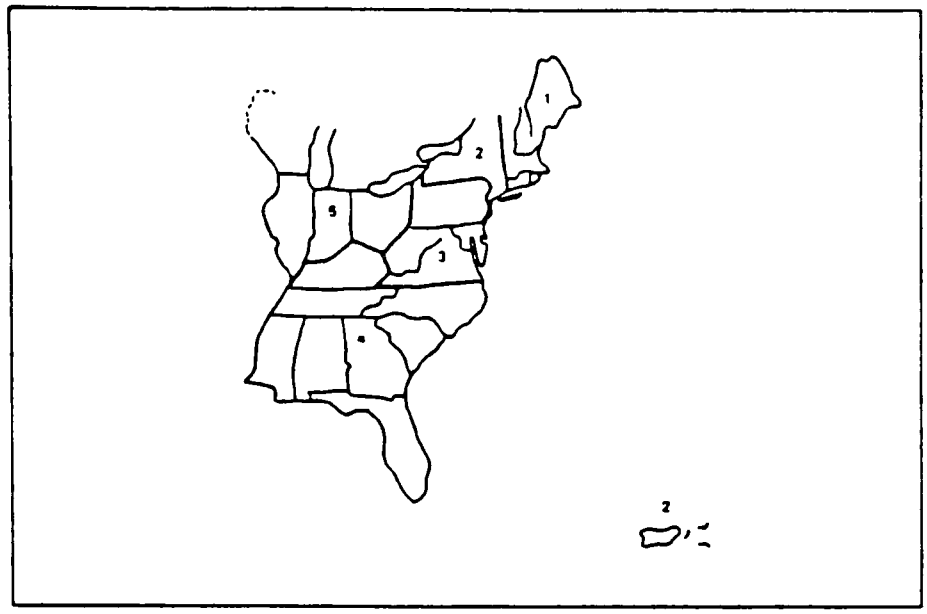




Figure 5-14. (Top) Nationwide trends in annual mean total suspended particulate concentrations from 1972 to 1977 are shown for 2707 sampling sites. (Bottom) Conventions for box plots.



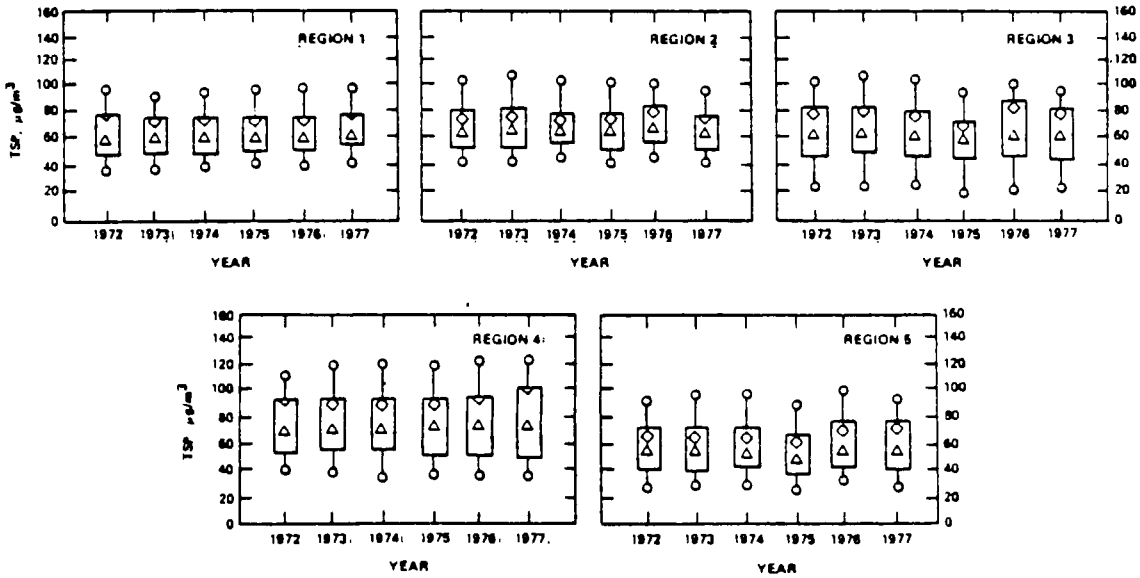
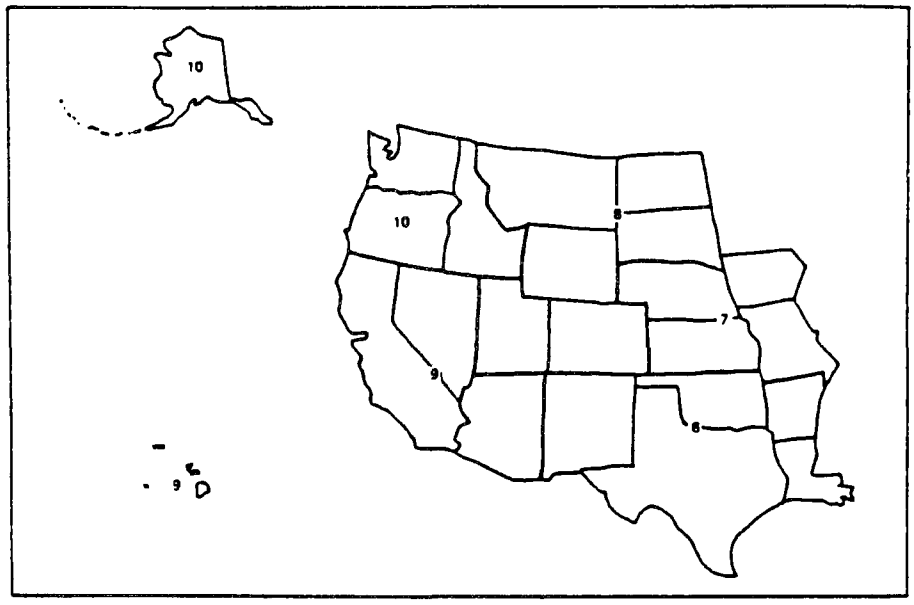




Figure 5-15. U.S. Environmental Protection Agency air quality control regions, and regional trends of annual mean TSP concentrations, are shown for Eastern States, 1972-77.



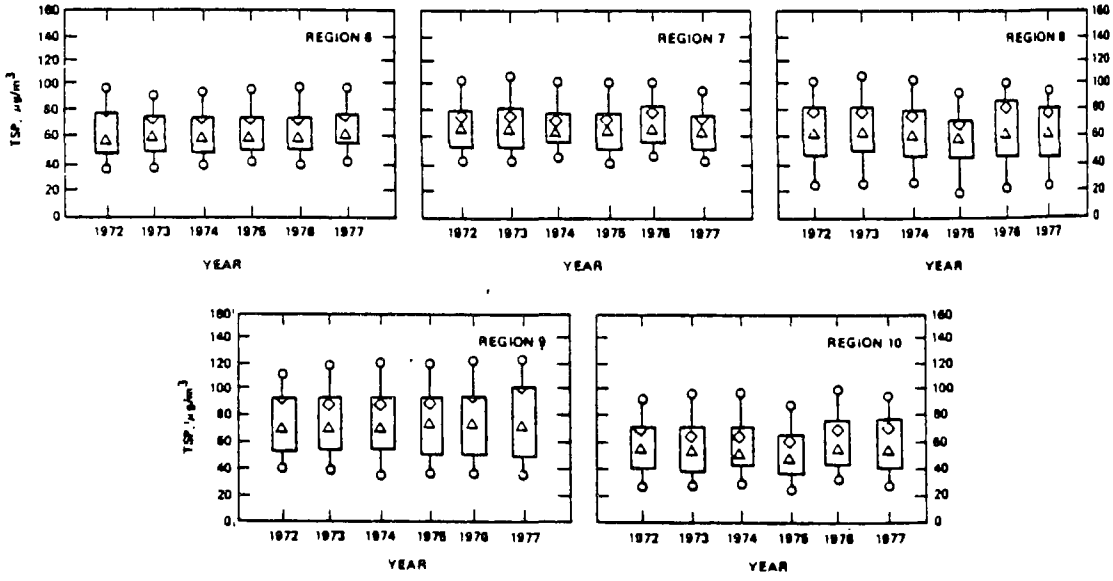




Figure 5-16. U.S. Environmental Protection Agency air quality control regions, and regional trends of annual mean TSP concentrations, are shown for Western States, 1972-77.

TABLE 5-14. REGIONAL SUMMARIES OF TSP VALUES FROM VALID MONITORS

| Number of sites | Region | Median | | | | 90th percentile | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Minimum | Mean | Maximum | SD[a] | Minimum | Mean | Maximum | SD[a] |
| 128 | I | 14.0 | 49.2 | 100.0 | 14.6 | 32.0 | 87.3 | 181.0 | 27.7 |
| 315 | II | 10.0 | 43.2 | 114.0 | 15.3 | 29.0 | 85.0 | 286.0 | 30.6 |
| 300 | III | 27.0 | 59.8 | 171.0 | 20.3 | 52.0 | 105.7 | 296.0 | 42.1 |
| 534 | IV | 22.0 | 55.3 | 137.0 | 17.2 | 41.0 | 93.5 | 256.0 | 30.9 |
| 781 | V | 13.0 | 64.1 | 189.0 | 22.0 | 26.0 | 122.4 | 383.0 | 42.8 |
| 294 | VI | 12.0 | 65.0 | 166.0 | 20.9 | 37.0 | 110.4 | 436.0 | 45.8 |
| 136 | VII | 34.0 | 69.7 | 154.0 | 20.2 | 58.0 | 123.6 | 359.0 | 44.2 |
| 152 | VIII | 7.0 | 54.8 | 164.0 | 32.8 | 18.0 | 107.8 | 412.0 | 64.0 |
| 89 | IX | 16.0 | 76.5 | 226.0 | 38.0 | 37.0 | 133.4 | 381.1 | 66.0 |
| 113 | X | 11.0 | 60.3 | 129.0 | 24.5 | 23.0 | 123.6 | 361.1 | 52.5 |
| 15 | Alaska | 11.0 | 48.1 | 94.0 | 22.7 | 35.0 | 137.1 | 250.0 | 68.7 |
| 9 | Hawaii | 25.0 | 39.7 | 70.0 | 13.7 | 40.0 | 63.6 | 99.0 | 18.9 |
| 10 | Puerto Rico | 32.0 | 54.3 | 85.0 | 13.9 | 66.0 | 90.7 | 134.0 | 18.9 |
| 2882 | Total[b] | 7.0 | 58.9 | 226.0 | 22.8 | 18.0 | 107.9 | 436.0 | 44.9 |

[a]SD, Standard deviation of the mean.
[b]Including American Samoa and Guam.

In Region III the composite average decreased from 78 to 60 $\mu g/m^3$, with the 90th percentile in the distribution of annual mean concentrations decreasing from slightly over 100 to about 95 $\mu g/m^3$. In Region IV the composite average decreased only slightly, from 65 to 60 $\mu g/m^3$, but has remained relatively stable or has even increased slightly since 1975. In Region V the composite average decreased from 80 to 70 $\mu g/m^3$, and the 90th percentile has decreased from 100 to 85 $\mu g/m^3$, reflecting the effectiveness of point source control.

The Western States make up Regions VI through X. In Region VI the composite average has remained at approximately 75 $\mu g/m^3$ and the 90th percentile has increased slightly since 1973, to about 100 $\mu g/m^3$. Industrial, utility, and related growth in this area as well as in Region IV is probably responsible for keeping TSP concentrations from decreasing. In region VII the composite average has been almost constant, varying only slightly between 80 and 75 $\mu g/m^3$. The 90th percentile has varied between 110 and 100 $\mu mg/^3$. Region VIII shows wide distribution in the concentrations. The 10th percentile, at about 20 $\mu g/m^3$, is the lowest among all regions. The 90th percentile, approximately 100 $\mu g/m^3$, is equal to about the highest concentrations in any region. The composite average has varied over the 6-year record, but is essentially the same, approximately 80 $\mu g/m^3$, in 1977 as it was in 1972. The background air quality in the upper States of this region (Montana, North and South Dakota, Wyoming) is among the highest in the country. Thus, some of the low levels (20 $\mu g/m^3$ and below) represent some of the lowest background concentrations measured in the United States. The high composite and high 90th percentile levels reflect the impact of locating monitors near industrial sources such as smelters and the fugitive dust emissions from windblown soils. Region IX has a composite average of 100 $\mu g/m^3$, which is up from 90 $\mu g/m^3$ in the early 1970's. The 90th percentile is also high, at 120 $\mu g/m^3$. Thus, Region IX has some of the highest levels in the

country. Region X has a composite average of approximately 70 $\mu g/m^3$, which is up slightly from a low of 60 $\mu g/m^3$ in 1975. The 90th percentile varies between 90 and 100 $\mu g/m^3$.

The overall trend in improvement from 1972 through 1975 was followed by a reversal in some regions in 1976. Despite this short-term reversal in 1976, 60 percent of the sites showed long-term improvement from 1972 to 1977. For those sites at which TSP concentrations violated annual standards, 77 percent showed long-term improvements. Approximately 25 percent of these sites reported their lowest annual values in 1977. Possibly, the short-term reversal in 1976 was due to unusually dry weather, resulting in windblown dust that may have contributed to elevated TSP levels throughout the Central Plains, Far West, Southwest, and Southeast.

5.2.1.5 National Status of NAAQS for TSP--The present primary NAAQS for TSP are 75 $\mu g/m^3$ annual geometric mean concentration and 260 $\mu g/m^3$ for the second-highest 24-hr concentration. There is a secondary standard of 60 $\mu g/m^3$ for an annual geometric mean and 150 $\mu g/m^3$ for the second-highest 24-hr concentration.

Of the 4008 stations reporting TSP values in 1977, only 2699 had enough samples per quarter to qualify for a valid annual average (EPA, 1978). From these stations 40 percent, or 1070, reported a violation of the secondary TSP annual standard (60 $\mu g/m^3$); 17 percent, or 456 stations, reported violations of the national primary annual standard (75 $\mu g/m^3$). Of all stations reporting at least minimum data, 36 percent, or 1424, showed violations of the 24-hr secondary TSP standards (second-highest value not to exceed 150 $\mu g/m^3$); 8 percent, or 314 monitoring stations, reported violations of the 24-hr primary standards for TSP (second-highest value not to exceed 260 $\mu g/m^3$). Table 5-15 shows the number of stations that recorded violations of the national primary or secondary standards

TABLE 5-15. NATIONAL SUMMARY OF TOTAL STATIONS REPORTING DATA AND NUMBER REPORTING VIOLATIONS OF AIR QUALITY STANDARDS FOR TSP, 1977 AND 1978

| Data record and standard exceeded | Number of sites | | Percent of sites exceeding NAAQS | |
|---|---|---|---|---|
| | 1977 | 1978 | 1977 | 1978 |
| Valid annual data[a] | 2699 | 2486 | | |
| Annual secondary (guide only) | 1070 | 1025 | 40 | 41 |
| Annual primary | 456 | 439 | 17 | 17 |
| At least minimal data[b] | 4008 | 3767 | | |
| 24-hr secondary | 1424 | 1191 | 36 | 32 |
| 24-hr primary | 314 | 215 | 8 | 6 |

[a]Must contain at least five of the scheduled 24-hr samples per quarter for EPA-recommended intermittent sampling (once every 6 days) or 75 percent of all possible values in a year for continuous intruments.
[b]At least three 24-hr samples for intermittent sampling monitors.

Source: 1977 data from National Air Quality, Monitoring and Emission Trends Report, 1977, U.S. Environmental Protection Agency, EPA 450/2-78-052, December 1978.
1978 data from direct communication with OAQPS, U.S. Environmental Protection Agency.

for TSP in 1977 and 1978. Forty-two States plus the District of Columbia showed violations of the primary ambient air standard for TSP in at least one monitoring location.

Preliminary summaries of 1978 air quality TSP data indicate that 1025 of the 2486 sites with valid data for annual averages exceeded the secondary standard and 434 exceeded the primary standard. This represents essentially no change in the percentage of sites not complying between 1977 and 1978.

There were only 3767 stations reporting data in 1978. Of those with at least partial data, 32 percent, or 1191, violated the 24-hr secondary standard and 6 percent, or 215, violated the primary standard. This indicates a slight improvement over 1977.

Figure 5-17, based on 1977 NADB TSP data, shows the AQCR attainment status for the annual primary NAAQS. The AQCR's classified as nonattainment were determined by violations at at least one sampling site. Nonattainment determined on the scale of an entire AQCR could be misleading. Local sources may dominate the levels recorded at a particular site in an otherwise less polluted area. EPA has recognized this and has allowed States to subdivide AQCR's into attainment and nonattainment regions. For this refined analysis, the reader is referred to the State implementation plans revised as of January 1979 for each State.

It appears that no region is exempt from attainment problems for TSP. The North, Midwest, Southeast, Southwest, and Northwest all had monitors showing violations of annual standards.

Finer spatial resolution of TSP concentrations is shown in Figure 5-18, prepared by EPA from 1974-76 data. Again, it should be remembered that the concentrations attributed to each county were derived from the monitor in that

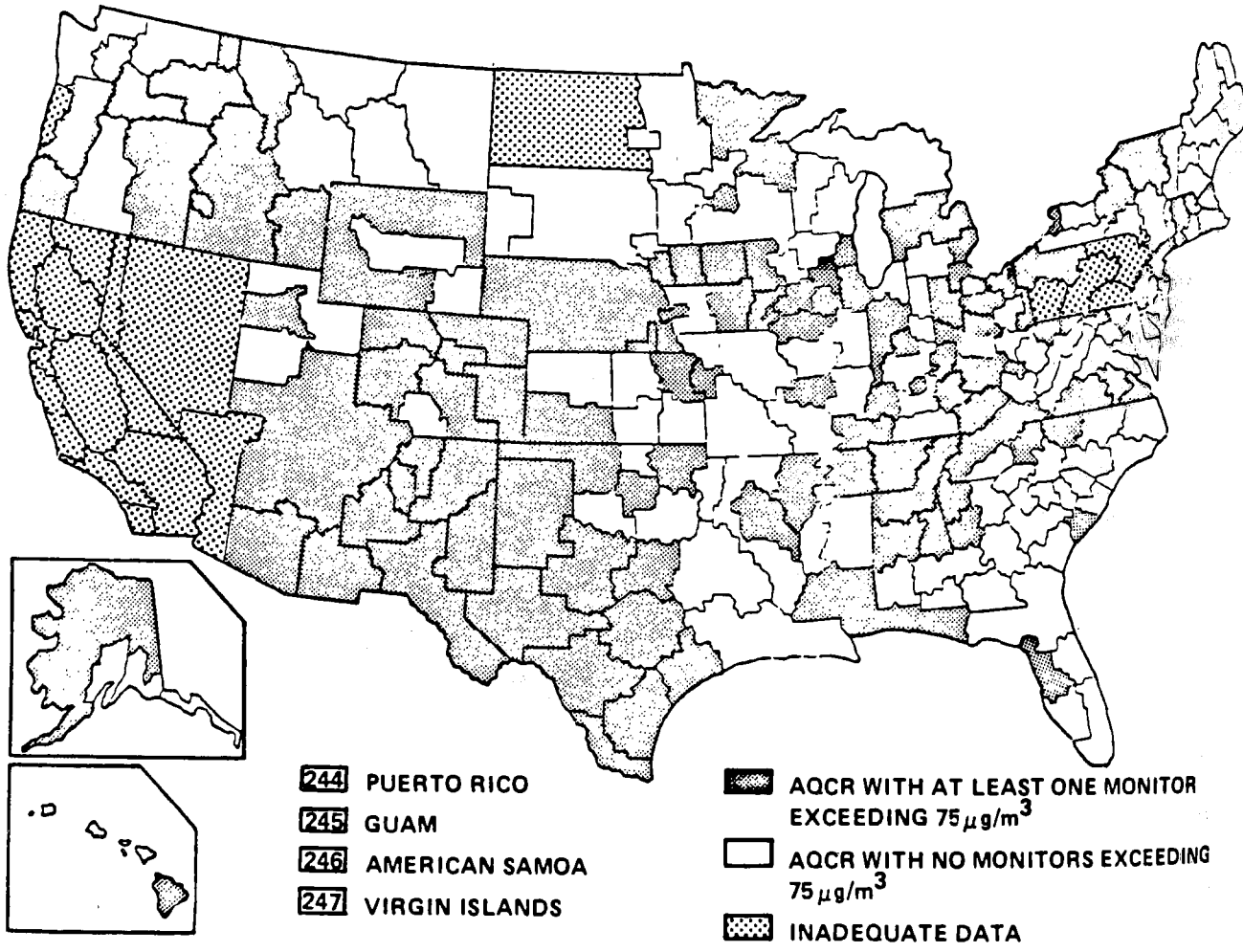



Figure 5-17. Map of the United States shows the AQCR's violating the primary annual TSP standard (> 75 $\mu g/m^3$), 1977.

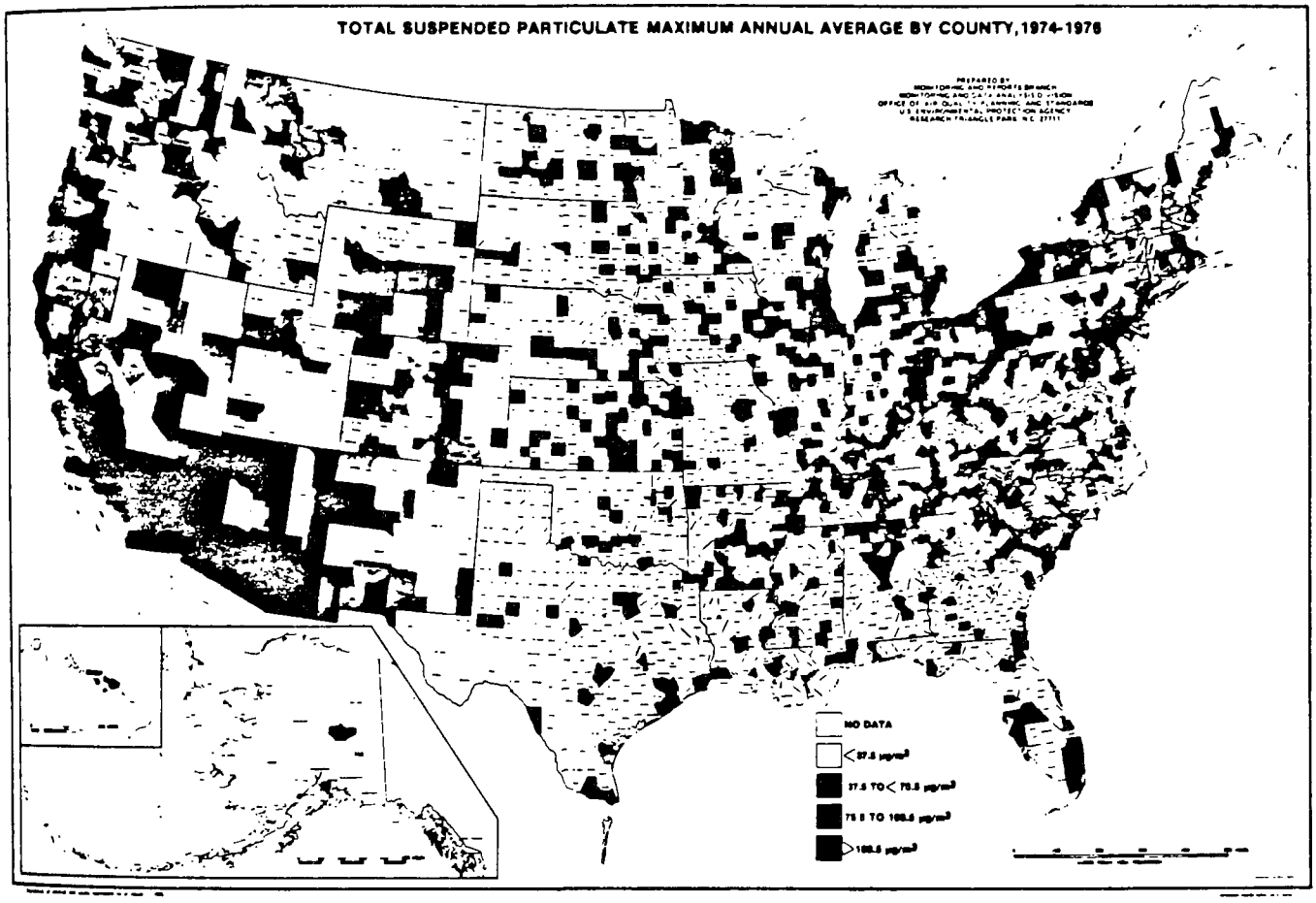



Figure 5-18. Maximum annual average of TSP concentrations for 1974-76 are shown by county. Note that the annual mean primary national ambient air quality standard is 75 $\mu g/m^3$, which is not to be exceeded.

county having the highest annual average value. It is not possible to determine whether concentrations are more or less uniform across the county or whether they are localized. However, several general impressions are obtained about national TSP conditions. High concentrations can be found in almost every State. Many populated counties have high concentrations (for example, New Jersey-New York City, Pittsburgh, Harrisburg, Chicago, and Los Angeles). Several sparsely populated counties also have high concentrations. Arid regions as well as industrialized counties have high levels.

The AQCR attainment status for the daily NAAQS is shown in Figure 5-19, which is based on the same 1977 NADB TSP data. The same comment made above applies to the 24-hr measurements. A violation of NAAQS for TSP at one location does not necessarily imply a higher health risk for the entire population of that area. The health implications even for those living near a site in violation are not clear. Populations living in attainment areas but exposed to TSP high in trace metals, for example, might have a high health risk.

A closer look at the site descriptions for stations that recorded violations suggests that the reasons for violation are quite variable. As discussed earlier, it seems clear that industrial sources contribute significantly to TSP levels at many sites. This is not so obvious at other sites, however. Some extremely high concentrations experienced at monitors in Arizona, New Mexico, and elsewhere are most likely associated with surface dust suspended by the wind. Without a careful site inventory or perhaps detailed analysis of TSP chemical and elemental composition, the specific reasons for TSP violations are unknown.

5.2.1.6 Severity of Peak TSP Concentrations--The geographic displays of attainment status are only one way of conveying the extent of the TSP pollution problem. To indicate the severity of TSP ambient exposures, the 90th percentile concen-

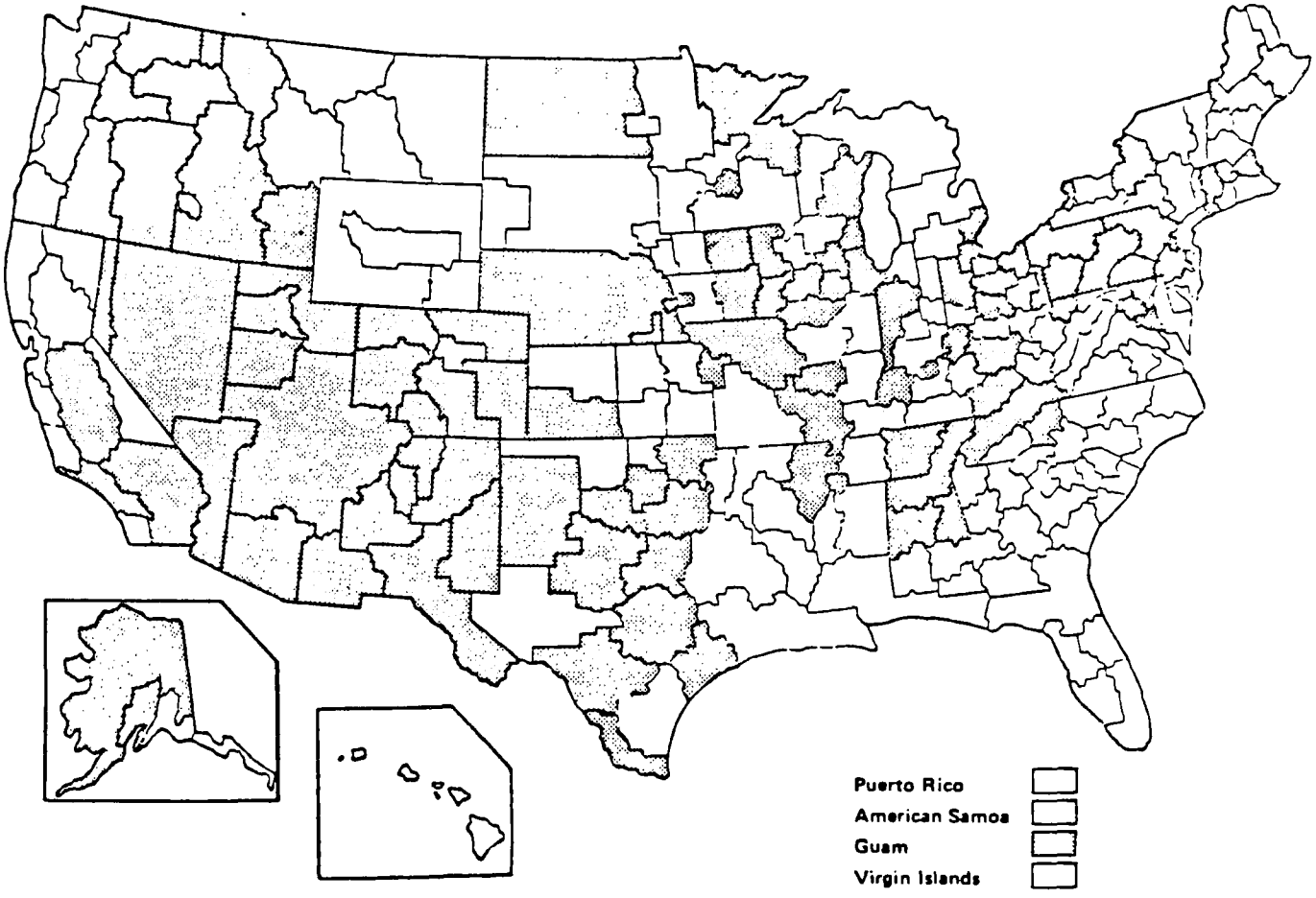



Figure 5-19. Map of the United States shows the AQCR's violating the primary 24-hr TSP standard (second highest, > 260 $\mu g/m^3$), 1977.

tration of the 24-hr measurements was examined for all 4008 sites in the 1977 NADB. The concentrations of TSP and other air pollutants have been widely reported to be log normally distributed (Larsen, 1971). This statistical relationship, however, appears inappropriate at the high and low ends of the distribution (Mage and Ott, 1978). Because the extreme values at the high end are subject to wide scatter, the 95th or 99th percentile was found to be less representative of the severity of high TSP levels. The 90th percentile was therefore chosen as being a more stable indicator. It represents the TSP level that is exceeded on approximately 36 days of the year.

Table 5-16 shows, for each AQCR, the number of TSP monitoring sites whose 90th percentile concentrations were <100, 100-200, 200-260, and >260 $\mu g/m^3$. In Figure 5-20 the AQCR's having at least one monitoring station whose 90th percentile exceeds 260 $\mu g/m^3$ are displayed. AQCR's in Montana, Arizona, and New Mexico have a large number of monitoring sites for a relatively sparse population (approximately twice EPA's minimum requirement). A number of these sites are near smelters. Hence, the high levels do not necessarily imply high population exposure to TSP. In addition, windblown soil contributes to the higher levels in these States. In the Northeast and East, the elevated TSP concentrations reflect the higher density of industrial and urban emissions. In these cases, the high levels (in Pennsylvania, Ohio, New Jersey, New York, Connecticut, and Massachusetts) indicate a larger population exposed to peak TSP concentrations. The high 90th percentile levels in North Dakota, Nebraska, Iowa, and Colorado perhaps reflect an influence of fugitive emissions from agriculture.

Figure 5-21 shows the number of AQCR's whose monitors have their 90th percentile TSP concentration within the various categories. Of the country's 254 AQCR's, only 20 had air quality to the extent that none of their 90th percentiles exceeded 100 $\mu g/m^3$. One hundred and fifty-four AQCR's had 90th percentile values in at

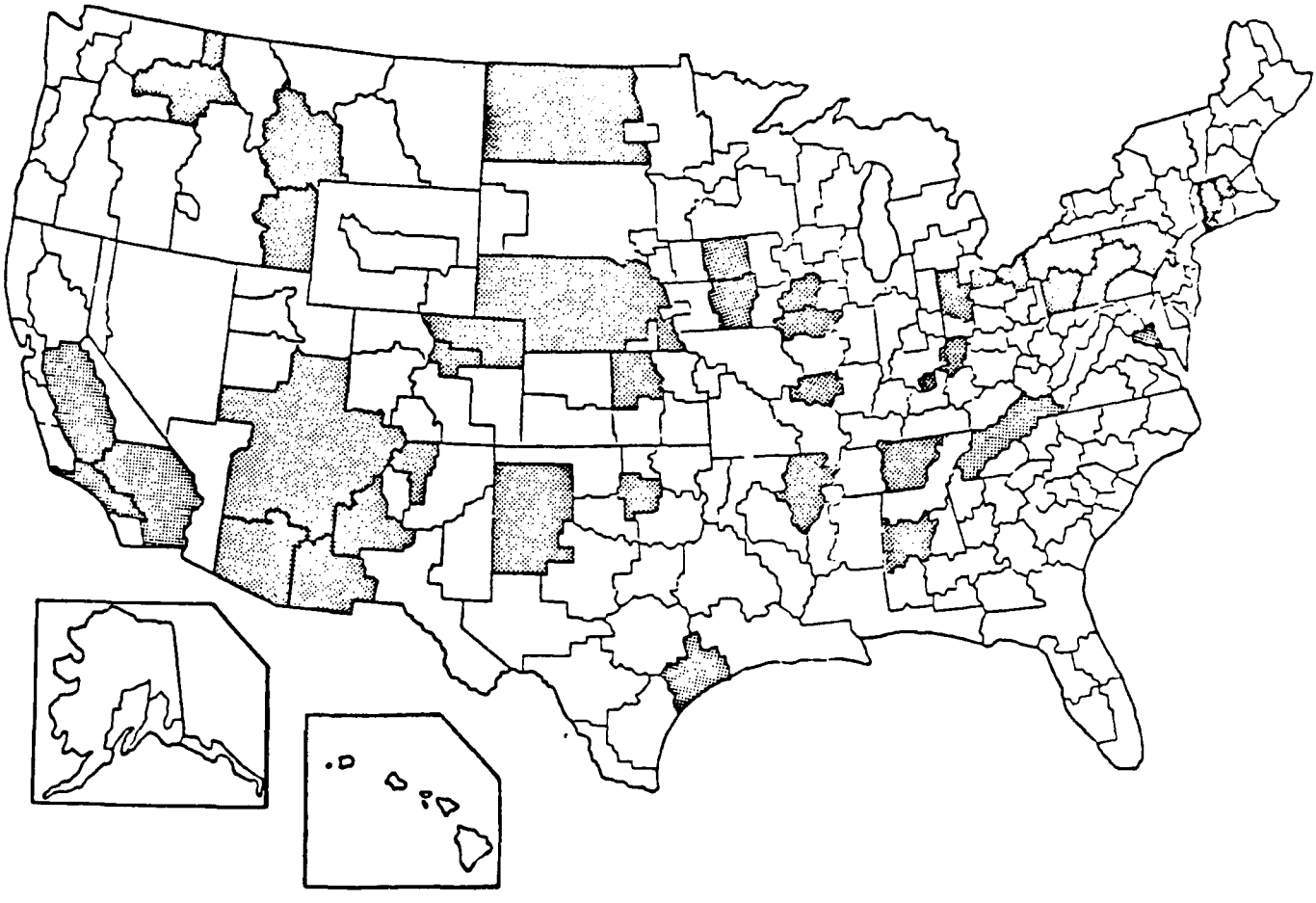


Figure 5-20. Shaded areas indicate AQCR's in which at least one monitoring site in 1977 had a 90th percentile TSP concentration exceeded 260 $\mu g/m^3$.

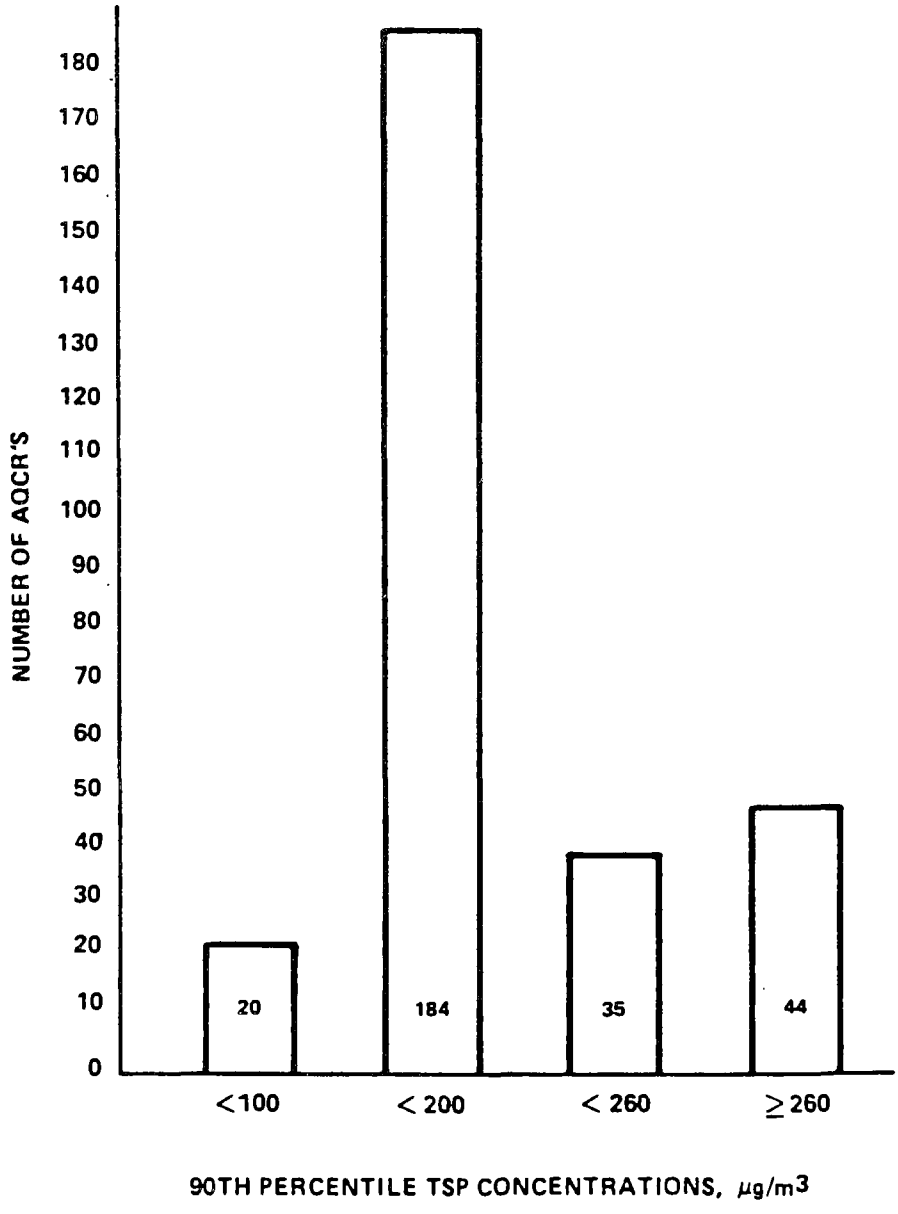



Figure 5-21. Severity of TSP peak exposures is shown on the basis of the 90th percentile concentration. Four AQCR's did not report.

TABLE 5-16. 1977 NATIONWIDE COMPLIANCE STATUS FOR TOTAL SUSPENDED PARTICULATE MATTER AND SEVERITY OF TSP EXPOSURES, BASED ON THE 90TH PERCENTILE CONCENTRATION OF 24-HR VALUES

| State | AQCR | Number of sites | Number of sites reporting 90th percentile concentrations ($\mu g/m^3$) of: <100 | 100-200 | 200-260 | >260 |
|---|---|---|---|---|---|---|
| AL | 1 | 5 | 3 | 2 | | |
| | 2(I)b | 8 | 7 | 1 | | |
| | 3 | 9 | 4 | 5 | | |
| | 4 | 20 | 6 | 10 | 2 | 2 |
| | 5(I) | 49 | 37 | 12 | | |
| | 6 | 4 | 2 | 2 | | |
| | 7(I) | 41 | 23 | 17 | 1 | |
| AK | 8 | 11 | 3 | 8 | | |
| | 9 | 8 | 4 | 4 | | |
| | 10 | 1 | 1 | | | |
| | 11 | 7 | 4 | 3 | | |
| AZ | 12(I) | 13 | 4 | 6 | | 3 |
| | 13(I) | 22 | 9 | 11 | 2 | |
| | 14(I) | 60 | 35 | 21 | 3 | 1 |
| | 15 | 38 | 9 | 18 | 3 | 3 |
| AR | 16 | 16 | 4 | 12 | | |
| | 17(I) | 8 | 4 | 4 | | |
| | 18(I) | 16 | 3 | 13 | | |
| | 19(I) | 6 | 4 | 2 | | |
| | 20 | 11 | | 9 | 1 | 1 |
| | 21 | 2 | 1 | 1 | | |
| | 22 | 15 | 9 | 6 | | |
| CA | 24 | 36 | 0 | 19 | 12 | 5 |
| | 25 | 3 | 3 | | | |
| | 27 | 2 | 2 | | | |
| | 28 | 7 | 5 | 2 | | |
| | 29 | 7 | 2 | 5 | | |
| | 30 | 20 | 16 | 4 | | |
| | 31 | 13 | 1 | 7 | 4 | 1 |
| | 32 | 1 | 1 | | | |
| | 33 | 8 | 1 | 4 | 2 | 1 |
| | 14(I) | | | | | |

TABLE 5-16 (continued)

| State | AQCR | Number of sites | Number of sites reporting 90th percentile concentrations ($\mu g/m^3$3) of <100 | 100-200 | 200-260 | >260 |
|---|---|---|---|---|---|---|
| CO | 34 | 4 | 1 | 3 | | |
| | 35 | 14 | 1 | 11 | 2 | |
| | 36 | 23 | 2 | 19 | 1 | 1 |
| | 37 | 13 | 3 | 8 | | 2 |
| | 38 | 9 | 1 | 8 | | |
| | 39 | 5 | 3 | 2 | | |
| | 40 | 5 | 2 | 1 | 2 | |
| CT | 41 | 4 | 4 | | | |
| | 42(I)[b] | 35 | 24 | 10 | | |
| | 43(I) | 135 | 105 | 30 | | |
| | 44 | 2 | 1 | 1 | | |
| DE | 45(I) | 59 | 40 | 19 | | |
| | 46 | 3 | 3 | | | |
| DC | 47(I) | 68 | 47 | 18 | 3 | |
| FL | 5(I) | | | | | |
| | 48 | 13 | 13 | | | |
| | 49(I) | 38 | 35 | 3 | | |
| | 50 | 61 | 54 | 7 | | |
| | 51 | 12 | 12 | | | |
| | 52 | 48 | 41 | 7 | | |
| GA | 2(I) | | | | | |
| | 49(I) | | | | | |
| | 53(I) | 7 | 6 | 1 | | |
| | 54 | 8 | 6 | 2 | | |
| | 55(I) | 16 | 10 | 6 | | |
| | 56 | 22 | 15 | 7 | | |
| | 57 | 1 | 1 | | | |
| | 58(I) | 10 | 6 | 3 | 1 | |
| | 59 | 3 | 2 | 1 | | |
| HI | 60 | 10 | 8 | 2 | | |
| ID | 61 | 14 | 1 | 9 | 1 | 3 |
| | 62(I) | 34 | 5 | 25 | 2 | 2 |
| | 63 | 5 | 1 | 2 | 1 | 1 |
| | 64 | 4 | | 2 | 2 | |
| IL | 65 | 11 | | 10 | | 1 |
| | 66 | 2 | | 2 | | |
| | 67(I) | 128 | 32 | 90 | 5 | 1 |
| | 68(I) | 8 | 5 | 3 | | |
| | 69(I) | 23 | 10 | 12 | | 1 |
| | 70(I) | 49 | 10 | 29 | 7 | 3 |
| | 71 | 6 | 3 | 2 | 1 | |
| | 72(I) | 27 | 10 | 15 | 2 | |
| | 73(I)" | 9 | 1 | 7 | 1 | |
| | 74 | 4 | | 4 | | |
| | 75 | 8 | 1 | 7 | | |

TABLE 5-16 (continued)

| State | AQCR | Number of sites | Number of sites reporting 90th percentile concentrations ($\mu g/m^3$) of: <100 | 100-200 | 200-260 | >260 |
|---|---|---|---|---|---|---|
| IN | 67(I)[b] | | | | | |
| | 76 | 9 | 7 | 2 | | |
| | 77(I) | 27 | 9 | 17 | | |
| | 78(I) | 20 | 4 | 14 | | |
| | 80 | 18 | 5 | 13 | | |
| | 81 | 3 | 2 | 1 | | |
| | 82(I) | 17 | 12 | 5 | | |
| | 83 | 4 | 2 | 2 | | |
| | 84 | 13 | 3 | 9 | | 1 |
| IA | 65(I) | | | | | |
| | 68(I) | | | | | |
| | 69(I) | | | | | |
| | 85(I) | 18 | 5 | 13 | | |
| | 86(I) | 5 | 1 | 4 | | |
| | 87(I) | 5 | 3 | 2 | | |
| | 88 | 13 | 2 | 11 | | |
| | 89 | 6 | 2 | 3 | | 1 |
| | 90 | 3 | 2 | 1 | | |
| | 91 | 5 | 1 | 4 | | |
| | 92 | 17 | 3 | 12 | 1 | 1 |
| | 93 | 1 | | 1 | | |
| KS | 94(I) | 35 | 7 | 26 | 2 | |
| | 95 | 14 | 10 | 4 | | |
| | 96 | 6 | 4 | 1 | | 1 |
| | 97 | 6 | 3 | 3 | | |
| | 98 | 5 | 2 | 3 | | |
| | 99 | 14 | 9 | 5 | | |
| | 100 | 5 | 1 | 4 | | |
| KY | 72(I) | | | | | |
| | 77(I) | | | | | |
| | 78(I) | | | | | |
| | 79(I) | 64 | 20 | 42 | 1 | 1 |
| | 101 | 9 | 1 | 4 | 4 | |
| | 102 | 12 | 7 | 5 | | |
| | 103(I) | 43 | 11 | 28 | 4 | |
| | 104 | 14 | 11 | 3 | | |
| | 105 | 6 | 4 | 2 | | |
| LA | 19(I) | | | | | |
| | 106(I) | 29 | 23 | 6 | | |
| ME | 107(I) | 30 | 22 | 6 | 2 | |
| | 108 | 2 | 1 | 1 | | |
| | 109 | 21 | 14 | 7 | | |
| | 110 | 7 | 7 | | | |

TABLE 5-16 (continued)

| State | AQCR | Number of sites | Number of sites reporting 90th percentile concentrations ($\mu g/m^3$) of: <100 | 100-200 | 200-260 | >260 |
|---|---|---|---|---|---|---|
| MD | 47(I)[b] | | | | | |
| | 112 | 9 | 6 | 3 | | |
| | 113(I) | 16 | 9 | 7 | | |
| | 114 | 3 | 2 | 1 | | |
| | 115 | 42 | 23 | 16 | 4 | |
| | 116 | 8 | 7 | | | 1 |
| MA | 117 | 5 | 2 | 3 | | |
| | 118 | 10 | 8 | 1 | | 1 |
| | 119 | 18 | 14 | 4 | | |
| | 120(I) | 22 | 17 | 5 | | |
| | 121(I) | 26 | 22 | 4 | | |
| MI | 82(I) | | | | | |
| | 122 | 47 | 30 | 17 | | |
| | 123 | 44 | 10 | 31 | 3 | |
| | 124 | 23 | 7 | 16 | | |
| | 125 | 15 | 9 | 6 | | |
| | 126 | 25 | 18 | 7 | | |
| MN | 127 | 7 | 7 | | | |
| | 128(I) | 17 | 11 | 6 | | |
| | 129(I) | 47 | 35 | 11 | 1 | |
| | 130 | 4 | 2 | 2 | | |
| | 131 | 21 | 11 | 10 | | |
| | 132 | 4 | 1 | 3 | | |
| | 133 | 1 | | 1 | | |
| MS | 5(I) | | | | | |
| | 18(I) | | | | | |
| | 134 | 4 | 1 | 3 | | |
| | 135 | 7 | 3 | 4 | | |
| MO | 70(I) | | | | | |
| | 94(I) | | | | | |
| | 137 | 7 | 2 | 5 | | |
| | 138 | 6 | 2 | 4 | | |
| | 139 | 18 | 11 | 7 | | |
| MT | 140 | 7 | 7 | | | |
| | 141 | 5 | 2 | 3 | | |
| | 142 | 11 | 5 | 5 | | 1? |
| | 143 | 15 | 13 | 2 | | |
| | 144 | 15 | 9 | 5 | 1 | |
| NE | 85(I) | | | | | |
| | 86(I) | | | | | |
| | 145 | 15 | 8 | 6 | 1 | |
| | 146 | 21 | 3 | 17 | | 1 |

TABLE 5-16 (continued)

| State | AQCR | Number of sites | Number of sites reporting 90th percentile concentrations ($\mu g/m^3$) of: <100 | 100-200 | 200-260 | >260 |
|---|---|---|---|---|---|---|
| NV | 13(I)[b] | | | | | |
| | 147 | 8 | | 2 | 6 | |
| | 148 | 21 | 8 | 11 | 2 | |
| NH | 107(I) | | | | | |
| | 149 | 2 | 2 | | | |
| NJ | 43(I) | | | | | |
| | 45(I) | | | | | |
| | 150 | 8 | 8 | | | |
| | 151(I) | 33 | 20 | 12 | | 1 |
| NM | 12(I) | | | | | |
| | 14(I) | | | | | |
| | 152 | 16 | 6 | 9 | 1 | |
| | 153(I) | 28 | 2 | 18 | 5 | 3 |
| | 154 | 3 | | 3 | | |
| | 155 | 7 | 1 | 6 | | |
| | 156 | 7 | 1 | 4 | 1 | 1? |
| | 157 | 8 | 3 | 4 | | 1 |
| NY | 43(I) | | | | | |
| | 158 | 41 | 35 | 6 | | |
| | 159(I) | 20 | 19 | 1 | | |
| | 160 | 38 | 37 | 1 | | |
| | 161 | 48 | 45 | 3 | | |
| | 162 | 50 | 28 | 19 | 3 | |
| | 163 | 13 | 13 | | | |
| | 164 | 23 | 20 | 3 | | |
| NC | 136(I) | 24 | 11 | 13 | | |
| | 165 | 12 | 8 | 4 | | |
| | 166 | 10 | 8 | 2 | | |
| | 167 | 31 | 19 | 12 | | |
| | 168 | 5 | 3 | 2 | | |
| | 169 | 12 | 9 | 3 | | |
| | 170 | 8 | 7 | 1 | | |
| | 171 | 14 | 8 | 6 | | |
| ND | 130(I) | | | | | |
| | 172 | 36 | 29 | 5 | 1 | 1 |
| OH | 79(I) | | | | | |
| | 103(I) | | | | | |
| | 124(I) | | | | | |
| | 173 | 24 | 3 | 20 | 1 | 1 |
| | 174 | 107 | 25 | 72 | 8 | 2 |
| | 175 | 20 | 3 | 16 | 1 | |
| | 176 | 18 | 3 | | | |

TABLE 5-16 (continued)

| State | AQCR | Number of sites | Number of sites reporting 90th percentile concentrations ($\mu g/m^3$) of: <100 | 100-200 | 200-260 | >260 |
|---|---|---|---|---|---|---|
| OH | 176 | 18 | 4 | 14 | | |
| | 177 | 21 | 6 | 14 | | 1 |
| | 178(I)[b] | 35 | 5 | 22 | 5 | 3 |
| | 179(I) | 6 | 2 | 4 | | |
| | 180 | 19 | 4 | 14 | | 1 |
| | 181(I) | 35 | 1 | 28 | 6 | |
| | 182 | 8 | 2 | 6 | | |
| | 183 | 13 | 4 | 9 | | |
| OK | 17(I) | | | | | |
| | 22(I) | | | | | |
| | 184 | 21 | 10 | 10 | | 1 |
| | 185 | 3 | 2 | 1 | | |
| | 186 | 19 | 8 | 10 | 1 | |
| | 187 | 4 | | 4 | | |
| | 188 | 6 | 3 | 3 | | |
| | 189 | 5 | 1 | 3 | 1 | |
| OR | 190 | 3 | 1 | 2 | | |
| | 191 | 3 | | 1 | 2 | |
| | 192 | 2 | 2 | | | |
| | 193(I) | 34 | 17 | 16 | 1 | |
| | 194 | 6 | 1 | 5 | | |
| PA | 45(I) | | | | | |
| | 151(I) | | | | | |
| | 178(I) | | | | | |
| | 195 | 10 | 1 | 6 | 2 | 1 |
| | 196 | 20 | 8 | 11 | 1 | |
| | 197 | 39 | 5 | 19 | 5 | 10 |
| PR | 244 | 11 | 5 | 6 | | |
| RI | 120(I) | | | | | |
| SC | 53(I) | | | | | |
| | 58(I) | | | | | |
| | 167(I) | | | | | |
| | 198 | 4 | 3 | 1 | | |
| | 199 | 10 | 5 | 5 | | |
| | 200 | 9 | 8 | 1 | | |
| | 201 | 3 | | 3 | | |
| | 202 | 19 | 16 | 3 | | |
| | 203 | 2 | 2 | | | |
| | 204 | 9 | 4 | 5 | | |
| SD | 87(I) | | | | | |
| | 205 | 11 | 8 | 3 | | |
| | 206 | 8 | 5 | 3 | | |

TABLE 5-16 (continued)

| State | AQCR | Number of sites | Number of sites reporting 90th percentile concentrations ($\mu g/m^3$) of: <100 | 100-200 | 200-260 | >260 |
|---|---|---|---|---|---|---|
| TN | 7(I)[b] | | | | | |
| | 18(I) | | | | | |
| | 55(I) | | | | | |
| | 207(I) | 54 | 16 | 36 | 1 | 1 |
| | 208 | 39 | 9 | 27 | 2 | 1 |
| | 209 | 10 | 4 | 6 | | |
| TX | 22(I) | | | | | |
| | 106(I) | | | | | |
| | 153(I) | | | | | |
| | 210 | 4 | 1 | 3 | | |
| | 211 | 4 | 1 | 2 | | 1 |
| | 212 | 11 | 7 | 4 | | |
| | 213 | 11 | 1 | 9 | 1 | |
| | 214 | 18 | 9 | 9 | | |
| | 215 | 43 | 22 | 21 | | |
| | 216 | 61 | 15 | 41 | 2 | 3 |
| | 217 | 11 | 4 | 4 | 3 | |
| | 218 | 5 | | 5 | | |
| UT | 14(I) | | | | | |
| | 219 | 4 | 2 | 2 | | |
| | 220 | 23 | 4 | 17 | 2 | |
| VT | 159(I) | | | | | |
| | 221 | 8 | 8 | | | |
| VA | 47(I) | | | | | |
| | 207(I) | | | | | |
| | 222 | 34 | 24 | 10 | | |
| | 223 | 20 | 11 | 9 | | |
| | 224 | 9 | 9 | | | |
| | 225 | 23 | 14 | 9 | | |
| | 226 | 32 | 22 | 10 | | |
| WA | 62(I) | | | | | |
| | 193(I) | | | | | |
| | 227 | 5 | | 5 | | |
| | 228 | 8 | 6 | 2 | | |
| | 229 | 21 | 12 | 9 | | |
| | 230 | 8 | 1 | 7 | | |
| WV | 103(I) | | | | | |
| | 113(I) | | | | | |
| | 179(I) | | | | | |
| | 181(I) | | | | | |
| | 232 | 1 | | 1 | | |
| | 233 | 1 | | 1 | | |
| | 234 | 12 | 5 | 7 | | |
| | 235 | 6 | 3 | 3 | | |
| | 236 | 3 | 1 | 2 | | |

TABLE 5-16 (continued)

| State | AQCR | Number of sites | Number of sites reporting 90th percentile concentrations ($\mu g/m^3$) of: <100 | 100-200 | 200-260 | >260 |
|---|---|---|---|---|---|---|
| WI | 68(I)[b] | | | | | |
| | 73(I) | | | | | |
| | 128(I) | | | | | |
| | 129(I) | | | | | |
| | 237 | 22 | 13 | 9 | | |
| | 238 | 17 | 12 | 5 | | |
| | 239 | 47 | 21 | 25 | 1 | |
| | 240 | 17 | 10 | 7 | | |
| WY | 241 | 6 | 5 | 1 | | |
| | 242 | 8 | 8 | | | |
| | 243 | 40 | 37 | 3 | | |
| GU | 246 | 3 | 1 | | 1 | 1 |
| VI | 247 | 4 | 2 | 2 | | |

Source: Based on Air Quality Data, 1977 Annual Statistics. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, EPA-450/2-78-040, September 1978.

least one site between 100 to 200 $\mu g/m^3$. These data and those in Table 5-16, indicate that most of the U.S. population might experience ambient TSP concentrations exceeding 100 $\mu g/m^3$ for at least 36 days of the year.

5.2.2 Composition of Ambient Particulate Matter

Atmospheric particles can be characterized in a variety of ways, including the number of particles per volume of air, the mass of particles per volume, the concentration of chemical species, the elemental composition of particles, or the acidity of the aerosol. Characterizing particles in different ways may be important in analyzing health significance and welfare effects. In addition, the further characterization of atmospheric particles beyond the traditional mass-per-volume measurements may provide useful information on source contributions and thus be of use in the design of effective control strategies. The following section will summarize information on the concentrations of TSP by various fractional components.

Particles can be classified into five general categories: Inorganic salts such as sulfates and nitrates; minerals, such as silica and silicates; fibrous materials (mineral, natural organic, or synthetic organic); organic compounds; biological material. The concentrations of TSP sulfates, nitrates, various organic constituents, and certain metals will be described. The availability of data on these constituents varies widely. Sulfate has been measured for some time. Recent studies have added much to our understanding of its spatial and temporal variation. However, data on the organic fractions of TSP are sparse. Finally, this section presents results of studies that have identified the source contributions to urban and rural TSP's.

5.2.2.1 Ambient sulfates--The term "atmospheric sulfates" describes a variety of sulfur compounds, including ammonium sulfate, ammonium bisulfate, sulfuric

acid, calcium sulfate, and a variety of metal salts. Most of the historic data on atmospheric concentrations of sulfates is based on the water-soluble extract of TSP filters and measurements of the sulfate ion. These measurements were subject to artifact formation on the glass fiber filters used in the early NASN measurements. In attempts to overcome this problem, Teflon and special neutral glass fiber filters have been introduced. They have not been trouble-free. Hydrophobic surfaces do not wet sufficiently to ensure that all water-soluble sulfates are removed. In general, it is now accepted that pre-1974 or -1975 TSP sulfate measurements using the traditional glass fiber filters may have overestimated sulfates by as much as 2 $\mu g/m^3$ in areas where ambient $SO_2$ concentrations were high.

The range of annual average TSP sulfate concentrations is from less than 1 $\mu g/m^3$ in some states to almost 20 $\mu g/m^3$ in urban industrial areas of the Northeast. For 24-hr average concentrations, sulfate concentrations have ranged from near zero to more than 80 $\mu g/m^3$.

5.2.2.1.1 Spatial and temporal distribution. The spatial distribution of sulfate concentration for 1974 is displayed in Figure 5-22. Figure 5-22A presents the annual average concentrations. An area having an annual average of more than 15 $\mu g/m^3$ extends from the lower Ohio Valley through the upper Ohio Valley, including major portions of Kentucky, West Virginia, Ohio, and western Pennsylvania. The areas with annual averages exceeding 10 $\mu g/m^3$ include almost all of the United States east of the Mississippi, except for the South Atlantic States and the upper New England area.

Through the central Midwest area, values of 4 to 9 $\mu g/m^3$ are reported. The high values seen in the Rocky Mountain States may originate from local smelters and coal-fired power plants. The Far Western States and the Pacific Northwest experience annual sulfate levels below 2 to 3 $\mu g/m^3$, except for the Los Angeles

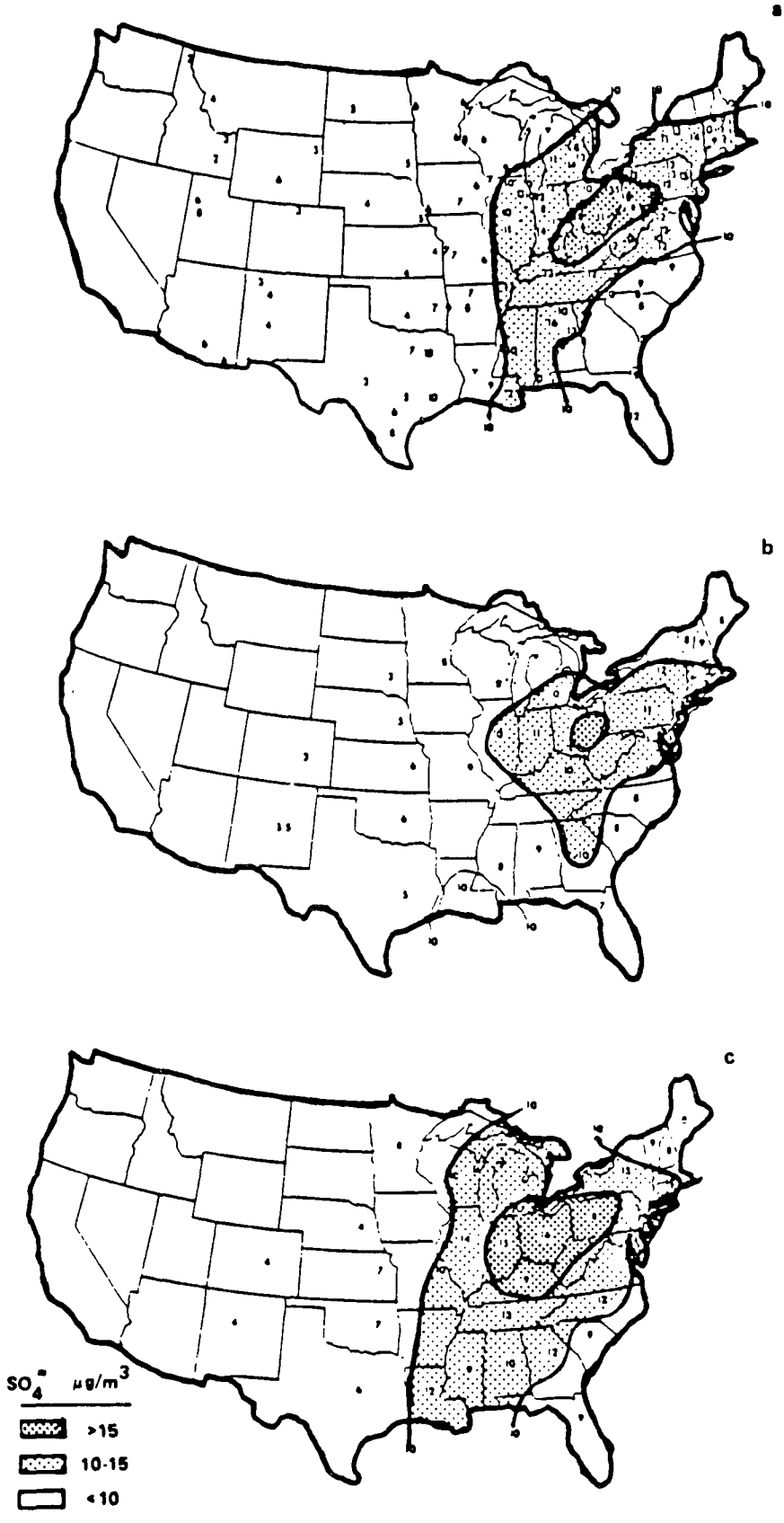



Figure 5-22. Contour maps of sulfate concentrations for 1974 are shown for: (a) annual average; (b) winter average; (c) summer average.

Source: National Research Council, Sulfur Oxides, National Academy Washington, DC, 1977.

area. The Los Angeles levels are not shown in this figure, but a 1975 National Academy of Sciences report on air quality and stationary source emission controls indicates that they are between 7 and 13 $\mu g/m^3$ (National Academy of Sciences, 1975).

Seasonal variations in sulfate concentrations are shown in Figures 5-22B and 5-22C for the winter months and the summer months. The area of elevated sulfate greatly expands during the summer months. As demonstrated by several regional studies on atmospheric sulfate transport, sulfate concentrations can be elevated over large geographical regions under certain meteorological conditions (Elisassen, 1978; Lyons and Dooley, 1978; Perhak, 1978; Whelpedale, 1978). This is support for the transport and conversion beyond the source regions of sulfur dioxide emissions. It is clear from these contour maps of high sulfate levels that a large portion of the U.S. population is exposed to annual sulfate concentrations in the ambient air of more than 10 $\mu g/m^3$. In view of the increasing sulfur dioxide emissions from increased use of coal throughout the United States, particularly in the South Central States, the area of maximum sulfate levels might expand and shift to the lower Ohio Valley area and the Southeast.

In a large-scale study of atmospheric sulfate in eastern Canada, Whelpedale (1978) reports mean levels of 10 $\mu g/m^3$ over southern Ontario. The mean levels of sulfates dropped to less than 2.5 $\mu g/m^3$ above the 49th parallel. Figure 5-23 displays these values for the period of study. During episodic conditions that affect primarily the lower Great Lakes region, the 24-hr concentrations have been reported as high as 40 to 50 $\mu g/m^3$. These episodic conditions are associated with the position of a high-pressure cell over eastern Canada with southwest flow occurring on the back side of the high pressure. This synoptic situation favors transport of sulfur dioxide and sulfates from the high sulfur dioxide source regions of the industrialized Northeastern United States.

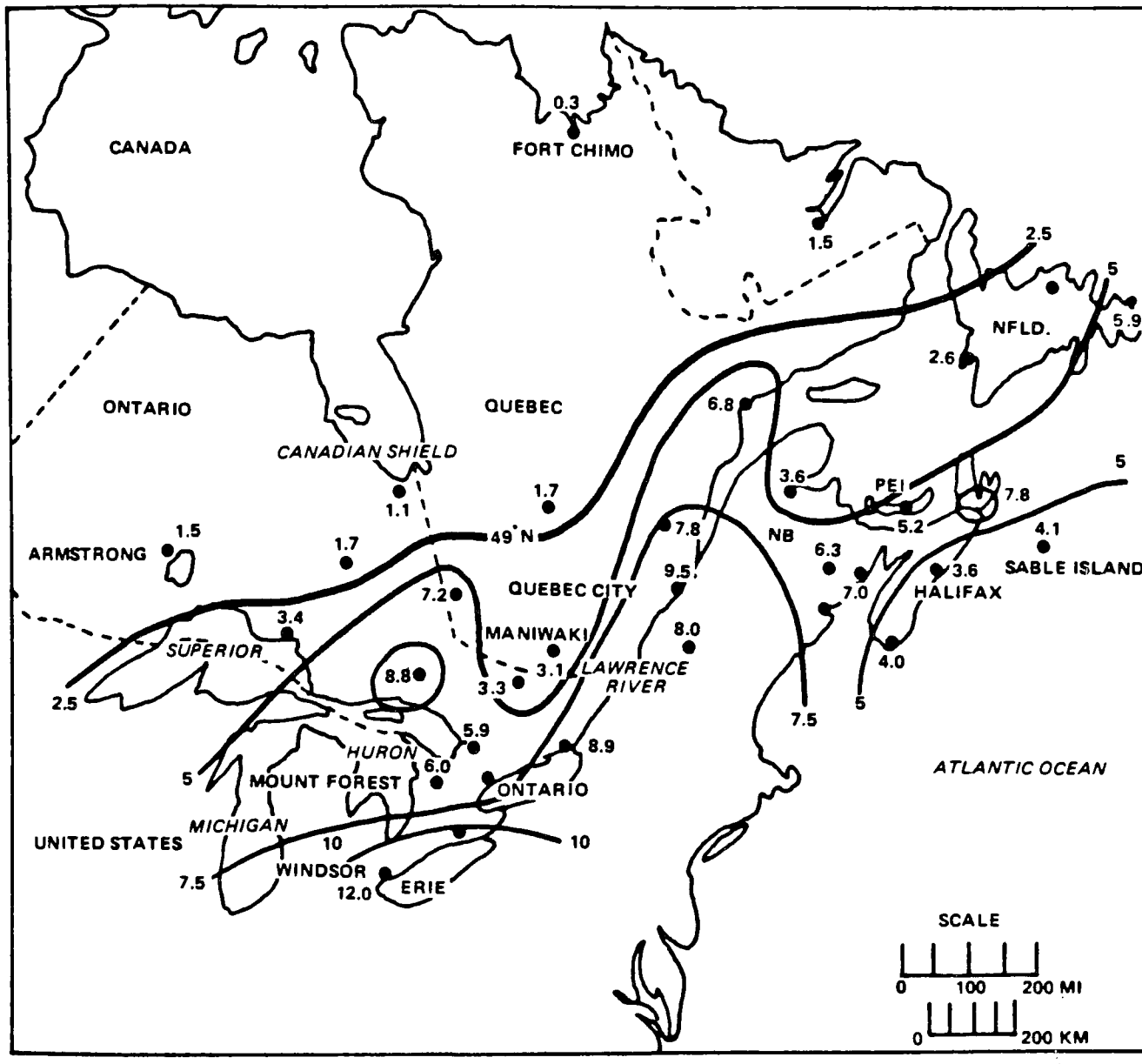



Figure 5-23. Intensive Sulfate Study area in Eastern Canada shows the geometric mean of the concentration of particulate soluble sulfate during the study period. Units are micrograms of sulfate per cubic meter.

Source: Whelpedale (1978).

Recently new information on the interrelationship of sulfur dioxide, nitrogen dioxide, ozone, TSP, sulfates, and nitrates has become available from large-scale regional study. The Electric Power Research Institute (EPRI) Sulfate Regional Experiment (SURE) involves intensive monitoring from some 54 rural stations and an aircraft sampling program. The area being studied is 2400 x 1840 km; it extends from Kansas to the Atlantic coast and from mid-Alabama to southeastern Canada (see Figure 5-24) (Hidy et al., 1979).

Mueller et al (1979) reported on the earlier SURE data collected in 1974 and 1975 and presented the preliminary results of an intensive field study made during July 1977 through February 1978. Using the limited historic data base, they indicate that the rural stations experience a frequency of occurrence of sulfates similar to that observed around large metropolitan areas such as New York City. As seen in Figure 5-25, 24-hr values greater than 10 $\mu g/m^3$ occurred in approximately half the data, and the occurrence of 24-hr sulfate levels exceeding 20 $\mu g/m^3$ was about 10 to 12 percent.

Based on concentrations of 10 to 20 $\mu g/m^3$ as an indicator of elevated exposure, the average concentrations over the SURE data were estimated by a linear interpolation procedure with a resolution of 80 x 80 km grids. The occurrence and spatial extent of elevated sulfates is displayed in Figure 5-26. Episodes of elevated sulfates are extensive; during an episode in early August 1977, the area where sulfate levels exceeded 20 $\mu g/m^3$ expanded to more than 500,000 $km^2$. The month of August shows elevated sulfates over a large area as compared with the month of October. In spite of the lower mean values during the winter months, large regions of elevated sulfur can occur. Two regional episodes occurred in January and early February 1977. In August, 39 percent of the sulfate values exceeded 10 $\mu g/m^3$; in January the figure was 30 percent. Five percent of the values exceeded 20 $\mu g/m^3$. In October, 20 percent of the

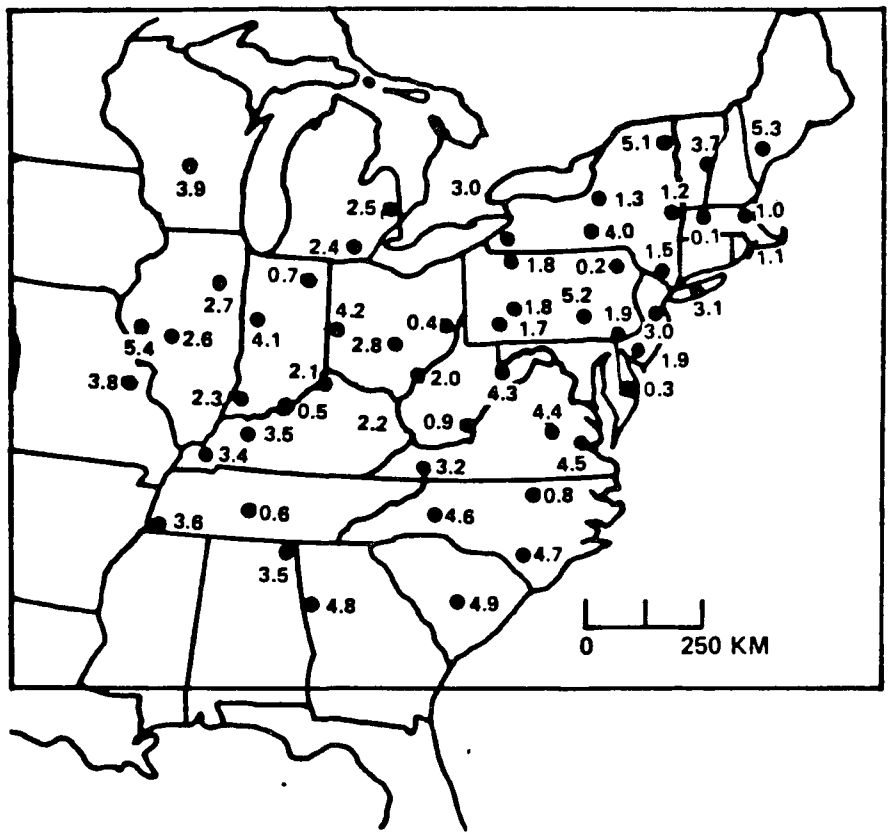



Figure 5-24. Map of SURE regions shows locations and numbers of ground measurement stations.

Source: Hidy et al. (1979).

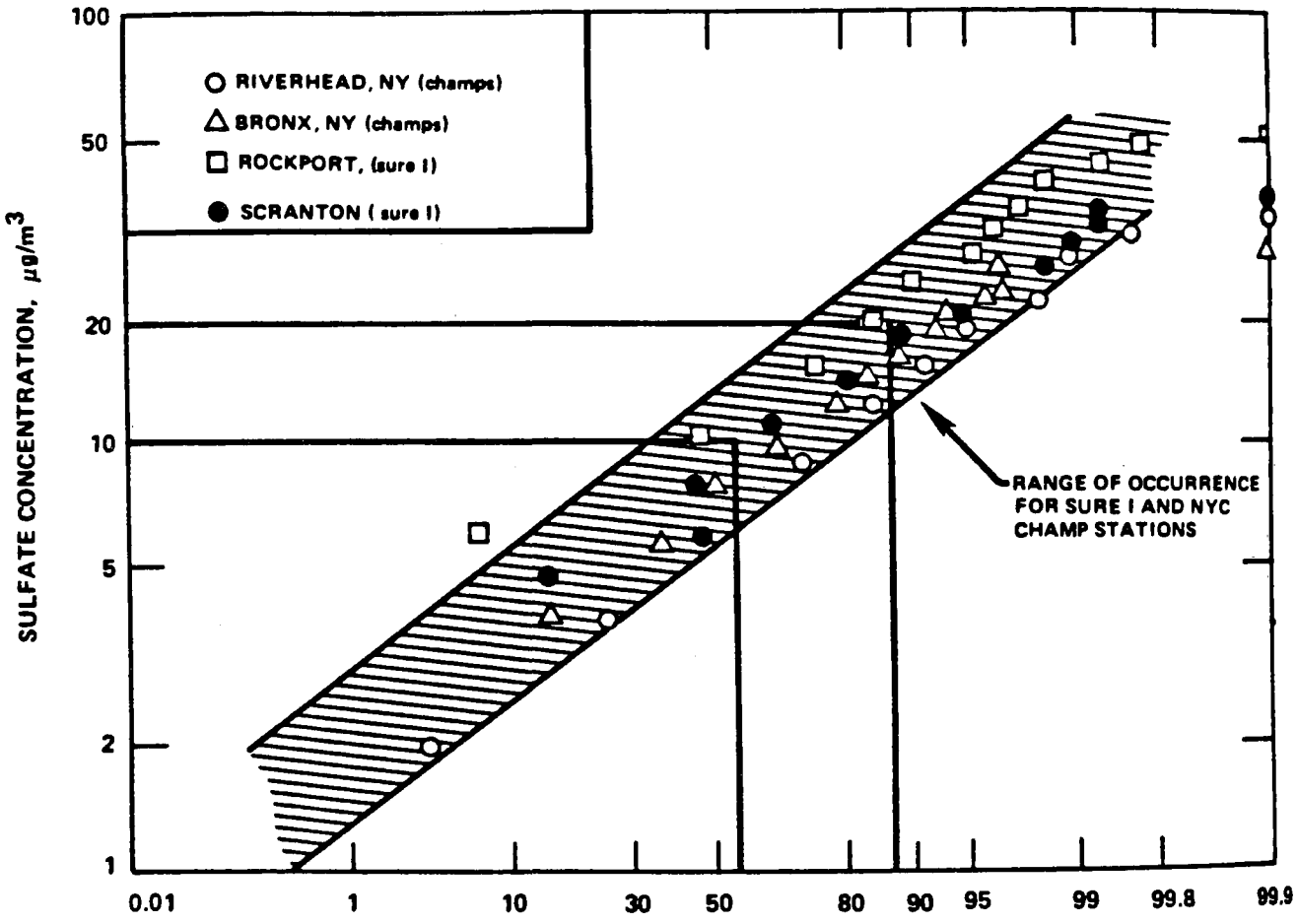



Figure 5-25. Cumulative plots show the frequency of sulfate concentrations in the SURE region on the basis of the 1974-75 historical data.

Source: Mueller et al. (1979).

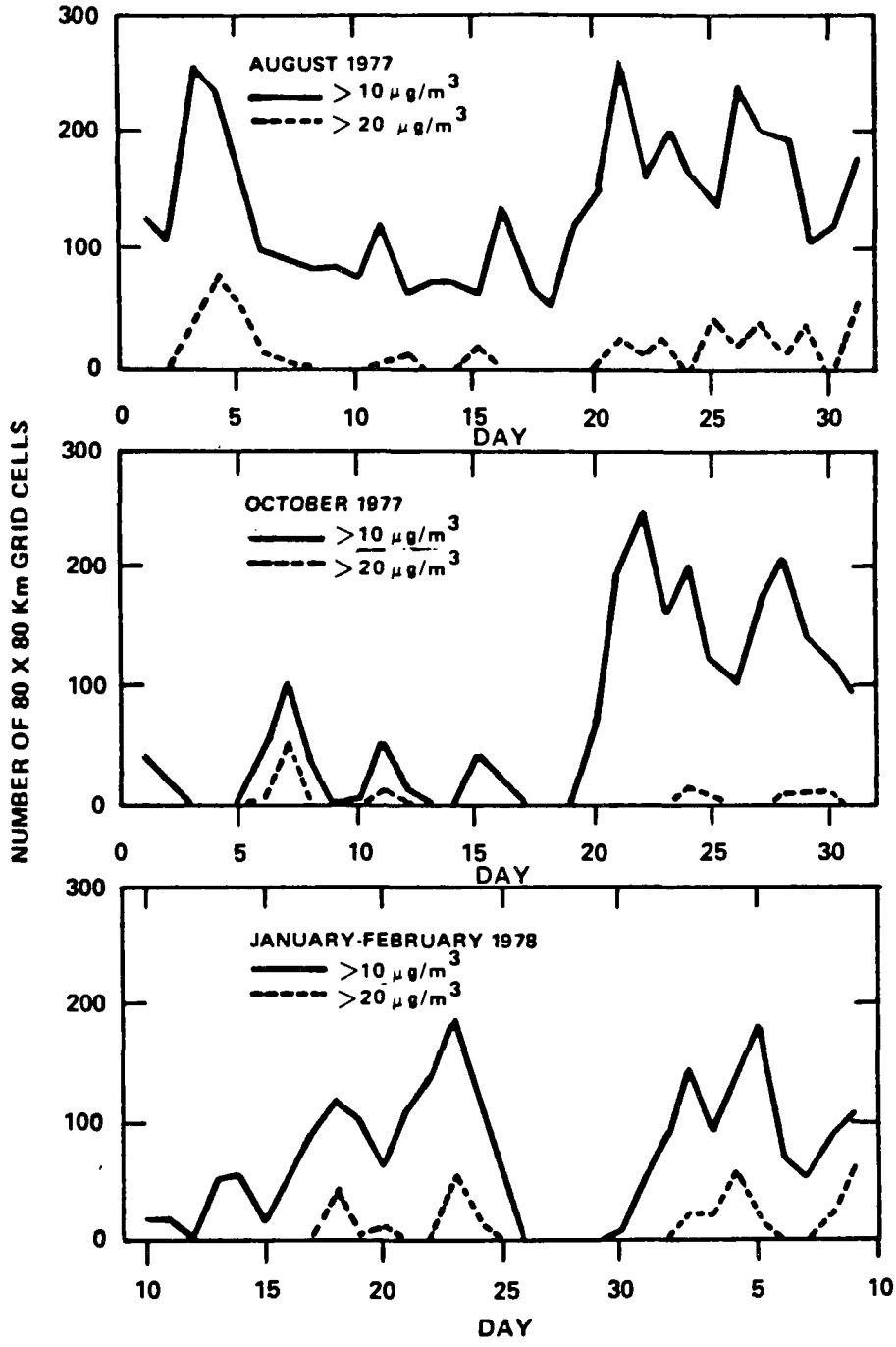


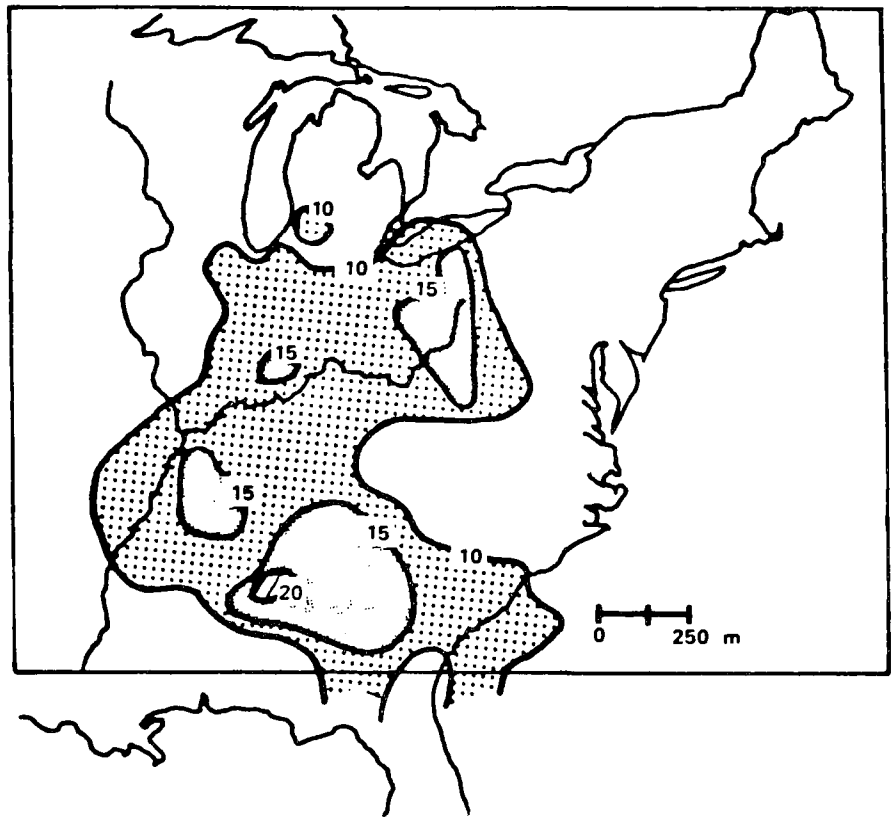

Figure 5-26. Plot shows the number of grid cells in which sulfate concentration equaled or exceeded 10 and 20 $\mu g/m^3$ for 24-hr mean in the SURE region for August 1977, October 1977, and January-February 1978. Total number of grid cells was 690.

Source: Mueller et al. (1979).

values exceeded 10 $\mu g/m^3$, and less than 1 percent of the values exceeded 20 $\mu g/m^3$. Figure 5-27 shows the estimated number of days exceeding 10 $\mu g/m^3$, for August 1977 and January-February 1978. In August, almost the entire Northeast had at least 10 days with sulfate concentrations greater than 10 $\mu g/m^3$. The area having 20 or more days with more than 10 $\mu g/m^3$ involved Ohio, West Virginia, Maryland, Pennsylvania, and New York. By contrast, in the winter months the area of prolonged elevated sulfate concentrations shifts toward the West and Southeast. The upper Ohio Valley remains high, and an increase in the number of days with more than 10 $\mu g/m^3$ also occurs over Tennessee, Alabama, and Georgia.

Studies of seasonal variations have reported elevated concentrations in the summer months (Hitchcock, 1976; Hidy, 1976). The summer monthly mean concentrations of sulfate in some regions can be twice those for the winter months. These distinct variations (Figures 5-28 and 5-29) for New York City and Los Angeles are less distinct in the Southeast and Midwest. Although biological production of hydrogen sulfide has been offered as an explanation for high summer values, more credence is now given to increased photochemical and chemical reactions.

Figure 5-30 is based an daily observations of sulfur oxides and sulfates obtained in 1974 and 1975 from stations in Indiana and Illinois eastward to Albany, NY. The data show a summer maximum in 24-hr monthly average sulfate concentrations over a distance of 1600 km (Hidy et al., 1978). All of the stations showed increased monthly mean sulfate levels during the summer months, the highest value occurring in July and centered near Wheeling, WV. For July 1975, daily values exceeding 30 $\mu g/m^3$ are quite frequent. Measurements of the 24-hr values for sulfates as high as 80 $\mu g/m^3$ have been recorded in the Wheeling, WV, area.



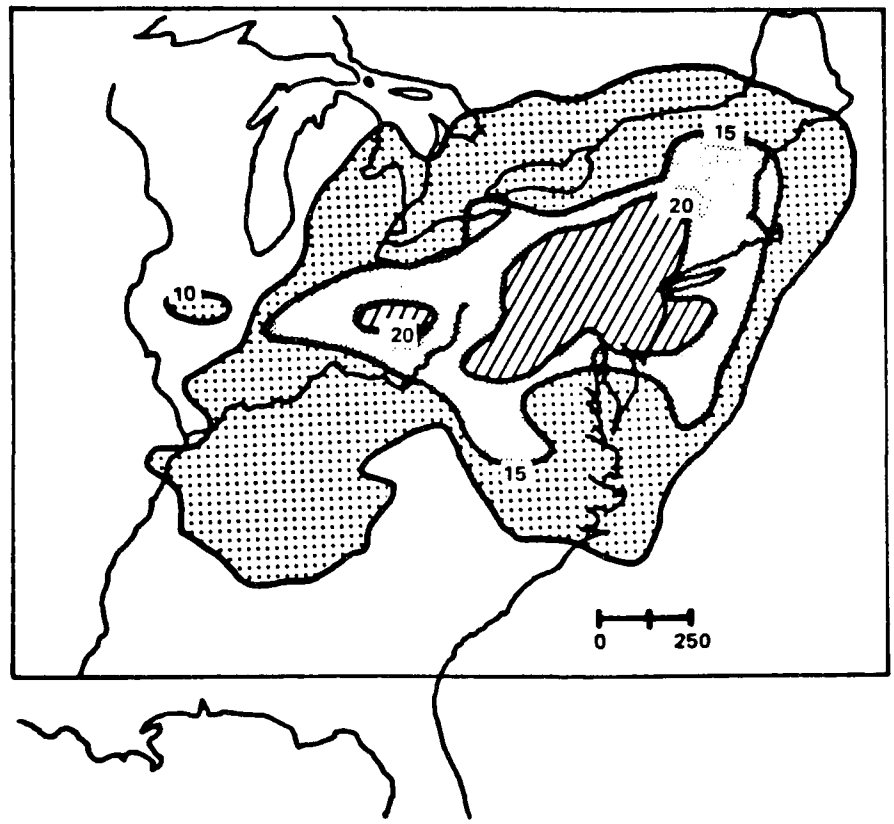




Figure 5-27. Map shows the spatial distribution of number of days per month that the sulfate concentration equaled or exceeded 10 $\mu g/m^3$. Station data were extrapolated according to $r^{-2}$. (A) January-February 1978 (31 days)? (B) August 1977 (31 days).

Source: Mueller et al. (1979).

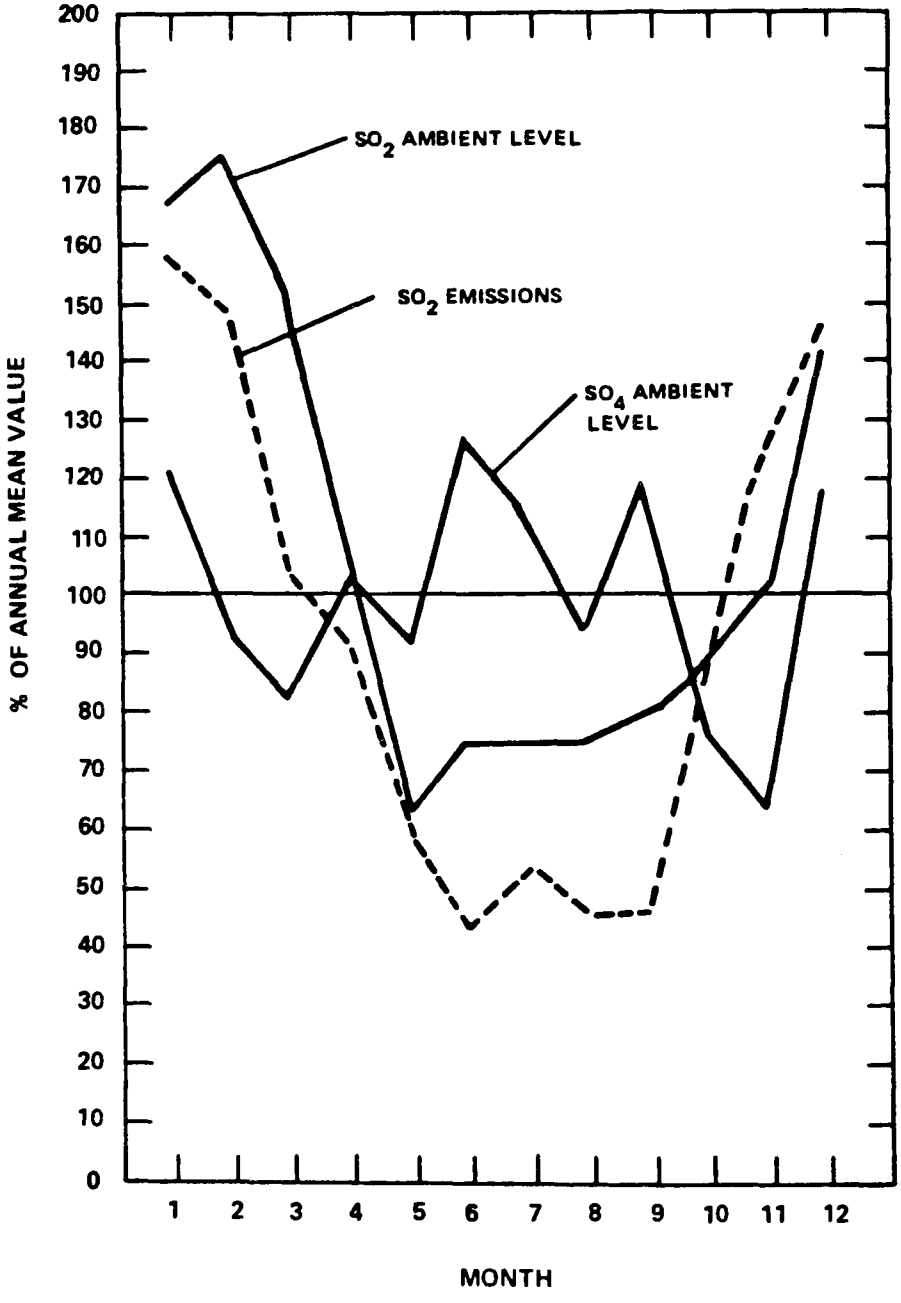



Figure 5-28. 1977 seasonal patterns of $SO_2$ emissions and 24-hr average $SO_2$ and $SO_4$ ambient levels in the New York area are normalized to the annual average values.

Source: Lynn et al. (1975).

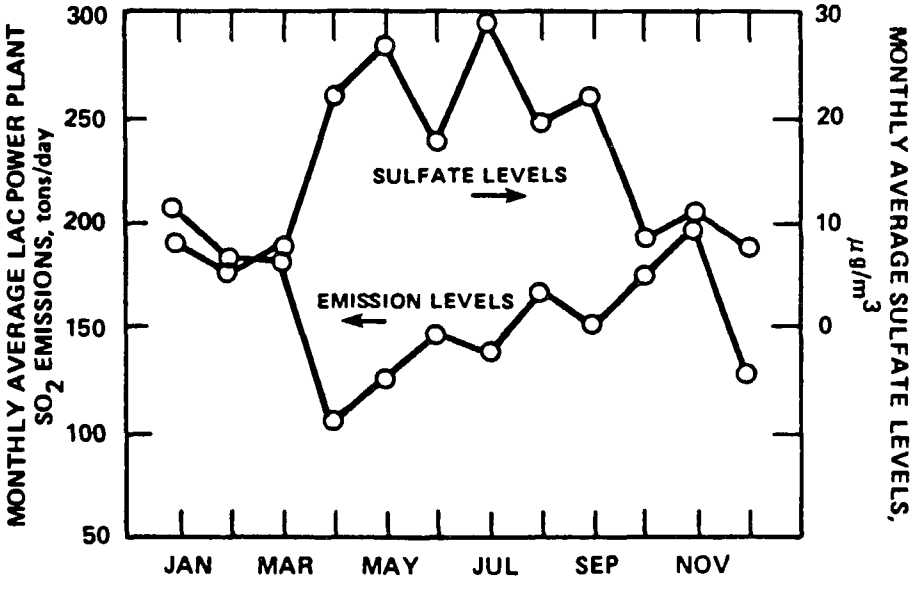



Figure 5-29. Monthly variation in monthly mean of 24-hr average sulfate concentration at downtown Los Angeles is compared with monthly mean 1973 Los Angeles County power plant $SO_2$ emissions.

Source: Mirabella (1977).

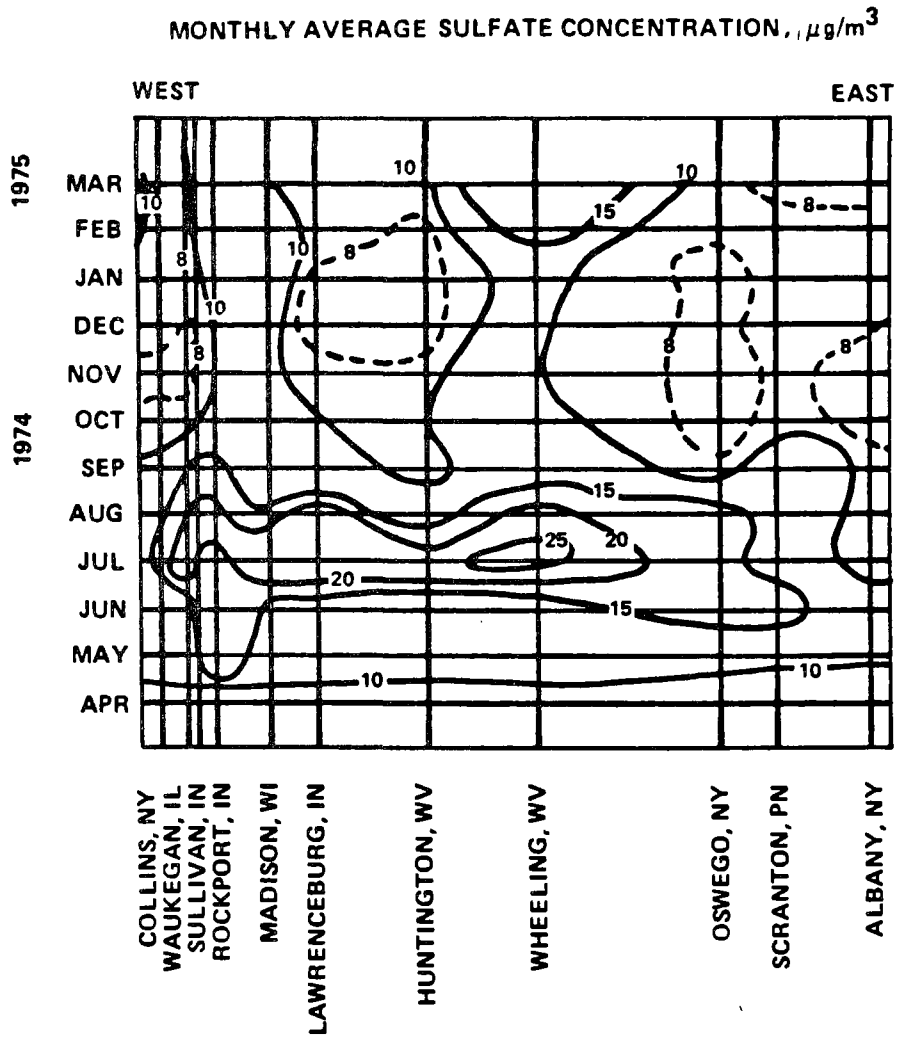



Figure 5-30. Regional and seasonal distributions of sulfate concentrations are shown for the Northeast quadrant of the United States.

Source: Hidy et al. (1976).

The seasonal differences are elucidated further in the daily time-distance plots for July 1974 and January 1975 in Figures 5-31 and 5-32. In winter, the high sulfate concentrations are localized, and generally the maximums are lower than those in summer. The winter episodes appear to last only 1 or 2 days, but the summer episodes have much greater geographical extent and seem to have durations of 1 to 5 days. Hidy et al. (1979) point out that the intense episodes may occur every 5 to 10 days on a cycle roughly equivalent to the passage of synoptic-scale high-pressure systems.

Lavery et al. (1979) postulate the existence of two meteorological conditions that result in regional accumulation of particulate sulfate concentrations above 20 $\mu g/m^3$ in the Northeastern United States:

> The first regime consists of cases where widespread stagnation occurs with a large high pressure area slowly moving eastward over the midwestern and eastern United States. Zones of polluted air collect over areas within 100-300 kilometers of high sulfur dioxide emissions sources. These zones maintain themselves over periods of one to four days in warm, moist air, with light winds, around the southern and western parts of the high pressure area. The second regime appears to be conducive to long-range (greater than 500 km) sulfate transport and involves a channeling of air flow between the west side of the Appalachian Mountains and weak cold fronts approximately oriented west-southwest to east-northeast and traveling south-eastward. The channeling appears to be combined with capped vertical mixing associated with subsidents around the frontal system. These episodes can last up to four days.

5.2.2.1.2 Urban variations. The preceding discussion of spatial and temporal variations of sulfate was derived for the most part from widely spaced rural monitoring stations. It is of interest to note spatial variations on the much smaller scale of a metropolitan area. The sulfate measured on this scale may consist of a natural background component, a long-distance transported component, a component formed locally in the atmosphere, and/or an artifact formed on the filter. Hidy et al. (1978) compare urban sulfate distributions from the previously reported works of Lynn et al. (1975) for the New York City area, and

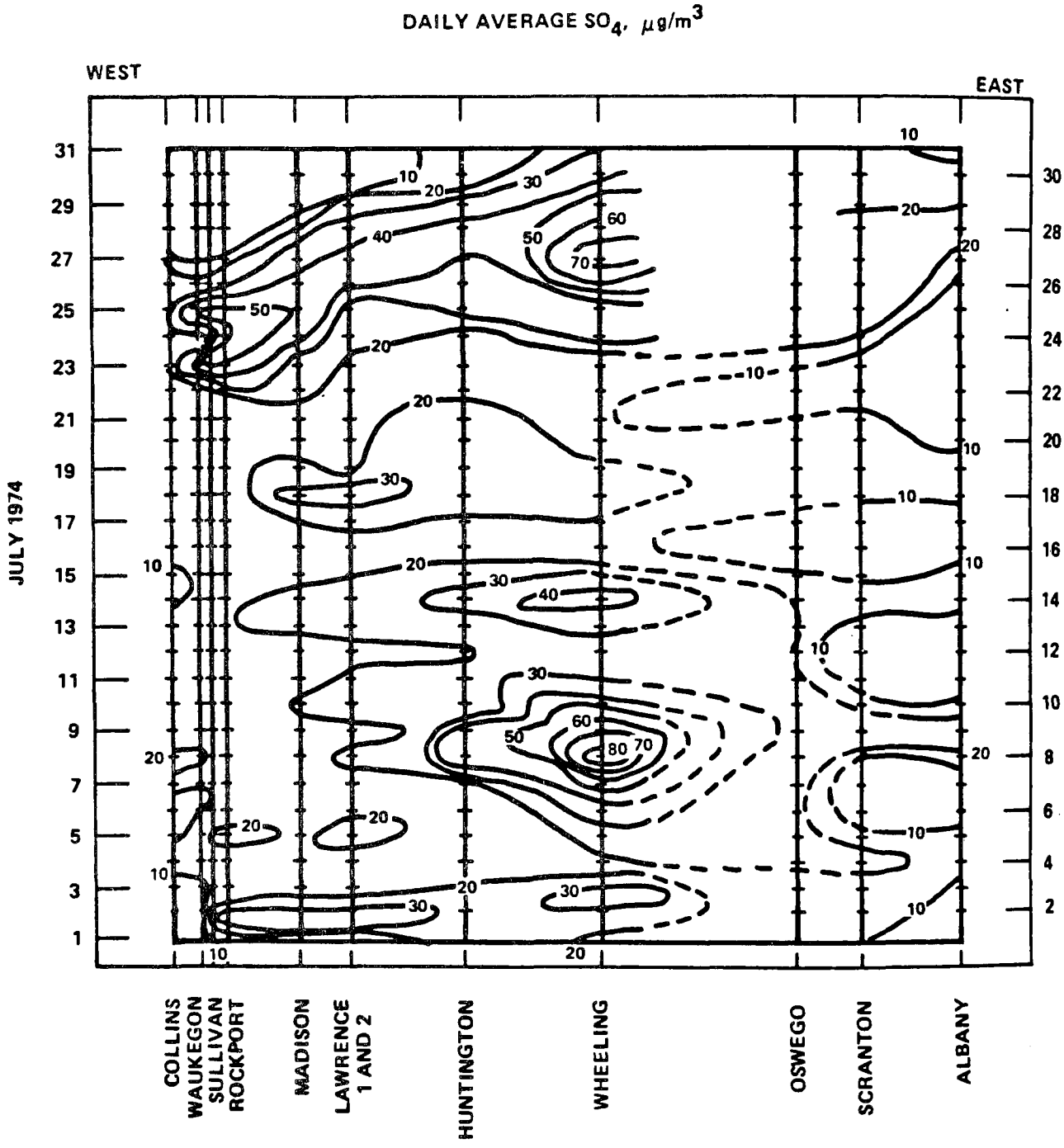



Figure 5-31. Spatial and temporal distributions of daily mean sulfate concentrations over the Northeast quadrant of the United States are shown for July 1974.

Source: Hidy et al. (1976).

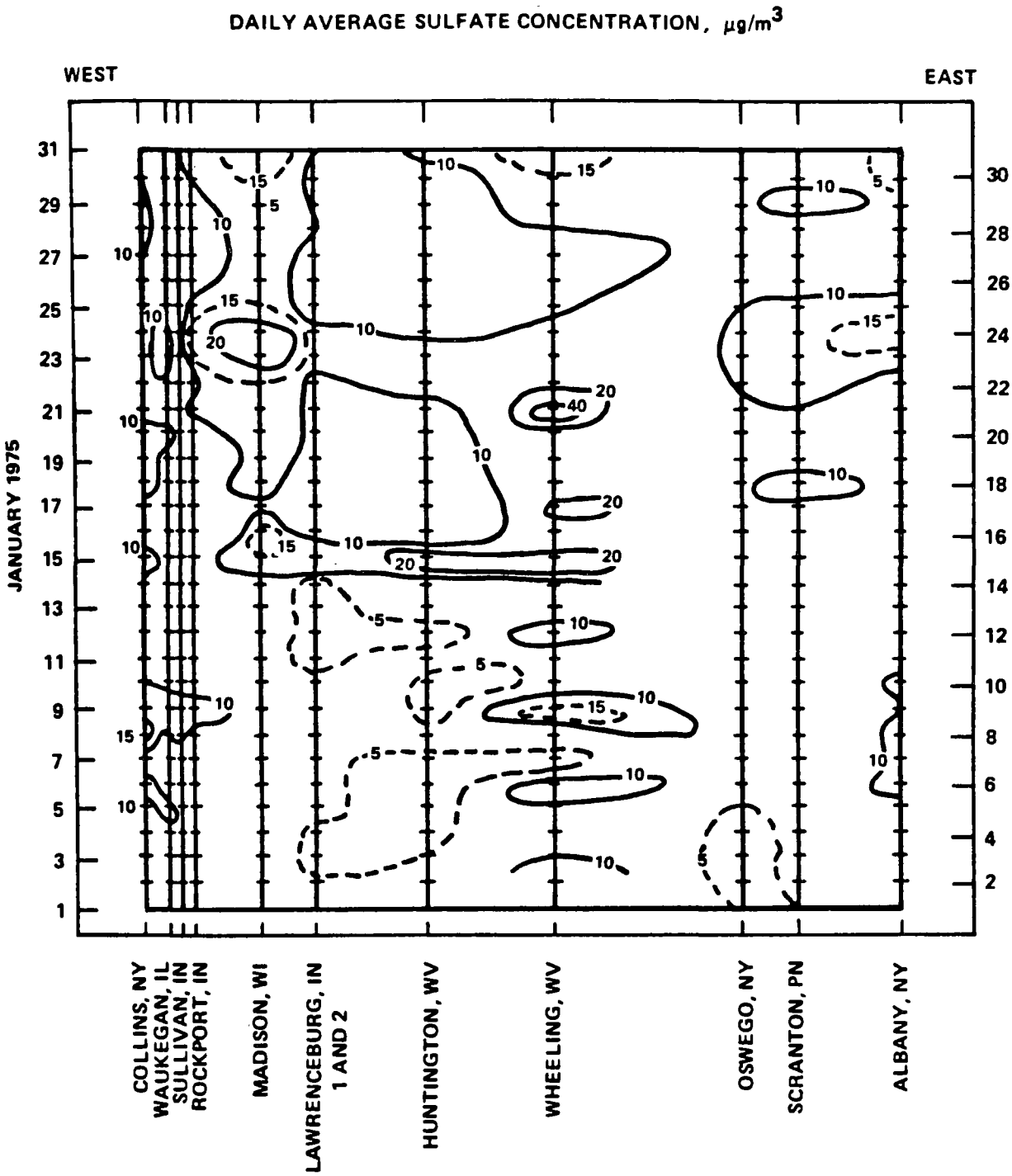



Figure 5-32. Spatial and temporal distributions of daily mean sulfate concentrations over the Northeast quadrant of the United States are shown for January 1975.

Source: Hidy et al. (1976).

Kurosaka (1976) did the same of the Los Angeles area. These areas differ in meteorology and climate, but the population and total sulfur dioxide emissions are similar.

The population density and sulfur dioxide emission densities are greater for the New York City area, however (see Table 5-17). As seen in Figure 5-33, there is a significant difference in sulfate concentrations across the New York urban area, with the highest values observed in a strip from Staten Island northeast into Brooklyn. The highest concentrations of sulfur dioxide emissions are in eastern New Jersey, Staten Island, Brooklyn, and the high-density areas of Manhattan. Within a distance of 10 to 50 km from the sources of highest concentration, the sulfate concentrations have decreased by 30 to 40 percent from their maximum values.

As shown in Figure 5-34, the mean annual average concentrations derived from 24-hr values in Los Angeles show a relatively uniform distribution across the Los Angeles basin area. A weak maximum is seen in the area near Burbank, and another maximum may occur in the San Bernardino area. The areas of major sulfur dioxide emissions are El Segundo and Long Beach areas and Fontana. A pattern similar to New York is found in the Los Angeles area; at distances exceeding 50 km from the areas of highest concentration, the sulfate levels drop off significantly.

Spengler et al. (1979) have measured respirable sulfates from a network of 10 to 12 sites in each of six cities for periods of up to 2 years. Analysis of variance shows no significant variations among sites within the cities of Topeka, KS; Portage, WI; Kingston, TN; and Watertown, MA. Some slight variations occur among the sites in St. Louis, and significant variations occur among the sites in Steubenville, OH. Only the Corondolet area of southeast St. Louis was monitored, not the entire city. There is a coke plant and a lead pigment plant

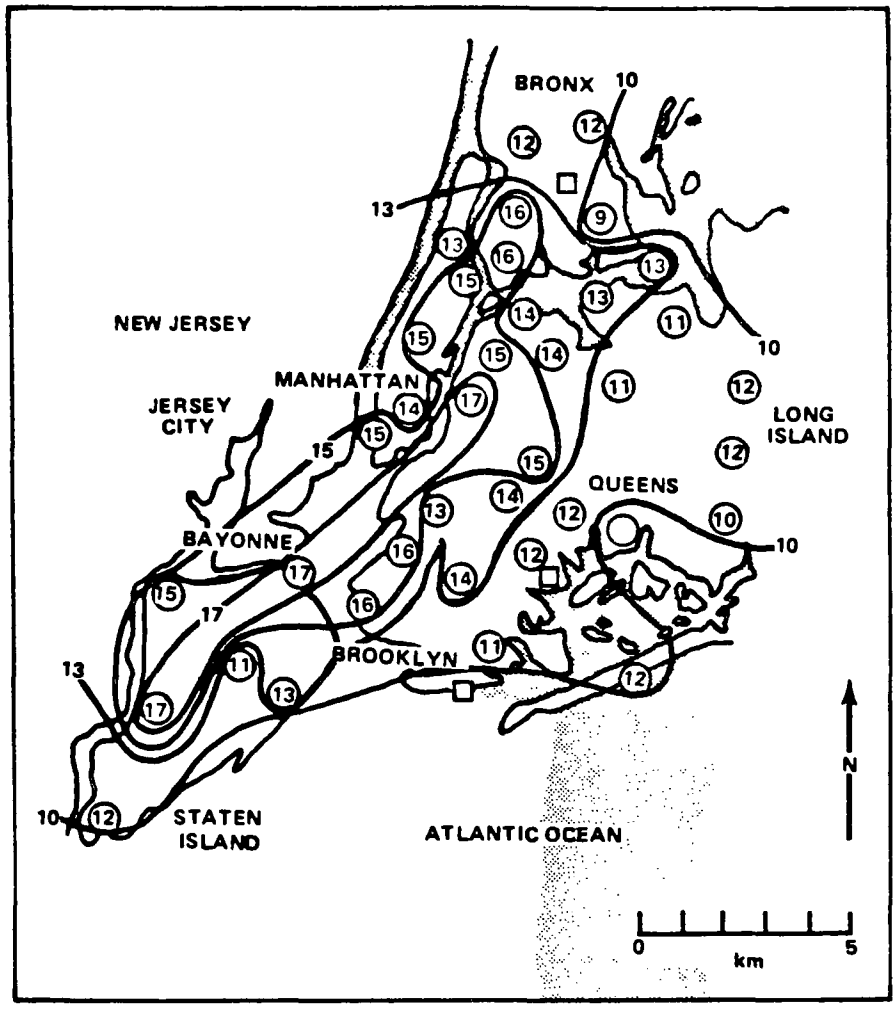



Figure 5-33. Map shows annual mean 24-hr average sulfate levels in micrograms per cubic meter in the New York area, based on 1972 data from Lynn et al. (1975). Triangles are locations of three CHAMP site stations. The fourth station is at the tip of Long Island about 160 km from Manhattan.

Source: Hidy et al. (1978).

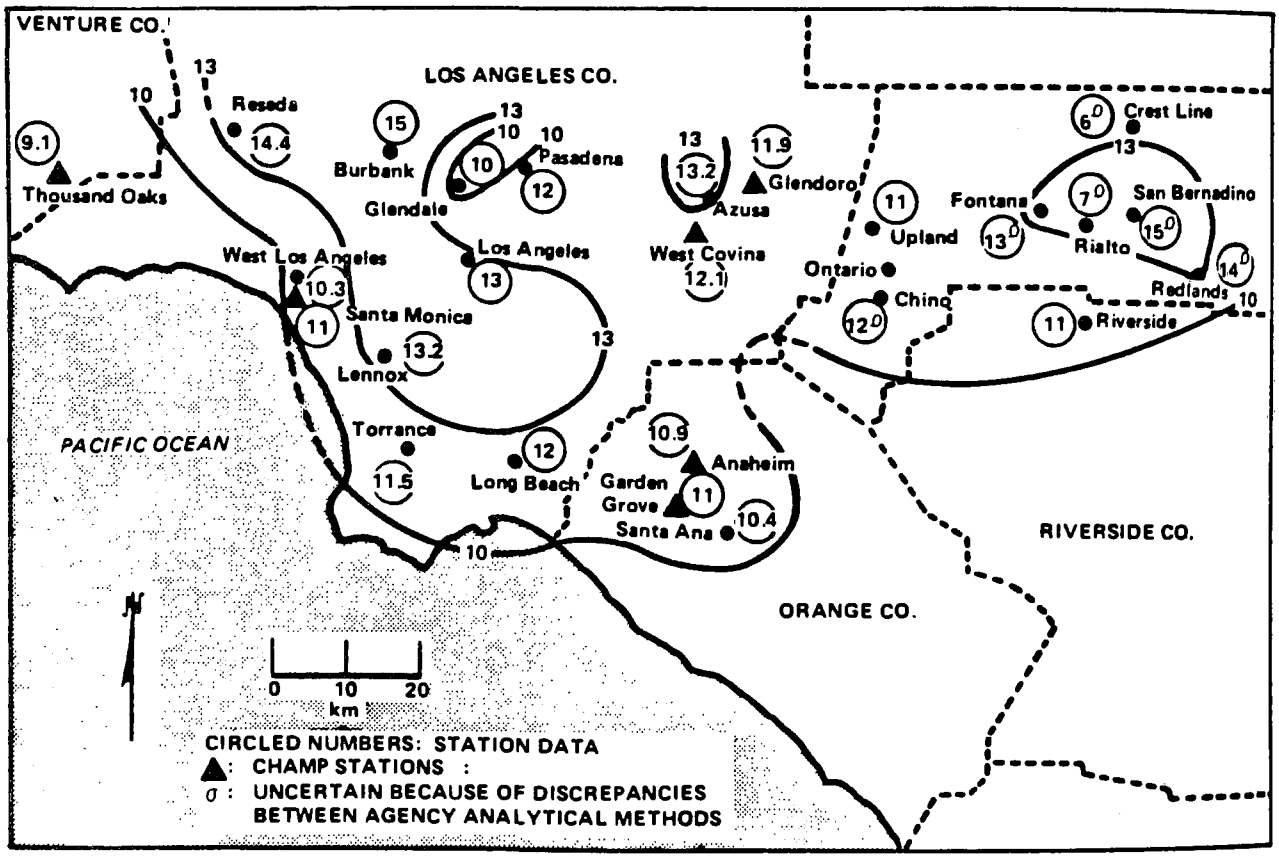



Figure 5-34. Distribution of annual average sulfate concentration in micrograms per cubic meter in the greater Los Angeles area is based on 1972-74 data.

Source: Kurosaka (1976).

TABLE 5-17. SOME CHARACTERISTICS OF POLLUTION IN THE NEW YORK AND LOS ANGELES AREAS

| Parameter | Los Angeles | New York |
|---|---|---|
| Surface area considered,[a] $km^2$ | 21,000 | 17,000 |
| Population estimate (1970)[b] | 9,000,000 | 12,000,000 |
| Population density, no./$km^2$ | 430 | 710 |
| $SO_2$ emissions, tons/yr | 238,000 | 266,000 |
| $SO_2$ emission density, kg/$km^2$/yr | 10,300 | 14,200 |
| Maximum temperature, °C[c] | 22.8 (5.5)[d] | 15.0 (7.4) |
| Minimum temperature, °C[c] | 10.8 (4.6) | 9.3 (8.4) |
| Relative humidity, %[e] | 50.2 (17.0) | 59.6 (16.5) |
| Normal precipitation, cm | 36 | 106 |
| Mean wind speed, m/sec[f] | 3.3 (1.4) | 5.8 (2.3) |
| Mixing height, m[g] | 849 (472) | 1290 (906) |
| Ventilation, $m^2$/sec | 2690 (2160) | 7460 (6200) |
| $SO_2$, μg/$m^3$ [h] | 12.5 (19.9) | 42.9 (45.0) |
| Water-soluble sulfate ($SO_4^{2-}$), μg/$m^3$ [h] | 10.1 (7.9) | 8.9 (5.7) |
| $NO_2$, μg/$m^3$ [h] | 83.9 (44.3) | 67.6 (36.0) |
| Water-soluble nitrate ($NO_3^-$), μg/$m^3$ [h] | 9.1 (7.7) | 2.6 (2.1) |
| $O_3$, μg/$m^3$ [h] | 52 (34) | 20 (22) |
| Total particulate mass concentration (TSP) less sulfate and nitrate, TSPM, μg/$m^3$ | 64.5 (27.4) | 40.4 (19.9) |

[a]Greater metropolitan areas; Los Angeles, South Coast Air Basin; New York, tri-state metropolitan area.
[b]Based on EPA Air Quality Control Regions.
[c]Annual mean of daily maximum or minimum hourly temperature.
[d]Numbers in parentheses are standard deviations.
[e]Annual mean of daily minimum humidity.
[f]Annual mean of noon wind speed at surface.
[g]Defined by annual mean of daily midday radiosonde sounding.
[h]Annual mean of 24-hr averaged values, 1974-75; Los Angeles, seven stations, New York, four stations (see Hidy et al., 1977b for details).

Source: Hidy et al. (1978).

nearby, which causes large $SO_2$ gradients and perhaps also sulfate gradients. In Steubenville, the TSP and $SO_2$ values near the river are approximately twice the concentrations 5 km to the west of the river. For respirable sulfates the pattern is similar and the gradient is not as pronounced, but the differences among sites are significant.

An attempt has been made to explain the variability in sulfate data for both the Los Angeles area and the New York City area by means of stepwise linear regression. Table 5-18 displays the three principal independent variables and the r values associated with them in explaining the variance of the daily sulfate concentrations. The results are very consistent in both areas except for Vista, CA, a community about 100 miles southeast of Los Angeles.

The results indicate that the most important variables are the 24-hr ozone level, the midday relative humidity, and the total mass concentration, minus the sulfate and nitrate fraction. Hidy et al. (1978) also suggest that these three factors are important in determining the daily variations of sulfate concentrations. The ozone or oxidant levels are an indication of photochemical oxidation, the relative humidity is an indication of water content of the air mass, and TSP is an indication of reactions involving particulate matter.

The local sulfur dioxide concentrations did not enter into the correlation sequence as one of the three principal variables. The findings of Spengler et al. (1979) appear quite consistent with these findings since the only city with a significant spatial variation among sites for sulfates also had a variation among sites for the respirable particles and TSP.

5.2.2.2. Ambient Nitrate Aerosols--Nitrate aerosols make up a varying amount of the total suspended particulate matter. Although widely reported to be signifi-

TABLE 5-18. PRIMARY RANKING OF VARIABLES FOR CORRELATING AIRBORNE SULFATE IN TWO CITIES BASED ON A STEPWISE LINEAR REGRESSION OF 15 VARIABLES FROM CHAMP AND RELATED MONITORING STATIONS

A. Los Angeles area

| | Anaheim | Garden Grove | West Covina | Glendora | Santa Monica | Thousand Oaks | Vista[a] |
|---|---|---|---|---|---|---|---|
| Variable | | | | | | | |
| 1 | $O_3$ | $O_3$ | $O_3$ | TSPM | $O_3$ | TSPM | $T_{min}$ |
| 2 | TSPM | TSPM | TSPM | RH[b] | RH | RH | $O_x$ |
| 3 | RH | RH | RH | $O_3$ | TSPM | $O_x$ | RH |
| Correlation coefficient (R) | 0.71 | 0.77 | 0.79 | 0.79 | 0.79 | 0.72 | 0.56 |

B. New York

| | Brooklyn | Queens | Bronx | Riverhead, L.I. |
|---|---|---|---|---|
| Variable | | | | |
| 1 | TSPM | TSPM | TSPM | TSPM |
| 2 | RH | RH | $O_3$ | RH |
| 3 | $O_3$ | $O_3$ | RH | $O_3$ |
| Correlation coefficent (R) | 0.60 | 0.63 | 0.54 | 0.62 |

[a]Located 50 km north of San Diego and 16 km inland from the coast.
[b]RH, Relative humidity.
[c]OX, 1-hr daily maximum ozone value.

Source: Hidy et al. (1978).

cantly less than the sulfate fraction, nitrates nevertheless represent an important constituent. Most nitrates in the atmosphere are formed in gas-to-aerosol reactions, principally involving nitrogen dioxide and nitric oxide. These reactions may yield nitric acid (gas or aerosols), ammonium nitrate, sodium nitrate, and lesser amounts of other compounds. A minor fraction of the nitrate aerosols measured in the atmosphere can be attributed to wind erosion of soil and resuspension of fertilizers (National Research Council, 1978). These sources may be more important locally near fertilizer plants or transfer facilities, as well as munition factories. A study in Chattanooga dramatizes the influence of local sources (Helms et al., 1970; National Research Council, 1977). The average nitrate concentration from a site close to the Volunteer Army Ammunition Plant was 48.9 $\mu g/m^3$. This is more than three times the NASN maximum station average for 1965 (13.5 $\mu g/m^3$). This station average was 15 to 20 times higher than that of the four other Chattanooga sites presumably not influenced directly by the munitions plant. Their averages ranged from 2.4 to 3.8 $\mu g/m^3$.

Accurate measurement of nitrates has been difficult (EPRI, 1979). Much of the historic data is of uncertain quality because of the formation of "particulate" nitrate on glass fiber filters. Spicer (1976) found that the concentration of nitrate "aerosols" was 3 to 10 times higher on glass fiber high-volume filters than on quartz fiber filters. Quartz filters are neutral and are thought to collect only particulate nitrates, but glass fiber filters contain basic sites and impurities that apparently extract at least some nitric acid vapor, increasing "particulate" nitrate readings. For several years the NASN stations operated by EPA have been analyzing the nitrate ion from high-volume samples. Again, because these samplers used glass fiber filters for collection, some of the historic data may overestimate the nitrate concentrations because

of absorption of nitric acid. The reader is referred to Table 5-14 of the National Research Council's study of nitrogen oxides (1977). This table presents the annual mean and maximum concentrations of nitrate ion for 92 NASN sites from 1958 through 1970.

The annual mean nitrate aerosol concentrations from 55 urban and 17 non-urban NASN sites is summarized in Figure 5-35. Concentrations in urban air are substantially higher than those in nonurban air. Although year-to-year variations are substantial, both urban and nonurban averages show upward trends. These trends are consistent with the increase in emissions of nitrogen dioxide.

These measurements are limited in that the analytical methods for aerosol nitrate analysis do not differentiate among particles containing neutral ammonium nitrate, sodium nitrate, and nitric acid. It is therefore impossible to estimate the relative quantities of neutral and acid nitrates in the aerosol.

The spatial distributions of nitrate ions are shown in Figure 5-36 for mostly urban sites and in Figure 5-37 for nonurban sites. The annual average concentrations are in micrograms per cubic meter, as measured from high-volume samples. A zone of high urban concentrations exceeding 4 $\mu g/m^3$ extends eastward from Chicago through the industrialized Northeast through Pennsylvania to the Philadelphia area. Other zones of high nitrates are found in southern Louisiana, around Birmingham, AL, and near Little Rock, AR. In general, a zone of high urban nitrates 3 $\mu g/m^3$ and larger extends up from southeastern Texas through the Midwest and across through the Northeast.

It is obvious from this display that the data base is quite incomplete for the west coast. No data are reported for the Los Angeles area, nor for the large metropolitan areas of San Francisco, Seattle, and Portland. The areas of high nitrate are similar to the areas of high nitrogen dioxide emissions (Figure 5-38). Areas of localized nitrogen dioxide emission from automobiles, electric

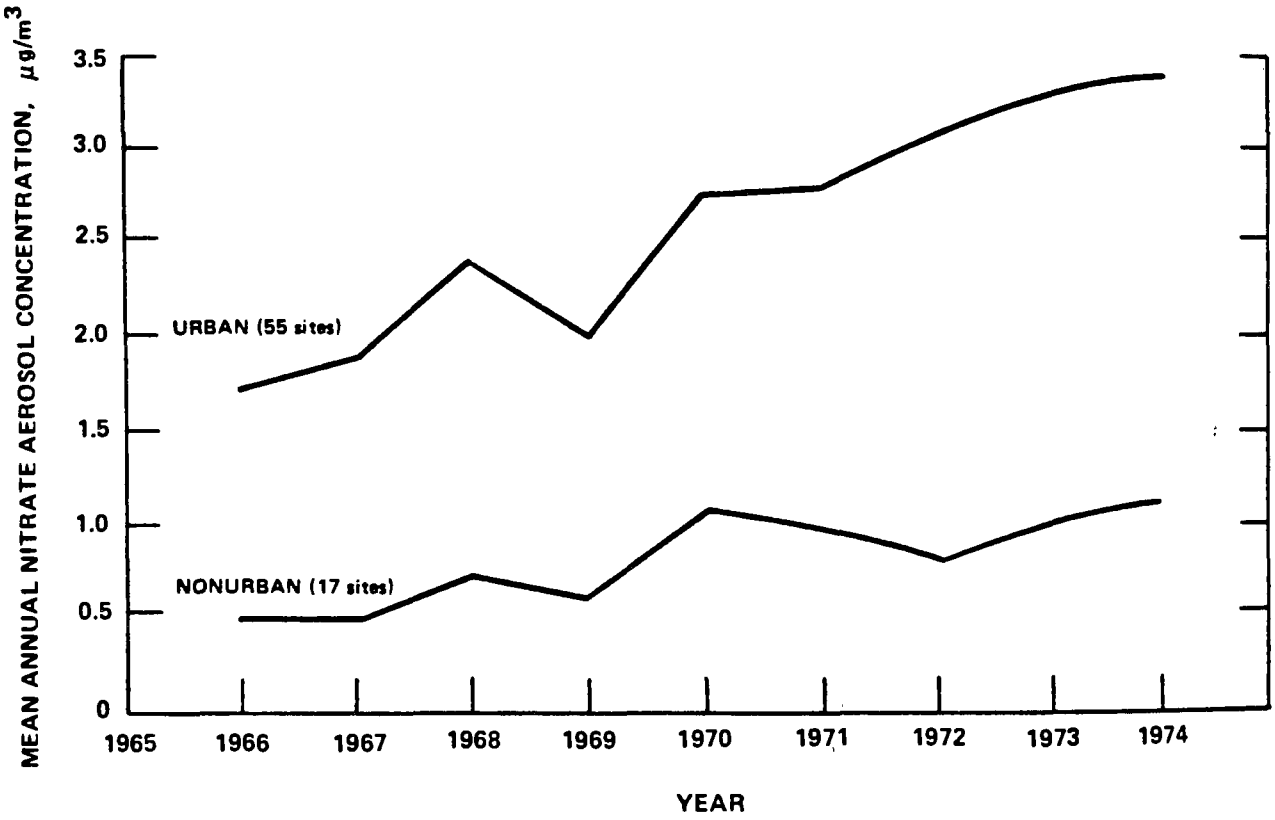



Figure 5-35. Mean annual nitrate aerosol concentrations in urban and nonurban air were obtained by the National Air Surveillance Network.

Source: Data from up to 1970 are from U.S. Environmental Protection Agency (1974). Data for 1971-74 are from Akland (1977).

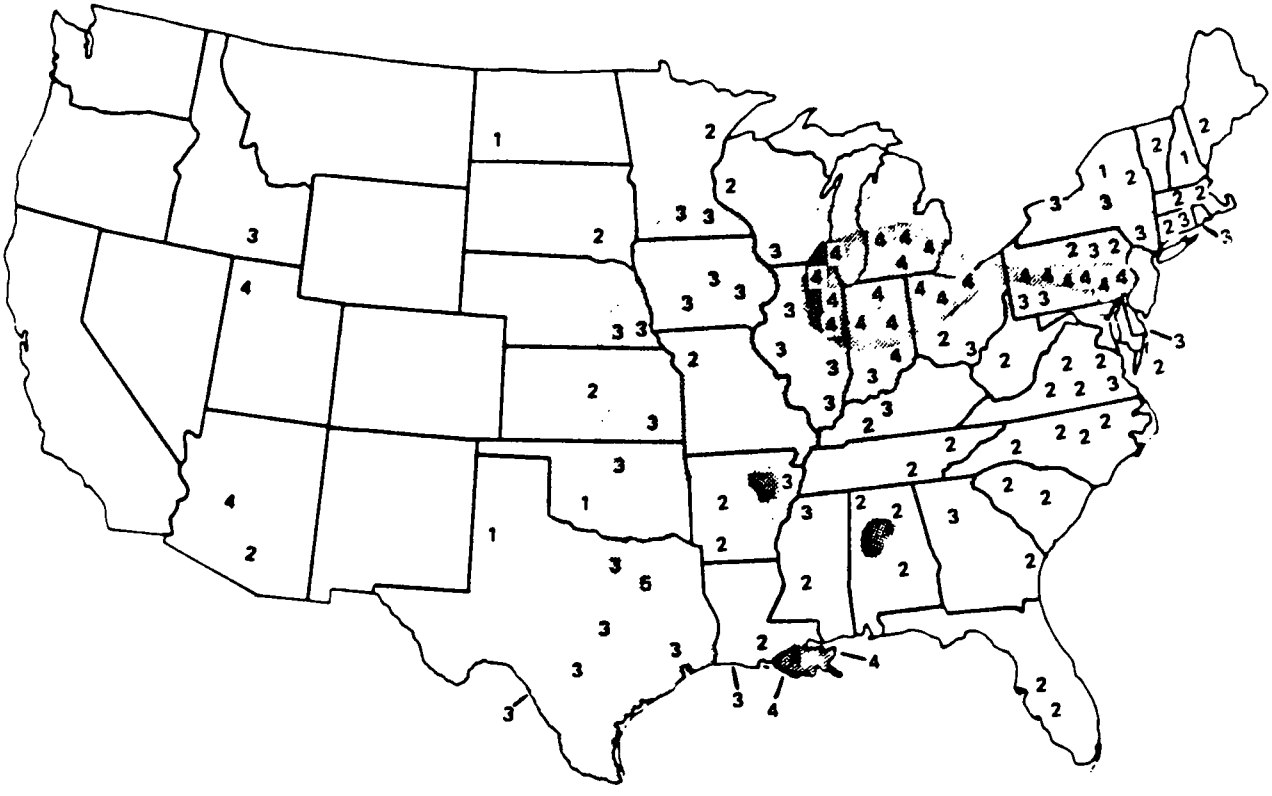


Figure 5-36. Map shows U.S. mean annual ambient nitrate levels in micrograms per cubic meter.

Source: Akland (1977).

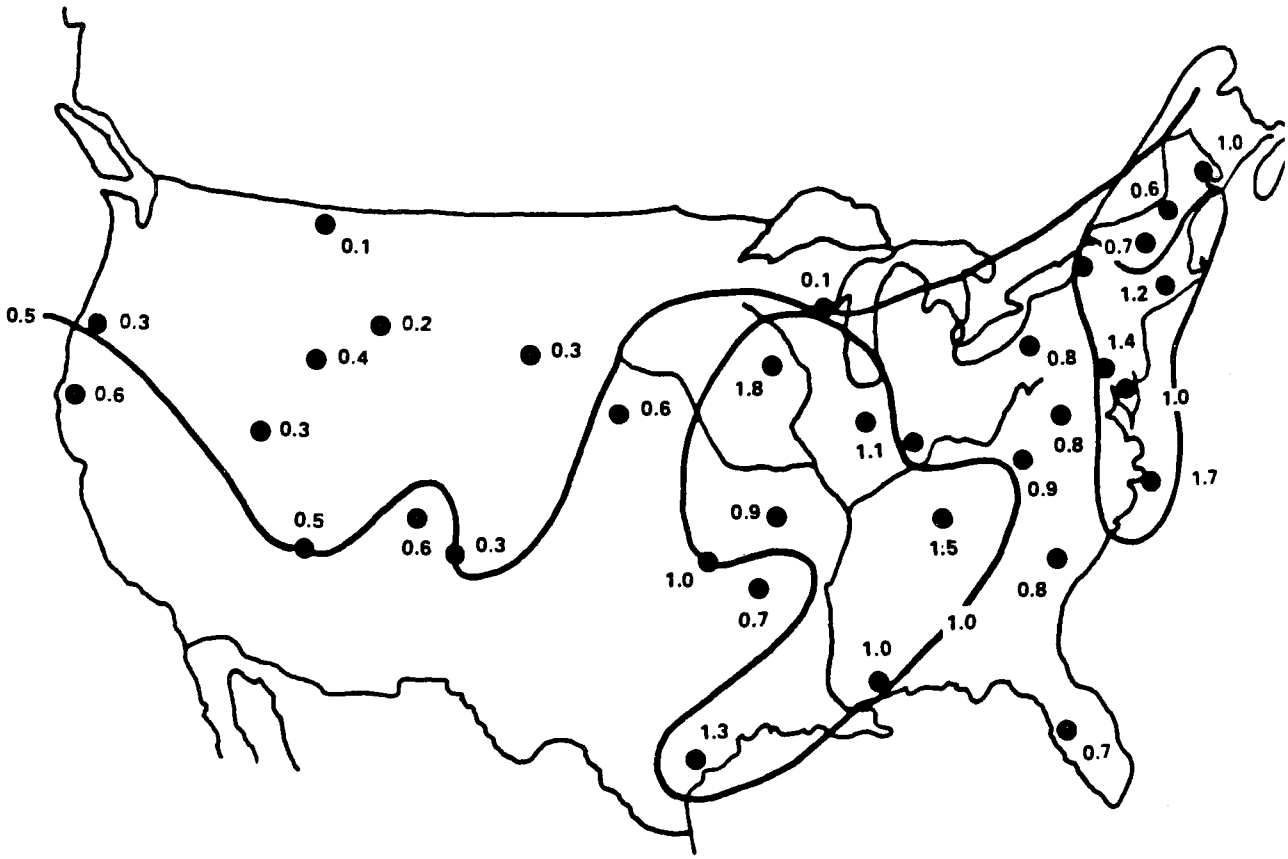



Figure 5-37. Mean nitrate concentrations in micrograms per cubic meter were measured at nonurban sites by the U.S. Environmental Protection Agency (unpublished data).

Source: National Research Council (1979).

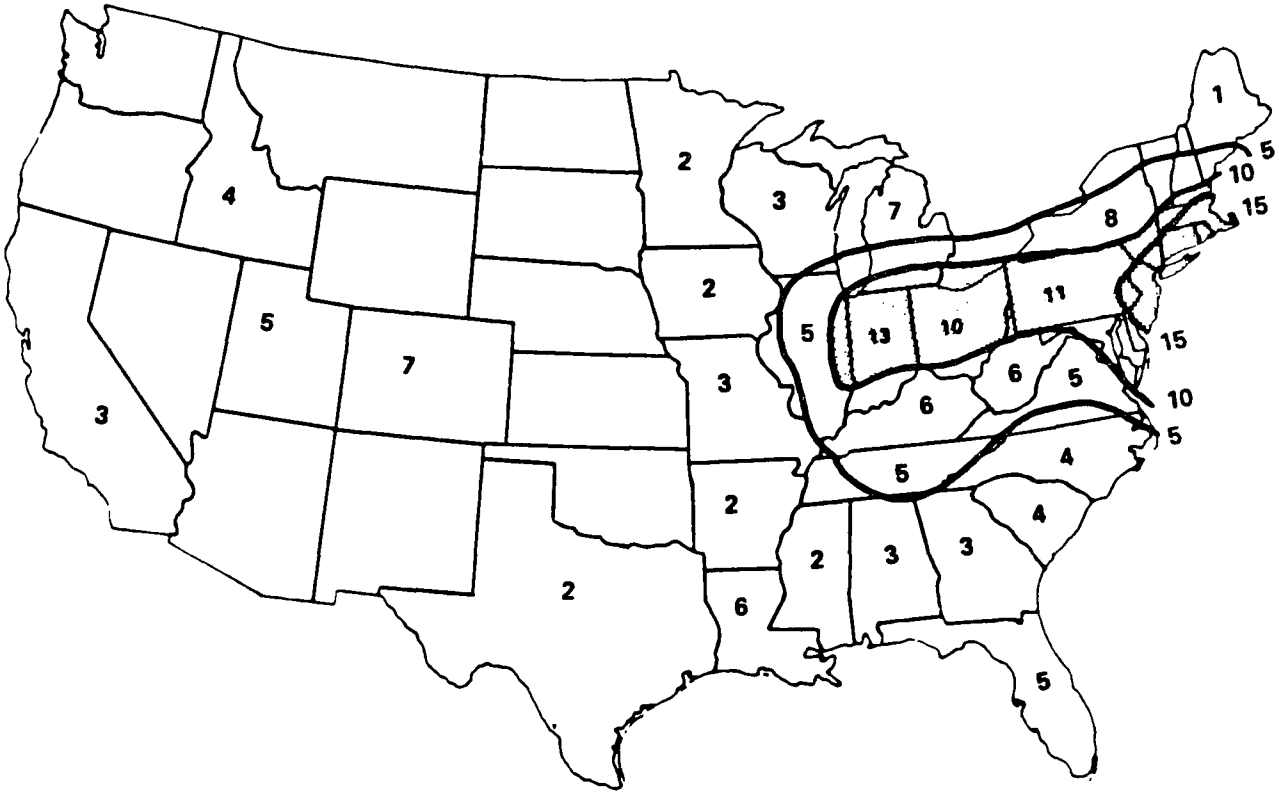



Figure 5-38. Map shows U.S. ambient emission densities for nitrogen dioxide in grams per square meter per year.

Source: Akland (1977).

utilities, and petroleum refineries might be expected to have elevated nitrate concentrations.

A few studies have sought information on nitrate concentrations by composition and particle size. Orell and Seinfeld (1977) compared the formation, sizes, and concentrations of ambient sulfate and nitrate particles. Unlike sulfuric acid, the nitric acid that is formed tends to remain in the gaseous phase, although it may be an important component of acid precipitation. The EPRI SURE Project (1979) reports nitrate ion concentrations one-tenth the concentration of sulfate ions. The monthly mean values for August and October 1977 are less than 0.6 $\mu g/m^3$ ammonium nitrate at three locations across the Northeast (see Figure 5-39). On a few occasions the daily levels exceded 1.5 $\mu g/m^3$.

Data from the sulfate and nitrate data base of the California Aerosol Characterization Experiment are reported by Appel et al. (1978). Summer measurements for 1972 and 1973 from five fixed and one mobile site indicate that the mass mean diameter for nitrates is between 0.3 and 1.6 $\mu m$.

Twenty-four-hour averaged concentrations of nitrate ion varied across the Los Angeles basin, increasing to 15 to 30 $\mu g/m^3$ in the eastern communities of Rubidoux and Riverside. Table 5-19 shows the averaged values from high-volume sampling for different times during 1972-73. The values do not reflect the annual concentrations; in fact, the highest concentrations are now in doubt because of an artifact involving the filters. The authors do report 1968 NASN data in the South Coast Basin as corroborating evidence of high nitrate ion concentrations and spatial variations (see Table 5-20). In contrast to sulfate, the diurnal pattern for nitrate often has a maximum during the morning close to the maximum for gas-phase nitrogen oxides. They concluded that the ratios of

TABLE 5-19. AEROSOL CHARACTERIZATION EXPERIMENT DATA FOR NITRATE AND SULFATE IN THE CALIFORNIA SOUTH COAST BASIN 1972-73 (24-h average values)[a]

| Sampling location | No. episodes | $NO_3^-$ | | $SO_4^{2-}$ | |
|---|---|---|---|---|---|
| | | μg/m$^3$ | % of mass | μg/m$^3$ | % of mass |
| Dominguez Hills | 2 | 4.1 | 3.1 | 17.8 | 13.6 |
| Harbor Freeway | 2 | 6.3 | 5.6 | 5.7 | 5.1 |
| Pasadena | 6 | 6.5 | 9.0 | 7.0 | 9.7 |
| West Covina | 5 | 8.2 | 4.5 | 21.8 | 12.0 |
| Pomona (1972) | 5 | 19.8 | 14.6 | 9.6 | 7.1 |
| Pomona (1973) | 2 | 7.9 | 4.8 | 11.5 | 7.0 |
| Rubidoux | 3 | 31.5 | 12.5 | 10.7 | 4.2 |
| Riverside | 9 | 15.2 | 13.4 | 7.7 | 6.8 |

[a]Analysis of high-volume samples collecter on Whatman 41 filters during July-October periods.

Source: Appel et al. (1978).

TABLE 5-20. NASN NETWORK DATA FOR NITRATE AND SULFATE IN THE CALIFORNIA SOUTH COAST BASIN FOR 1968 (annual 24-h average values)[a]

| Sampling location | $No^3$ | | $SO_4^{2-}$ | |
|---|---|---|---|---|
| | $\mu g/m^3$ | % of mass | $\mu g/m^3$ | % of |
| Long Beach | 5.7 | 5.0 | 12.7 | 11.1 |
| Los Angeles | 7.7 | 6.0 | 10.2 | 7.9 |
| Ontario | 9.1 | 7.9 | 9.0 | 7.8 |
| Riverside | 10.2 | 8.8 | 8.3 | 7.2 |

[a]Data based on geometric mean of 26 24-h sampling periods.

Source: U.S. Environmental Protection Agency (1972).

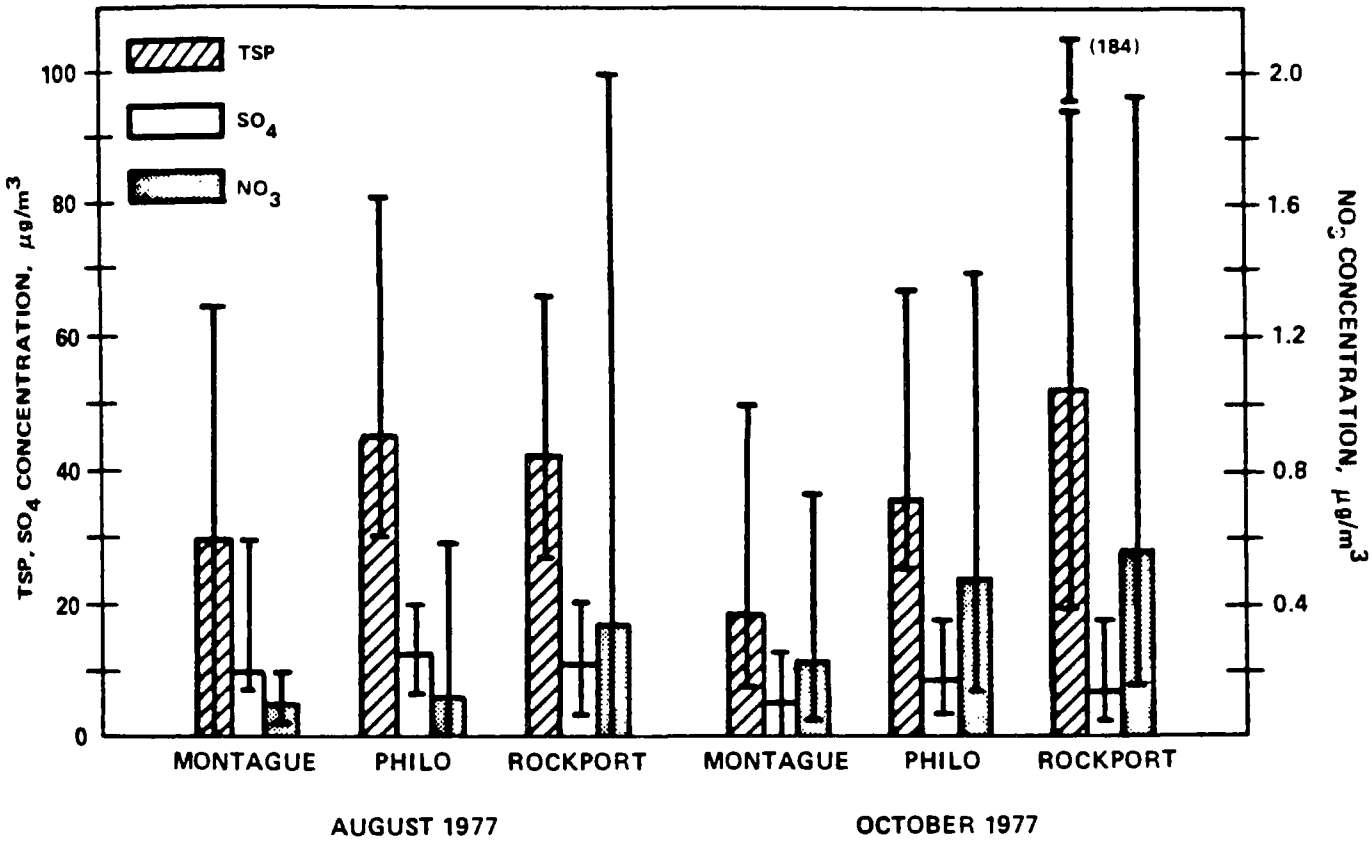



Figure 5-39. Histogram shows monthly mean and extremes of 24-hr particle concentrations for August and October 1977 at three sites in the SURE region.

Source: Hidy et al. (1979).

ionic constituents and ambient ammonia levels suggested that ammonium salts were the principal form of sulfate and nitrate.

Until recently such high nitrate levels were not suspected in other regions of the United States. However, the Environmental Protection Agency has just completed the first analysis from a dichotomous particle sampling program in Denver, CO. The 24-hr nitrate levels, primarily in the fine fraction, often exceeded 10 $\mu g/m^3$ (Stevens, 1979).

Japanese workers have been investigating atmospheric nitrates for some time. Kadawaki (1977) has found a bimodal distribution of nitrates in the Ngoya area of Japan. The submicron particles (0.4 to 0.6 $\mu m$ in diameter) are ammonium nitrate, and the course particles (3 to 5 $\mu m$ in diameter) are sodium nitrate. Background nonurban levels on the outer islands of Japan have been reported as low as 0.8 to 0.9 $\mu g/m^3$ (Kito, 1977). Much higher concentrations were reported in the city of Kawasaki, as high as maximum average concentrations of almost 7 $\mu g/m^3$ (Terabe, 1977).

In summary, our knowledge of nitrates in the atmosphere is rather limited. No comprehensive data set exists. The NASN measures nitrate ion every 12th day at relatively few sites; spatial and short-term temporal variations cannot be discerned. In fact, many cities have no measured values of nitrates reported. Furthermore, historic data before 1977 are in doubt because of the artifact formation on the filters. It is now believed that most of the aerosol nitrate is in the form of ammonium nitrate. There is some evidence that ammonium nitrate is in the fine fraction, while the artifact is predominantly in the coarse fraction. There are spatial patterns in nitrate concentrations. Cities tend to have higher levels of nitrates than do rural regions. Both the Chattanooga study and the Los Angeles study indicate that localized areas may have substantially higher nitrate levels. High average levels (>10 $\mu g/m^3$) of nitrates

found in Denver raise the concern that available data on nitrate concentrations may underestimate the actual population exposure. In the near future, new sampling and analysis techniques should substantially expand our knowledge of nitrate aerosols, nitric acid, and other nitrogen compounds.

5.2.2.3 Airborne Organic Particulate Matter--This section will be included in later draft.

### 5.2.3 Ambient Sulfur Dixoide Concentrations

Ambient concentrations of sulfur dioxide are determined by the following factors: (1) the density of emissions sources; (2) the source characteristics such as stack height, exit velocity, and source strength (3) the local meteorological conditions (4) the local topography and surrounding buildings (5) the reaction rate of sulfur dioxide in the plume, and (6) the removal rates by precipitation, deposition at the surface, and other reactions. These factors interact in such a way that in urban and industrialized areas with high densities of $SO_2$ emissions, the $SO_2$ emissions, the $SO_2$ concentrations are much higher than in surrounding rural areas. It is quite common to find gradients in $SO_2$ concentration within these industrialized and areas, with a central core area reporting the highest $SO_2$ concentrations. This pattern is shown diagrammatically in Figure 5-40.

Where $SO_2$ emissions are dominated by a single or a few point sources, the pattern of $SO_2$ concentrations could be different from the pattern displayed in Figure 5-40. Depending on topography, meteorology, and source characteristics, the concentration patterns may be asymmetrical and the temporal distribution may be skewed to low mean values with a few intermittent high peaks. These differences in concentration patterns may be important to the effects experienced in exposed human populations.

It will be shown in this section that significant progress has been made toward meeting the primary NAAQS for $SO_2$. By 1978 there remained only a few AQCRS with daily $SO_2$ levels above 365 $\mu g/m^3$, or annual averages above 80 $\mu g/m^3$. Most urban areas experienced dramatic improvements in air quality as a result of: (1) restrictions on sulfur in fuel (2) better controls on existing sources; (3) displacement of sources and the building of new sources in less populated regions; and (4) the building of taller stacks.

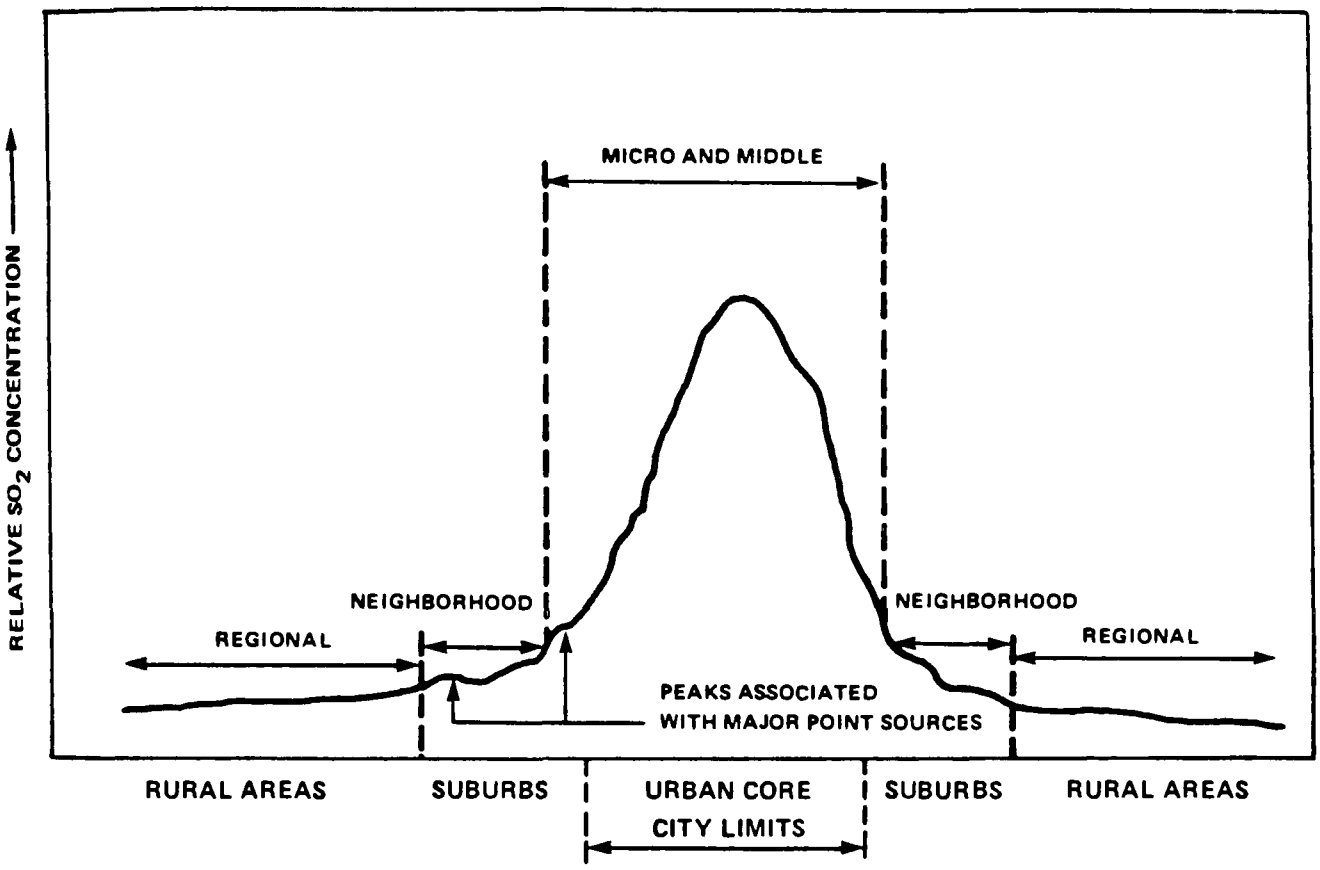



Figure 5-40. Relative locations for sites measuring concentrations represent several spatial scales of measurement in an urban complex, with respect to annual averaging times.

This section presents $SO_2$ concentration data for specific locations and areas where levels are currently high. The national status of $SO_2$ concentrations is reviewed, along with trends data. A comparison is made between $SO_2$ levels in six cities in the early 1960's and the concentration in the late 1970's. Insights on factors that are important determinants of population exposures are presented in the discussion of diurnal and seasonal $SO_2$ concentration patterns. Since $SO_2$ can be measured by a variety of methods (see chapter 3), a brief discussion of $SO_2$ monitoring and instruments precedes the substantive sections on concentrations.

5.2.3.1 Sulfur Dioxide Monitoring--The Environmental Protection Agency is now in the process of revising Federal, State, and local air monitoring networks. By 1981, States will be operating a selected number of sites in the National Air Monitoring Station (NAMS) Network. These sites are to be located in the areas of highest pollution concentrations and areas of high population density. They are designed to serve in assessing the trends and progress in meeting standards. By 1983, the State and local agencies are to be operating the State and Local Air Monitoring Station (SLAMS) Network. This network is designed to be part of each State's implementation plan. It is expected that this will mean fewer sites than are currently in operation; however, the effort of Federal coordination of air monitoring should provide the much-needed quality control. The trend to reduction in the number of stations is already apparent in the 1977 sulfur dioxide data. There were almost 120 fewer monitoring sites reporting data in 1977 than in 1976 (2365 vs. 2482). For sulfur dioxide this trend is becoming more pronounced. Many States terminated all or most of their 24-hr West-Gaeke bubbler sampling in 1978. It is well documented that sulfur dioxide measurements by this method are subject to degradation at

high temperature. Rather than modify the West-Gaeke bubbler method and maintain the dense network of bubblers and continuous monitors, State and local agencies, where they can, are relying continuous monitoring equipment. (See chapter 3). Table 5-21 give the number and type of $SO_2$ monitors operated by Federal, State, and local agencies during 1976, 1977, and 1978. It should be noted that in addition to those included on the tabulation there are many sulfur dioxide monitors operated by electric utilities, paper companies, smelting companies, and others. The data collected by these industries are not, however, part of the National Aerometric Data Bank. Table 5-21 indicates the wide variety of sampling methods currently used to measure $SO_2$ in the atmosphere There are some serious, unresolved questions about the direct comparability of these methods. By 1978 it was recognized that $SO_2$ could bias the calibrations of the flame photometric instruments. It was also recognized that hydrocarbons were an important interference for the pulse fluorescent instruments.

Nationally, $SO_2$ monitoring is not as extensive as TSP monitoring. In 1978 there were 947 sites with continuous monitoring equipment and 1298 bubbler sites. Every State conducted $SO_2$ monitoring. Table 5-22 lists the number of $SO_2$ monitors operating in each State in 1978. All operating sites are eligible for comparison with 3-hr and 24-hr NAAQS. However, only those sites with a sufficient number of hourly or daily observations are considered valid for comparison with the annual NAAQS. To be considered valid for this purpose, a continuous monitor must have been operational for at least 6570 hours during the year. A bubbler must have operated at least 5 days in each of the four calendar quarters. It is with respect to the number of vaild $SO_2$ sites that the national coverage appears inadequate. Only 99 of the 1298 bubbler sites or 7.6 percent are considered valid in 1978. Only 385 of the 947 (or 40.7

TABLE 5-21. TOTAL MONITORS REPORTING $SO_2$, BY METHOD, 1976-1977

| Type | 1976 | 1977 | 1978 |
|---|---|---|---|
| Continuous | | | |
| Colorimetric (West-Gaeke) | 82 | 95 | --[a] |
| Conductometric | 20 | 25 | -- |
| Coulometric | 339 | 365 | -- |
| Flame Photometric | 121 | 105 | -- |
| Hydrogen Peroxide (Titrimetry) | 11 | 76 | -- |
| Catalyst-flame photometric | 1 | 1 | -- |
| Pulsed fluorescent | 17 | -- | -- |
| Second Derivative spectrophotometry | 2 | -- | -- |
| Sequential-conductimetric | 10 | 9 | -- |
| | 603 | 676 | 947 |
| 24-Hour Bubbler | | | |
| Paraarosaniline | 1879 | 1689 | 1298 |
| Total | 2482 | 2365 | 2245 |

[a]Data not available.

TABLE 5.22. NUMBER OF BUBBLER AND CONTINUOUS $SO_2$ MONITORING SITES IN OPERATION IN 1978 AND VALID FOR 1978 ANNUAL MEANS

| | State | Bubblers | | Continuous | |
|---|---|---|---|---|---|
| | | Operational | Valid | Operational | Valid |
| 1. | Alabama | 10 | | 30 | 12 |
| 2. | Alaska | 7 | | 4 | |
| 3. | Arizona | 0 | | 15 | |
| 4. | Arkansas | 21 | | 1 | 1 |
| 5. | California | 0 | | 55 | 19 |
| 6. | Colorado | 0 | | 8 | 5 |
| 7. | Connecticut | 0 | | 24 | 5 |
| 8. | Delaware | 3 | | 15 | |
| 9. | District of Columbia | 0 | | 4 | 2 |
| 10. | Florida | 106 | 25 | 41 | 18 |
| 11. | Georgia | 23 | | 14 | 2 |
| 12. | Hawaii | 9 | | 0 | |
| 13. | Idaho | 0 | | 14 | 13 |
| 14. | Illinois | 36 | | 57 | 22 |
| 15. | Indiana | 64 | 25 | 42 | 15 |
| 16. | Iowa | 35 | | 16 | 4 |
| 17. | Kansas | 0 | | 5 | 2 |
| 18. | Kentucky | 153 | | 45 | 26 |
| 19. | Louisiana | 15 | | 0 | |
| 20. | Maine | 38 | 5 | 11 | 1 |
| 21. | Maryland | 43 | | 19 | 1 |
| 22. | Massachusetts | 49 | | 19 | 12 |
| 23. | Michigan | 0 | | 30 | 28 |
| 24. | Minnesota | 31 | 20 | 22 | 10 |
| 25. | Mississippi | 0 | | 4 | |
| 26. | Missouri | 8 | | 16 | 7 |
| 27. | Montana | 1 | | 21 | 2 |
| 28. | Nebraska | 20 | | 1 | |
| 29. | Nevada | 0 | | 1 | |
| 30. | New Hampshire | 16 | 11 | 10 | 2 |
| 31. | New Jersey | 12 | 2 | 23 | 19 |
| 32. | New Mexico | 25 | | 9 | 4 |
| 33. | New York | 0 | | 64 | 32 |
| 34. | North Carolina | 52 | | 2 | |
| 35. | North Dakota | 15 | | 2 | |
| 36. | Ohio | 156 | 10 | 46 | 21 |
| 37. | Oklahoma | 12 | | 6 | 2 |
| 38. | Oregon | 7 | | 4 | 1 |
| 39. | Pennsylvania | 4 | | 43 | 14 |
| 40. | Puerto Rico | 22 | | 0 | |
| 41. | Rhode Island | 5 | | 4 | 1 |
| 42. | South Carolina | 24 | 1 | 8 | |
| 43. | South Dakota | 9 | | 0 | |
| 44. | Tennessee | 0 | | 59 | 42 |
| 45. | Texas | 123 | | 16 | 6 |
| 46. | Utah | 0 | | 15 | 5 |
| 47. | Vermont | 0 | | 4 | 1 |
| 48. | Virginia | 64 | | 23 | 7 |
| 49. | Washington | 8 | | 11 | 4 |
| 50. | West Virginia | 26 | | 4 | 2 |
| 51. | Wisconsin | 20 | | 57 | 15 |
| 52. | Wyoming | 15 | | 3 | |
| 53. | American Samoa | 0 | | 0 | |
| 54. | Guam | 4 | | 0 | |
| 55. | Virgin Islands | 7 | | 0 | |
| | TOTAL | 1298 | 99 | 947 | 385 |

percent) continuous sites are considered valid. There are 7 States with no valid $SO_2$ monitoring for 1978. EPA is currently taking steps to improve the quality of $SO_2$ data and increase the number of representative sites reporting valid data.

For valid bubbler sites, the average number of 24-hr observations in 1978 was 60. The number of observations per site ranged from 28 to 322. For the valid continuous sites the mean number of observations was 7806 hourly measurements. This ranged from a minimum of 6578 hr to a maximum of 8755 hr.

Overall, the $SO_2$ monitoring should improve as EPA requires quality control procedures of State and local agencies. However, the historic data are of unknown accuracy. Presumably the West-Gaeke bubbler data were subject to comparable exposures, collection, and analysis procedures by the collecting agencies. To the extent that errors are consistent in time $SO_2$ bubbler data may still be useful for trend analysis, health studies and welfare effect studies, using the same methods.

5.2.3.2 Distribution of Sulfur Dioxide Concentrations--Although there are natural sources of $SO_2$ such as volcanoes (see chapter 4), they are of minor importance. Sulfur dioxide has a rather short half-life in the troposphere (see chapter 6). Background levels are often measured as zero. Therefore it is not surprising that the annual mean $SO_2$ concentration is 3 $\mu g/m^3$ in some locations.

Monitoring in urbanized areas near industrial sources that use sulfur-bearing fuels shows rather high concentrations of $SO_2$. In 1978 the annual mean concentrations obtained by $SO_2$ bubblers ranged from 3 to 79 $\mu g/m^3$. The valid continuous monitors registered 1978 annual mean concentrations ranging from 3 to 152 $\mu g/m^3$ .

The concentration of $SO_2$ like that of TSP is affected by meteorological variables influencing transport, dispersion, and removal, as well as by topography and the configuration of sources. Spatial and temporal variations in these parameters are reflected in the range of maximum concentration and of the 90th percentiles reported across the Nation. For bubbler sites, the lowest 24-hr maximum value reported by a site was 3 $\mu g/m^3$ and the highest was 907 $\mu g/m^3$. For the valid continuous sites the spread of 24-hr maximum values was greater, ranging from 10 $\mu g/m^3$ at one site to 2512 $\mu g/m^3$ another site. Among all continuous sites reporting in 1978, regardless of validity, the extreme 24-hour value was 3931 $\mu g/m^3$. These "daily" maxima are derived from moving 24-hr means.

Table 5-23 provides summaries of statistics on $SO_2$ from valid 1978 sites. Note the differences between bubbler and continuous data for the annual mean values. There appears to be a substantial difference in the overall mean concentrations as well as the maximum annual mean concentrations. The statistics on the 90th percentile and maximum concentrations also vary greatly between methods. Explanations of these differences are offered in a later section.

5.2.3.3 Sulfur Dioxide Concentration By Location

5.2.3.3.1 1978 highest annual average concentrations. The reasons for $SO_2$ variability have been mentioned in earlier sections. This section examines the locations with the highest annual averages and the highest maximum concentrations, and analyzes the distribution of $SO_2$ concentration nationally by site descriptors. However, because of the differences in $SO_2$ concentrations between bubbler and continuous monitoring, the distributions by site descriptor will be treated separately for each method.

TABLE 5-23. STATISTICS ON THE VALID $SO_2$ MONITORING SITES FOR 1978

| Statistic | Observations | Annual Mean, $\mu g/m^3$ | 90th Percentile $\mu g/m^3$ | Maximum Concentration $\mu g/m^3$ |
|---|---|---|---|---|
| Bubblers (N=99) | | | | |
| Mean | 60.0 | 19.5 | 43.6 | 112.2 |
| Standard Deviation | 38.0 | 15.4 | 37.5 | 126.5 |
| Minimum | 28.0 | 3.0 | 2.0 | 3.0 |
| Maximum | 322.0 | 79.0 | 176.0 | 907.0 |
| Continuous (N=385) | | | | |
| Mean | 7806 | 31.5 | 65.2 | 221.8 |
| Standard Deviation | 654 | 19.3 | 42.1 | 189.7 |
| Minimum | 6578 | 3.0 | 3.0 | 10.0 |
| Maximum | 8755 | 152.0 | 488.0 | 2512.0 |

Table 5-24 lists the annual mean and the maximum 24-hr concentration for the 11 valid continuous monitoring sites with the highest annual means in 1978. The highest annual mean concentration was 152 $\mu g/m^3$. This site in Montana was situated 2 miles northeast of a smelter. It also had the highest 24-hr concentration (2512 $\mu g/m^3$) of any valid continuous monitor. The maximum hour was 7205 $\mu g/m^3$, and the second highest hour was 6026 $\mu g/m^3$ at this site. Of the highest 11 sites, 5 are associated with smelters, 5 are associated with industrialized areas or towns, and one, New York City, is a densely populated city. In New York City, $SO_2$ emissions from space heating, power plants, and a variety of industrial sources resulted in a high annual mean concentration.

5.2.3.3.2 <u>1978-highest daily average concentrations</u>. Listed in Table 5-25 are the 45 continuous sites with the highest single-day 24-hour $SO_2$ concentrations. All but one of these sites have a second highest daily value exceeding 265 $\mu g/m^3$. Several of these sites are in the same general areas. Most likely the high levels in these areas are the result of a single source. For example, the sites in Deer Lodge County, Montana are experiencing high maximum 24-hr concentrations as a result of $SO_2$ emissions from a local smelter.

Many of these sites having high maximum daily values are located near specific industrial sources such as smelters, steel manufacturers, and paper mills. A few of the sites like Toledo, Ohio, Hammond, Indiana, Pittsburgh, Pennsylvania, and East Lake, Ohio, are in urbanized industrial areas. Most of the other sites are in less populated rural regions.

High 24-hr $SO_2$ concentrations occur in all regions of the country but not in all States. Ten of the high sites are in Montana, six in Wisconsin and six in Minnesota. In Table 5-25, listing the 45 sites with the highest maximum readings, only 17 states are included.

TABLE 5-24. $SO_2$ MONITORING SITES WITH THE HIGHEST 11 ANNUAL MEAN CONCENTRATIONS IN 1978 (VALID CONTINUOUS SITES ONLY)

| Location | Annual Means $\mu g/m^3$ | Maximum 24-hr, $\mu g/m^3$ | Description |
|---|---|---|---|
| Helena, Deer Lodge Co., Montana | 152 | 2512 | Rural-mine smelter |
| Pittsburgh, Pennsylvania | 140 | 602 | Center city industrial |
| Helena, Deer Lodge County, Montana | 95 | 1450 | Rural-industrial 1.6 miles east of smelter |
| Magna, Salt Lake Co., Utah | 93 | 811 | Suburban-industrial |
| Toledo, Ohio | 84 | 915 | Center city industrial |
| Pittsburgh, Pennsylvania | 79 | 376 | Suburban-industrial |
| Buffalo, New York | 78 | 267 | Suburban-industrial |
| Kellogg, Shoshone Co., Idaho | 78 | 294 | Suburban-residential |
| Shoshone Co., Idaho | 77 | 493 | Suburban-industrial |
| New York City, New York | 77 | 296 | Center city residential |
| Mingo Junction, Ohio | 76 | 329 | Center city industrial |

TABLE 5-25. THE 45 MONITORING SITES WITH THE HIGHEST 24 HOUR $SO_2$ CONCENTRATIONS IN 1978 (Continuous methods.)

| | Location | Maximum 24 hr, $\mu g/m^3$ | Second Highest 24-hr, $\mu g/m^3$ | Description |
|---|---|---|---|---|
| 1. | Eau Claire County Wisconsin | 3931 | 3266 | ? |
| 2. | Deer Lodge County Montana | 2512 | 1880 | Rural agricultural 2.75 mine of smelter |
| 3. | Deer Lodge County Montana | 1450 | 1185 | Rural-industry 1.6 mi. E of smelter |
| 4. | Unknown Montana | 1084 | 700 | ? |
| 5. | Dakota County Minnesota | 1030 | 850 | Rural-industry |
| 6. | Deer Lodge County Montana | 1015 | 862 | Rural-industry |
| 7. | Dougherty County Georgia | 945 | 440 | Rural-industry |
| 8. | Dakota County Minnesota | 933 | 653 | Rural-industry |
| 9. | Berlin New Hampshire | 925 | 721 | Center city-residential |
| 10. | Marathon County Wisconsin | 918 | 791 | Rural-industry |
| 11. | Toledo Ohio | 915 | 613 | Center city-industry |
| 12. | Millinocket Maine | 894 | 792 | Suburban-industrial |
| 13. | Tarpon Springs Florida | 816 | 653 | Rural-commercial |
| 14. | Magna, Utah | 811 | 706 | Suburban-industry |

TABLE 5-25. (continued)

| | Location | Maximum 24 hr, $\mu g/m^3$ | Second Highest 24-hr, $\mu g/m^3$ | Description |
|---|---|---|---|---|
| 15. | Laurel County Montana | 808 | 736 | Suburban-residential 3/8 mi. NE of refinery |
| 16. | Milwaukee Wisconsin | 799 | 482 | Center city-industry |
| 17. | St. Charles County Missouri | 782 | 751 | Rural-agricultural |
| 18. | Gila County Miami, Arizona | 779 | 677 | Rural-agricultural |
| 19. | Unknown Minnesota | 753 | 689 | ? |
| 20. | Deer Lodge County Montana | 720 | 530 | Center city-commercial |
| 21. | Unknown Montana | 711 | 415 | ? |
| 22. | St. Paul Park Minnesota | 703 | 663 | Center city-commercial |
| 23. | Oregon Lucas County Ohio | 697 | 414 | Suburban-residential |
| 24. | Deer Lodge County Montana | 689 | 682 | Rural-industry |
| 25. | Unknown Minnesota | 683 | 603 | ? |
| 26. | Laurel Montana | 670 | 279 | Suburban-residential 3/8 mi. NE of refinery |
| 27. | Deer Lodge County Montana | 668 | 659 | Rural-industry |
| 28. | Greenlee County Arizona | 668 | 561 | Rural-industry |

TABLE 5-25. (continued)

| | Location | Maximum 24 hr, $\mu g/m^3$ | Second Highest 24-hr, $\mu g/m^3$ | Description |
|---|---|---|---|---|
| 29. | St. Paul Park Minnesota | 655 | 429 | Center city-commercial |
| 30. | Millinocket Maine | 647 | 612 | Rural-industry |
| 31. | Pittsburgh Pennsylvania | 602 | 556 | Center city-industry |
| 32. | Millinocket Maine | 569 | 556 | Rural-industry |
| 33. | Wood River Illinois | 553 | 354 | Suburban-industry |
| 34. | Philadelphia Pennsylvania | 548 | 393 | Suburban-industry |
| 35. | Philadelphia Pennsylvania | 534 | 405 | Center city commercial |
| 36. | Iron County Cedar City, Utah | 526 | 439 | Suburb-residential |
| 37. | Pima County Ajo, Arizona | 522 | 481 | Suburb-industry |
| 38. | Hammon Lake County Indiana | 521 | 458 | Center city-industry-Gary area |
| 39. | Milwaukee Wisconsin | 518 | 401 | Center city-residential |
| 40. | Greenlee County Arizona | 510 | 347 | Rural industry 1.3 mi. NW of smelter |
| 41. | Shoshone County Idaho | 493 | 398 | Suburban-industry |
| 42. | Unknown Alabama | 486 | 401 | ? |

TABLE 5-25. (continued)

| | Location | Maximum 24 hr, $\mu g/m^3$ | Second Highest 24-hr, $\mu g/m^3$ | Description |
|---|---|---|---|---|
| 43. | Bannock County Idaho | 486 | 497 | Rural-industry |
| 44. | Greenbay County Wisconsin | 482 | 405 | ? |
| 45. | Greenbay County Wisconsin | 470 | 374 | ? |

[a]Privately operated

5.2.3.3.3 Sulfur dioxide concentrations by site. In this section the distributions of annual mean and 90th percentile concentrations by site descriptors are presented for bubbler and for continuous methods. As with TSP, a two-descriptor code has been associated with each site. Distributions for every combination of Type 1 (population, source, background) and for Type 2 (central city, suburban, rural, remote) will not be presented. In some cases the designations are contradictory, such as "population-remote" or "background-central city." The purpose of presenting these distributions is to permit comparison of these two categories of sampling methods and to examine the $SO_2$ concentrations as a function of location.

In Table 5-26 the cross-tabulation of mean concentrations by method is presented for "population-central city" and "population-source" sites. The third and fourth numbers in each cell are the column percentage and total percentage of sites having concentrations within the designated range. Examination of each of these numbers reveals that bubblers are, on the average, reporting lower concentrations than the continuous instruments. Three explanations are plausible:

1. Continuous monitors are systematically overestimating $SO_2$ concentrations.
2. Bubbler monitors are systematically underestimating $SO_2$ concentrations
3. Continuous monitors are biased upwards by placement in areas with higher levels.

In light of the reported temperature decay problems with $SO_2$ bubblers (chapter 3), the most likely explanation is that bubblers are underestimating $SO_2$. In Table 5-26, 14.4 percent of the continuous monitors report mean concentrations above 62 $\mu g/m^3$ while only 1.6 percent of the bubblers report

TABLE 5-26. CROSSTABULATION OF ANNUAL MEAN $SO_2$ CONCENTRATION BY METHOD (BUBBLER OR CONTINUOUS) FOR POPULATION-ORIENTED AND FOR SOURCE-ORIENTED CENTER CITY SITES

| Annual mean $SO_2$ concentration, $\mu g/m^3$ | Purpose of Site: Population Bubbler | Population Continuous | Population Row Total | Source Bubbler | Source Continuous | Source Row Total |
|---|---|---|---|---|---|---|
| 2-7 | | | | | | |
| Number of sites | 139 | 15 | 154 | 9 | 3 | 12 |
| Percent of row | 90.3 | 9.7 | | 75.0 | 25.0 | |
| Percent of column | 27.6 | 5.3 | | 16.1 | 6.3 | |
| Percent of total | 17.7 | 1.9 | 19.6 | 8.7 | 2.9 | 11.5 |
| 7-18 | | | | | | |
| Number of sites | 159 | 32 | 191 | 18 | 10 | 28 |
| Percent of row | 83.2 | 16.8 | | 64.3 | 35.7 | |
| Percent of column | 31.6 | 11.3 | | 32.1 | 20.8 | |
| Percent of total | 20.2 | 4.1 | 24.3 | 17.3 | 9.6 | 26.9 |
| 18-33 | | | | | | |
| Number of sites | 106 | 86 | 192 | 12 | 14 | 26 |
| Percent of row | 55.2 | 44.8 | | 46.2 | 53.8 | |
| Percent of column | 21.1 | 30.3 | | 21.4 | 29.2 | |
| Percent of total | 13.5 | 10.9 | 24.2 | 11.5 | 13.5 | 25.0 |
| 33-62 | | | | | | |
| Number of sites | 91 | 110 | 201 | 13 | 15 | 28 |
| Percent of row | 45.3 | 54.7 | | 46.4 | 53.6 | |
| Percent of column | 18.1 | 38.7 | | 23.2 | 31.3 | |
| Percent of total | 11.6 | 14.0 | 25.5 | 12.5 | 14.4 | 26.9 |
| >62 | | | | | | |
| Number of sites | 8 | 41 | 49 | 4 | 6 | 10 |
| Percent of row | 16.3 | 83.7 | | 40.0 | 60.0 | |
| Percent of column | 1.6 | 14.4 | | 7.1 | 12.5 | |
| Percent of total | 1.0 | 5.2 | 6.2 | 3.8 | 5.8 | 9.6 |

TABLE 5-26. (continued)

| Annual mean $SO_2$ concentration, $\mu g/m^3$ | Purpose of Site | | | | | |
|---|---|---|---|---|---|---|
| | Population | | | Source | | |
| | Bubbler | Continuous | Row Total | Bubbler | Continuous | Row Total |
| Column total | | | | | | |
| Number of sites | 503 | 284 | 787 | 56 | 48 | 104 |
| Percent of total | 63.9 | 36.1 | 100.0 | 53.8 | 46.2 | 100.0 |

these higher concentrations. Of the "source-center city" sites a higher percentage (7.1 percent) of the bubblers are above 62 $\mu g/m^3$, but this is still less than the 12.5 percent of the continuous monitors in this category.

The pattern is consistent with the display of the "population-suburban" and "source-suburban" distributions in Table 5-27. Where monitors were located in rural regions near industrial sources, only 2 percent of the bubblers reported means greater than 33 $\mu g/m^3$, while 17 percent of the continuous sites in similar locations were above this level.

Similar distributions were tabulated for the 90th percentiles. Table 5-28 displays these distributions for all "source"-oriented monitors in central cities, suburban, rural and remote areas. The concentrations reported by bubbler sites tends to be lower than those reported by continuous sites. This can be seen by comparing the row and column percentages between methods in Table 5-28. In part this may be due to the low sensitivity of the bubbler method. EPA reports that the method is not very reliable below 24 $\mu g/m^3$.

A systematic difference between methods is more apparent in the cross-tabulation of the "population" sites in Table 5-29. Disregarding for a moment the difference between methods, only 4.6 percent of the central-city population-oriented monitors reported 90th percentiles over 127 $\mu g/m^3$. Less than 4 percent of the suburban population-oriented monitors reported 90th percentile levels over 127 $\mu g/m^3$. Again, this does not necessarily imply that less than 5 percent of the population is exposed less than 10 percent of the time to concentrations above 127 $\mu g/m^3$. Referring to the previous table of source oriented monitors, the percentage of monitors in central cities and suburban locations that exceed 127 $\mu g/m^3$ for their 90th percentile concentration is somewhat greater (5 to 7 percent) than for the population-oriented monitors.

TABLE 5-27. CROSSTABULATION OF ANNUAL MEAN $SO_2$ CONCENTRATION BY METHOD (BUBBLER OR CONTINUOUS) FOR POPULATION-ORIENTED AND FOR SOURCE-ORIENTED SUBURBAN SITES

| Annual mean $SO_2$ concentration, $\mu g/m^3$ | Purpose of Site | | | | | |
|---|---|---|---|---|---|---|
| | Population | | | Source | | |
| | Bubbler | Continuous | Row Total | Bubbler | Continuous | Row Total |
| 2-7 | | | | | | |
| Number of sites | 139 | 16 | 155 | 21 | 2 | 23 |
| Percent of row | 89.7 | 10.3 | | 91.3 | 8.7 | |
| Percent of column | 36.5 | 6.6 | | 23.9 | 2.7 | |
| Percent of total | 22.3 | 2.6 | 24.9 | 13.0 | 1.2 | 14.2 |
| 7-18 | | | | | | |
| Number of sites | 101 | 40 | 141 | 35 | 13 | 48 |
| Percent of row | 71.6 | 28.4 | | 72.9 | 27.1 | |
| Percent of column | 26.5 | 16.5 | | 39.8 | 17.6 | |
| Percent of total | 16.2 | 6.4 | 22.6 | 21.6 | 8.0 | 29.6 |
| 18-33 | | | | | | |
| Number of sites | 88 | 82 | 170 | 16 | 34 | 50 |
| Percent of row | 51.8 | 48.2 | | 32.0 | 68.0 | |
| Percent of column | 23.1 | 33.9 | | 18.2 | 45.9 | |
| Percent of total | 14.1 | 13.2 | 27.3 | 9.9 | 21.0 | 30.9 |
| 33-62 | | | | | | |
| Number of sites | 50 | 83 | 133 | 13 | 17 | 30 |
| Percent of row | 37.6 | 62.4 | | 43.3 | 56.7 | |
| Percent of column | 13.1 | 34.3 | | 14.8 | 23.0 | |
| Percent of total | 8.0 | 13.3 | 21.3 | 8.0 | 10.5 | 18.5 |
| >62 | | | | | | |
| Number of sites | 3 | 21 | 24 | 3 | 8 | 11 |
| Percent of row | 12.5 | 87.5 | | 27.3 | 72.7 | |
| Percent of column | 0.8 | 8.7 | | 3.4 | 10.8 | |
| Percent of total | 0.5 | 3.4 | 3.9 | 1.9 | 4.9 | 6.8 |

TABLE 5-27. (continued)

| Annual mean $SO_2$ concentration, $\mu g/m^3$ | Purpose of Site | | | | | |
|---|---|---|---|---|---|---|
| | Population | | | Source | | |
| | Bubbler | Continuous | Row Total | Bubbler | Continuous | Row Total |
| Column total | | | | | | |
| Number of sites | 381 | 242 | 623 | 88 | 74 | 162 |
| Percent of total | 61.2 | 38.8 | 100.0 | 54.3 | 45.7 | 100.0 |

TABLE 5-28. CROSSTABULATION OF 90TH PERCENTILE OF DAILY AVERAGE CONCENTRATIONS OF $SO_2$ BY METHOD (BUBBLER OR CONTINUOUS) FOR SOURCE-ORIENTED SITES IN CENTER CITY, SUBURBAN, RURAL, AND REMOTE LOCATIONS

| 90th Percentile of daily average $SO_2$ concentration, $\mu g/m^3$ | Location | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Center City | | | Suburban | | | Rural | | | Remote | | |
| | Bubbler | Continuous | Row Total | Bubbler | Continuous | Row Total | Bubbler | Continuous | Row Total | Bubbler | Continuous | Row Total |
| 2-14 | | | | | | | | | | | | |
| Number of sites | 13 | 4 | 17 | 24 | 3 | 27 | 36 | 19 | 55 | 1 | 1 | 2 |
| Percent of row | 76.5 | 23.5 | | 88.9 | 11.1 | | 65.5 | 34.5 | | 50.0 | 50.0 | |
| Percent of column | 23.2 | 8.3 | | 27.3 | 4.1 | | 43.4 | 10.1 | | 100.0 | 14.3 | |
| Percent of total | 12.5 | 3.8 | 16.3 | 14.8 | 1.9 | 16.7 | 13.2 | 7.0 | 20.2 | 12.5 | 12.5 | 25.0 |
| 14-39 | | | | | | | | | | | | |
| Number of sites | 14 | 7 | 21 | 28 | 15 | 43 | 30 | 51 | 81 | 0 | 5 | 5 |
| Percent of row | 66.7 | 33.3 | | 65.1 | 34.9 | | 37.0 | 63.0 | | 0.0 | 100.0 | |
| Percent of column | 25.0 | 14.6 | | 31.8 | 20.3 | | 36.1 | 27.0 | | 0.0 | 71.4 | |
| Percent of total | 13.5 | 6.7 | 20.2 | 17.3 | 9.3 | 26.5 | 11.0 | 18.8 | 29.8 | 0.0 | 62.5 | 62.5 |
| 39-68 | | | | | | | | | | | | |
| Number of sites | 10 | 18 | 28 | 18 | 29 | 47 | 12 | 60 | 72 | 0 | 1 | 1 |
| Percent of row | 35.7 | 64.3 | | 38.3 | 61.7 | | 16.7 | 83.3 | | 0.0 | 100.0 | |
| Percent of column | 17.9 | 37.5 | | 20.5 | 39.2 | | 14.5 | 31.7 | | 0.0 | 14.3 | |
| Percent of total | 9.6 | 17.3 | 26.9 | 11.1 | 17.9 | 29.0 | 4.4 | 22.1 | 26.5 | 0.0 | 12.5 | 12.5 |
| 68-127 | | | | | | | | | | | | |
| Number of sites | 13 | 14 | 27 | 14 | 16 | 30 | 3 | 42 | 45 | | | |
| Percent of row | 48.1 | 51.9 | | 46.7 | 53.3 | | 6.7 | 93.3 | | | | |
| Percent of column | 23.2 | 29.2 | | 15.9 | 21.6 | | 3.6 | 22.2 | | | | |
| Percent of total | 12.5 | 13.5 | 26.0 | 8.6 | 9.9 | 18.5 | 1.1 | 15.4 | 16.5 | | | |
| >127 | | | | | | | | | | | | |
| Number of sites | 6 | 5 | 11 | 4 | 11 | 15 | 2 | 17 | 19 | | | |
| Percent of row | 54.5 | 45.5 | | 26.7 | 73.3 | | 10.5 | 89.5 | | | | |
| Percent of column | 10.7 | 10.4 | | 4.5 | 14.9 | | 2.4 | 9.0 | | | | |
| Percent of total | 5.8 | 4.8 | 10.6 | 2.5 | 6.8 | 9.3 | 0.7 | 6.3 | 7.0 | | | |

TABLE 5-28. (continued)

| 90th Percentile of daily average $SO_2$ concentration, $\mu g/m^3$ | Location | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Center City | | | Suburban | | | Rural | | | Remote | | |
| | Bubbler | Contin-uous | Row Total | Bubbler | Contin-uous | Row Total | Bubbler | Contin-uous | Row Total | Bubbler | Contin-uous | Row Tota |
| Column total | | | | | | | | | | | | |
| Number of sites | 56 | 48 | 104 | 88 | 74 | 162 | 83 | 189 | 272 | 1 | 7 | 8 |
| Percent of total | 53.8 | 46.2 | 100.0 | 54.3 | 45.7 | 100.0 | 30.5 | 69.5 | 100.0 | 12.5 | 87.5 | 100.0 |

TABLE 5-29. CROSSTABULATION OF 90TH PERCENTILE OF DAILY AVERAGE CONCENTRATIONS OF $SO_2$ BY METHOD (BUBBLER OR CONTINUOUS) FOR POPULATION-ORIENTED MONITORS CENTER CITY, SUBURBAN, AND RURAL LOCATIONS.

| 90th Percentile of daily average $SO_2$ concentration, $\mu g/m^3$ | Location | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Center City | | | Suburban | | | Rural | | |
| | Bubbler | Continuous | Row Total | Bubbler | Continuous | Row Total | Bubbler | Continuous | Row Total |
| 2-14 | | | | | | | | | |
| Number of sites | 167 | 17 | 184 | 146 | 18 | 164 | 25 | 4 | 29 |
| Percent of row | 90.8 | 9.2 | | 89.0 | 11.0 | | 86.2 | 13.8 | |
| Percent of column | 33.2 | 6.0 | | 38.3 | 7.4 | | 43.1 | 14.8 | |
| Percent of total | 21.2 | 2.2 | 23.4 | 23.4 | 2.9 | 26.3 | 29.4 | 4.7 | 34.1 |
| 14-39 | | | | | | | | | |
| Number of sites | 136 | 39 | 175 | 95 | 49 | 144 | 23 | 4 | 27 |
| Percent of row | 77.7 | 22.3 | | 66.0 | 34.0 | | 85.2 | 14.8 | |
| Percent of column | 27.0 | 13.7 | | 24.9 | 20.2 | | 39.7 | 14.8 | |
| Percent of total | 17.3 | 5.0 | 22.2 | 15.2 | 7.9 | 23.1 | 27.1 | 4.7 | 31.8 |
| 39-68 | | | | | | | | | |
| Number of sites | 104 | 96 | 200 | 90 | 76 | 166 | 9 | 11 | 20 |
| Percent of row | 52.0 | 48.0 | | 54.2 | 45.8 | | 45.0 | 55.0 | |
| Percent of column | 20.7 | 33.8 | | 23.6 | 31.4 | | 15.5 | 40.7 | |
| Percent of total | 13.2 | 12.2 | 25.4 | 14.4 | 12.2 | 26.6 | 10.6 | 12.9 | 23.5 |
| 68-127 | | | | | | | | | |
| Number of sites | 85 | 107 | 192 | 48 | 80 | 128 | 1 | 7 | 8 |
| Percent of row | 44.3 | 55.7 | | 37.5 | 62.5 | | 12.5 | 87.5 | |
| Percent of column | 16.9 | 37.7 | | 12.6 | 33.1 | | 1.7 | 25.9 | |
| Percent of total | 10.8 | 13.6 | 24.4 | 7.7 | 12.8 | 20.5 | 1.2 | 8.2 | 9.4 |
| >127 | | | | | | | | | |
| Number of sites | 11 | 25 | 36 | 2 | 19 | 21 | 0 | 1 | 1 |
| Percent of row | 30.6 | 69.4 | | 9.5 | 90.5 | | 0.0 | 100.0 | |
| Percent of column | 2.2 | 8.8 | | 0.5 | 7.9 | | 0.0 | 3.7 | |
| Percent of total | 1.4 | 3.2 | 4.6 | 0.3 | 3.0 | 3.4 | 0.0 | 1.2 | 1.2 |

TABLE 5-29. (continued)

| 90th Percentile of daily average $SO_2$ concentration, $\mu g/m^3$ | Location | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Center City | | | Suburban | | | Rural | | |
| | Bubbler | Continuous | Row Total | Bubbler | Continuous | Row Total | Bubbler | Continuous | Row Total |
| Column total | | | | | | | | | |
| Number of sites | 503 | 284 | 787 | 381 | 242 | 623 | 58 | 27 | 85 |
| Percent of total | 63.9 | 36.1 | 100.0 | 61.2 | 38.8 | 100.0 | 68.2 | 31.8 | 100.0 |

These comparisons are quite general. In order to make more accurate approximations of the population exposures to high ambient $SO_2$ concentrations, two steps must be taken. First the discrepancy in $SO_2$ sampling methods must be resolved so that measurements can be compared. Second, a careful analysis around each high monitor must be performed. Perhaps this would included dispersion modeling, but as a minimum the population actually exposed should be tabulated. The last point deserves emphasis. The current data bases contain no information on the population each monitoring site is intended to represent.

5.2.3.4 Sulfur Dioxide Cycles

5.2.3.4.1 Diurnal patterns. In some locations $SO_2$ concentrations have distinct temporal patterns. These patterns depend on the variability of meteorological factors and on the variability of source emissions.

Diurnal variations in $SO_2$ concentrations reflect the changing dispersion characteristics of the lower atmosphere and variations in mixing height. If emissions are predominantly from low-level sources such as residential and and institutional space heating, the highest hourly concentrations will frequently occur at night and in the early-morning hours. At these times, low mixing height and decreased wind speeds lead to higher concentrations. During the day more vertical mixing usually occurs and wind speeds increase; this results in the dilution of low-level emissions. Figure 5-41 give the monthly mean hourly concentrations for $SO_2$ in December 1978 in Watertown, MA. The pattern just described is apparent.

In locations where $SO_2$ emissions from taller stacks are the major $SO_2$ source, a different diurnal pattern can occur. In these situations, typical of power plants and smelters, the highest concentrations usually occur in the

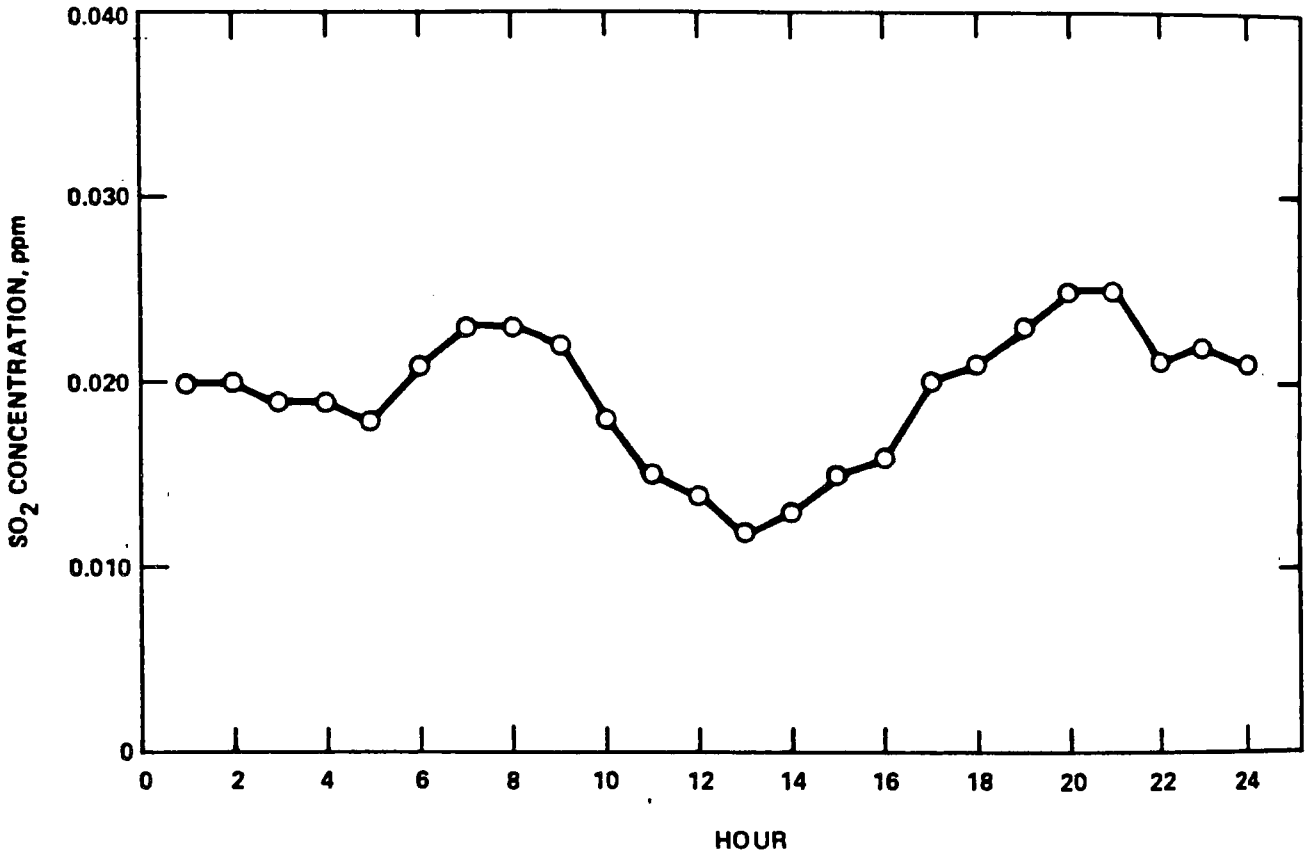



Figure 5-41. Monthly means of hourly sulfur dioxide concentrations are shown for Watertown, MA, for December 1978.

morning hours just after sunrise. Levels can be almost zero at night if the source is emitting into a stratified region above a lower level inversion. Upon inversion breakup, when heating at the surface causes vertical mixing, an elevated plume can be mixed to the ground. Fumigation conditions lasting from several minutes to several hours can occur. The monthly mean hourly plot of $SO_2$ concentrations at a site in Kingston, TN, illustrates this point (See Figure 5-42). In 1975, a nearby 1500-MW power plant was emitting through nine stacks less than 320 ft high. In 1978 the emission had been switched over to two 1000-ft stacks. Analysis by Montgomery and Coleman (1975) of the effects of tall stacks on the peak-to-mean ratios for different averaging times discusses the influence of inversion breakup. In essence, even with tall stacks, inversion breakup that catches the plume and brings it to the surface can occur. So the peak-to-mean ratio is almost independent of stack height. The frequency of occurrences on the other hand would most likely be less with taller stacks.

In Figure 5-42 the plot for the monthly mean of hourly values reveals a different pattern from that found in Watertown, MA. The maximum hours occur in the late morning. By 1978, the emissions from the nearby power plant were discharged through two 1000-ft towers. The monthly mean of the hourly observations in January 1978 shows a less pronounced diurnal cycle. Some similarity can be found in comparing the monthly mean hourly averages for Watertown, Massachusetts (Figure 5-41), and St. Louis, Missouri (Figure 5-43). In February, 1977, a major local source of $SO_2$ was still in operation in St. Louis. The midmorning and late night maxima are again associated with diurnal variations of meteorological factors. By February, 1978, the source had shut down and the $SO_2$ levels at the monitoring stations reflect this fact. The absence of low-level stacks emitting into a stable layer of air near the

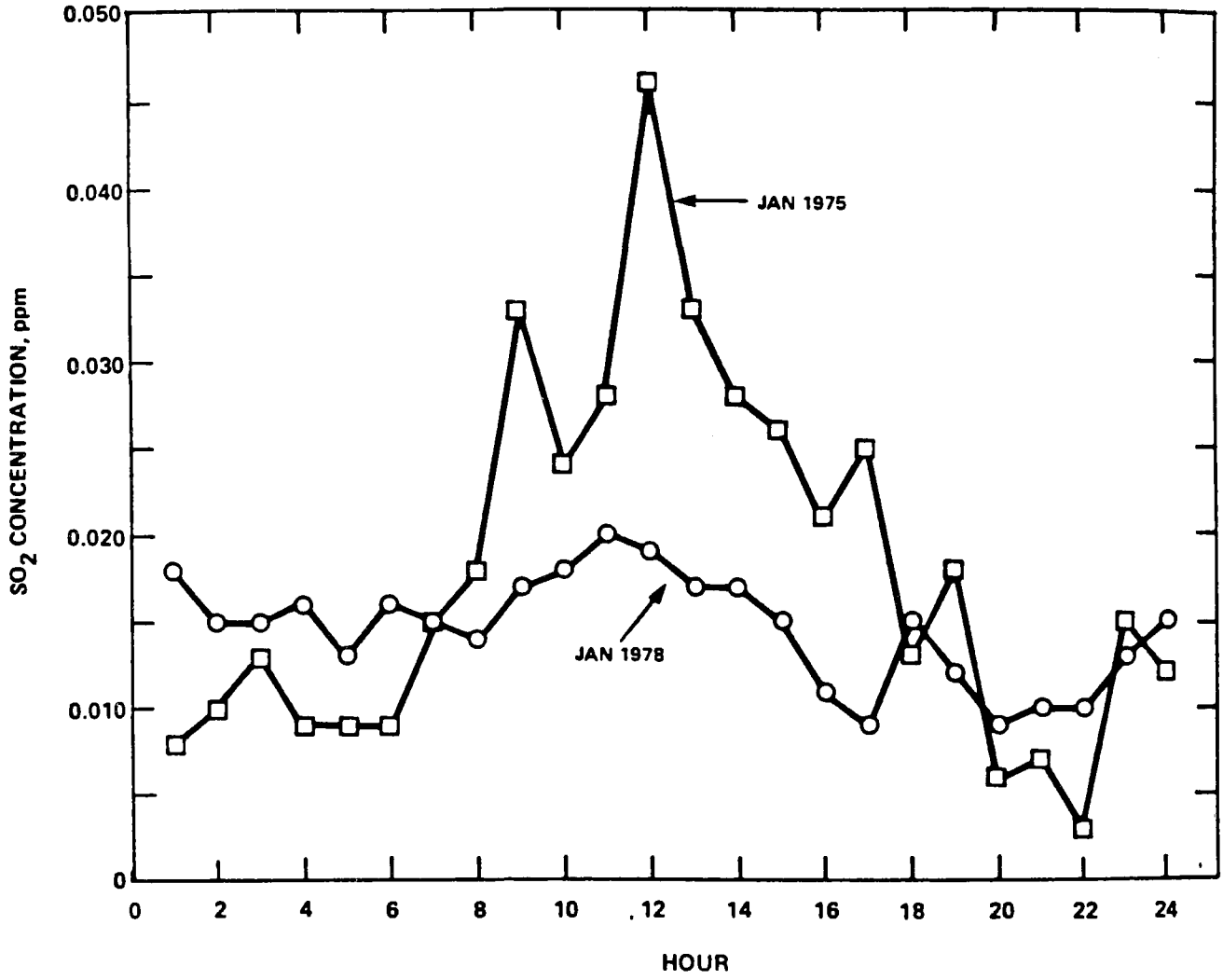



Figure 5-42. Monthly means of hourly sulfur dioxide concentrations are shown for Kingston (TVA site 44-1714-003, "Laddie Village") for January 1975 and 1978.

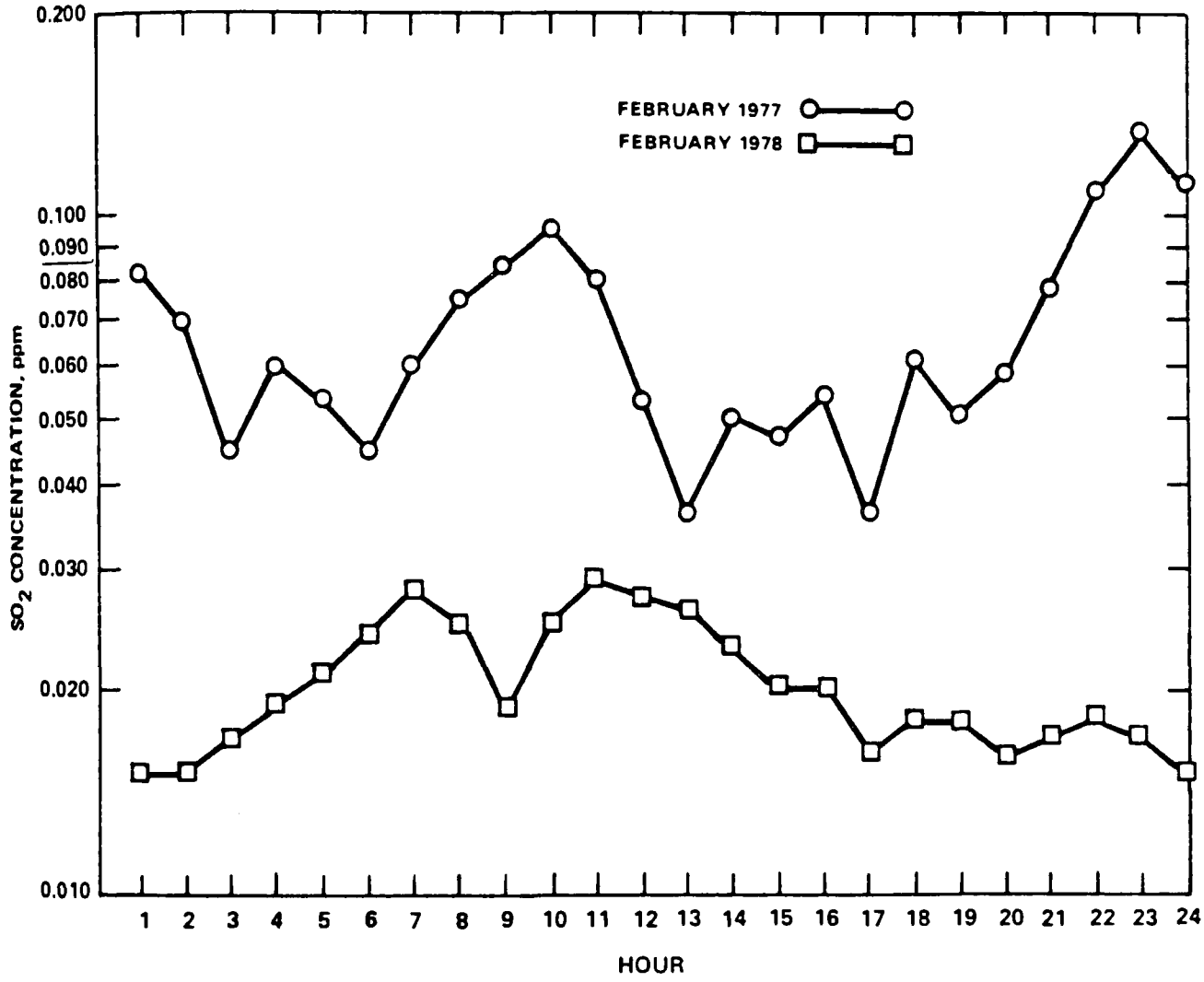



Figure 5-43. Monthly means of hourly sulfur dioxide concentrations are shown for St. Louis (city site no. 26-4280-007, "Broadway & Hurck") for February 1977 and 1978.

surface at night is noticeable. Concentrations do not build up at night as in the previous year.

The $SO_2$ monthly mean hourly values for the industrialized river valley town of Steubenville, OH, are shown in Figure 5-44. In June of 1976, a distinctive maximum in the diurnal pattern appears. In July of 1977 there is no apparent variation across the hours.

In concluding this section it can be said that the variations in hourly concentrations are influenced by source configuration and meteorological dispersion. Therefore, it is difficult to generalize about the pattern of the hourly concentrations. It has been shown that, although there may be some similarities, the daily patterns in $SO_2$ concentrations are different for different locations and can change in time for a given location.

5.2.3.4.2 Seasonal Patterns. Concentrations of $SO_2$ display seasonal variability. The variability is most pronounced in areas in which there is strong seasonal variation in the emission-source strength or in meteorological conditions. Obviously, in urban areas where space heating is the major source of $SO_2$, the levels will be much higher during the heating season. Figure 5-45 illustrates just such situations in Watertown, MA and Steubenville, OH. The highest monthly mean concentrations occur in the winter months.

Figure 5-45 also shows the data for St. Louis, Missouri, where the seasonal pattern is different. Here a local industrial source dominates $SO_2$ concentration patterns around the monitor. The higher monthly mean concentrations occur in the months with the higher frequency of south winds. The source is to the south of the monitoring station. Any increase in $SO_2$ concentrations as a result of the winter heating season is not apparent.

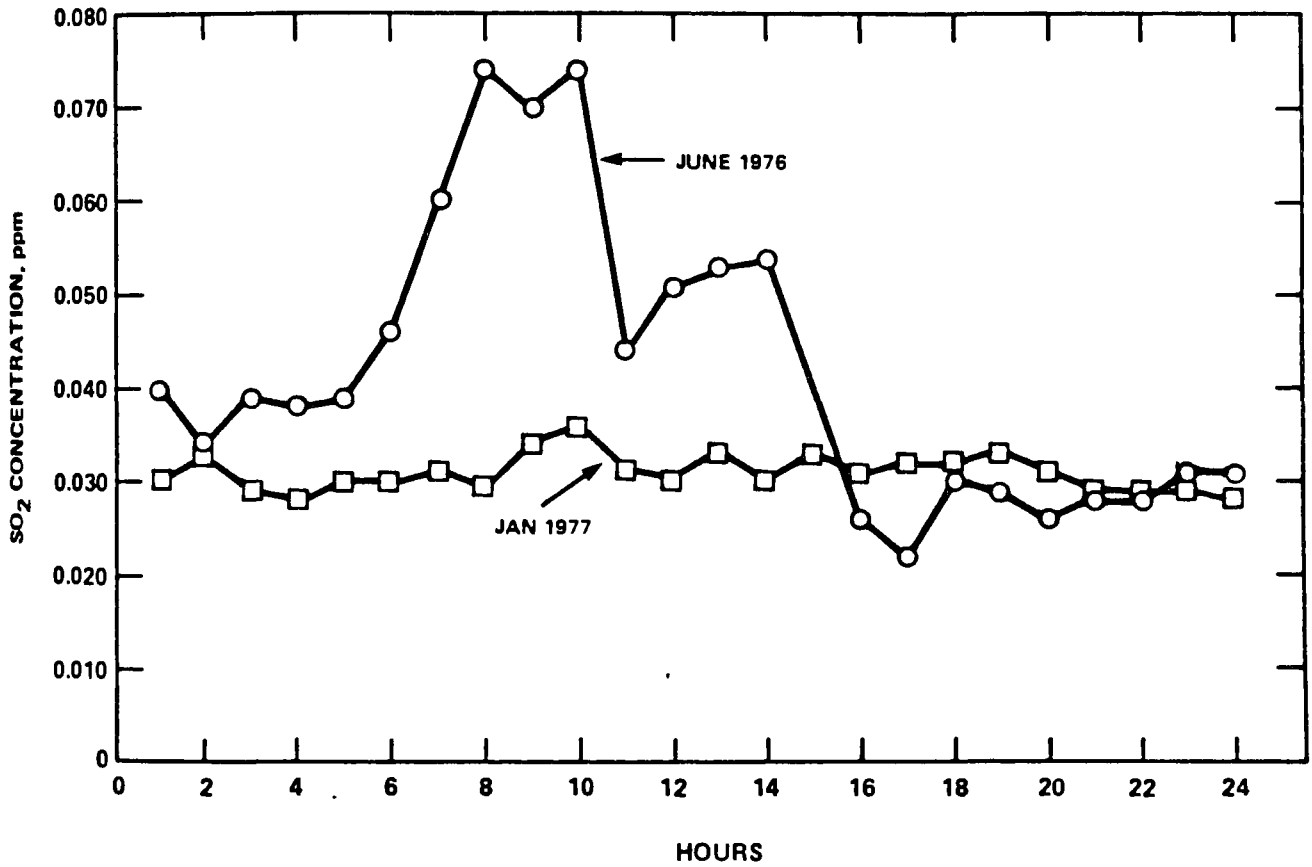



Figure 5-44. Monthly means of hourly sulfur dioxide concentrations are shown for Steubenville, OH (NOVAA site 36-6420-012) for June 1976 and 1977.

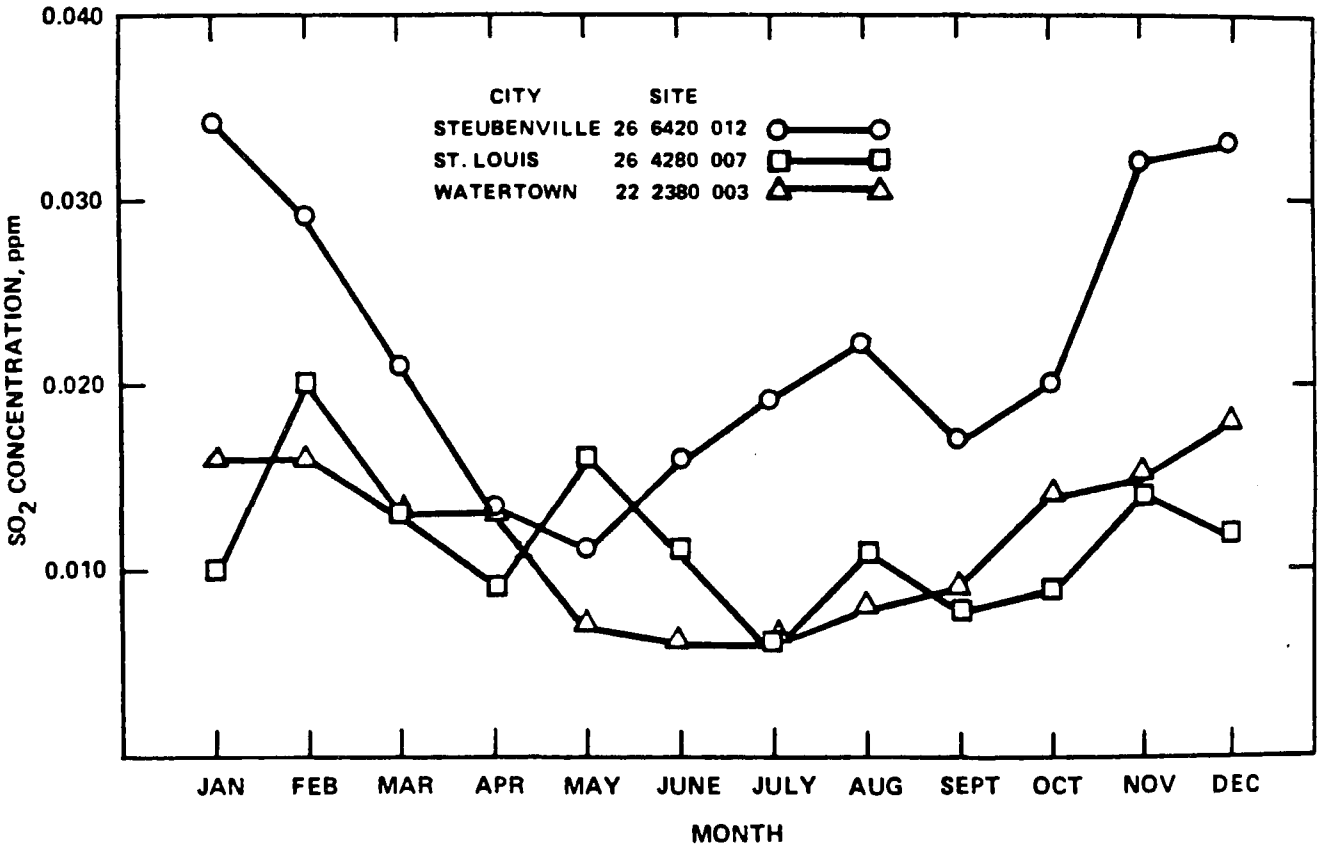



Figure 5-45. Seasonal variations in sulfur dioxide levels are shown for Steubenville, St. Louis, and Watertown.

5.2.3.5 National Status of Sulfur Dioxide Concentrations

5.2.3.5.1 National View. Of the 2365 monitoring sites reporting data in the year 1977, only 1355 had sufficient data in each quarter and for the entire year to support a valid annual mean. Of these sites, nineteen reported values above the primary annual mean standard for sulfur dioxide of 80 $\mu g/m^3$ (0.03 ppm). This represents approximately 1 percent of all the stations reporting. Of 2365 monitoring stations, fifty-eight reported levels above the 24-hr primary standard. This is based on the second-highest 24-hour average exceeding 365 $\mu g/m^3$. These 58 stations represent only 2 percent of all the reporting stations. Thirty sites reported levels above the 3-hr secondary standard of 1300 $\mu g/m^3$ or 0.5 ppm. Again this represents approximately 1 percent of all the monitoring sites. (See Table 5-30).

In 1978, five of the 484 valid sites reported values above the annual standard. This is only 1 percent of valid sites. Forty-four continuous-analyzer and two bubbler sites report a second-highest daily concentration above 365 $\mu g/m^3$. Again, this is approximately the same proportion of nonattainment sites as in 1977.

Areas of the country where $SO_2$ levels exceed NAAQS are usually associated with large point sources or a complex of industrial sources. However, many nonindustrialized or lightly industrialized urban areas in the Northeast have elevated $SO_2$ because of widespread use of high-sulfur fuels for space heating and in power plants. In the South, emissions from industrial sources are important sources of $SO_2$. In the West, power plants and smelters are the dominant sources of $SO_2$. Over the entire Nation, $SO_2$ exposures vary greatly in complexity. A single source in flat or complex terrain can cause $SO_2$ concentrations with a large standard deviation, depending on wind direction

TABLE 5-30. NATIONAL SUMMARY FOR SULFUR DIOXIDE TOTAL STATIONS REPORTING DATA, NUMBER AND PERCENTAGE OF SITES REPORTING CONCENTRATIONS ABOVE THE NATIONAL AMBIENT AIR QUALITY STANDARDS 1977-1978

| Data record and Standard exceeded | Number of Sites Reporting 1977 | Number of Sites Reporting 1978 | Number of Sites Violating 1977 | Number of Sites Violating 1978 | Percent of sites exceeding NAAQS 1977 | Percent of sites exceeding NAAQS 1978 |
|---|---|---|---|---|---|---|
| Valid annual data[a] annual standard | 1355 | 484 | 19 | 5 | 1 | 1 |
| Minimal data[b] 24-hr standard | 2365 | 2245 | 58 | 44 | 2 | 2 |
| 3-hr Standard | | | 30 | 18 | 1 | <1 |

[a]Valid annual data record must contain at least five of the scheduled 24-hour samples per quarter for EPA-recommended intermittent sampling (once every 6 days) or 75 percent of all possible values in a year for continuous instruments.

[b]Minimal data consist of at least three 24-hour samples for intermittent sampling monitors or 400 hourly values for continuous instruments.

and mixing conditions. In contrast those living in nonindustrial-urban communities could experience seasonal variability with high concentrations in the winter. Those living in an industrialized river valleys could experience persistently high $SO_2$ levels.

The regions experiencing elevated $SO_2$ concentrations are displayed in a series of national maps. Figure 5-46 shows the AQCR's where valid monitors in 1977 reported annual concentrations greater than 80 $\mu g/m^3$. The eastern AQCR's were associated with industrial urban areas for the most part, many of them in river valley settings. The AQCR's in the west have strong point sources in complex terrain settings. Unfortunately, 59 AQCR's had insufficient data. Another 179 AQCR's had monitoring, with all sites reporting annual levels below 80 $\mu g/m^3$.

The AQCR's where at least one monitor reported its second highest daily value above 365 $\mu g/m^3$ (0.14 ppm) is 1977 are shown in Figure 5-47. More AQCR's appear to have a problem with daily concentrations. Twenty-nine AQCR's had a monitor whose second highest concentration was greater than 365 $\mu g/m^3$. Eighteen AQCR's had insufficient or no data, and in the remaining 200 all sites reported second highest daily values below 365 $\mu g/m^3$.

Although the data base used in compiling Figure 5-48 was collected between 1974 and 1976, it does offer finer spatial resolution of national $SO_2$ concentrations. The second highest 24-hr average $SO_2$ concentration by county is displayed. Some areas in the west with extremely high concentrations are still problem areas in the late 1970's. Comparing this figure with Table 5-25, which shows the 45 sites with the highest concentrations, confirms that several counties and cities are still reporting high concentrations. As with the previous figures showing $SO_2$ levels by AQCR's, one should not infer spatial averaging.

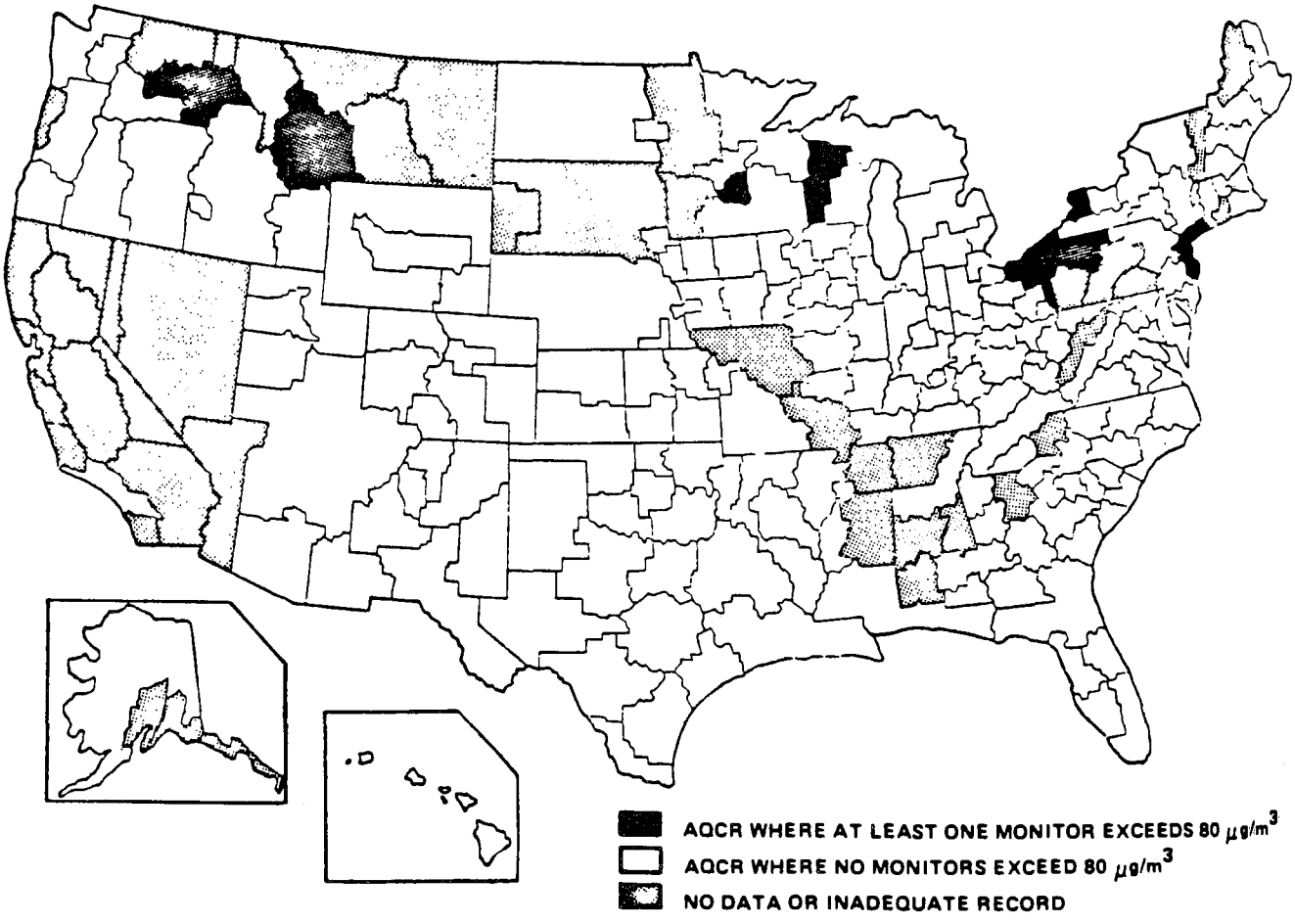



Figure 5-46. National status is shown for average annual (1977) sulfur dioxide concentrations; less than 100, 100 to 200, 200 to 365, and greater than 365 $\mu g/m^3$.

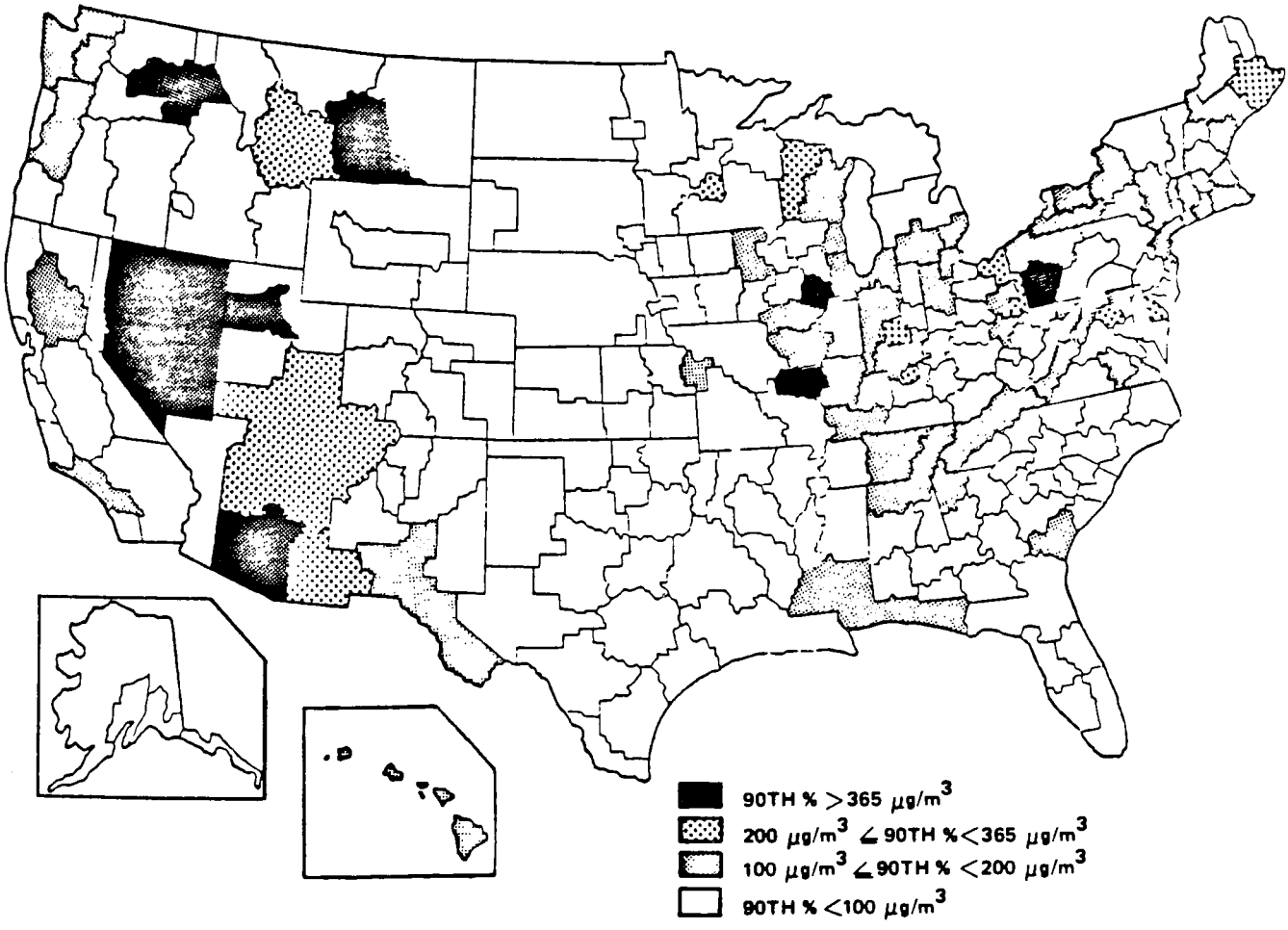



Figure 5-47. Statistical characterization of 1977 national sulfur dioxide status is shown by 90th percentile concentrations.

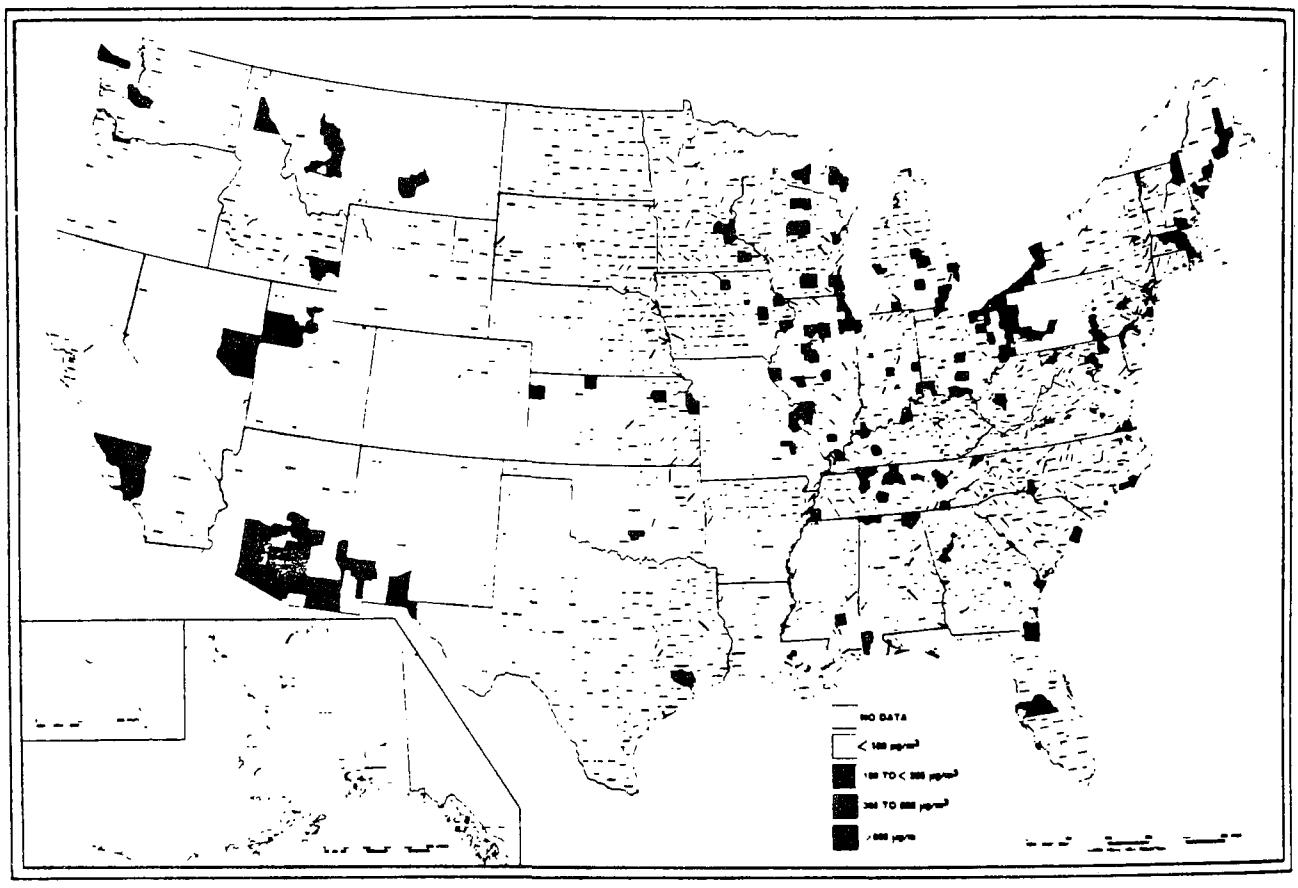



Figure 5-48. Characterization of 1974-76 national $SO_2$ status is shown by second highest 24-hr average concentration. The 24-hr primary national ambient air quality standard is 365 $\mu g/m^3$, which is not to be exceeded more than once per year.

Source: Monitoring and Reports Branch, Monitoring and Data Analysis Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency.

High readings may exist at one or more monitoring sites (for example, Deer Lodge County, MT), but it is likely that there are substantial gradients across the county, and almost certainly across an AQCR.

As indicated earlier, the range of valid annual averages from continuous monitors in 1978 extends from 3 to 158 $\mu g/m^3$. The range for bubblers is from 3 to 79 $\mu g/m^3$. Hence no bubbler site exceeds the NAAQS, whereas five continuous-monitor sites, or roughly 1 percent did exceed 100 $\mu g/m^3$ in 1978. Plotting the distribution of the percentage of sites less than a specific concentration offers further evidence of the discrepancy in sampling methods. Figure 5-49 plots the cumulative frequency distribution for valid 1978 bubbler and continuous monitor sites. Figures 5-50 and 5-51 are histograms of the annual average $SO_2$ concentrations ($\mu g/m^3$) for the valid bubbler and valid continuous-monitor sites in 1978.

According to the bubbler method, 50 percent of the monitors are averaging less than 12 $\mu g/m^3$. The 50th percentile for continuous monitors is 27 $\mu g/m^3$. A few interesting observations can be made from these distributions. If the five continuous-monitor sites represent special situations, such as smelter monitoring, and were set aside, then the distributions for both methods would be very similar. Second, the appearance of a "light tail" to the bubbler distributions indicates that the concentrations are not lognormally distributed. Presumably if the bubbler method is understimating $SO_2$ ambient concentrations it is biasing the higher values to a greater extent.

Figure 5-52 shows the cumulative frequency distributions of the 90th percentiles for valid bubbler and continuous-monitor sites. The distributions indicate 5 percent of the sites had approximately 10 percent of their reported 24-hr averaged concentrations exceeding 120 $\mu g/m^3$. One percent of the sites

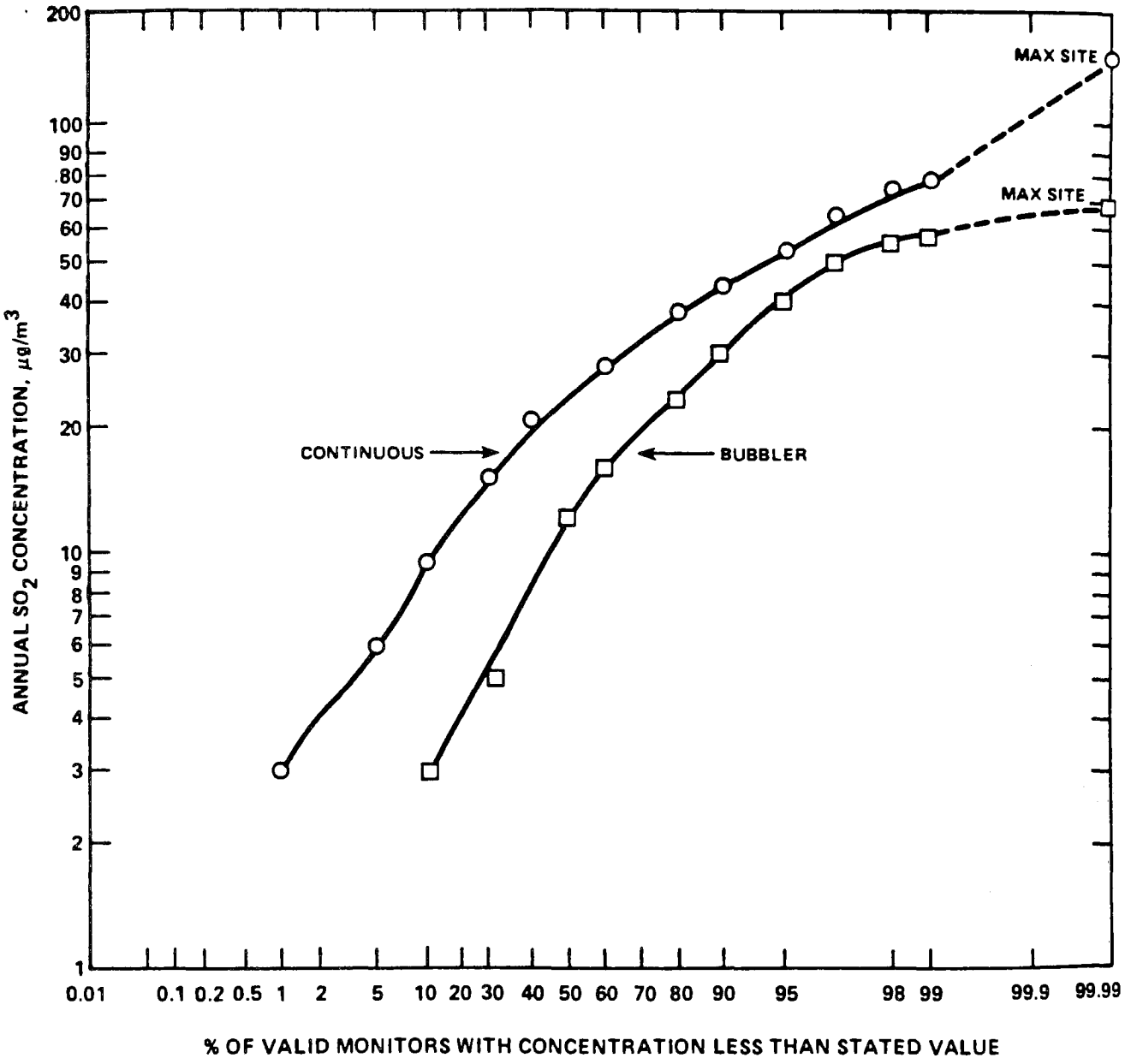



Figure 5-49. Distribution of annual average sulfur dioxide concentration in 1978 is shown for continuous and bubbler methods.

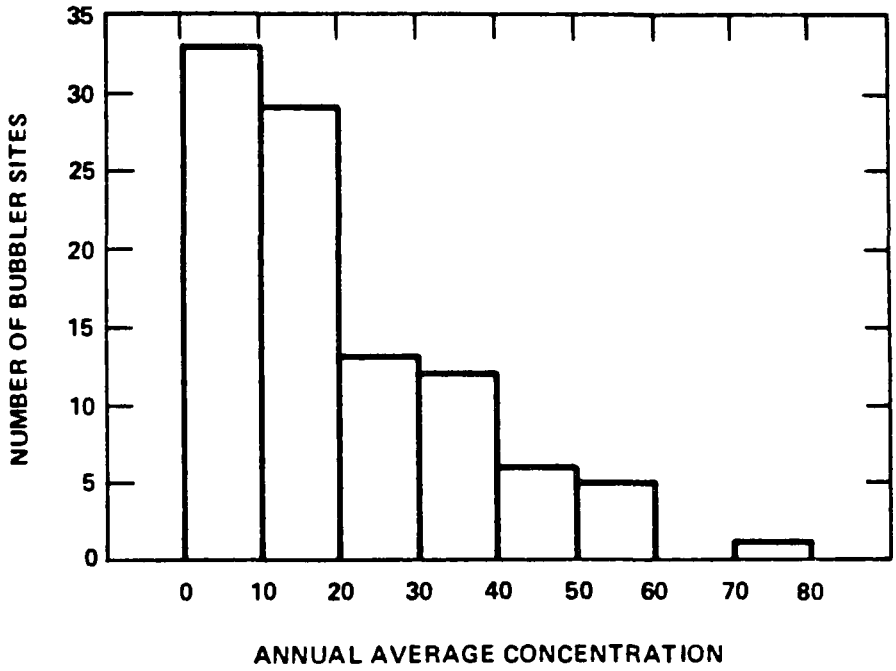



Figure 5-50. Histogram shows annual average sulfur dioxide concentrations for valid bubbler sites, 1978.

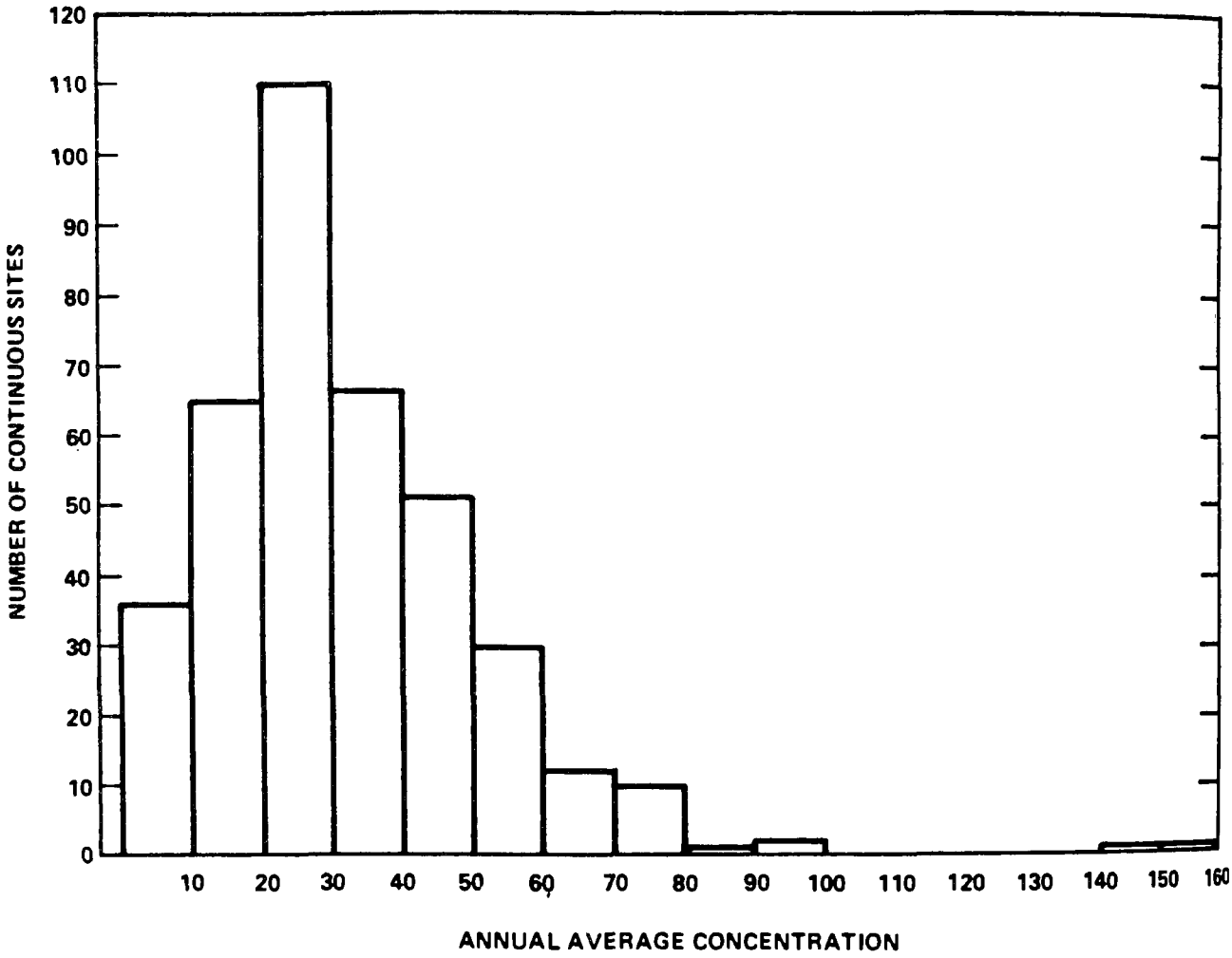



Figure 5-51. Histogram shows annual average sulfur dioxide concentrations for valid continuous sites, 1978.

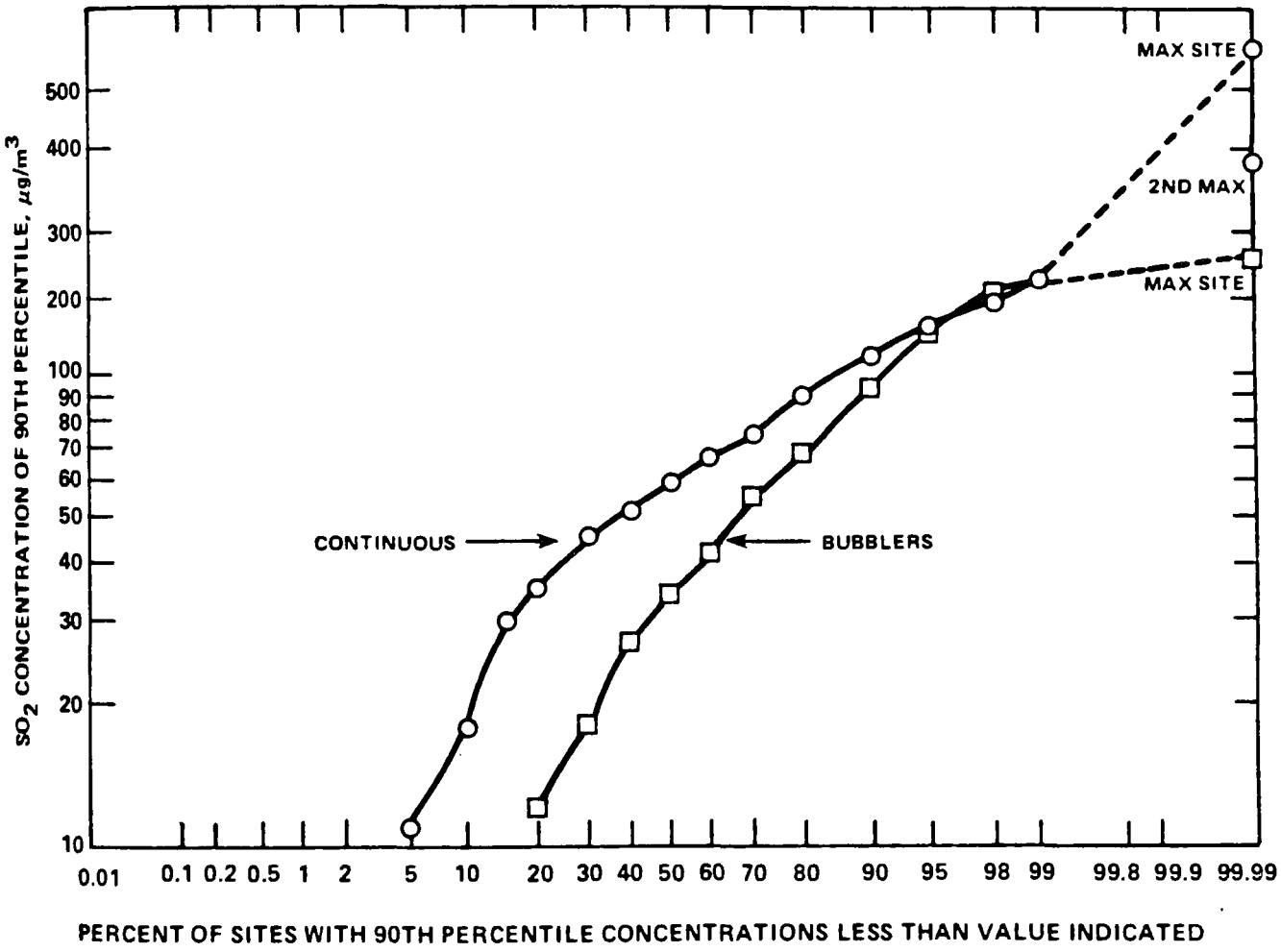



Figure 5-52. Cumulative frequency distribution of the 90th percentile is shown for valid bubblers and continuous monitors.

had daily observations exceeding 150 μmg/m$^3$ 10 percent of the time (equivalent to 36 days per year at each of these sites).

The convergence of the distributions for bubbler and continuous-monitor measurements at higher concentrations is intriguing. At first, it appears to contradict the distributions of the annual averages. However, if bubbler results are primarily affected at high temperatures then there is an explanation. For bubbler sites located in areas where $SO_2$ emissions and higher $SO_2$ concentrations occur primarily in the winter, the temperature effect would not substantially reduce the higher concentrations. However, high measurements in warmer weather would be affected. In addition, if the laboratories using bubblers to determine $SO_2$ were to report all values below the lower detectable limit as zero, the distribution would be affected in a similar manner.

The upper end of the distributions in Figures 5-49 and 5-52 represent very few sites. It is therefore not surprising to find that the maximum or second-highest site is not consistent with the full distribution.

5.2.3.5.2 Regional distribution of $SO_2$

Regional differences in $SO_2$ concentrations are not striking. In part, this is the result of the locational dependency of the monitor. In previous sections it was shown that high $SO_2$ levels are found around smelters in otherwise clean areas. In the eastern and northern states, most continuous $SO_2$ monitoring is in urbanized areas. Mean concentrations across all continuous monitors in Regions I, II, III, IV, and V range from 23 μg/m$^3$ to 51 μg/m$^3$. (See Table 5-32). The maximum annual mean for a single site in these regions ranges from 59 μg/m$^3$ in Region I to 140 μg/m$^3$ in Region III among the valid sites. In the less industrialized or populated regions (VI through X), the mean annual concentration across all sites in each region ranges from 8 μg/m$^3$ to 40 μg/m$^3$.

TABLE 5-31. BUBBLER $SO_2$ MONITOR RESULTS BY REGION

| Region | Type | Number of sites | Number of observations per site | | | | Arithmetic Means | | | | 90th Percentile | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Min. | Mean | Max. | s.d. | Min. | Mean | Max. | s.d. | Min. | Mean | Max. | s.d. |
| I | Valid | 16 | 40 | 92 | 322 | 90 | 15 | 22 | 54 | 10 | 13 | 47 | 146 | 31 |
| | All | 108 | 2 | 34 | 322 | 50 | 3 | 27 | 111 | 18 | 2 | 51 | 245 | 35 |
| II | Valid | 2 | 28 | 30 | 31 | 2 | 5 | 7 | 8 | 2 | 13 | 15 | 16 | 2 |
| | All | 12 | 5 | 13 | 31 | 9 | 3 | 21 | 57 | 18 | 2 | 46 | 96 | 33 |
| III | Valid | 0 | - | - | - | - | - | - | - | - | - | - | - | - |
| | All | 140 | 1 | 27 | 181 | 20 | 3 | 22 | 70 | 13 | 2 | 49 | 209 | 33 |
| IV | Valid | 26 | 30 | 52 | 61 | 8 | 3 | 9 | 57 | 13 | 2 | 18 | 127 | 29 |
| | All | 368 | 1 | 23 | 111 | 15 | 3 | 13 | 68 | 12 | 2 | 28 | 173 | 27 |
| V | Valid | 55 | 41 | 56 | 61 | 5 | 3 | 24 | 79 | 15 | 2 | 56 | 176 | 37 |
| | All | 307 | 1 | 33 | 181 | 18 | 3 | 27 | 104 | 16 | 2 | 58 | 210 | 35 |
| VI | Valid | 0 | - | - | - | - | - | - | - | - | - | - | - | - |
| | All | 196 | 1 | 18 | 44 | 9 | 3 | 5 | 32 | 4 | 2 | 9 | 102 | 14 |
| VII | Valid | 0 | - | - | - | - | - | - | - | - | - | - | - | - |
| | All | 63 | 5 | 24 | 47 | 11 | 3 | 9 | 48 | 7 | 2 | 18 | 149 | 22 |
| VIII | Valid | 0 | - | - | - | - | - | - | - | - | - | - | - | - |
| | All | 40 | 2 | 21 | 38 | 10 | 3 | 3 | 8 | 1 | 2 | 3 | 22 | 4 |
| IX | Valid | 0 | - | - | - | - | - | - | - | - | - | - | - | - |
| | All | 0 | - | - | - | - | - | - | - | - | - | - | - | - |
| X | Valid | 0 | - | - | - | - | - | - | - | - | - | - | - | - |
| | All | 15 | 6 | 12 | 15 | 4 | 11 | 27 | 63 | 21 | 13 | 34 | 76 | 25 |

TABLE 5-31. (continued)

| Region | Type | Number of sites | Number of observations per site | | | | Arithmetic Means | | | | 90th Percentile | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Min. | Mean | Max. | s.d. | Min. | Mean | Max. | s.d. | Min. | Mean | Max. | s.d. |
| Alaska | Valid | 0 | - | - | - | - | - | - | - | - | - | - | - | - |
| | All | 7 | 1 | 21 | 29 | 11 | 5 | 9 | 11 | 2 | 10 | 18 | 31 | 9 |
| Hawaii | Valid | 0 | - | - | - | - | - | - | - | - | - | - | - | - |
| | All | 9 | 10 | 13 | 15 | 2 | 3 | 10 | 36 | 11 | 2 | 18 | 73 | 24 |
| Nation | Valid | 99 | | | | | | | | | | | | |
| | All | 1265 | | | | | | | | | | | | |

TABLE 5-32. CONTINUOUS $SO_2$ MONITOR RESULTS BY REGION.

| Region | Type | Number of sites | Number of observations per site | | | | Arithmetic Means | | | | 90th Percentile | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Min. | Mean | Max. | s.d. | Min. | Mean | Max. | s.d. | Min. | Mean | Max. | s.d. |
| I | Valid | 22 | 6665 | 7519 | 8416 | 567 | 16 | 33 | 59 | 12 | 34 | 65 | 147 | 27 |
| | All | 72 | 185 | 4582 | 8416 | 2720 | 8 | 39 | 138 | 23 | 14 | 77 | 340 | 52 |
| II | Valid | 51 | 6597 | 7540 | 8697 | 546 | 15 | 37 | 78 | 16 | 35 | 72 | 159 | 30 |
| | All | 87 | 140 | 5815 | 8697 | 2380 | 15 | 41 | 94 | 19 | 35 | 78 | 173 | 33 |
| III | Valid | 26 | 6578 | 7562 | 8638 | 670 | 12 | 51 | 140 | 23 | 34 | 97 | 282 | 46 |
| | All | 108 | 94 | 4381 | 8638 | 2534 | 7 | 45 | 140 | 21 | 14 | 86 | 282 | 40 |
| IV | Valid | 100 | 6678 | 8305 | 8755 | 574 | 5 | 23 | 63 | 12 | 9 | 54 | 135 | 27 |
| | All | 203 | 421 | 5754 | 8755 | 2848 | 3 | 23 | 77 | 13 | 3 | 49 | 180 | 29 |
| V | Valid | 111 | 6580 | 7640 | 8715 | 625 | 7 | 36 | 84 | 16 | 10 | 70 | 167 | 30 |
| | All | 254 | 129 | 5512 | 8715 | 2327 | 3 | 37 | 192 | 25 | 5 | 73 | 501 | 50 |
| VI | Valid | 13 | 6631 | 7443 | 8452 | 607 | 3 | 13 | 31 | 7 | 3 | 31 | 69 | 19 |
| | All | 32 | 1669 | 5461 | 8452 | 2072 | 3 | 12 | 56 | 13 | 3 | 29 | 160 | 38 |
| VII | Valid | 13 | 6769 | 7540 | 8325 | 439 | 6 | 31 | 47 | 14 | 13 | 62 | 94 | 25 |
| | All | 38 | 334 | 4676 | 8325 | 2624 | 4 | 25 | 82 | 20 | 5 | 52 | 155 | 41 |
| VIII | Valid | 12 | 6741 | 7739 | 8624 | 514 | 3 | 40 | 152 | 47 | 3 | 100 | 488 | 146 |
| | All | 49 | 373 | 4694 | 8624 | 2358 | 3 | 34 | 152 | 39 | 3 | 89 | 488 | 113 |
| IX | Valid | 19 | 6857 | 7952 | 8638 | 507 | 3 | 8 | 29 | 6 | 3 | 16 | 48 | 12 |
| | All | 52 | 105 | 4973 | 8638 | 2525 | 3 | 24 | 87 | 20 | 3 | 49 | 213 | 49 |
| X | Valid | 18 | 6651 | 7854 | 8677 | 464 | 13 | 34 | 78 | 18 | 35 | 90 | 150 | 38 |
| | All | 29 | 625 | 6158 | 8677 | 2526 | 13 | 33 | 78 | 17 | 29 | 72 | 150 | 38 |

TABLE 5-32. (continued)

| Region | Type | Number of sites | Number of observations per site | | | | Arithmetic Means | | | | 90th Percentile | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Min. | Mean | Max. | s.d. | Min. | Mean | Max. | s.d. | Min. | Mean | Max. | s.d. |
| Alaska | Valid | 0 | - | - | - | - | - | - | - | - | - | - | - | - |
| | All | 4 | 1965 | 2057 | 2114 | 65 | 3 | 8 | 17 | 6 | 3 | 13 | 22 | 8 |
| Hawaii | Valid | 0 | - | - | - | - | - | - | - | - | - | - | - | - |
| | All | 0 | - | - | - | - | - | - | - | - | - | - | - | - |
| Nation | Valid | 385 | | | | | | | | | | | | |
| | All | 928 | | | | | | | | | | | | |

Even with the summary of the 1978 continuous $SO_2$ data as displayed in Table 5-32, it is difficult to speculate on regional differences in $SO_2$ concentrations. Concentrations are influenced primarily by local sources. The locations of monitors have clearly not been randomly chosen in each region, nor have they been systematically deployed for source population or background sampling. Therefore, a better indicator of regional differences in $SO_2$ concentrations and population exposures can be obtained from examining sulfur emission patterns. (See Chapter 4).

Another approach to examining the differences between regions in $SO_2$ concentrations is offered in Table 5-33. In this table the number of sites exceeding an annual average of 80 $\mu g/m^3$ and the number of sites where the second highest 24-hour average exceeds 365 $\mu g/m^3$ are tabulated. The "potential" for higher $SO_2$ concentrations can be inferred from the number of all sites (valid and invalid) that fall into these two categories. The definition of "valid site" in this case refers to the number of observations, not the accuracy of the data.

Table 5-33 indicates that Region V has the greatest number of sites with a second highest daily value exceeding 365 $\mu g/m^3$. This is followed by Region VIII with 12 "potentially" high sites.

The general conclusions that might be drawn from this table are that the regional and national status of $SO_2$ attainment of standards might be substantially underestimated. There are two possible reasons. One is that bubbler $SO_2$ monitors do not report the same proportion of violations as do continuous monitors. The second is that only 41 percent of the continuous monitors are considered valid for determining annual averages; additional locations with high $SO_2$ concentrations are not noted in national summaries.

TABLE 5-33. COMPARISON OF BUBBLER AND CONTINUOUS $SO_2$ MONITOR RESULTS BY REGION

| Region | Type | Total number of sites | | Number of sites with arithmetic mean $\geq$ 80 μg/m$^3$ | | Number with second highest value $\geq$ 365 μg/m$^3$ | |
|---|---|---|---|---|---|---|---|
| | | continuous | bubbler | continuous | bubbler | continuous | bubbler |
| I | Valid | 22 | 16 | 0 | 0 | 1 | 0 |
| | All | 72 | 108 | 4 | 1 | 4 | 1 |
| II | Valid | 51 | 2 | 0 | 0 | 0 | 0 |
| | All | 87 | 12 | 4 | 0 | 0 | 0 |
| III | Valid | 26 | 0 | 1 | 0 | 2 | 0 |
| | All | 108 | 140 | 6 | 0 | 3 | 0 |
| IV | Valid | 100 | 26 | 0 | 0 | 6 | 1 |
| | All | 203 | 368 | 0 | 0 | 7 | 1 |
| V | Valid | 111 | 55 | 1 | 0 | 8 | 0 |
| | All | 254 | 307 | 11 | 2 | 20 | 0 |
| VI | Valid | 13 | 0 | 0 | 0 | 0 | 0 |
| | All | 32 | 196 | 0 | 0 | 0 | 0 |
| VII | Valid | 13 | 0 | 0 | 0 | 0 | 0 |
| | All | 38 | 63 | 1 | 0 | 2 | 0 |
| VIII | Valid | 12 | 0 | 3 | 0 | 3 | 0 |
| | All | 49 | 40 | 6 | 0 | 12 | 0 |
| IX | Valid | 19 | 0 | 0 | 0 | 0 | 0 |
| | All | 52 | 0 | 2 | 0 | 4 | 0 |
| X | Valid | 18 | 0 | 0 | 0 | 4 | 0 |
| | All | 29 | 15 | 0 | 0 | 4 | 0 |
| Alaska | Valid | 0 | 0 | 0 | 0 | 0 | 0 |
| | All | 4 | 7 | 0 | 0 | 0 | 0 |
| Hawaii | Valid | 0 | 0 | 0 | 0 | 0 | 0 |
| | All | 0 | 9 | 0 | 0 | 0 | 0 |
| Nation | Valid | 385 | 99 | 5 | 0 | 24 | 1 |
| | All | 928 | 1265 | 34 | 3 | 56 | 2 |

5.2.3.6 Severity of Ambient Exposures--The 90th percentile of the 1977 sulfur dioxide data was examined for every AQCR. The number of $SO_2$ monitors in each AQCR and the subsets that reported their 90th percentile level <100 μg/m$^3$, between 100 and 200, between 200 and 365, and >365 μg/m$^3$ are tabulated in Table 5-34. The 90th percentile serves as an indicator of the severity of the $SO_2$ ambient concentrations. It represents the concentrations that the population might be repeatedly exposed to as frequently as once each ten days. In other words, it represents an ambient $SO_2$ concentration that might be experienced some 870 hr/yr, or for 36 days of the year.

The severity of $SO_2$ exposure, according to the 90th percentile level is displayed for each AQCR in Figure 5-53. On the basis of the 1977 aerometric data, most of the urban areas of the East and Northeast frequently have $SO_2$ levels exceeding 100 μg/m$^3$. The urban areas around Washington, D.C., western Pennsylvania, eastern Ohio, southern Indiana, northern Kentucky, St. Louis, and Indianapolis have levels that repeatedly exceed 200 mg/m$^3$ and some are even greater than 365 mg/m$^3$. Close examination of the aerometric data indicates that the peak concentrations are often two to five times the 90th percentile value. Again, the large point sources in the West are responsible for the high 90th percentile levels in Montana, Nevada, Idaho, Arizona, and New Mexico. Throughout the Midwest and high Plains States, the 90th percentile levels are less than 100 mg/m$^3$, indicating very low means in these areas.

5.2.3.7 Sulfur Dioxide Concentrations And Historic Trends

5.2.3.7.1 National trends. The $SO_2$ levels in most urban areas in the United States have improved steadily since the mid-1960's. The trend of decreasing $SO_2$ concentrations can be resolved into three distinct periods. From 1964-69 the improvement was gradual. In the middle period, between 1969 and 1972, the

TABLE 5-34. NINTIETH-PERCENTILE SULFUR DIOXIDE LEVELS, 1977.
(NADB 1977, $SO_2$ 24-HR BUBBLERS AND 1-HR CONTINUOUS)

| State | AQCR | Number of sites | Number of Sites Reporting 90th percentile concentrations ($\mu g/m^3$) | | | |
|---|---|---|---|---|---|---|
| | | | < 100 | 100-200 | 200-365 | > 365 |
| Alabama | 1 | 1 | 1 | | | |
| | 2[a] | 1 | 1 | | | |
| | 3 | 1 | 1 | | | |
| | 4 | 5 | 5 | | | |
| | 5[a] | 69 | 68 | 1 | | |
| | 6 | 2 | 2 | | | |
| | 7[a] | 17 | 16 | 1 | | |
| Alaska | 8 | 1 | 1 | | | |
| | 9 | 1 | 1 | | | |
| | 10 | | | | | |
| | 11 | 4 | 4 | | | |
| Arizona | 12[a] | 13 | 10 | 1 | 2 | |
| | 13[a] | 3 | 3 | | | |
| | 14[a] | 16 | 15 | | 1 | |
| | 15 | 18 | 15 | 1 | | 2 |
| Arkansas | 16 | 7 | 7 | | | |
| | 17[a] | 3 | 3 | | | |
| | 18[a] | 9 | 9 | | | |
| | 19[a] | 2 | 2 | | | |
| | 20 | 1 | 1 | | | |
| | 21 | 1 | 1 | | | |
| | 22[a] | 6 | 6 | | | |
| California | 24 | 34 | 29 | 5 | | |
| | 25 | | | | | |
| | 26 | | | | | |
| | 27 | | | | | |
| | 28 | 2 | 1 | 1 | | |
| | 29 | 5 | 5 | | | |
| | 30 | 16 | 16 | | | |
| | 31 | 4 | 4 | | | |
| | 32 | 3 | 3 | | | |
| | 33 | 1 | 1 | | | |
| Colorado | 34 | | | | | |
| | 35 | | | | | |
| | 36 | 8 | 8 | | | |
| | 37 | | | | | |
| | 38 | | | | | |
| | 39 | | | | | |
| | 40 | | | | | |

[a]Interstate AQCR, reported once

TABLE 5-34 (continued)

| State | AQCR | Number of sites | Number of Sites Reporting 90th percentile concentrations ($\mu g/m^3$) < 100 | 100-200 | 200-365 | > 365 |
|---|---|---|---|---|---|---|
| Connecticut | 41 | 3 | 2 | 1 | | |
| | 42[a] | 34 | 31 | 3 | | |
| | 43[a] | 100 | 93 | 7 | | |
| | 44 | 1 | 1 | | | |
| Delaware | 45[a] | 47 | 13 | 23 | 1 | |
| | 46 | 3 | 3 | | | |
| D.C. | 47 | 75 | 56 | 17 | 2 | |
| Florida | 48 | 11 | 11 | | | |
| | 49[a] | 48 | 48 | | | |
| | 50 | 28 | 28 | | | |
| | 51 | 11 | 11 | | | |
| | 52 | 53 | 50 | 2 | 1 | |
| Georgia | 53[a] | 8 | 8 | | | |
| | 54 | 7 | 7 | | | |
| | 55[a] | 15 | 12 | 3 | | |
| | 56 | 15 | 14 | 1 | | |
| | 57 | 1 | 1 (1 obs) | | | |
| | 58[a] | 13 | 12 | 3 | | |
| | 59 | 3 | 3 | | | |
| Hawaii | 60 | 60 | 10 | 9 | 1 | |
| Idaho | 61 | 4 | 2 | 2 | | |
| | 62[a] | 14 | 8 | 1 | 3 | 2 |
| | 63 | 1 | 1 | | | |
| | 64 | 2 | 2 | | | |
| Illinois | 65[a] | 14 | 11 | 3 | | |
| | 66 | 3 | 3 | | | |
| | 67 | 114 | 96 | 18 | | |
| | 68[a] | 4 | 4 | | | |
| | 69[a] | 7 | 7 | | | |
| | 70 | 29 | 15 | 11 | 2 | 1 |
| | 71 | 4 | 4 | | | |
| | 72[a] | 29 | 27 | 2 | | |
| | 73 | 3 | 3 | | | |
| | 74 | 5 | 3 | 2 | | |
| | 75 | 10 | 8 | 2 | | |
| Indiana | 76 | 6 | 6 | | | |
| | 77[a] | 28 | 28 | | | |
| | 78[a] | 31 | 18 | 10 | 3 | |
| | 79[a] | 36 | 30 | 6 | | |
| | 80 | 22 | 13 | 8 | 1 | |
| | 81 | 2 | 2 | | | |
| | 82[a] | 17 | 12 | 5 | | |
| | 83 | 5 | 4 | 1 | | |
| | 84 | 11 | 10 | 1 | | |

TABLE 5-34. (continued)

| State | AQCR | Number of sites | Number of Sites Reporting 90th percentile concentrations ($\mu g/m^3$) < 100 | 100-200 | 200-365 | > 365 |
|---|---|---|---|---|---|---|
| Iowa | 69[a] | | | | | |
| | 85[a] | 9 | 9 | | | |
| | 86[a] | 2 | 2 | | | |
| | 87[a] | 3 | 3 | | | |
| | 88 | 4 | 3 | 1 | | |
| | 89 | 1 | 1 | | | |
| | 90 | 1 | 1 | | | |
| | 91 | 2 | 2 | | | |
| | 92 | 13 | 13 | | | |
| | 93 | 1 | 1 | | | |
| Kansas | 94[a] | 20 | 19 | 1 | | |
| | 95 | 14 | 14 | | | |
| | 96 | 2 | 2 | | | |
| | 97 | 3 | 3 | | | |
| | 98 | 2 | 2 | | | |
| | 99 | 14 | 14 | | | |
| | 100 | 2 | 2 | | | |
| Kentucky | 72[a] | | | | | |
| | 77[a] | | | | | |
| | 78[a] | | | | | |
| | 79[a] | | | | | |
| | 101 | 7 | 7 | | | |
| | 102 | 13 | 13 | | | |
| | 103[a] | 25 | 25 | | | |
| | 104 | 8 | 8 | | | |
| | 105 | 6 | 6 | | | |
| Louisiana | 19[a] | | | | | |
| | 22[a] | | | | | |
| | 106[a] | 24 | 24 | | | |
| Maine | 107[a] | 25 | 23 | 2 | | |
| | 108 | 2 | 2 | | | |
| | 109 | 20 | 17 | 1 | 2 | |
| | 110 | 8 | 6 | 2 | | |
| Maryland | 47[a] | | | | | |
| | 112 | 7 | 7 | | | |
| | 113[a] | 20 | 17 | 3 | | |
| | 114 | 6 | 6 | | | |
| | 115 | 46 | 44 | 2 | | |
| | 116 | 3 | 3 | | | |
| Massa-chusetts | 42[a] | | | | | |
| | 117 | 6 | 6 | | | |
| | 118 | 13 | 13 | | | |
| | 119 | 26 | 25 | 1 | | |
| | 120[a] | 24 | 22 | 2 | | |
| | 121[a] | 28 | 25 | 3 | | |

TABLE 5-34. (continued)

| State | AQCR | Number of sites | Number of Sites Reporting 90th percentile concentrations ($\mu g/m^3$) < 100 | 100-200 | 200-365 | > 365 |
|---|---|---|---|---|---|---|
| Michigan | 82[a] | | | | | |
| | 122 | 15 | 15 | | | |
| | 123 | 21 | 19 | 2 | | |
| | 124[a] | 14 | 12 | 2 | | |
| | 125 | 6 | 5 | 1 | | |
| | 126 | 1 | 1 | | | |
| Minnesota | 127 | 3 | 3 | | | |
| | 128[a] | 9 | 9 | | | |
| | 129[a] | 25 | 25 | | | |
| | 130[a] | 1 | 1 | | | |
| | 131 | 15 | 13 | 1 | 1 | |
| | 132 | 2 | 2 | | | |
| | 133 | 1 | 1 | | | |
| Missis-sippi | 5[a] | | | | | |
| | 18[a] | | | | | |
| | 134 | 2 | 2 | | | |
| | 135 | 1 | 1 | | | |
| Missouri | 70[a] | | | | | |
| | 94[a] | | | | | |
| | 137 | 3 | 3 | | | |
| | 138 | 1 | 1 | | | |
| | 139 | 6 | 6 | | | |
| Montana | 140 | 4 | 1 | 1 | 1 | 1 |
| | 141 | 1 | 1 | | | |
| | 142 | 9 | 5 | 3 | 1 | |
| | 143 | 5 | 5 | | | |
| | 144 | | | | | |
| Nebraska | 85[a] | | | | | |
| | 86[a] | | | | | |
| | 145 | 3 | 3 | | | |
| | 146 | 4 | 4 | | | |
| Nevada | 13[a] | | | | | |
| | 147 | 1 | | | | 1 |
| | 148 | 1 | 1 | | | |
| New Hampshire | 107[a] | | | | | |
| | 121[a] | | | | | |
| | 149 | 1 | 1 | | | |
| New Jersey | 43[a] | | | | | |
| | 45[a] | | | | | |
| | 150 | 2 | 2 | | | |
| | 151 | 1 | 1 | | | |

TABLE 5-34. (continued)

| State | AQCR | Number of sites | Number of Sites Reporting 90th percentile concentrations ($\mu g/m^3$) < 100 | 100-200 | 200-365 | > 365 |
|---|---|---|---|---|---|---|
| New Mexico | 12[a] | | | | | |
| | 14[a] | | | | | |
| | 152 | 2 | 2 | | | |
| | 153[a] | 15 | 14 | 1 | | |
| | 154 | 1 | 1 | | | |
| | 155 | 4 | 4 | | | |
| | 156 | 1 | 1 | | | |
| | 157 | 1 | 1 | | | |
| New York | 43[a] | | | | | |
| | 158 | 15 | 14 | 1 | | |
| | 159[a] | 7 | 7 | | | |
| | 160 | 17 | 12 | 5 | | |
| | 161 | 17 | 13 | 4 | | |
| | 162 | 35 | 26 | 8 | 1 | |
| | 163 | 4 | 4 | | | |
| | 164 | 10 | 7 | 3 | | |
| North Carolina | 136[a] | 11 | 11 | | | |
| | 165 | 6 | 6 | | | |
| | 166 | 6 | 6 | | | |
| | 167[a] | 25 | 25 | | | |
| | 168 | 3 | 3 | | | |
| | 169 | 3 | 3 | | | |
| | 170 | 6 | 6 | | | |
| | 171 | 11 | 10 | 1 | | |
| North Dakota | 130[a] | | | | | |
| | 172 | 16 | 16 | | | |
| Ohio | 79[a] | | | | | |
| | 103[a] | | | | | |
| | 124[a] | | | | | |
| | 173 | 13 | 13 | | | |
| | 174 | 91 | 55 | 31 | 5 | |
| | 175 | 9 | 9 | | | |
| | 176 | 14 | 14 | | | |
| | 177 | 6 | 5 | 1 | | |
| | 178 | 13 | 9 | 4 | | |
| | 179[a] | 5 | 4 | 1 | | |
| | 180 | 2 | 2 | | | |
| | 181[a] | 27 | 5 | 21 | 1 | |
| | 182 | 5 | 5 | | | |
| | 183 | 7 | 5 | 2 | | |
| Oklahoma | 17[a] | | | | | |
| | 184 | 8 | 8 | | | |
| | 185 | 1 | 1 | | | |
| | 186 | 12 | 12 | | | |
| | 187 | 1 | 1 | | | |
| | 188 | 2 | 2 | | | |
| | 189 | 3 | 3 | | | |

TABLE 5-34. (continued)

| State | AQCR | Number of sites | Number of Sites Reporting 90th percentile concentrations ($\mu g/m^3$) < 100 | 100-200 | 200-365 | > 365 |
|---|---|---|---|---|---|---|
| Oregon | 190 | 1 | 1 | | | |
| | 191 | 1 | 1 | | | |
| | 192 | 2 | 2 | | | |
| | 193[a] | 10 | 8 | 2 | | |
| | 194 | 1 | 1 | | | |
| Penn-sylvania | 45[a] | | | | | |
| | 195 | | | | | |
| | 196 | | | | | |
| | 197 | 7 | | 3 | 3 | 1 |
| Puerto Rico | 244 | 9 | 9 | | | |
| Rhode Island | 120[a] | | | | | |
| South Carolina | 53[a] | | | | | |
| | 58[a] | | | | | |
| | 167[a] | | | | | |
| | 198 | 4 | 4 | | | |
| | 199 | 9 | 9 | | | |
| | 200 | 7 | 7 | | | |
| | 201 | 2 | 2 | | | |
| | 202 | 15 | 15 | | | |
| | 203 | 3 | 3 | | | |
| | 204 | 6 | 6 | | | |
| South Dakota | 87[a] | | | | | |
| | 205 | 3 | 3 | | | |
| | 206 | 2 | 2 | | | |
| Tennessee | 7[a] | | | | | |
| | 18[a] | | | | | |
| | 55[a] | | | | | |
| | 207 | 46 | 44 | 5 | | |
| | 208 | 29 | 27 | 2 | | |
| | 209 | 1 | 1 | | | |
| Texas | 22[a] | | | | | |
| | 106[a] | | | | | |
| | 153[a] | | | | | |
| | 210 | 4 | 4 | | | |
| | 211 | 3 | 3 | | | |
| | 212 | 12 | 12 | | | |
| | 213 | 2 | 2 | | | |
| | 214 | 14 | 14 | | | |
| | 215 | 20 | 20 | | | |
| | 216 | 55 | 55 | | | |
| | 217 | 8 | 8 | | | |
| | 218 | 6 | 6 | | | |
| Utah | 14[a] | | | | | |
| | 219 | 4 | 4 | | | |
| | 220 | 14 | 7 | 3 | | 4 |
| Vermont | 159[a] | | | | | |
| | 221 | 2 | 2 | | | |

TABLE 5-34. (continued)

| State | AQCR | Number of sites | Number of Sites Reporting 90th percentile concentrations ($\mu g/m^3$) < 100 | 100-200 | 200-365 | > 365 |
|---|---|---|---|---|---|---|
| Virginia | 47[a] | | | | | |
| | 207[a] | | | | | |
| | 222 | 10 | 10 | | | |
| | 223 | 14 | 11 | 3 | | |
| | 224 | 1 | 1 | | | |
| | 225 | 17 | 15 | 2 | | |
| | 226 | 9 | 8 | 1 | | |
| Washington | 62[a] | | | | | |
| | 193[a] | 1 | 1 | | | |
| | 227 | 1 | 1 | | | |
| | 228 | 3 | 2 | 1 | | |
| | 229 | 10 | 9 | 1 | | |
| | 230 | 1 | 1 | | | |
| West Virginia | 103[a] | | | | | |
| | 113[a] | | | | | |
| | 179[a] | | | | | |
| | 181[a] | | | | | |
| | 232 | 1 | 1 | | | |
| | 233 | 1 | 1 | | | |
| | 234 | 6 | 6 | | | |
| | 235 | 4 | 4 | | | |
| | 236 | 1 | 1 | | | |
| Wisconsin | 128[a] | | | | | |
| | 129[a] | | | | | |
| | 237 | 14 | 13 | 1 | | |
| | 238 | 13 | 11 | | 2 | |
| | 239 | 11 | 10 | 1 | | |
| | 240 | 15 | 15 | | | |
| Wyoming | 241 | 4 | 4 | | | |
| | 242 | 3 | 3 | | | |
| | 243 | 9 | 9 | | | |
| Guam | 246 | 4 | 4 | | | |
| Virgin Islands | 247 | 4 | 4 | | | |

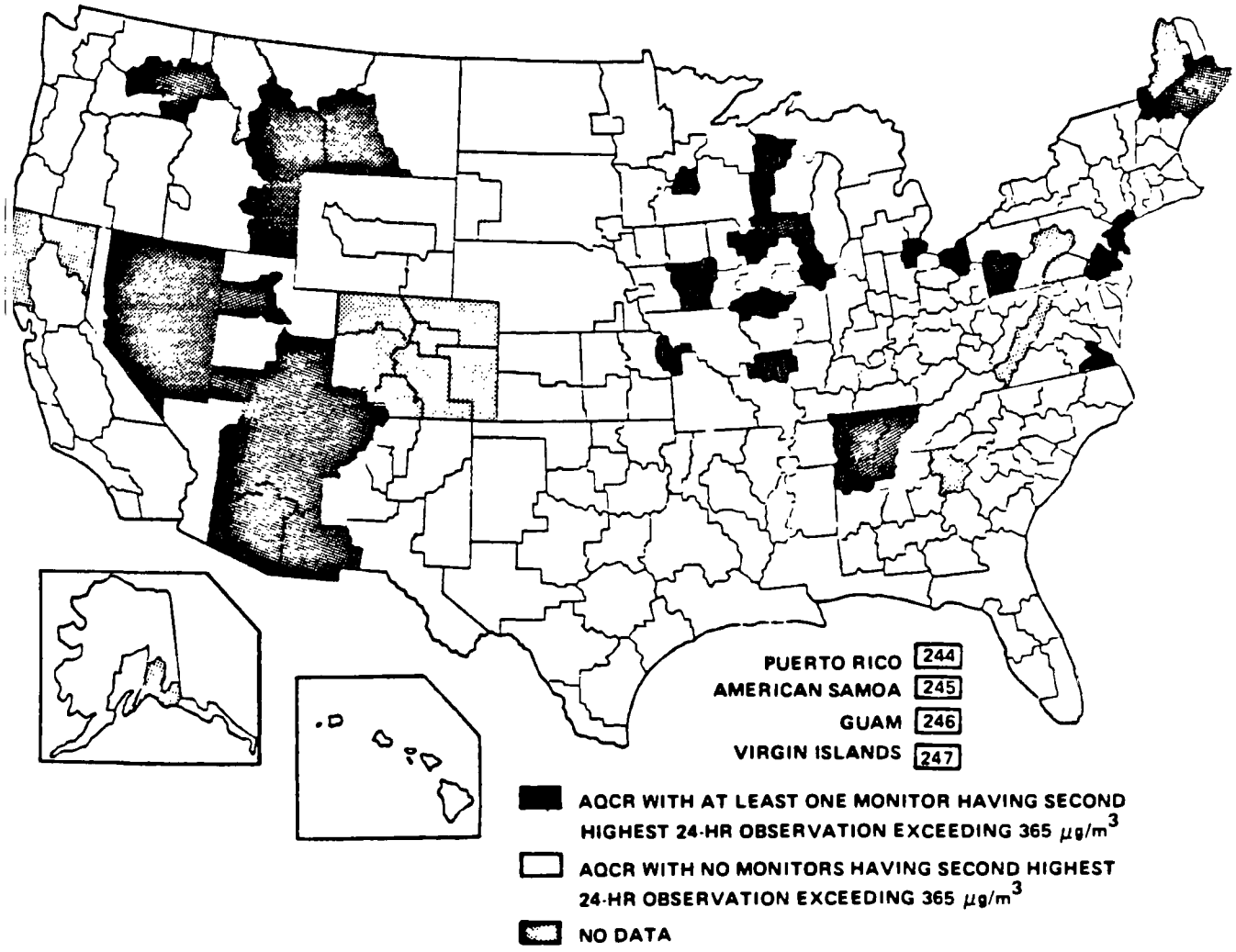



Figure 5-53. Characterization of 1977 national sulfur dioxide status is shown by 24-hr average concentrations.

improvement in most urban areas was more pronounced. Since 1973 the improvement has again become slower. The 1977 EPA trends report states: "In most urban areas, this is consistent with the switch in emphasis from attainment of standards to maintenance of air quality; that is, the initial effort was to reduce pollution to acceptable levels followed by efforts to maintain air quality at these lower levels." From 1972 through 1977 annual averaged $SO_2$ levels dropped by 17 percent, or an annual improvement rate of about 4 percent per year. Figure 5-54 summarizes the annual averaged $SO_2$ concentrations for 32 urban NASN stations for the years 1964-71. In this figure the first two periods are apparent. In Figure 5-55 the national trends in annual average $SO_2$ concentrations from 1972-1977 at 1333 sampling sites are displayed. The symbols in Figure 5-55 are the same as those used in earlier figures on TSP trends. The diamond symbolizes the composite annual average concentration; the triangle is the median value.

Over the period of 1970-77 $SO_2$ emissions are reported to have decreased only slightly (EPA, 1978). In 1970 the estimated annual manmade $SO_2$ emissions were 29.8 million metric tons. By 1977 this was reduced only to 27.4 million metric tons. The improvement in the ambient air quality levels for $SO_2$ reflects displacement of sources from urban areas to rural areas, the restriction of sulfur content of fuels used in low-level area sources, and the building of newer sources with taller stacks.

5.2.3.7.2 Urban trends. The first air quality criteria document for sulfur oxides, published in 1969, presented the frequency distributions for sulfur dioxide levels in selected American cities for 1962-1967 (U.S. Department of Health, Education, and Welfare, 1969). Improvements in sulfur dioxide levels in each of the six cities can be demonstrated by comparing the available

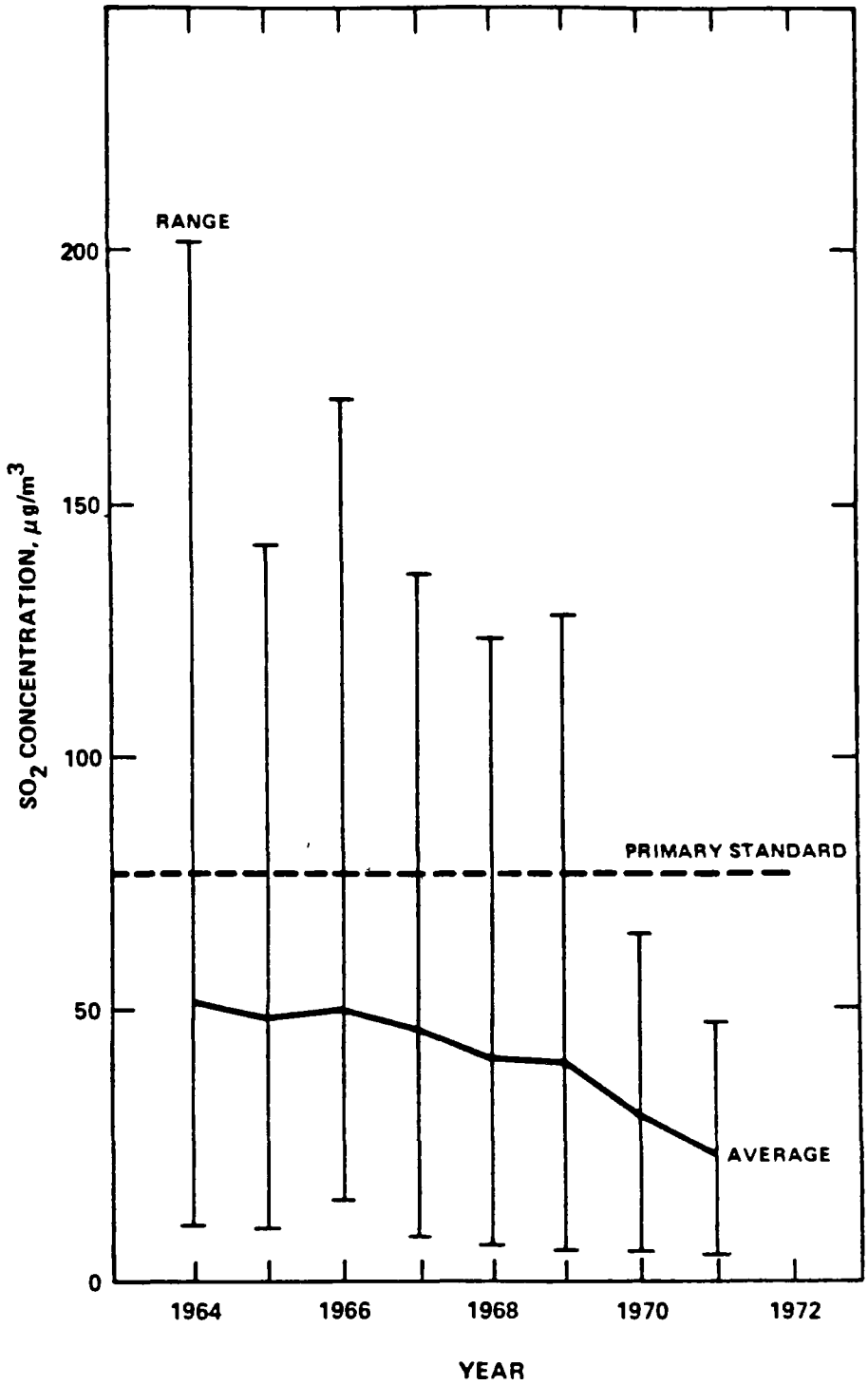



Figure 5-54. Average sulfur dioxide concentrations are shown for 32 urban NASN stations.

Source: National Academy of Sciences (1975).

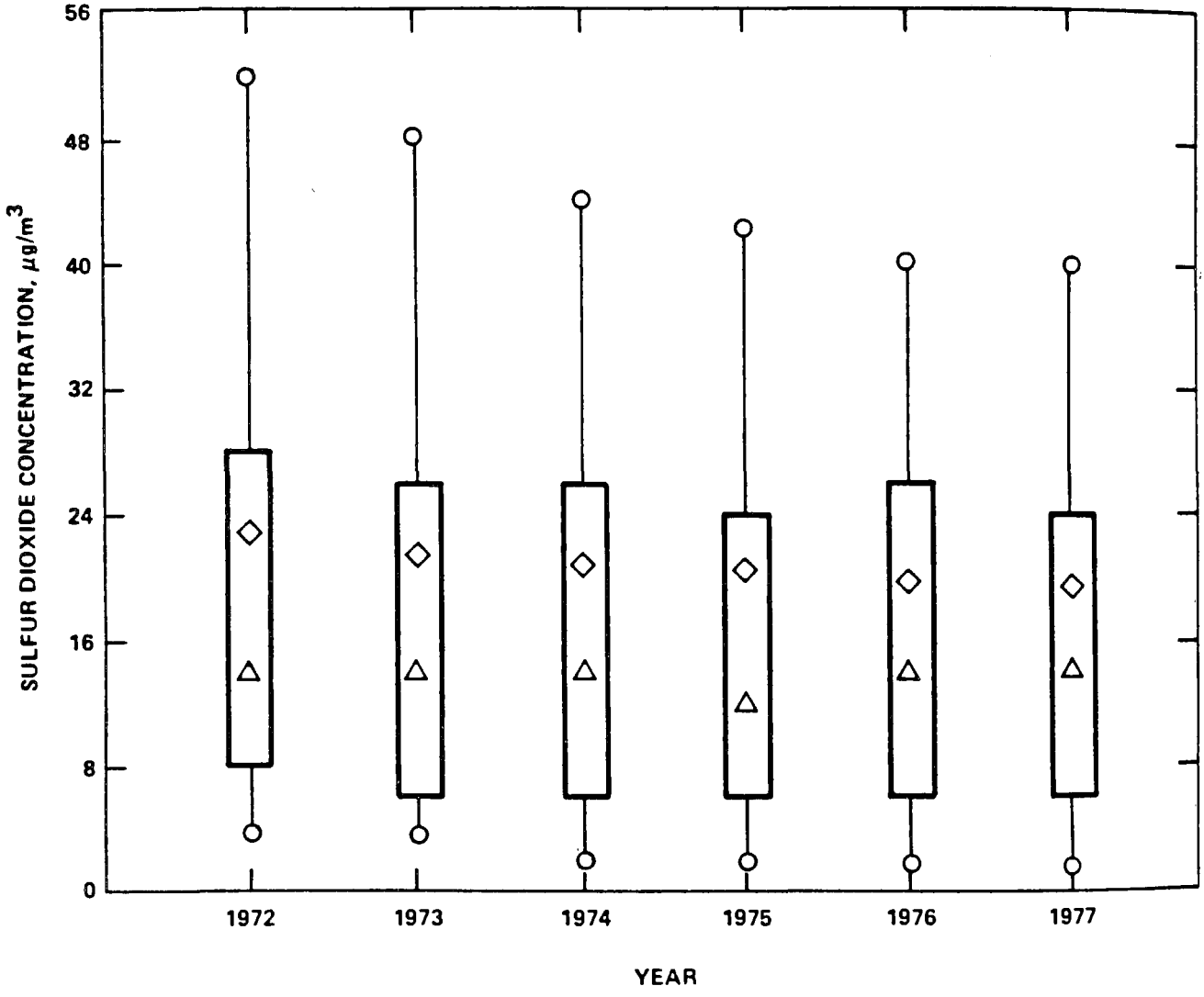



Figure 5-55. Nationwide trends in annual average sulfur dioxide concentrations from 1972 to 1977 are shown for 1233 sampling sites.

Source: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards (1978).

recent $SO_2$ data. The 1960's data came from the Continuous Air Monitoring Project (CAMP), which operated continuous monitors in a few of the largest U.S. cities. The cities are: Chicago, Philadelphia, St. Louis, Cincinnati, Los Angeles, and San Francisco. In each city there is more than one continuous monitor now operating. The station reporting the highest levels was used in order not to overemphasize any improvement. The comparison is only an approximation because the locations of the monitors and the instrumental methods used were not the same in the 1969 document (see Table 5-35).

In each city the peak concentration has decreased. In most cities the peak is less than one-half of the earlier values. The only exception is St. Louis, where the earlier peak was 0.72 ppm and the 1977 peak was 0.67 ppm. The result is not unexpected in that the earlier summary is a composite frequency distribution of 5 years of monitoring.

A better indicator of improved air quality would be the 50th, 70th, and 90th percentile concentration. In Chicago, the 50th percentile concentration dropped from 0.08 ppm to 0.022 ppm; the primary annual standard is met but there are still violations of the 24-hr $SO_2$ NAAQS. In Philadelphia the levels have improved substantially; the 50th, 70th, and 90th percentile concentrations are less than one-half the earlier values. Modest improvement is shown for St. Louis and Cincinnati; their 50th percentile concentrations are lower now than they were in the mid-1960's. The highest concentrations occur as frequently in St. Louis as they did before, but in Cincinnati they occur less frequently. Review of the St. Louis $SO_2$ data shows improved air quality for most of the city. The high concentrations now reported are typical of only a smaller section of the city. Los Angeles shows improvement in reducing the high concentrations, but the 50th percentile concentration is actually slightly

TABLE 5-35. COMPARISON OF FREQUENCY DISTRIBUTION OF $SO_2$ CONCENTRATION (PPM) DURING 1962-67[a] AND DURING 1977[b].

| City | Year | Frequency Distribution of $SO_2$ (ppm) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 30 | 50 | 70 | 90 | 99 | Maximum |
| Chicago | 1962-67 | 0.03 | 0.08 | 0.17 | 0.32 | 0.65 | 0.95 |
| | 1977 | 0.01 | 0.022 | 0.032 | 0.06 | 0.12 | 0.25 |
| Philadelphia | 1962-67 | 0.03 | 0.05 | 0.09 | 0.21 | 0.45 | 0.85 |
| | 1977 | 0.01 | 0.02 | 0.04 | 0.08 | 0.23 | 0.44 |
| St. Louis | 1962-67 | 0.02 | 0.03 | 0.05 | 0.11 | 0.26 | 0.72 |
| | 1977 | 0.005 | 0.01 | 0.03 | 0.1 | 0.37 | 0.67 |
| Cincinnati | 1962-67 | 0.01 | 0.018 | 0.03 | 0.07 | 0.18 | 0.53 |
| | 1977 | 0.013 | 0.02 | 0.025 | 0.04 | 0.085 | 0.29 |
| Los Angeles | 1962-67 | 0.01 | 0.015 | 0.02 | 0.04 | 0.08 | 0.25 |
| | 1977 | 0.01 | 0.02 | 0.02 | 0.03 | 0.05 | 0.09 |
| San Francisco | 1962-67 | | | 0.01 | 0.03 | 0.07 | 0.17 |
| | 1977 | | 0.001 | 0.01 | 0.01 | 0.03 | 0.03 |

[a]Concentrations from CAMP stations as reported in Air Quality Criteria for Sulfur Oxides document, U.S. Dept. of Health, Education, and Welfare, NAPCA, 1969.

[b]Concentrations from NADB, U.S. Environmental Protection Agency, 1977.

higher than it was the previous decade. Similar, San Francisco, has trimmed the peaks, but is has a very low median value.

5.2.3.8 Summary--The frequency of peak levels has been reduced in most urban areas. The steady improvement of $SO_2$ ambient air quality has been slowed somewhat in recent years. Currently, only 1 percent of the sulfur dioxide monitoring sites show levels above the annual NAAQS. In 1974 the annual mean sulfur dioxide standard was exceeded in 3 percent of the monitoring stations (31 of 1030), compared with 16 percent in 1970. In 1977 and 1978, 2 percent of the sites reported violations of the 24-hr standard. In 1974 this standard was exceeded in 4.4 percent of the reporting stations (99 of 2241), compared with 11 percent in 1970. Many of these sites reporting violations of the 24-hr standard are in remote areas near large point sources. A large percentage of the U.S. population is exposed to ambient concentrations of sulfur dioxide exceeding 100 $mg/m^3$ some 10 percent of the time.

## 5.3 REFERENCES


Ahmed, A. Karim. PCBs in the Environment. Environment, p. 6, March 1976.

Air Quality Criteria for Particulate Matter, U.S. DHEW, Public Health Service, Washington, DC, Pub. No. AP-49, 1969; and National Ambient Air Quality Standards: 40 CRF §550.6.

Akland, G. G. Air quality for non-metallic inorganic loss 1971-1974 from the National Air Surveillance Networks, Report No. EPA-600/4-77-003. RTP, NC: U.S. EPA, 1977.

Altshuller, A. P. Characteristics of the chemical composition of the five particulate fraction in the atmosphere. May 1976 (unpublished paper).

Alzona, J., B. L. Cohen, H. Rudolph, H. N. Jow and J. O. Frohliger. Indoor-outdoor relationships for airbourne particulate matter of outdoor origin. Atmospheric Environment 13: 55-60, 1979.

Amdur, M. O. The physiological response of guinea pigs to atmospheric pollutants. Institute of Air Pollution 1: 170, 1959.

Anderson, I. Relationships between outdoor and indoor air pollution. Atmospheric Environment 6: 275-8, 172.

Appel, Bruce R., E. L. Kothny, Emmanuel M. Hoffer, Geroge M. Hidy, Jerome J. Wesolowski. Sulfate and nitrate data from California Aerosol Characterization Experiment (ACHEX) ES&T 12:418-25, 1978.

Atmospheric Nitrosamine Assessment Report. Office of Air and Waste Management, Draft, March 12, 1976.

Benson, F. B., J. J. Henderson, and D. E. Caldwell. Indoor-Outdoor Air Pollution Relationships: A Literature Review. Publication No. AP-112. RTP, NC: U.S. EPA, 1972.

Berdyev, Kh. B., N. V. Pavlovich, and A.A. Tuzhilina. Effect of motor vehicle exhaust gases on atmospheric pollution in dwelling and in a main street. Hygiene and Sanitation (Moscow) 32:424-426.

Biersteker, K., H. de Graaf, and C.A. G. Nass. Indoor air pollution in Rotterdam homes. Intl. Journal of Air and Water Pollution 91232-50, 1965.

Binder, R. E., C.A. Mitchell, H. R. Hosein, and A. Bouhuip. Importance of the indoor environment in air pollution exposure. Arch. Environmental Health 31:277, 1976.

Blifford, I. H. and G. O. Meeker. A factor analysis model of large scale pollution. Atmospheric Environment 1:147-157, 1967.

Bradow, Ron. Emissions measurement and charterization division. Environmental Sciences Research Laboratory, RTP, EPA, 1976.

Bretschreider, K. and J. Matz. Nitrosamines in the atmospheric air at places of employment. Arch. Gesh. 13:1974 and Exc. Medica Sec. 46., Environmental Health & Pollution Control, 6, 1974.

Bridbord, K. et. al. Human exposure to polynuclear aromatic hydrocarbons. In: Carcinogenesis: Vol. I, Polynuclear aromatic hydrocarbons: chemistry, metabolism and carcinogenesis, ed. R. I. Freudenthal and P. W. Jones. New York: Raven Press, 1976.

Brosette, C. (1976) Airborne particulates: Black and white episodes. Ambio 5: 157-163, 1976.

Cahill, T. Personal remarks. Committee on Particulate Control Technology, National Research Council, 2nd Meeting, March 29-30, 1979, Los Angeles, California.

Calvert, Jack G. Hydrocarbon involvement in photochemical smog formation in Los Angeles atmosphere. ES&T 10:256, 1976.

"Cancer and the Environment," N. J. Dept. of Env. Prot., May 25, 1976.

Carey, G. C. R., J. J. Phair, R. J. Shephard, and M. L. Thomson: The effects of air pollution on human health. Amer. Ind. Hyg. Assn. J. 19:363-370, 1958.

Cavanugh, G. et. al. Potentially hazardous emissions from the extraction and processing of coal and oil. Columbus, Ohio: Batelle Columbus Laboratories, prepared for the U.S. EPA, 1975.

Charlson, R. J., A. H. Vanderpol, D. S. Covert, A. P. Waggoner, and N. C. Ahlquist. Sulfuric acid - ammonium sulfate aerosol: Optical detection in the St. Louis region. Science 184: 156-158, 1974.

Charlson, Robert J., David S. Covert, Timothy V. Larson, and Alan P. Waggoner, "Chemical properties of tropospheric sulfur aerosols," Atm. Env. 12:39-53, 1978.

Coburn, W. G., R. B. Huzar, and J. D. Huzar. Continuous in situ monitoring of ambient particulate sulfur using flame photometry and thermal analysis. Atm. Env. 12: 89-98, 1978.

Colome, S. D. and J. D. Spengler. Instrumental neutron activation analysis of indoor/outdoor respirable aerosols. APCA, Cincinnati, Ohio, 72nd Annual Meeting, June 1979, pp. 24-29.

Colucci, J. M. and C. R. Begeman. The automotive contribution to airborne polynuclear aromatic hydrocarbons in air. Natl. Cancer Institute Monogr. 9:225, 1962.

Corn, M. Aerosols and the primary air pollution - nonviable particles: their occurrence, properties, and effects, Ch. 3 in Stern, A. C. (ed.), Air Pollution, v. I (3d ed.). New York: Academic Press, 1976.

Corn, M. Nonviable particles in the air. In: A. C. Stern, ed., Air Pollution. v. I: Air pollution and its effects. (2nd ed.) New York: Academic Press, 1968, pp. 47-94.

Cote, W. A., W. A. Wade III, and J. E. Yocom: Final report on a study of indoor air quality. EPA Contract 68-02-0745, TRC Project No. 32247. Wethersfield, Conn.: Quality Assurance and Environmental Monit. Lab and Human Studies Lab, U.S. EPA, 1974.

Cox, R. A. and S. A. Perikett. Effect of relative humidity on the disappearance of ozone and sulphur dioxide in contained systems. Atmospheric Environment 6:365-68, 1972.

Cunningham, P. T. and S. A. Johnson (1976). Spectroscopic observation of acid sulfate in atmospheric particulate samples. Science 191:77-79, 1976.

De Maio, L. and M. Corn. Polynuclear aromatic hydrocarbons associated with particulates in Pittsburgh air. JAPCA 16:67, 1966.

Dockery, Douglas W. Personal exposure to respirable particulates and sulfates: measurement and prediction. Doctoral Thesis, Harvard University, School of Public Health, May 1975.

Dzubay, T. G. Chemical-elemental balance method applied to dichotomous samples data. Symposium, Annals of the N.Y. Acad. of Sci., Jan. 9-12, 1979.

Dzubay, T. G. and R. K. Stevens. Ambient air analysis with dichotomous sampler and x-ray fluorescence spectrometer. Envir. Sci. Tech. 9:663-668, 1975.

Dzubay, T. G., R. K. Stevens, and C. M. Peterson. Application of the dichotomous sampler to the characterization of ambient aerosols. In T. G. Dzubay, Ed. X-Ray Fluorescence Analysis of Environmental Samples. Ann Arbor: Ann Arbor Science Publishers, Inc., 1977, pp. 95-106.

Economic Commission for Europe. Working Party on Air Pollution Problems. Task Force on Fine Particulate Pollution. Report. Geneva, WHO, December 1977.

Gartrell, G., Jr. and S. K. Friedlander. Relating particulate pollution to sources: the 1972 California Aerosol Characterization Study. Atmospheric Environment 9:279-299, 1975.

Gate, D. F. Relative contributions of different sources of urban aerosols: aplications of a new estimation method to multiple sources in Chicago. Atmospheric Environment 9:1-18, 1975.

Goldwater, L. J., A. Manoharan, and M. B. Jacobs: Suspended particulate matter, dust in "domestic" atmospheres. Arch. Envir. Health 2: 511-515, 1961.

Gordon, Robert J. Distribution of Airborne Polycyclic Aromatic Hydrocarbons throughout Los Angeles. ES&T 10:370, 1976.

Haagen-Smib, A. J. et. al. The State of California plan for achieving and maintaining the National Ambient Air Quality Standards, January 30, 1972.

Hardy, K. A., R. A. Kselsson, J. W. Nelson, J. W. Winchester. Elemental constituents of Miami aerosol as function of particle size. ES&T 10:176-182, 1976.

Hauser, Thomas R. and John N. Pattison. Analysis of aliphatic fraction of air particulate matter. ES&T 6:549, 1972.

Heidelberger, Charles. Chemical carcinogenesis. Ann. Rev. Biochem. 44:79, 1975.

Helms, G. T., J. H. Southerland, K. R. Woodward, J. V. Hinda?, D. H. Coventry, and C.D. Robson. Chattanooga, Tennessee -- Rossville, Georgia. Interstate Air Quality Study, 1967-68. National Air Pollution Control Administration Publication No. APTD-0583. Washington, DC:GPO, 1970.

Hetling, L., E. Horn and J. Tofflemire. Summary of Hudson River PCG Study Results. NY State Department of Environmental Conservation, Bureau of Water Research, April 1978.

Hidy, G. M., B. Appel, R. J. Charlson, W. E. Clark, D. Covert, D. Dockweiler, S. K. Friedlander, P. Friedman, R. Giauque, S. Green, S. Heisler, W. W. Ho, J. J. Hunt-Ficker, R. B. Husar, K. Kubler, G. Lauer, P. K. Mueller, T. Novakov, R. Ragaini, L. W. Richards, T. B. Smith, E. R. Stephens, G. Sverdrup, S. Twiss, A. Waggoner, S. Wall, H. H. Wang, J. J. Wesolowski, K. T. Whitby, and W. White (1974). Characterization of Aerosols in California (ACHEX). Final Report. Vols. I-IV. Submitted to the Air Resources Board, State of California, Sept. 30, 1974.

Hidy, G. M., B. R. Appel, R. J. Charlson, W. E. Clark, S. K. Friedlander, D. H. Hutchison, T. B. Smith, J. Suder, J. J. Wesolowski, and K. T. Whitby (1975). Summary of the California aerosol characterization experiment. J. APCA 25:1106-1114.

Hidy, G. M., P. K. Mueller, V. Dio, and K. C. Detor. Study and implementation of the Sulfate Regional Experiment (SURE). Proc., 4th Symposium on Turbulence and Diffusion and Air Pollution, AMS, Jan. 1979.

Hidy, G. M., P. K. Mueller, and E. Y. Tong. Design of Sulfate Regional Experiment (SURE), v. 1 & 2, Electric Power Research Institute, Report EC-125, Palo Alto, California, 1976.

Hidy, G. M., P. K. Mueller & E. Y. Tong. Spatial and temporal distributions of airborne sulfates in parts of the United States. Atm. Env. 12:735-752, 1978.

Hitchcock, D. Atmospheric sulfates from biological sources. JAPCA 26: 210-215, 1976.

Hoegg, U. R. Cigarette smoke in closed spaces. Envir. Health Persp. 117-128, 1972.

Hollowell, C. D., R. J. Beednitz, and G. M. Traynor. Combustion generated indoor air pollution. 4th International Clean Air Congress, Tokyo. May 16-20, 1977.

Hopke, P. K. et. al. The use of multivariate analysis to identify sources of selected elements in the Boston urban aersol. Atmospheric Environment 10:1015-1025, 1976.

Husar, R. B., W. E. Wilson, Jr., and G. J. D'Alessia. Sulfate: Alternative means of reducing their atmospheric concentrations. AICLE. 85th National Meeting, Philadelphia. June 4-8, 1978.

Inter-Agency Energy-Environment Research and Development Program. Survey of Indoor Air Quality Health Criteria and Standards. Publication #EPA-600/7-78-027. Research Triangle Park: Office of Research and Development, U.S. Environmental Protection Agency, March 1978.

Ishido, S. Variations in indoor and outdoor dust intensities. Bull. Dept. Home Econ., Osaka City University. 6:53-59, 1959.

Ishido, S., K. Kamada, and ____ Nakagawa: Free dust particles and airborne microflora. Bull. Dept. Home Econ., Osaka City Univ. 21: 31-37, 1956.

Jacobs, M. B., L. J. Goldwater, and A. Fergany: Comparison of suspended particulate matter of indoor and outdoor air. Intl. J. Air Water Pollution 6:377-380, 1962.

Junge, C. Die Konstitution der atmospharischen aerosole. Ann. Meteorol. 5 (Beiheft) 1-55, 1952.

Kadawaki, Atoshi. Size distributions and chemical composition of atmospheric particulate nitrate in the Ngoya area. Atm. Env. 11: 671-5, 1977.

Kerteszhe-Saringer, M. et. al. On the size distribution of B(a)P containing particles in urban air. Atm. Env. 5:429, 1971.

Ketchum, Brian T. et. al. Final report to the National Highway Traffic Administration, Non-passenger Automobile Average Fuel Economy Standards Model Years 1980-81. (Docket No. FE. 77-05, Notice 1) by Citizens for Clean Air, In. and Environmental and Resources Technology, February 7, 1978.

Ketchum, Brian T. et. al. Final Report to the National Highway Traffic Administration. U.S. Dept. of Transportation, 1981-84. Passenger Automobile Average Fuel Economy Standards (Docket No, FE-76-1), April 11, 1977.

Kito, T. Survey of air pollution on outlying islands. Kuki Seijo 15(2): 10-21, 1977.

Kleinman, M. T. The use of long term and seasonal trends of elemental compounds as an aid to the identification of sources of airborne pollutants. Conference on Aerosols, N.Y. Acad. of Sciences, January 1979.

Kotin, P. and H. L. Falk. Atmospheric factors in pathogenesis of lung cancer. Adv. in Cancer Res. 7:475, 1963.

Kowalcyzk, G. S., C. E. Choquette, and G. E. Gordon. Chemical element balances and identification of air pollution sources in Washington, D.C. College Park , MD: Dept. of Chemistry, University of Maryland, 1979 (draft).

Krost, Ken. Atmospheric Chemistry and Physics Division, Environmental Sciences Research Lab. Personal commun. RTP:EPA, 1977.

Kurosaka, D. Sulfate concentrations in the South Coast Air Basin. Report DTS-76-1, Calif. Air Resources Board, Sacramento, Calif. 1976.

LaBelle, C. W., J. A. Long, and E. E. Christofano. Synergistic effects of aerosols: particulates as carriers of toxic vapors. Arch. Ind. Health II; 197, 1955.

Larsen, Ralph I. A mathematical model for relating air quality measurements to air quality standards. EPA Publ. AP-89. RTP, NC: EPA, 1971.

Lavery, T. F., G. M. Hidy, R. L. Basket, and J. Thrasher. Occurrence of long-range transport of sulfur oxides in the northeastern United States. Proc., 4th Symposium on Turbulence Diffusion and Air Pollution AMS, Reno, Nevada, Jan. 15-18, 1979.

Lee, R. E., Jr. The size of suspended particulate matter in air. Science 178:567-575. 1972.

Lee, R. E., Jr., S. S. Joranson, R. E. Enrione, and G. B. Morgan. National Air Surveillence cascade impactor network. II. Size distribution measurements of trace metal components. Environ. Sci. Tech. 6:1025-1030 1972.

Lee, R. E., Jr., R. K. Patterson, and J. Wagman. Particle-size distribution of metal components in urban air. Environ. Sci. Tech. 2:288-290 1968.

Lefcoe, N. M. and I. I. Inculet: Particulates in domestic premises: I. Ambient levels and central air filtration. Arch. Envir. Health 22:230-238, 1971.

Lefcoe, N. M. and I. I. Inculet: Particulates in domestic premises: II. Ambient levels and indoor-outdoor relationships. Arch. Environ. Health 30:575, 1975.

Lijinsky, William and Samuel S. Epstein. Nitrosamines as environmental carcinogens. Nature 225:21, 1970.

Ludwig, J. H., G. B. Morgan, and T. B. McMullen. Trends in urban air quality. In W. H. Matthew, W. W. Kellogg, and G. O. Robinson, Eds. Man's Impact on Climate. Cambridge: MIT Press, 1971, pp. 321-338.

Lynn, D. A., G. L. Deane, R. C. Galkiewicz, and R. M. Bradway. National Assessment of the Urban Particulate Problem. Vol I. RTP, NC: U.S. EPA Office of Air Quality Planning and Standards. Publ. #EPA-450/3-76-024, July 1976.

Lynn, D. A., B. S. Epstein, and C. K. Wilcox. Analysis of New York City Sulfate Data. Final report EPA Contr. 68-02-1337, Task 10, GCA Corp., Bedford, MA, 1975.

Lyons, W. A. and J. C. Dooley, Jr. Satellite detection of long range pollution transport and sulfate aerosol haze. Atmos. Envt. 12:621-631, 1978.

MITRE Technical Report Series, EPA Contract No. 68-02-1495, Project No. 077B, Dept. W-54, prepared by the MITRE Corp., McLean, VA, 1976.

MSA Research Corporation. Hydrocarbon Pollutant Systems Study: I. Stationary Sources, Effects and Control. Final Report. MLA Research Corp., 1972.

Mage, D. T. and W. R. Ott. Refinements of the lognormal probability model for analysis of aerometric data. JAPCA 28:796-7 1978.

Maunsell, K. Concentration of airborne spores in dwellings under normal conditions and under repair. Intl. Arch. Allergy 5:373-376, 1954.

Megaw, W. S. The penetration of iodine into buildings. Intl. J. Air Pollution 5:121-128, 1962.

Miller, F. J. et. al. Particle size considerations for establishing a standard for inhaled particles. RTP, NC: U.S. EPA, Office of Air Quality Planning and Standards, January 1979 (draft).

Moschandreas, D. J., J. W. Winchester, J. W. Nelson, and R. M. Burton. Fine particle residential indoor air pollution. Atmospheric Environment (in press).

Mueller, P. K., R. W. Mosley, and L. B. Pierce. Chemical composition of Pasadena aerosol by particle size and time of day. J. Colloid and Interface Science 39:235, 1972.

Mueller, P. K. et al. Concentration of fine particulate and lead in car exhaust. Symposium on Air Pollution Measurement Methods, Philadelphia. American Society for Testing and Materials. Special technical publication, 1964.

Mueller, P. K., G. M. Hidy, T. F. Lavery, K. Warren, R. L. Bassett. Some early results from the Sulfate Regional Experiment (SURE). Proc. 4th Symposium on Turbulence Diffusion and Air Pollution, AMS, Reno, Nevada, Jan. 15-18, 1979, pp. 322-329.

Ragda, Niren, John R. Ward, Benjamin J. Mason and Leon S. Pocinki. Retrospective modeling of ambient concentrations of Benzo(a)pyrene. Pres., 71st Annual Meeting. Air Pollution Control Association, Houston, June 25-30, 1978.

National Academy of Sciences. Air Quality and Stationary Source Emissions Control. Ser. #94-4. March 1975.

National Academy of Sciences. Report by the Commission on Natural Resources. Air Quality and Stationary Source Emission Controls, March 1975.

National Academy of Sciences. Vapor-Phase Organic Pollutants. Washington, DC; NAS, 1976.

National Academy of Sciences. Committee on Biologic Effects of Atmospheric Pollutants. Particulate Polycyclic Organic Matter. Washington, D.C., NAS, 1972.

National Research Council. Airborne Particles, EPA-600/1-77-053. RTP, NC: U.S. EPA, 1977.

National Research Council. Nitrates: An Environmental Assessment. Washington, D.C.: National Academy of Sciences, 1978.

National Research Council. Nitrogen Oxides. Washington, D.C.: National Academy of Sciences, 1977.

National Research Council, Assembly on Life Sciences, Division of Medical Sciences, Committee on Medical and Biologic Effects of Environmental Pollutants, Subcommittee on Airborne Particles. Airborne Particles. Baltimore: University Park Press, 1979.

Natusch, David F. S. and John R. Wallace. Urban aerosol toxicity: the influence of particle size. Science 186:695, 1974.

Nitrosamines found in commercial pesticides. Chem & Eng News, p. 33, Sept. 20, 1976.

Oreel, A. and J. Seinfeld. Nitrate formation in atmospheric aerosols. Environmental Sci. & Tech. 11:1000-7, 1977.

Pace, T. G. U.S. EPA, personal communication. April 1979.

Pace, T. G. and E. L. Meyer, Jr. Preliminary characterization of inhalable particulate in urban areas. Proceedings, 79th Annual Meeting, Air Pollution Control Assn., Cincinnati, Ohio, June 1979.

Parvis, D. Condensation nuclei in the air of artificially heated environments. Annali della Sanita Publica 13:1569-1581, 1952.

Pellizzari, Ed. Development of Analytical Techniques for Measuring Ambient Carcinogen Vapors. RTP:Research Triangle Institute, EPA, 1976.

Perera, F. P. and A. K. Ahmed. Respirable particulates: impact of airborne fine particulates on health and the environment. New York: Natural Resources Defense Council, Inc., 1978.

Perhack, Ralph M. Sulfate regional experiment in northeastern United States: The "SURE" program. Atm. Env. 12:641-647, 1978.

Preussman, R. Formation of carcinogens from precursors occurring in the environment: new aspects of nitrosamine induced tumorigenesis. Rec. Results Cancer Res. 44:9, 1974.

Record, Frank M., R. M. Brodway, and K. W. Wiltsee, Jr. A study of ambient particulates in Massachusetts. Proc. Northeast Atlantic Internatl. Section, APCA, Fall Technical Meeting, Windsor, Conn., Oct. 18, 1978.

Romagnol, G. Studies on the climatic conditions in some elementary classrooms of Novara. Italian Rev. of Hyg. 21:410-419, 1961.

Organic Vapors Identified in Ambient Air. RTI Quartery Rept. No. 2, Table 9, 1976. And KIN-BUC Report, EPA, 1976.

Sawicki, E. The chemical composition and potential genotoxic aspects of polluted atmospheres. Workshop for the Investigation on the Carcinogenic Burden by Air Pollution in Man. Hanover, Germany. Oct. 22-24, 1975.

Sawicki, E. Dimethylnitrosamine in the Baltimore and Belle, West Virginia Environments. Proceedings, Meeting. Environmental Research Center, Environmental Protection Agency, RTP, Jan. 6, 1967.

Sawicki, Eugene. Atmospheric Chem. and Phys. Div. ESRL, RTP, EPA. Personal communication, April 1976.

Sawicki, E. et. al. Benzo(a)pyrene content of the air of American communities. Amer. Ind. Hyg. Assn. J. 21:443, 1960.

Sawicki, E. et. al. Polynuclear aromatic hydrocarbons: Composition of the atmosphere in some large American cities. Am. Ind. Hyg. Assn. J. 23: 137, 1962.

Sawicki, E. et. al. Quantitative composition of the urban atmosphere in terms of polynuclear aza heterocyclic compounds and aliphatic and polynuclear aromatic hydrocarbons. Int. J. Air & Water Poll. 9:515, 1965.

Scanlan, Richard. N-Nitrosamines in Foods. CRC Critical Reviews in Food Technology, April, 1975, p. 357.

Schaefer, V. S., V. A. Mohnen, and V. R. Veirs: Air quality of American homes. Science 175:133-175, 1972.

Scott Research Laboratory. 1970 Atmospheric Reaction Studies in the Los Angeles Basin, Vols. 1, 2, 4. Plumsteadville, Pa.: Scott Research Lab., 1970.

Seisaburo, S., K. Kiyoko, and N. Tatsuko: Free dust particles and airborne microflora. Bull. Dept. Home Econ., Osaka City Univ. 4:31-37, 1959.

Selected Environmental Carcinogens. Draft #1. New Jersey Dept. of Env. Prot., Oct. 1976.

Shapley, Deborah. Nitrosamines: scientists on the trail of prime subject in urban cancer. Science 191:235, 1976.

Shepherd, R. J., G. C. R. Carey and J. J. Phair: Critical evaluation of a filter-strip smoke sampler used in domestic premises. AMA Arch. Ind. Health 17:236-252, 1958.

Spedding, D. J. Sorption of sulphur dioxide by indoor suraces -- II. Wood. J. Appl. Chem. 20:226-28, 1970.

Spedding, D. J. and R. P. Rowlands. Sorption of sulphur dioxide by indoor surfaces -- I. Wallpapers. J. Appl. Chem. 20:143-46, 1970.

Spedding, D. J., R. P. Rowlands, and J. E. Taylor. Sorption of sulphur dioxide by indoor surfaces -- III. Leather. J. Appl. Chem. 21:68-70, 1971.

Spengler, J. Analysis of preliminary dichotomous sampling data, Harvard School of Public Health, Unpublished, 1979.

Spengler, John D. Preliminary analysis of dichotomous and TSP measurements in Topeka, Kansas and Kingston, Tennessee.

Spengler, J. D. and D. W. Dockery. Long term measurements of respirable sulfates and particles inside and outside homes. Electro 79 Professional Program Paper 2413, New York City, April 25, 1979.

Spicer, C. W. The fate of nitrogen oxides in the atmosphere. Ecological Research Series, Office of Research and Development Report No. EPA-60013-76-030. RTP, NC: U.S. EPA, 1976.

Sproul, Wayne T., Air Pollution and its Controls. NY: Exposition Press, 1970.

Steigerwald, B. J. Particulate control strategy. Office of Air Quality Planning and Standards, EPA, memo to Roger Strelow, Asst. Administrator for Air and Waste Management, July 2, 1975; submitted by EPA to the Subcommittee, House Committee on Interstate and Foreign Commerce.

Sterling, T. D. and D. M. Kobayashi. Exposure to pollutants in enclosed "living spaces." Envir. Res. 13:1-35, 1977.

Stevens, R., National Environmental Research Laboratory, U.S. EPA, Personal communication. May 1979.

Stevens, Robert K. and Thomas G. Dzubay. Sampling and analysis of atmospheric sulfate and related species. Atmospheric Envt. 12:55-68, 1978.

Summary Report on Nitrosamines (draft), RTP: Health Effects Research Lab., EPA, 1976.

Sverdrup, G. M., K. T. Whitby, and W. E. Clark: Characterization of California aerosols -- II. Aerosol size distribution measurements in the Mojave Desert. Atmos. Enviroment 9:483-494, 1975.

Terabe, M. Air pollution in Japan: present state area trends. Kuki Seizo 15(2):1-10, 1977.

Thomas, J. F., M. Mujai, and B. D. Tebbens. Fate of airborne benzo(a)pyrene. Envir. Sci. Tech. 2:33, 1968.

Thompson, C. R., E. G. Hensel, and G. K. Kats: Outdoor-Indoor levels of six air pollutants. JAPCA 23:881-6, 1973.

22 High Volume Industrial Chemicals (HIVOC). Preliminary Assessment for Air Pollution Potential, U.S. EPA, Office of Air Quality Planning and Standards, 1976.

U.S. Dept. of Health, Education & Welfare Public Health Service. Natl. Air Pollution Control Administration. Air Quality Criteria for Sulfur Oxides. Publication No. AP-50. Washington, D.C.: HEW, 1969.

U.S. Environmental Protection Agency. National Air Quality, Monitoring, and Emissions Trends Report, 1977. EPA-450/21-78-052, December 1978.

U.S. Environmental Protection Agency. National Assessment of the Urban Particulate Problem. Vol. I. National Assessment (EPA-450/3-76-024). July 1976.

U.S. Environmental Protection Agency. National primary and secondary ambient air quality standards. Federal Register 36(84):8186-8201, 1971.

U.S. Environmental Protection Agency. Report to Congress on the National Particulate Problem. Feb. 1979. Noted to be cited or quoted.

U.S. Environmental Protection Agency. Environmental Criteria and Assessment Office. Health Assessment Document for Polycyclic Organic Matter. RTP, NC:U.S. EPA, 1978. External review draft #1.

U.S. Environmental Protection Agency. Environmental Criteria and Assessment Office. Health effects of short-term exposure to nitrogen dioxide. EPA-600/8-78-009. RTP, NC: EPA, 1978.

U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Air Quality Data. 1977 Annual Statistics. EPA 450/2-78-040. RTP, Sept., 1978.

U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. National Air Quality, Monitoring and Emissions Trends Report, 1977. RTP, NC. Publ. #EPA-450/2-78-052. Dec. 1978.

U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Optimum Site Exposure Criteria for $SO_2$ monitoring. Publ. #EPA-450/3-77/013. RTP, NC, U.S. EPA, April 1977.

U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Preferred Standards Path Report for Polycyclic Organic Matter. Durham, NC: EPA, 1974.

Walker et al. Environmental Assessment of Atmospheric Nitrosamines. EPA Contract No. 68-02-1495, Feb. 1976.

Walsh, M., A. Black, and A. Morgan. Sorption of $SO_2$ by typical indoor sources including wool carpets, wallpaper, and paint. Atmospheric Environment, received to be published February 24, 1977.

Warren Springs Laboratory: British Standard 1747, Part 2. Stevenage, G. B., 1964.

Weatherly, M. L. Air pollution inside the home in symposium on Plume Behavior. Intl. J. Air-Water Poll. 10:404-09, 1966.

Whelpedale, D. M. Large scale atmospheric sulfur studies in Canada. Atm. Env. 12:661-670, 1978.

Whitby, K. T., A. B. Algren, R. C. Jordan, and J. C. Annis: The ASHAE airborne dust survey. Heating, Piping and Air-Cond. 29(11): 185-192, 1957.

Wigby, T. K. and B. Cantrell. Atmospheric Aerosols -- Characteristics and Measurements. Intl. Conference on Environmental Sensing and Assessment (ICESA) (75CH1004-1), 1975.

Wilson, M. L. G. Indoor air pollution. Proc. Royal Soc., Ser. A. (London) 307:215-221, 1968.

Winchester, J. W. and G. D. Nifong. Water pollution in Lake Michigan by trace elements from pollution aerosol fallout. Water, Air and Soil Pollution 1:50-64, 1971.

Yocom, J. R., W. L. Clink, and W. A. Cote: Indoor/Outdoor air quality relationships. JAPCA 21:251-259, 1971.

# 6. TRANSMISSION THROUGH THE ATMOSPHERE

## 6.1 INTRODUCTION

Relating ambient concentrations of $SO_x$ and particles to source emission rates is a central problem for the development of control measures. Processes occurring in the atmosphere play a dominant part in determining source-receptor relationships. Until the early 1970's, the atmosphere was regarded primarily as a medium that dispersed primary emissions, thereby reducing ambient concentrations downwind of individual sources by dilution. During this period, emission rates from major point sources were increasing; at the same time, however, stack heights were increasing, which improved the local ambient air quality because of increased atmospheric dilution.

Since the early 1970's, it has become increasingly apparent that the role of the atmosphere in the chemical transformation and removal of $SO_x$ and particles is also important. Many harmful environmental effects are now attributed to the reaction products of $SO_x$, $NO_x$, and hydrocarbons that are distributed and deposited by the atmosphere. To quantify these effects and their causes, it is necessary to understand many processes that occur in the atmosphere. Among these processes are physical and chemical transformations (section 6.2), dry and wet removal processes (section 6.3), and dispersion (section 6.4).

The process by which a pollutant is carred past a fixed point or across a fixed plane is called transport; this process is carried out by horizontal wind. The process by which a pollutant is mixed in the atmosphere is called diffusion; this process is caused by horizontal and vertical motions resulting from gradients of pressure and temperature and from surface roughness features. In air pollution meterology, it is common to use the term "dispersion" to describe transport and diffusion together. The term "transmission" is used for the joint effects of transport, diffusion, transformation, and deposition.

Listed below are the relevant factors that are discussed and substantiated in this chapter.

(1) Atmospheric particle mass is distributed bimodally with respect to particle size. Particles smaller than 2 μm in diameter are referred to as fine particles; particles 2 μm and larger are often referred to as coarse particles.

(2) Comparable masses of fine and coarse particles are measured within urban areas. With increasing distance downwind from urban areas, the fine-particle mass tends to exceed the coarse-particle mass, except in areas influenced by wind or vehicle generated fugitive dust from soil.

(3) Much of the fine-particle mass is secondary, i.e. formed in the atmosphere by the transformation of gases, mainly sulfur dioxide, nitrogen oxides, and organics containing more than six carbon atoms. The remainder of the fine-particle mass is due to primary emissions and consists mostly of combustion-derived sulfates and carbonaceous particles, lead aerosols, small amounts of other metal-containing particles from combustion and industrial processes, and small amounts of finely divided mineral dusts.

(4) The coarse particles are mostly primary and consist of substances emitted directly from industrial sources and from combustion processes, along with substantial amounts of suspended or resuspended dusts of various types. Some nitrate and sulfate is found in coarse particles.

(5) Because removal by deposition may take several days, fine particles may be transported for distances of 1000 km or more from their origin or the origin of precursor gases. Secondary fine particles are formed continuously by atmospheric reactions and are likely to undergo long-range transport.

(6) Urban-area sources and large-point sources contribute precursors of aerosols formed during atmospheric reactions; the contributions of these many sources are therefore superimposed downwind.

(7) Gas-to-particle conversion processes depend on a variety of environmental factors, such as solar radiation, concentrations of oxidizing radicals, and humidity. Precursor-gas emission rates alone are therefore of very limited usefulness in estimating the mass of secondary fine particles.

Because of these complexities, it is essential that several very different approaches be used to establish source-receptor relationships (section 6.5).

The annual U.S. emissions of $SO_x$ ranged from 20 to 23 x $10^6$ tons per year between 1940 and 1960 (chapter 4). Until 1950, $SO_x$ emissions from industrial sources were the largest; near-ground emissions from homes, commercial establishments, and locomotives were next; emissions from electric power plants were least. Between 1950 and 1960, $SO_x$ emissions from homes, commercial establishments, and locomotives decreased rapidly and those from industrial sources decreased somewhat, whereas those from electric power plants increased rapidly. By the 1960's, $SO_x$ emissions from electric power plants exceeded emissions from any other class of sources. The increase in $SO_x$ emissions from electric power plants continued into the 1970's; emissions from other classes of sources continued to decline or level off at much lower levels than in earlier years.

Sulfur dioxide concentrations in urban areas declined substantially during the 1970's. This decline reflects shifts in fuel usage toward lower sulfur fuels for most emission sources. In several urban areas, power plants also burned fules with lower sulfur content. The trends in sulfur dioxide concentrations reflect these changes. During the same period, urban sulfate levels decreased in the winter months, particularly in the Northeast, reflecting $SO_x$ emission trends. Sulfates increased during the warmer months in both urban and nonurban

areas into the 1970's, with some subsequent declines later in the decade in some regions. The differences among seasonal trends obscure the effect of $SO_x$ control on sulfate concentrations computed on an annual average basis. The high sulfate concentrations measured during the summer months in recent years are best explained by long-range transport and the transformation of $SO_x$ to sulfates. Historical trends during the winter months can be accounted for by shifts to lower sulfur fuels.

The historical data base for particulate nitrate is in doubt because of sampling difficulties. Positive artifacts on basic filter material due to absorption of nitric acid vapor and negative artifacts due to volitilization of $NH_4NO_3$ vapor make the existing data base unreliable until these problems have been defined quantitatively.

A downward trend in benzene-soluble organics was observed at most urban and nonurban sites during the 1960's. No trend data on carbon-containing aerosols are available for the 1970's. Nevertheless, carbon-containing aerosols still seem to be the second most abundant particulate species in the Eastern United States. At some western urban sites, carbon-containing aerosols exceed sulfates in concentration because of low $SO_x$ emissions.

The preceding discussion indicates the complexity in developing source-receptor relationships for the $SO_x$/aerosol/precursor complex.

## 6.2 TRANSFORMATIONS

### 6.2.1 Transformation of $SO_2$

The chemical transformation of $SO_2$ in the atmosphere generally leads to the formation of sulfuric acid or other sulfates, although the formation of metal sulfides and organic sulfite complexes has been reported (Eatough et al., 1978). The oxidation of $SO_2$ to sulfuric acid is of grave concern because it leads to

the acidification of aerosols, fogs, and rain (acidification of rain is treated separately in Chapter 8). However, the formation of these sulfates, commonly called secondary sulfates," is responsible for large quantities of submicron aerosols in the troposphere.

6.2.1.1 Atmospheric Investigations--Investigations of the plumes of coal-burning power plants have suggested pseudo-first-order conversion rates in the range of 0 to 8 percent per hour. However, Wilson (1978) critically reviewed most of these studies reported before 1978 and concluded that they do not provide reliable information on the rate of sulfate formation. In general, the investigators used insensitive instrumentation, improper sampling techniques, or inappropriate flight patterns. In 1978, more advanced studies were reported at the International Symposium on Sulfur in the Atmosphere. For example, Husar et al. (1978) reported data (see Figure 6-1) for the rate of sulfate formation as a function of solar radiation for the Labadie power plant plume. As can be seen in Figure 6-1, the conversion rate shows a strong correlation with solar radiation, which suggests that photochemical pathways are important. However, Gillani et al. (1978) also noticed that the rate was significantly affected by the background concentration of ozone and by the degree of mixing. For example, as shown in Figure 6-2, the Labadie plume received approximately the same solar radiation intensity on July 9 and 18. However, on July 18 the background $O_3$ concentration and mixing were greater; on that day the conversion rate was about twice that on July 9.

It is likely that the inability to replicate experiments as discussed above and the inability of various research laboratories to agree on experimental conversion rates are due to complex parameters such as mixing, solar radiation intensity, and background concentration of reactive species (Wilson, 1979). Also, it should be expected that other parameters, including temperature,

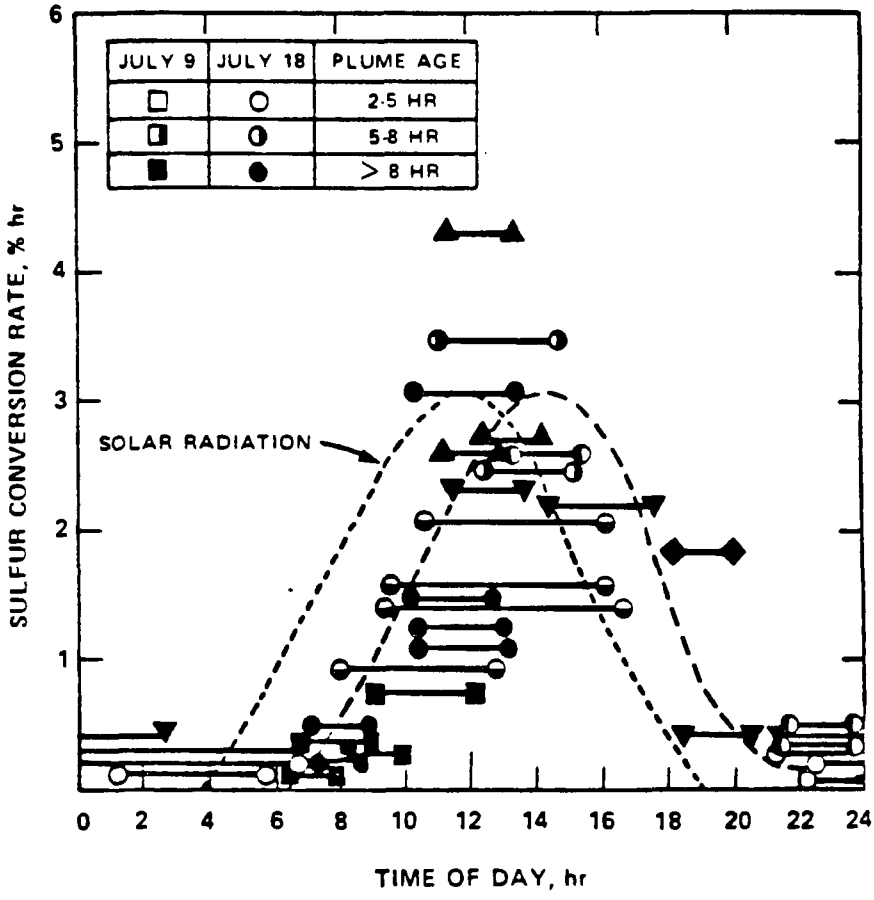



Figure 6-1. The daytime conversion rate in the MISTT study was quite variable, ranging from 1 to 4 percent per hour, whereas nighttime values were consistently below 0.5 percent per hour. Either photochemical conversion or liquid-phase oxidation in daytime cumulus clouds is consistent with the daytime peak of conversion rate.

Source: Husar et al. (1978).

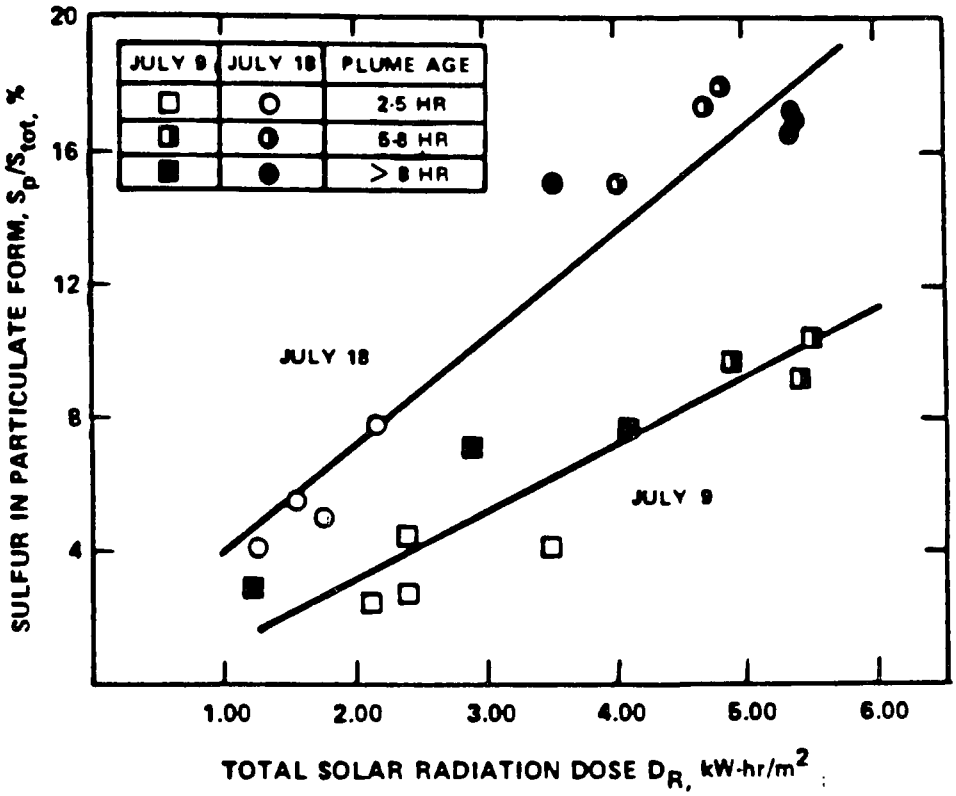



Figure 6-2. The ratio of particulate sulfur, Sp, to total sulfur concentrating $S_{tot}$, (consisting of particulate S in sulfates plus gaseous S in $SO_2$, average for traverse) is shown as a function of total plume solar radiation dose, $D_R$, (time integral of solar radiation, $R_T$, between plume release time and plume sampling time). The least squares regression lines shown have the following equations:

July 9: $y = 2.05x - 0.89$, $r = 0.92$;
July 18: $y = 3.22x + 0.75$, $r = 0.96$.

Source: Gillani et al. (1978).

relative humidity, and source operational parameters, will influence the rate of sulfate formation. These recent plume studies have established that atmospheric conversion rates of sulfate formation are in the range of 0 to 8 percent per hour (Husar et al., 1978). However, at this time, field observations of plumes have not been completely described in terms of the fundamental processes, including the chemical pathways, atmospheric mixing, and removal at the earth's surface. A model including variable first-order conversion, mixing, and removal has been presented (Gillani et al., 1978). Only data for the summertime are available at present.

There have been a limited number of investigations of $SO_2$ conversion rates in urban areas. Measurements in the Los Angeles area during the summer smog season suggested an $SO_2$ oxidation rate in the range of 1 to 13 percent per hour for the daylight hours (Roberts and Friedlander, 1976). Measurements using St. Louis air in a Teflon bag give maximum $SO_2$ oxidation rates of 1.6 to 5.5 percent per hour. These values, and the increase in rate with increasing ratio of non-methane hydrocarbons (NMHC) to nitrogen oxides, agree with the results of smog chamber studies at higher pollutant concentrations (Miller, 1978). For the St. Louis urban plume, White et al. (1976) measured the mass flow rate of ozone and particulate sulfur. Their measurements at discrete distances suggested that the overall sulfate formation rates varied from 1 to 15 percent per hour. That data set has been modeled by Isaksen et al. (1978), who obtained good agreement by assuming a photochemical pathway involving oxidation of $SO_2$ by OH, $HO_2$, and $RO_2$ radicals.

The oxidation rate of $SO_2$ in the troposphere on a regional scale of dispersion has not been measured directly, owing to the complexity of such an experiment. However, based on atmospheric concentration data from monitoring networks and an estimate of natural and manmade $SO_2$ source strengths, lifetimes

of $SO_2$ and sulfate are estimated to be 25 and 80 hr, respectively, at midlatitudes for Europe (Rodhe, 1978). Accounting for the relative importance of various $SO_2$ transformation and removal processes is difficult, but Rodhe (1978) estimated that the turnover times of $SO_2$ were partitioned between oxidation to sulfate (80 hr), dry deposition (60 hr), and wet deposition (100 hr), with about 30 percent of the $SO_2$ being oxidized and then removed as sulfate.

Measurement of oxygen isotope ratios has been applied to the study of $SO_2$ oxidation in the atmosphere in an attempt to elucidate the principal pathways: homogeneous gas-phase oxidation and heterogeneous oxidation (either in liquid aerosols or on the surface of solid aerosol). Measurements of oxygen isotope ratios for water vapor, precipitation water, sulfate in precipitation, sulfate in aerosols, and $SO_2$ as a function of season indicate that aerosol sulfate shows no correlation with the isotope ratio of water vapor or precipitation water, but sulfate in rain does (Holt et al., 1979). It now appears that the turnover times of water and sulfate are too dissimilar for oxygen isotope ratios to yield information on sulfate aerosol pathways. However, the correlation of isotope ratios for sulfate in precipitation and for precipitation water indicates that the major pathway for sulfate formation in raindrops is in the condensed phase.

Because of the complexity of atmospheric processes, it appears at this time that insight into the chemical pathways requires the study of simple systems in the laboratory in conjunction with smog chamber and field studies.

6.2.1.2 Laboratory Investigation and Modeling

6.2.1.2.1 Smog chamber studies. Smog chamber studies such as those conducted at Battelle's Columbus laboratories have provided information on the influence of pollutant concentrations and the NMHC/$NO_x$ ratio on sulfate formation (Miller, 1978).

Experiments in which NMHC and $NO_x$ concentrations were held constant while the $SO_2$ concentration was varied indicate that the conversion is first order in

$SO_2$, as would be expected for radical reactions. As shown in Figures 6-3A and 6-3B (Miller, 1978), the rates do vary somewhat with changes in NMHC and $NO_x$ concentrations. There is a greater variation in maximum rates (1.1 to 11 percent per hour) than in total sulfate formed during a 6-hr radiation period (23 to 65 $\mu g/m^3$). It is not clear which measure is most appropriate for plumes, since the smog chamber was operated under constant illumination instead of the diurnal cycle of solar radiation.

As shown in Figure 6-3C (Miller, 1978), the maximum rate increases as the $NMNC/NO_x$ ratio increases. This is relevant to plume conversion because the plume contains high concentrations of $NO_x$ and very low concentrations of NMHC. Thus, as background air with a higher $NMHC/NO_x$ ratio mixes with or diffuses into the plume, the conversion rate within the plume increases. This inhibiting effect of $NO_x$ on photochemical smog reactions occurs because $NO_x$ competes with $SO_2$ for OH and peroxy radicals. Since NO reacts rapidly with ozone, no ozone will be found in the plume until enough ozone has diffused into the plume to convert all the nitric oxide to nitrogen dioxide.

6.2.1.2.2 Plume simulation with a chemical kinetics model. A very simplified model of plume behavior has been used to investigate how diurnal variations in solar intensity, changes in solar intensity, and changes in amount of dilution affect sulfate formation (Easter et al., 1980). The chemical kinetics model was based on the average values of the pollutant concentrations in the plume and thus neglected cross-plume variations in concentration and reaction rates, which are thought to be very important. However, the simulation provides insight into the interaction between mixing and solar radiation.

The model predictions of $SO_2$ oxidation rates are presented in Figure 6-4 (Wilson, 1979). Each plot shows the $SO_2$ oxidation rate in ambient air and in

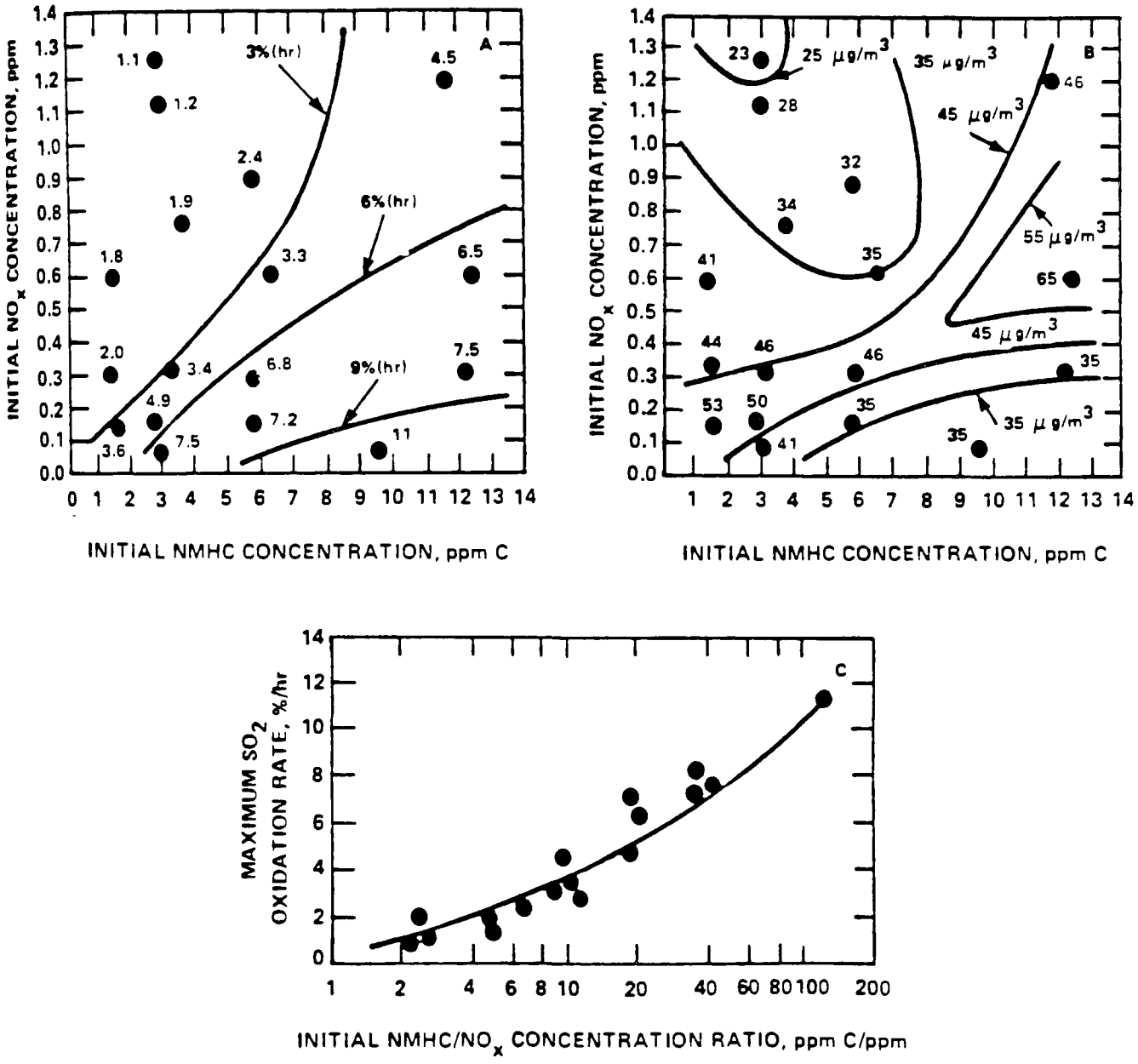



Figure 6-3. The initial NMHC and $NO_x$ concentrations affect (A) the maximum rates of $SO_2$ oxidation and (B) the total conversion of $SO_2$ to sulfate aerosol in a 6-hr irradiation interval. (C) The maximum rate of $SO_2$ oxidation is plotted as a function of initial NMHC/$NO_x$ ratio.

Source: Miller (1978).

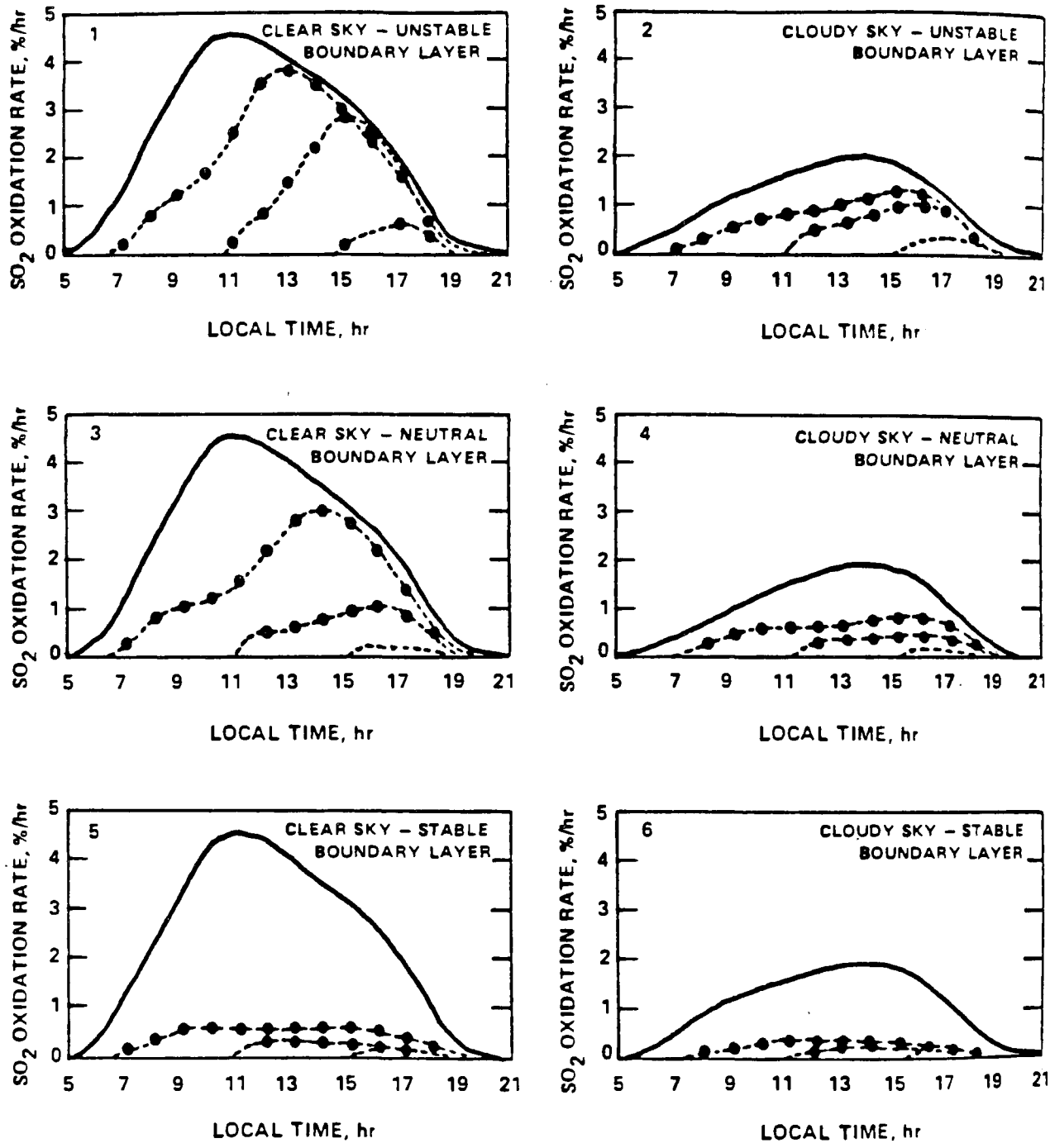



Figure 6-4. The rate of oxidation of $SO_2$ is simulated by kinetic modeling. The solid curve in each plot is the $SO_2$ oxidation rate in ambient air. The dashed curves are the net $SO_2$ oxidation rates predicted for power plant plumes emitted at 6 a.m., 11 a.m., and 3 p.m.

Source: Wilson (1979).

plumes emitted at 6 a.m., 11 a.m., and 3 p.m. for a particular set of solar-intensity and plume-dispersion conditions. The plume $SO_2$ oxidation rates were calculated using "net-plume" $SO_2$ and sulfate concentrations (average plume concentrations minus ambient concentrations). For determining dispersion rates, stability class was held constant for the neutral and stable conditions but was varied for the unstable condition by following the diurnal pattern of boundary layer evolution for a clear summer day.

The model predicts that the rate of $SO_2$ conversion to sulfate in plumes will be bounded by the conversion rate in the ambient, background air. This is not surprising since the plume contains higher levels of $NO_x$, which competes with $SO_2$ for the OH and peroxy radicals. Plume $SO_2$ oxidation rates show a distinct dependence on solar intensity: the rates are lowest near dawn and dusk, and they are significantly lower in the simulations of cloudy versus clear conditions. The 50 percent reduction in solar intensity for the cloudy conditions results in a somewhat greater than 50 percent decrease in the ambient $SO_2$ oxidation rates. According to the modeling estimates, the primary contributions to $SO_2$ oxidation come from the reaction of $SO_2$ with OH, $HO_2$ and $RO_2$. The OH concentration is dependent on solar intensity and on the concentration of other species which vary during the simulations.

The plume $SO_2$ oxidation rates are also predicted to be sensitive to the plume dispersion rate. Several hours are usually required after emission begins before the oxidation rate in the plume reaches the ambient rate, and this induction period is lengthened by slower plume dispersion. Free-radical concentrations in the plume are depressed below ambient levels during this initial period, until plume NO concentrations are reduced by dispersion and by reaction with ambient ozone. The induction period is also lengthened by lower solar

radiation because of the resulting lower ambient ozone levels. The induction period is also observed in field measurements and corresponds to the "early" and "intermediate" stages in the chemical life history of the plume (Wilson, 1979).

It is clear that measurements of plume conversion rates made during the periods from 7 to 9 a.m. and from 6 to 8 p.m. will give much lower rates than similar measurements during midday. The lower rates are due both to lower solar radiation and to reduced mixing.

6.2.1.3 Homogeneous Gas-Phase Reactions--The reactions involved in the homogeneous oxidation of $SO_2$ have been critically reviewed by Calvert et al. (1978). It is now thought that the oxidation is governed by reactions of photochemically generated OH, $HO_2$, and $CH_3O_2$ radicals. For midlatitudes in the Northern Hemisphere, the oxidation is mainly due to the OH radical (Figure 6-5). The oxidation rate is season dependent, with a maximum value of 0.2 percent per hour for July and a minimum value of 0.09 percent per hour for January (Northern Hemisphere average). Calculated conversion rates for the clean troposphere as a function of season and latitude have been computed by Altshuller (1980) as follows: July, 30°N, 0.43 percent per hour, 50°N, 0.24 percent per hour; January, 30°N, 0.10 percent per hour, 50°N, 0.01 percent per hour.

In polluted air masses, however, Calvert et al. (1978) estimated that the rates of oxidation by RCHOO, O, $CH_3O_2$, and $HO_2$ radicals greatly exceed the rate of oxidation by the OH radical (see Figure 6-5 for a specific example of the relative importance of these species in a polluted air mass). Recent laboratory measurements (Graham, 1979) suggest that the rate of reaction of $HO_2$ with $SO_2$ may not be as great as the value used by Calvert et al. (1978). However, smog chamber studies demonstrate that some species other than OH does convert $SO_2$ to sulfate (Kuhlman et al., 1978; McNelis, et al, 1975). Additional investigations are needed to obtain reliable rates for the reaction of the $HO_2$ and $RO_2$ radicals with $SO_2$.

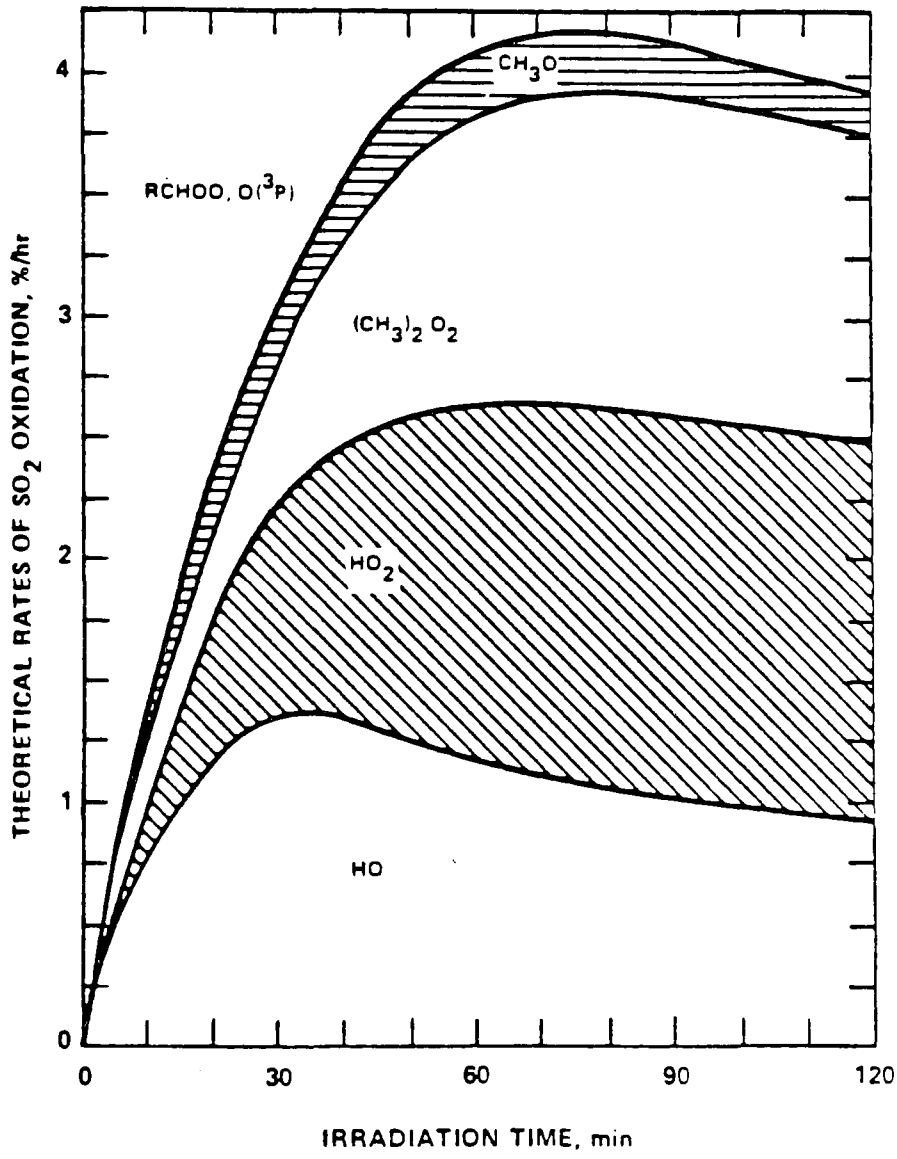



Figure 6-5. The theoretical rate of reaction (percent per hour) of various free-radical species on $SO_2$ is shown for a simulated sunlight-irradiated (solar zenith angle of 40°) polluted atmosphere. The initial concentrations (in ppm) were as follows: $SO_2$, 0.05; NO, 0.15; $NO_2$, 0.05; CO, 10; $CH_4$, 1.5; $CH_2O$, 0; $CH_3CHO$, 0. The relative humidity was 50 percent, and the temperature was 25°C.

Source: Calvert et al. (1978).

6.2.1.4 Heterogeneous Aqueous Reactions--Whereas photochemical gas-phase reaction rates appear to be high enough to dominate $SO_2$ oxidation during the summer and in daytime hours, the pathway in the winter and nighttime hours is not known at present. Although not well established, it appears that $SO_2$ oxidation in liquid aerosols and fogs can reasonably proceed during these periods through catalysis (by dissolved transition metal ions and carbon) and through reaction with dissolved oxidants (ozone, hydrogen peroxide, and nitrogen dioxide).

Studies of the autooxidation of dissolved $SO_2$ in pure water have yielded rates that are too low to be significant for the lower troposphere, although it has been suggested that this reaction may be important in clouds (Hegg and Hobbs, 1978). It is highly unlikely that aerosols and fogs in the lower troposphere consist of pure water, and it has not been demonstrated that the uncatalyzed autooxidation may be dominant in cloud water.

There have been many investigations of the metal-catalyzed oxidation of dissolved $SO_2$ species in water. The metals of main interest include manganese, iron, copper, and nickel. Unfortunately, vanadium, which is also of interest, has not been widely studied.

The kinetics of the manganese-catalyzed reaction have been investigated for over 75 years. One of the first to criticize such studies was Titoff in 1903, who remarked: "In Bigelow's (1898) work the reaction occurred between two phases, and the retardation could be determined by a change in the boundary layer or by a decrease in the solution rate of the oxygen." Although Titoff recognized the possibility that the oxidation is dominated by mass transport, many later investigators up to the present have not treated it adequately. Apart from work done in two-phase systems, there have been only three studies. It is unusual

that in none of these three reports were the rate expressions clearly stated; instead, it was left to the reader to extract the rate constant. Estimates of the rate expressions are presented in Table 6-1.

The work of Hoather and Goodeve (1934) and that of Coughanowr and Krause (1965) are in good agreement, each showing a second-order dependence on manganese concentration. However, Neytzell-de Wilde and Taverner (1958) reported a first-order dependence on manganese concentration. This difference is currently unresolved.

The iron-catalyzed oxidation of dissolved $SO_2$ species has not been investigated as extensively as that of manganese. The only studies not using two-phase systems (subject to mass transport limitations) are those of Neytzell-de Wilde and Taverner (1958) and of Karraker (1963). Hegg and Hobbs (1978) have pointed out that Karraker (1963) did not investigate the catalyzed oxidation in which dissolved oxygen is the oxidant, but instead the redox system associated with the couple $Fe^{3+} + e^- \rightarrow Fe^{2+}$ in an oxygen-free system. Thus, Karraker's work is not considered applicable. Neytzell-de Wilde and Taverner (1958) reported that the sulfate formation rate was second order for $[SO_3^{2-}]$, but Karraker (1963), who reanalyzed their data, demonstrated that it was in fact first order. As before, Neytzell-de Wilde and Taverner did not report the rate constant for their data; however, an estimate is presented in Table 6-1. To date, the kinetics of copper-catalyzed and vanadium-catalyzed oxidations have not been satisfactorily investigated.

For the metal ion-catalyzed oxidation of dissolved $SO_2$ in the absence of mass transport considerations, the reaction kinetics for managanese are in doubt, there is only one study for iron, and there are no satisfactory investigations for copper and manganese. For the few systems that have been studied,

TABLE 6-1. RATE EXPRESSIONS[a] FOR THE Mn-, Fe-, Cu-, AND V-CATALYZED OXIDATION OF DISSOLVED $SO_2$ IN WATER

| Expression | Investigators |
|---|---|
| 1a. $\frac{d[SO_4^{2-}]}{dt} \approx 44[Mn^{2+}]^{1.7}[SO_3^{2-}]^0$ pH 3-4 | Hoather and Goodeve (1934) |
| b. $\frac{d[SO_4^{2-}]}{dt} \approx 1.7 \times 10^{-5}[Mn^{2+}]\,[SO_3^{2-}]\,[H^+]^{-1}$ pH ~ 2.2 | Neytzell-de Wilde and Taverner (1958) |
| c. $\frac{d[SO_4^{2-}]}{dt} = 8[Mn^{2+}]^2[SO_3^{2-}]^0$ pH 3-4 | Coughanowr and Krause (1965) |
| 2. $\frac{d[SO_4^{2-}]}{dt} = 0.04\,[Fe^{3+}]\,[SO_3^{2-}]\,[H^+]^{-1}$ | Neytzell-de Wilde and Taverner (1958) |
| 3. For copper: none | |
| 4. For vanadium: none | |
| 5. Mixed catalysts (e.g., manganese plus iron): none | |

[a]Units = mole, liter, second.

the ranges of pH, temperature, ionic strength, and type and concentration of inhibitors have been insufficiently investigated. Also, the behavior of mixed-catalyst (e.g., manganese plus iron) systems needs to be investigated. The catalysis of the oxidation of dissolved $SO_2$ by carbon particles suspended in the water has been studied by Chang et al. (~~1979~~ 1978). It was found that the oxidation rate of dissolved $SO_2$ species was

$$\frac{d[SO_2 \cdot H_2O]}{dt} = k[C]\,[O_2]^{0.69}[SO_2 \cdot H_2O]^0 \exp(-E_a/RT)$$

With an activation energy of $E_a$ = 11.7 kcal/mol over the pH range of 1.45 to 7.5 for the carbon studied, which was Nuchar-190. (The investigators demonstrated that Nuchar-190 behaved similarly to soot from acetylene and natural gas flames.) An average value of $k = 1.17 \times 10^5$ $mol^{0.3} \times liter^{0.7}$/g-sec was reported. The kinetics have been interpreted in terms of the rate-limiting step being the formation of an activated complex between molecular oxygen and the carbon surface (Chang et al., 1978; Eatough et al., ~~1979~~ 1978a).

Chang et al. (1978) have estimated that for 10 μg of fine carbon soot suspended in 0.05 g of liquid water and dispersed in 1 $m^3$ of air, the atmospheric sulfate production would be about 1 μg/hr. At this time, it remains to be demonstrated that the laboratory soots used by Chang et al. (1978) correspond to those present in the atmosphere or that the suspension of soot at ambient levels (<10 μg/$m^3$) in aerosols, cloud droplets, or rain is similar to the laboratory system.

Hydrogen peroxide, ozone, and nitrogen dioxide may be important in the oxidation of $SO_2$ in aqueous aerosols and fogs. Although these compounds do not demonstrate high reactivity toward $SO_2$ in air, their reactivity is enhanced in the liquid phase. Again, caution is advised in accepting the results of studies

of two-phase systems in which the investigators have not completely accounted for the possibility of the mass transport limitation of the oxidation rate. Therefore, only the recent results for single-phase systems are discussed here.

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

$$\frac{d[SO_4^{2-}]}{dt} = k[H_2O_2]\,[HSO_3^-]\,[H^+] + k_a[H_2O_2]\,[HSO_3^-]\,[HA]$$

where $k = 5.2 \times 10^5$ liters/mol$^2$·sec, with k and $k_a$ being the third-order rate constants for the catalysis by free protons and proton-donating buffers, respectively. At pH $\leq 4$, it is found that $k/k_2 \geq 3200$. Therefore, the second term is probably not important for acid aerosols and fogs. It is of great significance that the reaction rate increases as the solution becomes more acidic, which is in contrast to aqueous oxidation by metal ions and by ozone. The activation energy and the effect of ionic strength on the reaction have been measured by Penkett et al. (1979).

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

$$\frac{d[SO_4^{2-}]}{dt} \approx k[HSO_3^-]\,[O_3]\,[H^+]^{-1}$$

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

$$\frac{d[SO_4^{2-}]}{dt} = k_1[SO_2 \cdot H_2O]\,[O_3]$$

$$\frac{d[SO_4^{2-}]}{dt} = k_2[HSO_3^-]\,[O_3]$$

$$\frac{d[SO_4^{2-}]}{dt} = k_3[SO_3^{2-}]\,[O_3]$$

where $k_1$ = 590 liters/mol·sec, $k_2 = 3.1 \times 10^5$ liters/mol·sec, and $k_3 = 2.2 \times 10^9$ liters/mol·sec. The differences between the results of Penkett et al. (1979) and Erickson et al. (1977) remain to be resolved.

The oxidation of $SO_2$ dissolved in water by $NO_2$ and $HNO_2$ may also be an important sulfate formation process. Ross (1978) has reported that nitrous acid completely oxidizes $SO_2$ dissolved in water at pH = 4 within 15 to 30 sec when both reactants are present in the $10^{-3}$ to $10^{-4}$ M range. At present, the reactions involved in the oxidation of $SO_2$ by nitrous acid and nitrogen dioxide are incompletely characterized, and their environmental significance is unknown.

At this time, the significance of reactions occurring in aqueous aerosols in unknown. That is due principally to the lack of laboratory data for properly designed two-phase reaction studies on complex chemical systems that simulate environmental conditions.

6.2.1.5 Heterogeneous Surface Reactions--Recent laboratory studies of the removal of $SO_2$ by airborne particulate matter have been conducted on a wide variety of pure solids (Chun and Quon, 1973; Judeikis and Siegel, 1973; Haury et al., 1978). Although reaction kinetics have not been identified, two general types of processes have been: a capacity-limited reaction for $SO_2$ removal and a catalytic $SO_2$ oxidation process. The initial contact of $SO_2$ with the solid produces a rapid loss of $SO_2$ from the gas phase; the reaction rate decreases

with time. For the capacity-limited reaction, the rate slowly approaches zero; for the catalytic process, the rate levels off for a time and then approaches zero. The latter phenomenon is attributed to a pH decrease caused by sulfuric acid formation.

Urone et al. (1968) and Smith et al. (1969) found a number of solids to be effective in removing $SO_2$. In Urone's studies, $SO_2$ admitted to a flask containing a particular solid, allowed to react with no mixing, and the product and remaining $SO_2$ were determined. Only the average reaction rates can be calculated from these experiments; more importantly, with this experimental procedure the rates will be diffusion limited. The highest rate determined was for $SO_2$ with ferric oxide; the value was >75 percent per minute. Other materials found to be slightly less reactive than ferric oxide were magnetite, lead oxide, lead dioxide, calcium oxide, and aluminum oxide. The rate for the ferric oxide experiment was for 20 mg of ferric oxide in a 2-liter flask; the ferric oxide concentration would thus be $10^7$ $\mu g/m^3$. Assuming a direct proportionality between rate and particle concentration, the $SO_2$ removal rate in the atmosphere would be calculated to be 0.04 percent per hour for 100 $\mu g/m^3$ of particles with the same reactivity as ferric oxide.

In Smith's experiments, an exploding-wire technique was used to generate aerosols. There was a rapid decrease in $SO_2$ concentration, the rate depending on the materials tested; the capacity for removal was in the order $PbO_x$ > $Al_2O_3$ > $Fe_3O_4$.

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

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

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

The most comprehensive study to date on $SO_2$ removal by pure solids was made by Judeikis (1974), who used a tubular flow reactor in which solids were supported on an axial cylinder to measure reactivities; the calculated removal rates for various solids are listed below.

| Substance | Removal rate, percent per hour |
|---|---|
| MgO | 32 |
| $Fe_2O_3$ | 18 |
| $Al_2O_3$ | 13 |
| $MnO_2$ | 10 |
| $PbO_2$ | 3 |
| NaCl | 0.1 |
| Charcoal | 1 |

The values were estimated based on a previously derived model (Judeikis and Siegel, 1973).

Charcoal is not a pure solid, but it is listed for comparison purposes. Because of the ubiquitous nature of carbonaceous matter in ambient air particulate samples, various workers have studied the $SO_2$ removal rate by carbon.

Because of the varieties of carbon available for study, such as activated charcoal, graphite, acetylene flame products, and combustion products of diesel oil and heating oil, a comparison of the results is rather difficult. We cite here a few investigations that deal with the gas-solid reaction of $SO_2$ with carbon.

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

Liberti et al. (1978) studied the adsorption and oxidation of $SO_2$ on various particles, including soot from an oil furnace and various atmospheric particulate samples. They concluded that the main interaction between the $SO_2$ and particulate matter is adsorption, with most catalytic reactions occurring at high temperatures, near the combustion source. Their experiments with atmospheric particulate samples led them to the conclusion that any heterogeneous nonphotochemical sulfate formation is strongly dependent on the reactivity of the aerosol surface, and hence the history (aged, freshly emitted), of the aerosol.

6.2.2 Physical Transformations

6.2.2.1 Aerosol Size Distribution--The size distribution of atmospheric aerosol is important because it influences the rate of dry and wet deposition, transport times, visibility impairment, and the site and extent of deposition in the lung. The existance of a bimodal distribution was suggested in the early 1970's based both on aerosol volume distributions derived from particle counts (Whitby et al., 1972) and on mass distributions measured with impactors (Whitby et al., 1974; reinterpretation of impactor data of Lee, 1972). There is now an overwhelming amount of evidence that not only are two modes usually observed in the mass

or volume distribution of well-mixed urban and rural aerosols, but that the fine and coarse modes are normally quite different in chemical composition.

The physical separation of the fine and coarse modes occurs because condensation/coagulation processes produce fine particles, while mechanical processes produce mostly coarse particles (Whitby, 1978).

This is shown in an idealized schematic in Figure 6-6. Individual sources of primary aerosols may produce fine or coarse aerosols; some chemical species in the coarse mode may have a tail extending into the fine mode. Secondary aerosols, formed in the atmosphere from primary gaseous emissions, will normally be fine. Recently it has been observed that fine particles may be further subdivided into a nuclei mode and an accumulation mode (Wilson et al., 1977; Whitby and Sverdrup, 1980).

The nuclei mode is observed only near combustion or other high temperature sources. These particles rapidly coagulate into the accumulation mode. The dynamics of particle growth normally prevent accumulation mode particles from growing larger than about 1 μm.

Figure 6-7 shows a typical urban-type size distribution presented in five different ways.

Typically, atmospheric aerosol number size distributions have been presented as log dN/d log $D_p$ vs log $D_p$, as shown in Figure 6-7(a). Because a good portion of such plots could be fitted by a power function of the form dN/d log $D_p = AD^k_p$, this has been used by many investigators to model the number-size distribution (Junge, 1953; Clark and Whitby, 1967). However, when such number distributions are transformed to surface area-size, or volume-size distributions [Figs. 6-7(d) and (e)], it is seen that the apparently minor deviations form the power law are actually significant modes.

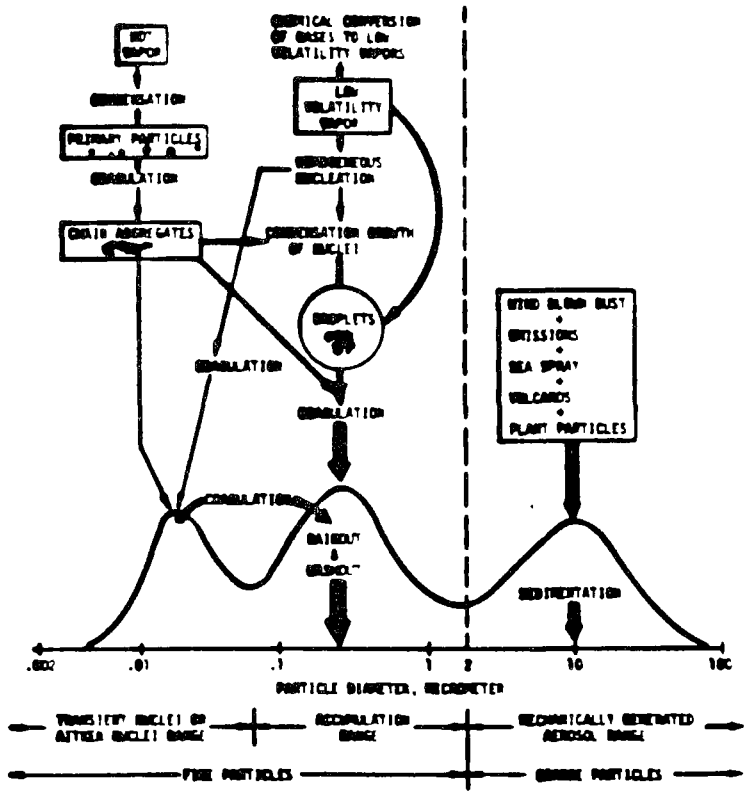



Figure 6-6. Schematic of an atmospheric aerosol size distribution showing the three modes, the main source of mass for each mode, and the principal processes involved in inserting mass into, and removing mass from, each mode.

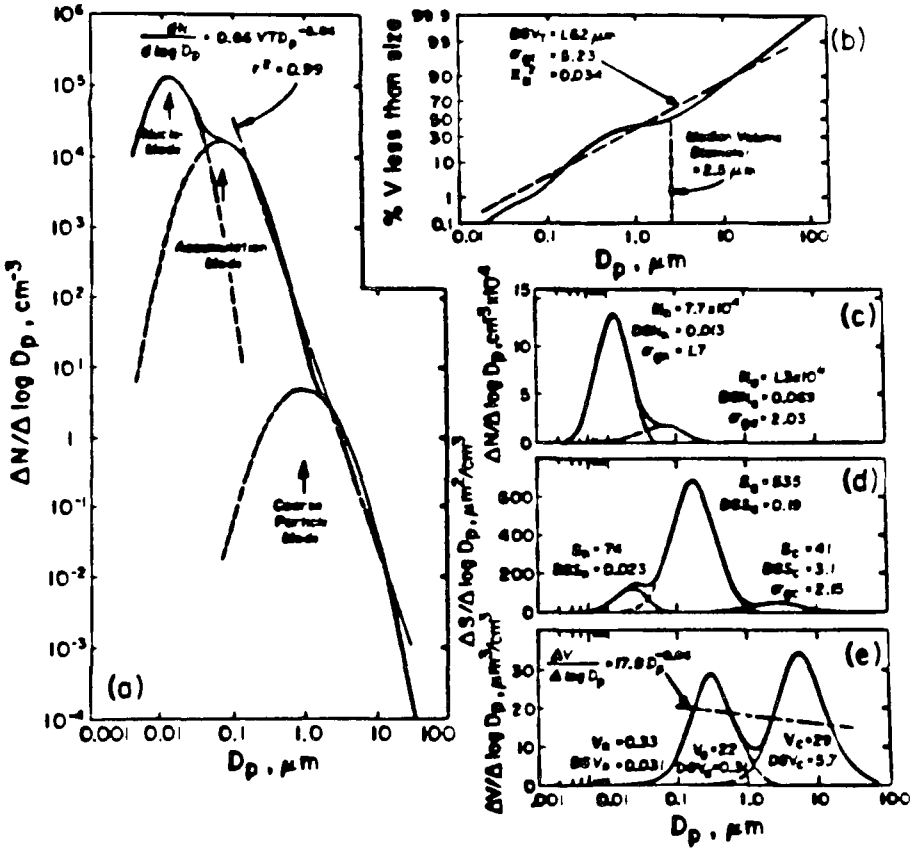



Figure 6-7. Average urban model aerosol distribution plotted in five different ways. In (a) a power function has been fitted to the number distribution over the size range 0.0 to 32 μm. In (b) a log-normal distribution has been fitted to the range 0.1 to 32 μm. It is evident that the modal nature of the aerosol is shown best by the plots of (c), (d), and (e).

The linear-log forms shown in Figs. 6-7(c), (d), and (e) are useful because the apparent area under the distribution curves is proportional to the integral in the size range. From these plots, it is possible to visually judge the relative N, S and V in the different modes of the distribution.

The form log dN/d log D, vs log $D_p$ is dominated by the nuclei mode for most urban and near-urban situations. For background aerosols, the number in the accumulation mode may occasionally dominate the distribution. This plot usually masks the model structure of aerosols, and erroneously suggest that the whole distribution can be modeled by a continuous function. Although a power function is often an adequate model for the number distribution in the 0.1-10 μm range, it is a poor model for the surface and volume distributions.

Cumulative plots of N, S, V, or m vs log $D_p$ [Fig. 6-7(b)] have widely used for the presentation of powder size distributions and for the presentation of impactor results (Wagman et al., 1967).

From such a plot of a unimodal distribution on logarithmic probability paper, it is possible to determine the geometric mean by inspection. However, the cumulative plot has several deficiencies. First, the cumulative form masks the modes in the distributions. Second, the median used to determine the geometric mean is a function of the upper and lower cutoffs of the measurement method, since the distribution must be normalized by the total N, S, or V.

Thirdly, the median obtained from a cumulative plot is kind of an average between the fine and coarse modes, and therefore does not have a clear-cut physical significance. For the distribution shown in Fig. 6-7(e) the geometric mean diameters by volume (DGV) of the accumulation and coarse particle modes are 0.31 and 5.7 μm, respectively. The volume median from the cumulative plot [Fig. 6-7(b)] is 2.5 μm.

The fundamentally modal nature of atmospheric size distribution was not seen until about 1970 because the majority of workers in aerosols only plotted

data as in Figs. 6-7(a) and (b). It is now clear that the N, S and V size distributions must be all examined and then plotted in several ways if a proper understanding is to be achieved (Whitby, 1978).

The fine and coarse particle modes in general: originate separately, are transformed separately, are removed from the atmosphere by different mechanisms, require different control techniques, have different chemical composition, and have different optical properties. Therefore, the distinction between fine and coarse particles is of fundamental importance to any discussion of the physics, chemistry, measurement, or air quality standards of aerosols. Of particular importance is the general division of acidic material into the fine fraction and of basic material into the coarse fraction. Measurements of acidity (pH) require that the sample be dissolved in water. If the fine and coarse fractions are collected in the same sample, the acid particles in the fine fraction will dissolve and be neutralized by coarse basic particles.

The existence of a bimodal distribution with fine and coarse modes has been clearly demonstrated by cascade impactor studies which yield mass-size distributions and by number distribution studies which may be converted into volume distribution. These size distribution studies suggest 1-3 μm as the most appropriate range for a cut-point for fine and coarse aerosols. However, practical considerations of reducing plugging of impactor orifices indicate that 2.5 μm is a more appropriate cut-point, especially for particle size fractionating devices such as the dichotomous sampler (Miller et al., 1979).

Impactor studies in which chemical composition has been determined as a function of particle size also demonstrate the division into fine and coarse modes and show the difference in chemical composition of the two modes. Except for a few trace elements, the chemical species are either primarily coarse,

primarily fine, or bimodal. On the basis of such studies, it is possible to divide the major chemical species observed in atmospheric aerosols into several groups shown in Table 6-2 (Miller et al., 1979).

The major components of the fine fraction of the atmospheric aerosol are sulfate, ammonium, nitrate ions, lead, carbon-containing material including soot, and condensed organic matter. Also, several studies have shown that potentially toxic carcinogenic species, such as polynuclear aromatic compounds, As, Se, Cd, Zn, which can exist as vapors, are more concentrated in the fine particle fraction. In urban areas the fine fraction, as a percent of total suspended particulate matter, varies from 15-25% in Denver to 40-60% in the Los Angeles area and New York-New Jersey urban areas. The percent of the fine particle fraction which is secondary varies from 60-80% in these urban areas. These percentages are based on short-term intensive studies (Miller et al. 1979).

Sulfate is usually considered a secondary aerosol. However, in a few cases in areas downwind of oil-fired power plants with relatively short stacks using high vanadium oil primary sulfate can make an appreciable contribution to the aerosol mass (Wilson et al, 1979).

The coarse fraction consist mainly of soil or curstal material, the major elements being oxides of Si, Al, Ca, and Fe. The major source in most sampling areas is soil or crustal material suspended by vehicular traffic from dirt roads, dirt deposited on paved roads, unpaved shoulders, and rock used as filler in pavement or from recreational or agricultural activity in rural areas (Harrison, 1976; Graf et al, 1977; Draftz, 1979; Hardy, 1979). Studies in Chicago have shown that on the average reflotation (soil suspension from terrestrial surfaces) accounts for approximately 20% of the annual TSP value in the city of Chicago. On an annual average basis it was found that vehicular traffic suspends about 14 $\mu g/m^3$, while winds averaging above 13 mph suspend 5 $\mu g/m^3$ (Newman et al., 1976)

TABLE 6-2. CLASSIFICATION OF MAJOR CHEMICAL SPECIES ASSOCIATED WITH ATMOSPHERIC AEROSOLS

| Normally Fine | Normally Coarse | Normally Bimodal | Variable |
|---|---|---|---|
| $So_4^{=}$, C (soot), organic (condensed vapors), Pb, $NH_4^+$, As, Se, $H^+$ | Fe, Ca, Ti, Mg K, $PO_4^{=}$, SI, Al organic (pollen, spores, plant parts) | $NO_3^-$, $Cl^-$ | Zn, Cu, Ni, Mn Sn, Cd, V, Sb |

Source: Miller et al., 1979.

In some samples from industrial areas or near specific sources the coarse particle fraction may be dominated by local industrial sources (Draftz and Severin, 1980). Other sources include wind erosion products, primary emissions, sea spray, volcanic eruptions, and biological material such as pollen and spores.

6.2.2.2 Aerosol Transformation--Aerosol dynamics concerns the evolution of the particle size distribution. At any given moment, the particle size distribution reflects the past history of the aerosol. It is determined by such physical processes as nucleation (formation of new particles), condensation on existing particles, coagulation (collision and subsequent adhesion), and depositional loss from the atmosphere. The state of theoretical work in describing these processes for application in phenomonological models appears to be satisfactory (Hidy and Brock, 1970; Middleton and Brock, 1976; Middleton et al., 1977; Suck et al., ~~1977~~ 1978; Gelbard and Seinfeld, 1979). Factors affecting the rate at which the particle size distribution changes include the mechanisms of chemical formation, the prexisting particle size distribution, and the relative humidity. Recent reviews of aerosol dynamics with special emphasis on the formation of sulfur compounds include those by Friedlander (1978), Whitby (1978), and Boulaud et al. (1978).

Aerosol formation in photochemical chambers has been frequently studied by measuring the particle size distribution. By intergrating and weighting the size distribution, the aerosol number concentration, N, area concentration, A, and volume concentration, V, can be measured as a function of time [Figure 6-8(b)] Friedlander, 1978).

For aerosol growth processes involving homogeneous gas-phase reactions as the source of condensable molecules, the growth can be divided into three time domains (Husar and Whitby, 1973; Friedlander, 1978). In the first domain,

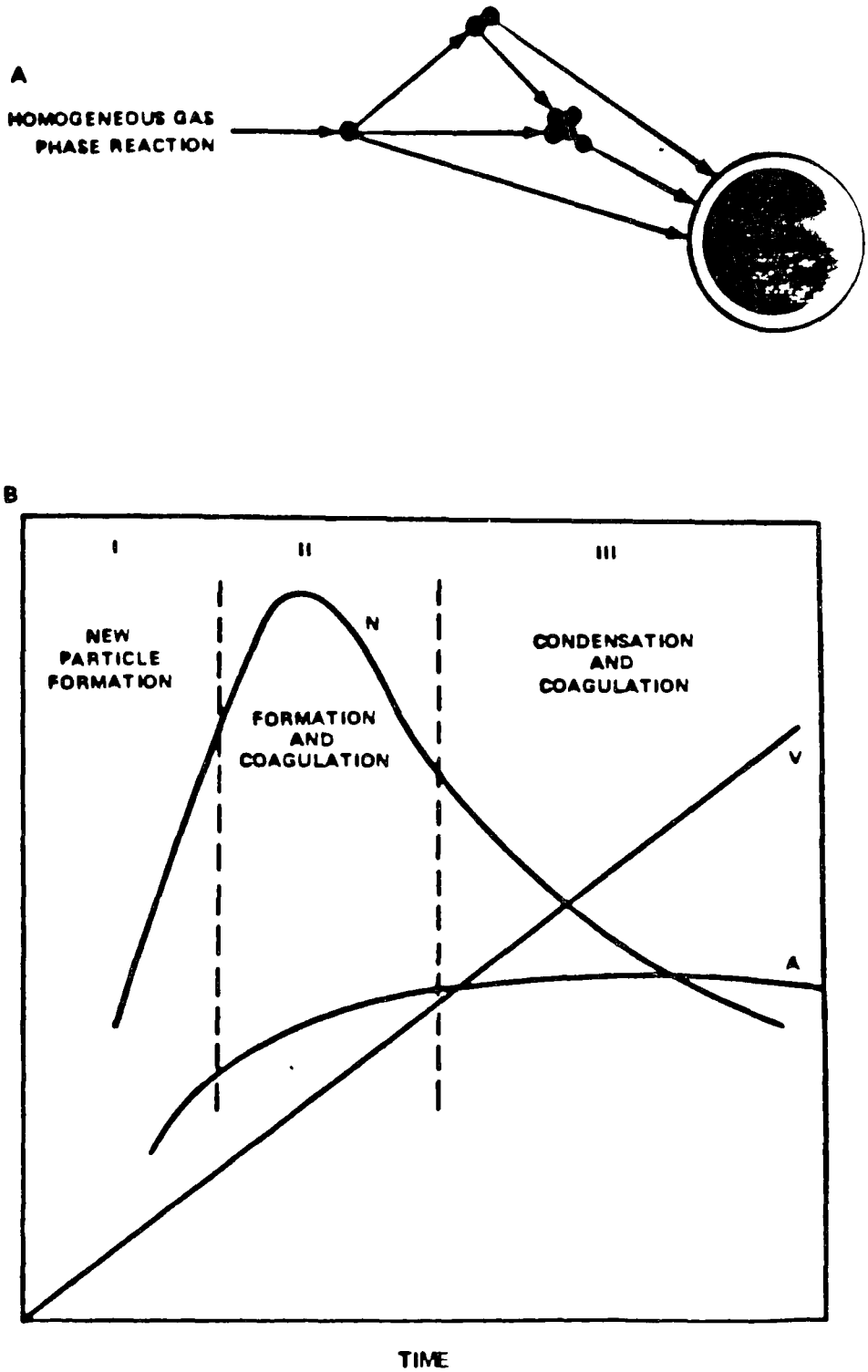



Figure 6-8. (A) Condensible molecules (monomer) produced by gas-phase reactions may either produce new particles or condense on larger preexisting particles. New particles (clusters) may also be scavenged by the preexisting particles. (B) Three time domains for aerosol formation in an irradiated chamber.

Sources: (A) McMurry and Friedlander (1978).
(B) Friedlander (1978), after Husar and Whitby (1973).

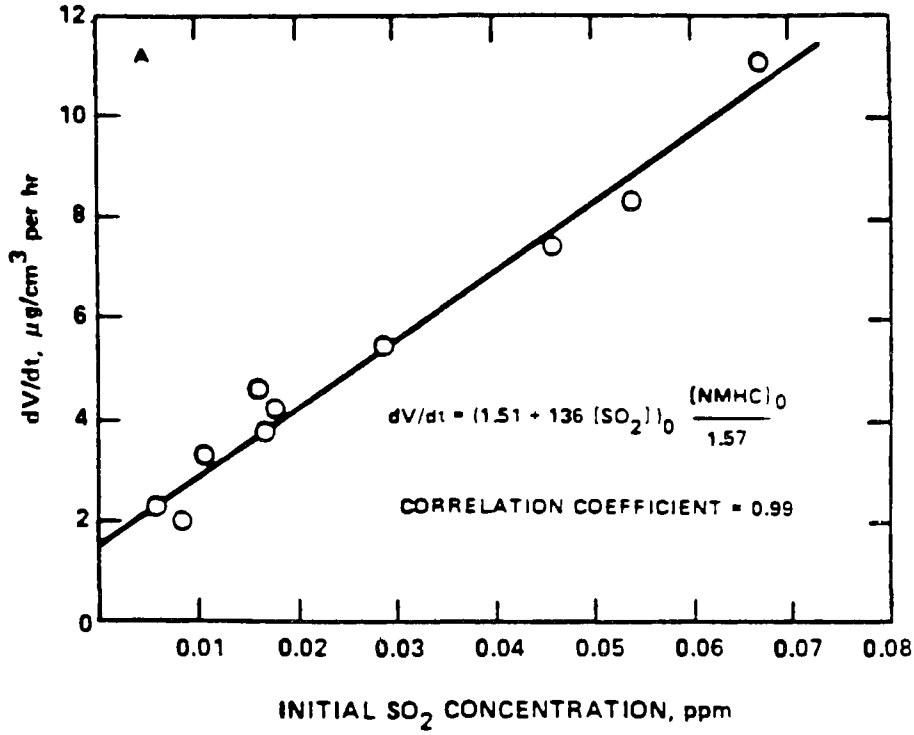
molecules are generated by gas-phase chemical reactions and collide to form particles (nucleation). The nucleation of sulfuric acid has received considerable attention (e.g., Middleton and Kiang, 1978), and there is a qualitative agreement between theory and experiment.

In the second domain, collision and adhesion (i.e., coagulation among the newly formed particles) become important. The aerosol surface area increases and then approaches an approximately constant value in the third domain, in which coagulation and condensation on the existing aerosol are the dominant processes (Figure 6-8; McMurry and Friedlander, 1978; Friedlander, 1978).

The growth processes are illustrated in Figure 6-8A (McMurry and Friedlander, 1978). If the surface area of the preexisting aerosol is sufficiently high, the formation of new particles will be suppressed by scavenging onto the existing particles. The scavenging of newly formed nuclei and condensable molecules constitutes the key mechanism by which "accumulation mode" aerosols are formed in the atmosphere (Whitby, 1978).

The gas-to-particle conversion rate can be measured directly by monitoring the rate of change of the aerosol volume concentration, dV/dt. The theory of aerosol dynamics for such a system was formulated by McMurray and Friedlander (1978). Clark et al. (1976) used such a system in Los Angeles, where they added $SO_2$ to ambient air containing hydrocarbons and $NO_x$. Their observations showed that aerosol formation is linearly proportional to the concentration of $SO_2$ (Figure 6-9A; Clark et al., 1976) and to that of nonmethane hydrocarbons (Figure 6-9B; Clark et al., 1976).

In summary, the phenomenology and theory of aerosol dynamics in photochemical systems are reasonably well understood. Nucleation, condensation, and coagulation are the dominant mechanisms, scavenging being responsible for the growth of



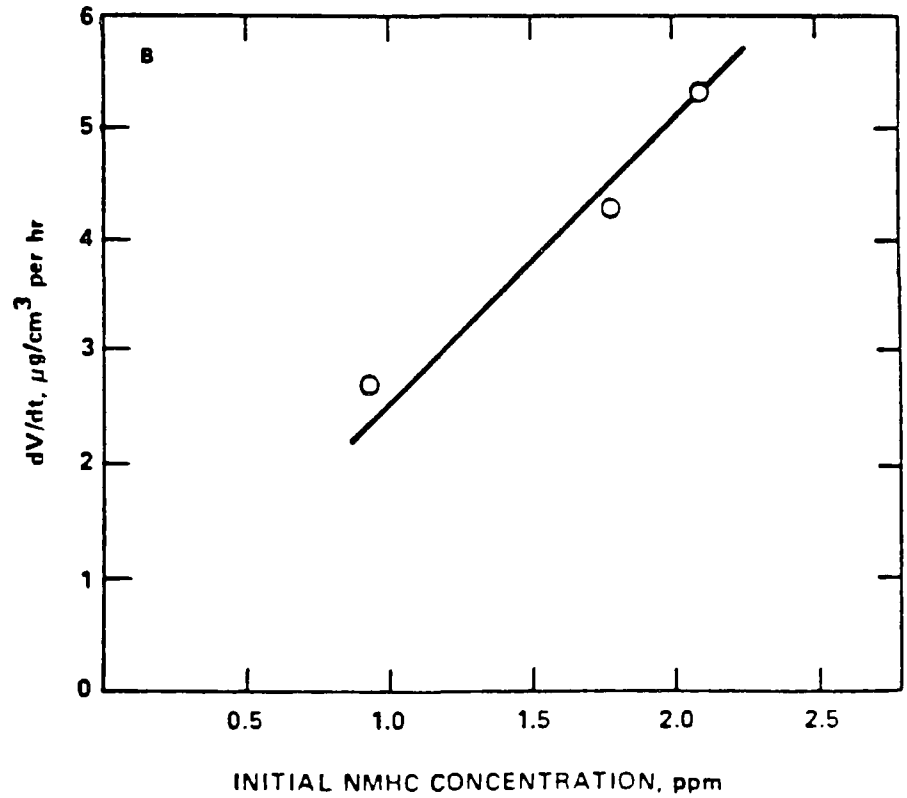




Figure 6-9. (A) Volumetric conversion rate is shown as a function of initial $SO_2$ concentration for an ultraviolet light intensity of 30.5 $W/m^2$ and an NMHC concentration of 1.57 ppm. (B) Volumetric conversion rate is shown as a function of initial NMHC concentration for $SO_2$ concentration of 0.017 ppm and an ultraviolet light intensity of 30.5 $W/m^2$.

Source: Clark et al. (1976).

accumulation-mode aerosols in the size range from 0.5 to 1.0 μm. Unfortunately, there is no comparable understanding of aerosol dynamics for liquid-phase or surface-controlled reactions.

### 6.2.3 Water Uptake and Release

An important form of physical transformation is the uptake or release of water vapor from atmospheric aerosols. Most atmospheric sulfates and nitrates are water soluble and hygroscopic. Concurrent with the identification of sulfates as major constituents of atmospheric fine particles, there has been considerable interest in the hygroscopic properties of pure and mixed sulfur compounds (Junge, 1952, 1963; Winkler, 1973; Charlson et al., 1974; Tang, 1976). The hygroscopic growth of sulfate-containing particles has a profound effect on their size, shape, refractive index, pH, and reactivity, which in turn influence their toxicity, removal efficiency, and effects on climate and weather.

The hygroscopic properties can be obtained from observation of aqueous solution properties such as equilibrium water vapor pressure or relative humidity (RH) as a function of solute/solvent mole fraction. The dependence of the sulfate mole fraction on RH for three different sulfate compounds is illustrated in Figure 6-10 (Charlson et al., 1978). (Raoult's law behavior assuming complete dissociation is included for comparison.) Sulfuric acid exhibits a monotonic curve characteristic of simple hygroscopic behavior. By contrast, ammonium bisulfate and ammonium sulfate exhibit stepwise increases at 39 and 81 percent RH, respectively, and monotonic curves at higher RH. This latter phenomenon, a sudden uptake of water when the RH exceeds a certain level, is termed "deliquescence" and is exhibited by these two compounds and a number of other organic and inorganic compounds, primarily salts. The existence of and differences in deliquescence points among compounds provide a possible basis for identification (e.g., Charlson et al., 1978).

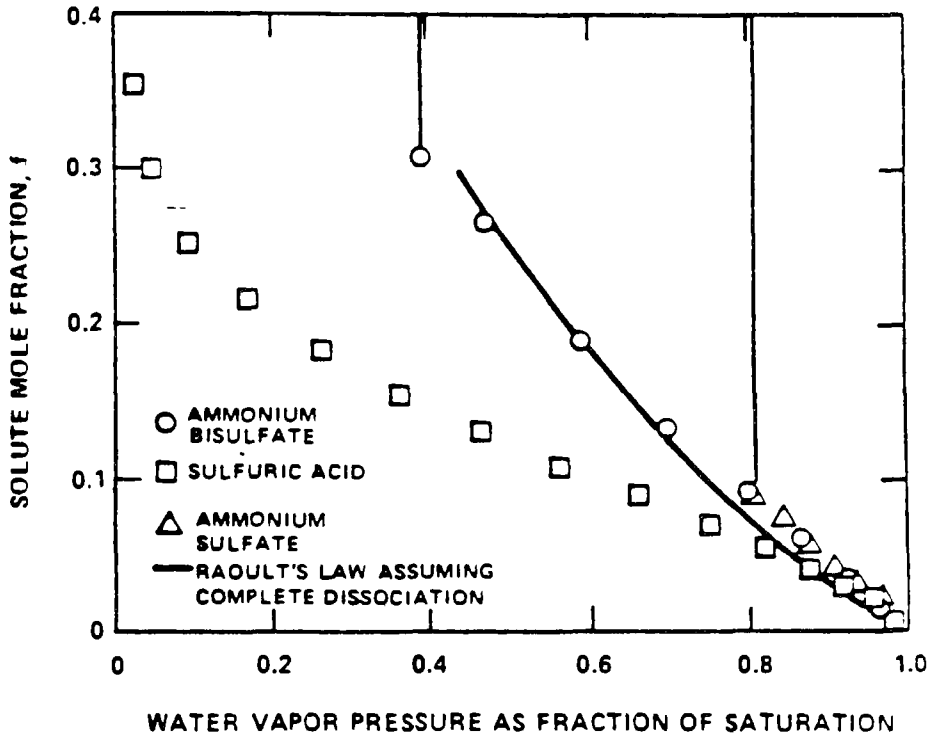



Figure 6-10. Solute mole fraction is shown as a function of water vapor pressure (as a fraction of saturation) for three sulfate compounds: sulfuric acid (Coordinating Research Council, 1968); ammonium bisulfate (Tang and Munkelwitz, 1977); and ammonium sulfate (Low, ~~1971~~ 1968). Curve showing data according to Raoult's law is from Charlson et al. (1978).

Under atmospheric conditions, hygroscopic/deliquescent compounds in the aerosol phase equilibrate rapidly with their surroundings and exhibit changes in size and other properties in response to RH changes. Figure 6-11 (Charlson et al., 1978) shows theoretical growth (increasing RH) curves for some sulfate compound aerosols based on vapor pressure data. In the aerosol phase, most compounds seem to remain as solution droplets at concentrations well above saturation, that is, at an RH well below the deliquescence point. This is caused by the phenomenon called hysteresis (Orr et al., 1958; Junge, 1963). Atmospheric aerosols probably exhibit hysteresis (Winkler and Junge, 1972), but this has been confirmed only on deposited aerosol samples. If so, they may contain considerably more water in the range 30 to 70 percent RH than would be expected from their deliquescence curves.

Since vapor pressure data are based on bulk measurements of pure compounds, corrections must be made for the increase in vapor pressure over curved surfaces (Kelvin effect) and, in the case of deliquescence, for the small number of crystal units present. For the complex mixture of compounds generally found in atmospheric aerosols, hygroscopic properties are rather difficult to model.

A number of techniques have been used to directly investigate the hygroscopic properties of aerosols (Orr et al., 1958; Tang and Munkelwitz, 1977; Kapustin et al., 1974; Sinclair et al., 1974; Winkler, 1973; Covert, 1974; Charlson et al., 1974). Charlson et al. (1974) have developed a humidograph that measures the light-scattering coefficient of the particulate matter, $b_{sp}$, as a function of increasing RH. This technique provides an <u>in situ</u> measurement of $b_{sp}$ and is most sensitive to the concentration of particles 0.3 to 1.0 μm in diameter.

Humidograms of pure laboratory-generated aerosols are shown in Figure 6-12 (Charlson et al., 1978). The humidograms for sulfuric acid and ammonium bisulfate

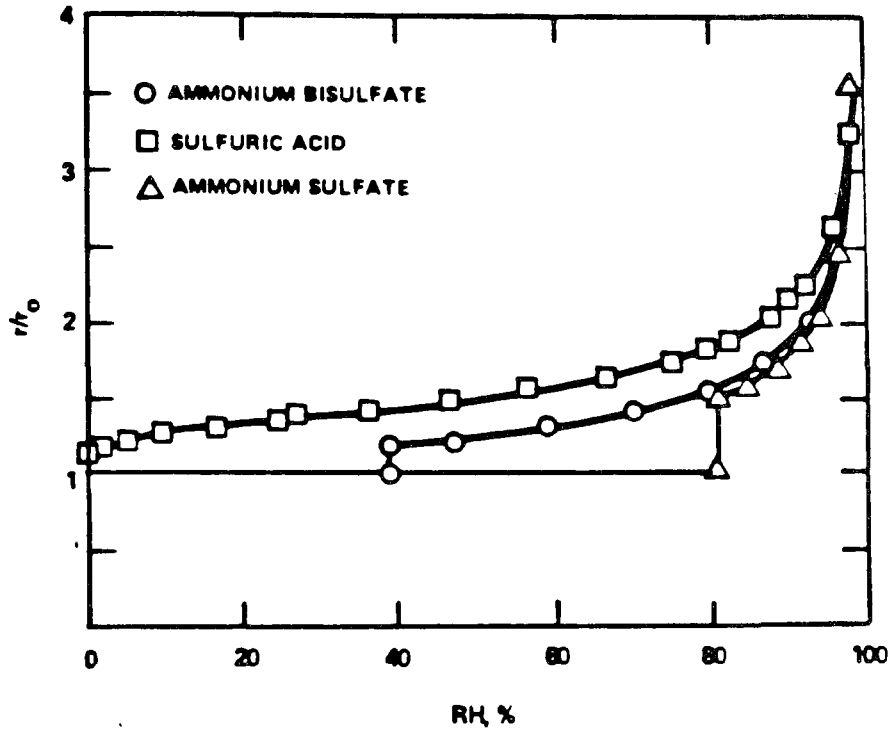



Figure 6-11. Theoretical growth curves based on vapor pressure data are shown for three sulfate aerosols exposed to increasing humidity. The dry particles have initial radius, ro, and they grow to radius, r, which is a function of relative humidity.

Source: Charlson et al. (1978).

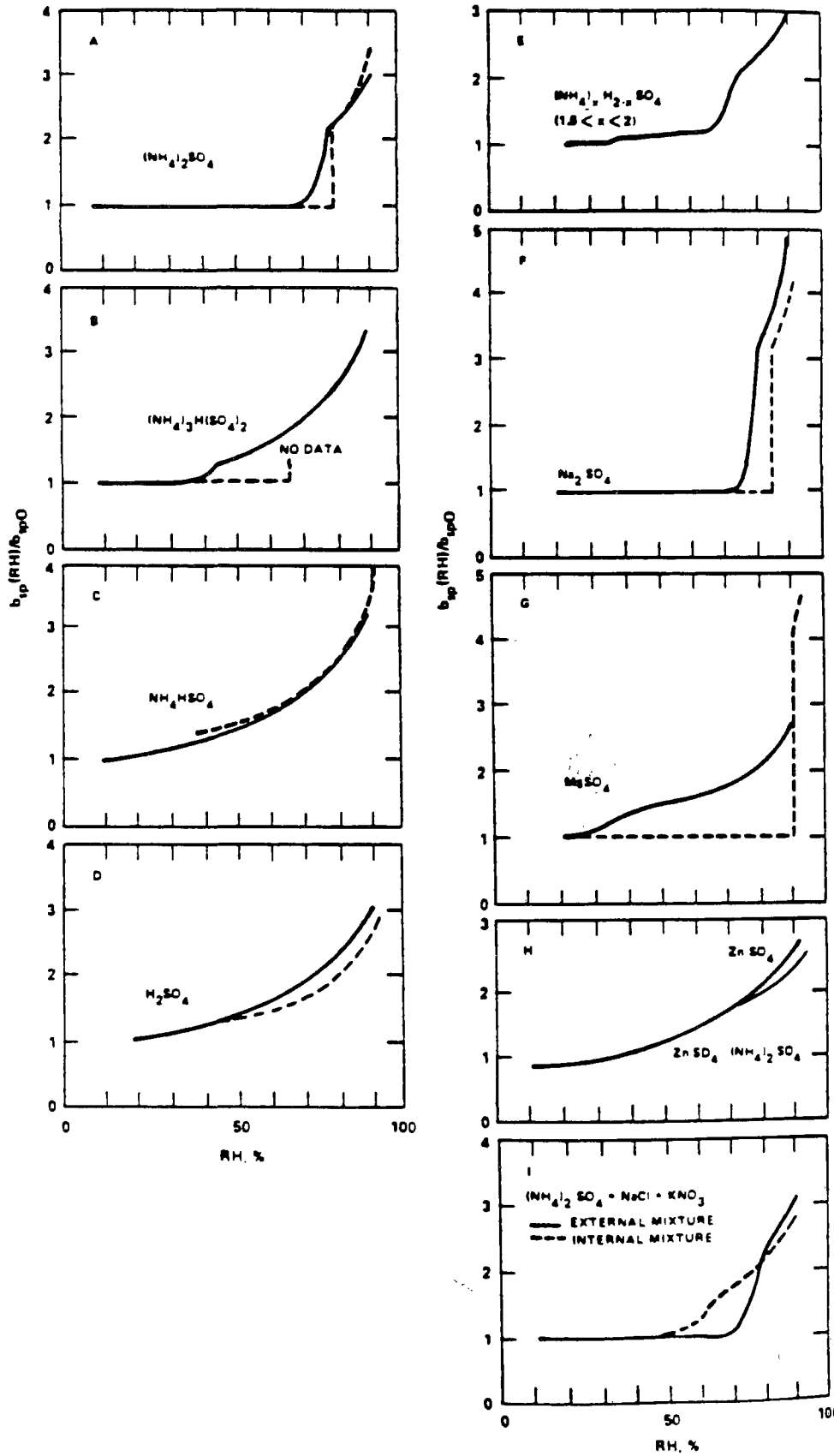



Figure 6-12. Humidograph data for pure, laboratory-generated sulfate compounds show deliquescence steps for some compounds. Dashed curves are calculated except in graph I.

Source: Charlson et al. (1978).

are for practical purposes indistinguishable, the expected deliquescence point for ammonium bisulfate was not observed experimentally. Those for both $(NH_4)_3H(SO_4)_2$ and ammonium sulfate are distinguishable from the rest because of the presence of their deliquescence steps. The mixture of these two salts (Figure 6-12E; Charlson et al., 1978) shows two deliquescence steps at 45 and 80 percent. If $(NH_4)_3H(SO_4)_2$ is not an important atmospheric species, these differences in response to relative humidity, coupled with the fact that the acid sulfate aerosols can be changed into ammonium sulfate (thus altering their hygroscopic nature) by in situ reaction with gaseous ammonia, provide a means for detecting sulfate and for distinguishing between ammonium sulfate and the more acidic forms (Charlson et al., 1974).

Atmospheric aerosols seldom consist of pure compounds, however. The "mixed aerosol" hypothesis advanced by Junge (1952) and extended by Winkler (1973) defines two extreme cases for chemical mixing in aerosols: (1) internal mixtures, in which each individual aerosol particle contains a mixture of compounds, and (2) external mixtures, in which each particle is a pure compound, yet the population of aerosol particles consists of various compounds.

All intermediate degrees of mixing are possible. External mixtures will have hygroscopic properties that are simple linear combinations of the individual compounds. Internal mixtures exhibit nonlinear behavior with respect to hygroscopic growth because of ion interactions, which tend to increase solubility. An example of this effect is illustrated in Figure 6-12I (Charlson et al., 1978) for external and internal mixtures of ammonium sulfate, sodium chloride, and potassium nitrate in mass ratios of 2:1:1.

In summary, the hygroscopic and deliquescent behavior of pure sulfate compounds in aerosol form can be predicted from solution equilibrium calculation. However, water uptake by mixed salts and atmospheric aerosols can be obtained only from aerosol measurements as a function of relative humidity.

### 6.2.4 Carbon-Containing Aerosols

The carbon in atmospheric aerosols consists of an elemental component (such as graphite or soot) and a nonvolatile, organic component. There are significant differences in the optical properties of these two components. Elemental carbon is formed during the combustion of fossil fuels and is emitted as primary particles (∿0.1 μm), which strongly absorb light. The nonvolatile, organic component consists of primary hydrocarbons emitted in combustion exhaust and of secondary organics formed by photochemical reactions. These primary hydrocarbons and secondary organic vapors either nucleate or condense on existing aerosols. They do not strongly absorb light, but usually make important contributions to light scattering in urban hazes.

The importance of elemental carbon has been emphasized in a conference on "Carbonaceous Particles in the Atmosphere" (Novakov, ~~1979~~ 1978). However, there are only limited data on the mass ratio of elemental/(primary + secondary) organics for a few cities. Appel et al (~~1979~~ 1978) found for a four-day period in July 1975 in Pasadena, Pomona, and Riverside that elemental carbon was the most abundent carbon species; also, the secondary organic mass was usually twice that of primary hydrocarbons. Of the secondary organics, adipic and glutaric acids were among the most abundent products; most likely they were oxidation products of cyclohexene and cyclopentene emitted by motor vehicles. For total carbon, benzene soluble organics, and hydrogen analyses of fine aerosols collected in Denver in Nov. 1971, it was estimated that the elemental carbon was 2.3-3.6 $\mu g/m^3$ for the episode days observed; from measured Pb concentration, it was suggested that in Nov. 1973 in Denver the elemental carbon in fine aerosol was 1.7-4.4 $\mu g/m^3$ (Durham et al, ~~1979~~ 1978). Also, for Denver in Nov. 1973, Pierson and Russell (1979) estimated from Hi-Vol samples the total elemental carbon to be 2.9-27.6 $\mu g/m^3$.

Although atmospheric measurements of carbon-containing aerosols are less complete than those of sulfates, available results suggest that carbon-containing

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

The National Academy of Sciences (Grosjean, 1977) has extensively reviewed the methods of primary and secondary organic aerosol identification, and the physical and chemical aspects of their formation. Primary organics emitted into the atmosphere by industrial sources, motor vehicles, agriculture activities, and natural sources include: linear and branched alkanes and alkenes, substituted benzenes and styrenes, quinones, acridines, quinolines, phenols, cresols, pthlalates, fatty acids, carbonyl compounds, polyaromatic hydrocarbons, terpenes and pesticides. Secondary organic aerosols are formed by the oxidation reactions of the primary organics, ozone, and nitrogen oxides. Typical products that have been identified are: aliphatic organic nitrates, dicarboxylic acids, benzoic and phenylacetic acids, and terpene products such as pinonic acid (Grosjean and Friedlander, 1975; Miller et al., 1972; Schuetzle et al., 1975). By using computer-controlled high-resolution mass spectrometry and thermal analysis Schuetzel et al. (1975) and Cronn et al. (1977) obtained diurnal variations of primary and secondary organics from two-hour size-resolved samples. The variations of hexanedioic acid and total amides with ozone are shown in Figure 6-13 for West Covina. The concentrations of these secondary organic aerosols and the ozone are highly correlated.

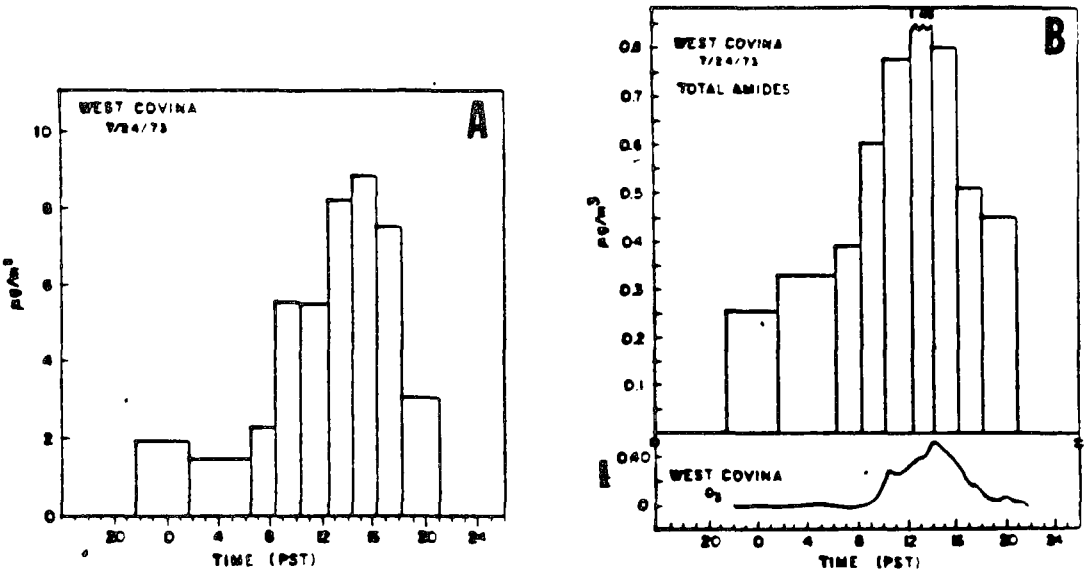



Figure 6-13. (a) Diurnal variation of hexanedioic acid, a presumed secondary component.

Figure 6-13. (b) Comparison of the diurnal variation of total amides (a presumed secondary component) with ozone.

Source: Cronn et al., (1977).

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

The chemical composition of "model" organic aerosols generated from single hydrocarbons is not well-established for suspected important aerosol precursors. Functional group analyses for the products of olefins, benzene and benzene substituted compounds, and terpenes that have reacted with ozone show that the bulk consists of high oxygenated compounds, which include: carbonyls, carboxylic acids, and nitrate esters. Only a few studies of species identification have been reported. Detailed aerosol product identification has been reported for the ozone-1-butene reaction (Lipeles, 1973); the $NO_x$-toluene, $NO_x$-cyclohexene, and $NO_x$-α-pinene photo-reactions (Schwartz, 1974), and the $NO_x$-cyclopetene, $NO_x$-cyclohexene, and 1-7-octadiene photo-reactions (Grosjean, 1977). Good agreement was indicated by Grosjean (1977) with Schwartz (1974) for the $NO_x$-cyclohexene photo-reaction, except that Grosjean observed adipic acid to be the major product (not found to be present by Schwartz). It is significant

that most of the polyfunctional compounds identified (see the cited papers and the NAS report for details) have also been identified as important constituents in ambient aerosols.

The secondary aerosols formed from alkenes having seven or more carbons (cyclic olefins, diolefins, and terpenes) grow into the light-scattering range and produce appreciable visibility reduction. For example, aerosols formed from cyclic olefins and diolefins have particle sizes between 0.1 and 0.3 μm. For such systems, the gas-to-aerosol conversion process consists of the formation of supersaturation in the gas phase and subsequent condensation on preexisting particles.

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

6.2.5 Particulate Nitrate

A number of topics related to the transport of nitrogen oxides and their transformation to gaseous and particulate nitrates are discussed in the Air Quality Criteria for Oxides of Nitrogen (to be published, 1980). These topics include visibility, environmental transport and transformation, and acidic precipitation.

At eastern urban sites such as St. Louis, Mo., Dayton, Oh., and Charleston, W.V., particulate nitrate concentrations did not exceed 1 to 2 $\mu g/m^3$, and these nitrate concentrations often were below 1 $\mu g/m^3$ (Spicer, 1976; Stevens et al., 1978). At several eastern nonurban sites, nitrates ranged from 0.1 to 0.6 $\mu g/m^3$ (Mueller et al., ~~1979~~ 1980). In the measurements in Charleston, W.V. (Stevens et al., 1978), the concentration of particulate sulfate was 5 to 50 times greater

than that of particulate nitrate. At the nonurban sites, the ratio of particulate sulfate to particulate nitrate ranged from 10:1 to 100:1 (Mueller et al., 1979). The results should not be extrapolated to western sites.

Atmospheric nitrates most likely result from photochemical reactions involving the oxidation of NO and $NO_2$ to yield $HNO_3$ and organic nitrates (Demerjian et al., 1974; Orel and Seinfeld, 1977). The measurement of ambient nitrate aerosols has been recognized to be subject to significant biases. Glass fiber filters may exhibit a positive bias due to the absorption of gaseous $HNO_3$ (Spicer and Schumacher, 1979; Appel et al, 1979), and negative biases may result from the evaporation of $NH_4NO_3$ in both solid (Stelson et al., 1979) and aqueous solution (Tang, 1979). Also, a negative bias may result from displacement of $HNO_3$ from particulate nitrate by $H_2SO_4$ aerosols being collected on the filter (Harker et al., ~~1979~~ 1977). The measurement methodology for $HNO_3$ and inorganic particulate nitrate measurement and their biases have been reviewed (Stevens, 1979). Until an understanding is gained for particulate nitrate sampling with glass fiber, quartz fiber and Teflon filters, nitrate data bases cannot be regarded as valid.

Because of the substantial increases anticipated in nitrogen oxide emissions from utility sources, current nitrate levels must be carefully determined and followed.

## 6.3 WET AND DRY REMOVAL OF $SO_2$ AND AEROSOLS

Deposition processes limit the lifetime of sulfur compounds and other compounds in the atmosphere, control the distance traveled before removal, and limit their atmospheric concentrations. In addition to fulfilling the essential role of cleansing the atmosphere, these processes are also important because

they deliver sulfur compounds to surface waters, soils, and ecosystems (see Chapter 8 on acidic precipitation). Because of these features and the growing concern over adverse physical and biological effects, the overall question of deposition has received increasing attention in the fields of atmospheric chemistry and biology.

$SO_2$ and aerosols are removed from the atmosphere by wet deposition (incorporation in precipitation) and dry deposition (direct transfer in the absence of precipitation). These two processes are of approximately equal magnitude. According to Rodhe (1978), the estimated overall turnover times of $SO_2$, $SO_4^{2-}$, and sulfur ($SO_2 + SO_4^{2-}$) in Europe at midlatitudes are roughly 25, 80, and 50 hr, respectively; the turnover times for wet and dry deposition are approximately 100 and 60 hr, respectively.

### 6.3.1 Dry Deposition

The dry deposition of pollutant gases and aerosols has been recently reviewed by Chamberlain (1975), Garland (1978), Slinn (~~1974~~ 1976), and Slinn et al. (1978). It is convenient to view the overall mass transfer rate as the product of a mass transfer coefficient ($V_d$) and the difference between the bulk concentration and the surface concentration (Garland, 1978). It it is also convenient to envision the deposition velocity as the inverse of the overall resistance to mass transfer. The total resistance is the sum of several independent resistances.

The surface resistance incorporates absorption, adsorption for gases, and adhesion for aerosol particles. It is generally believed that the surface of vegetation is responsible for most of the $SO_2$ uptake by dry deposition. The surface resistance of dry vegetation is governed primarily by the diffusion rate of $SO_2$ through the stomatal openings (Garland, 1978). The opening and closing of stomata depends on the type of vegetation, solar radiation, water stress, and other important variables. It has been proposed, however, that the $SO_2$ uptake

is closely related to the transfer of water vapor. Fowler and Unsworth (1974) point out that the surface resistance over vegetation wetted by dew is nearly zero until the deposition is limited by the decrease in the solubility of $SO_2$ as the pH of the dew decreases as a result of the oxidation of $SO_2$ to sulfuric acid.

For fine particles in the submicron size range, the collision efficiency with surfaces is unity; therefore their surface resistance is zero.

The aerodynamic resistance is determined by the turbulent eddy diffusion that delivers the pollutants from a height of several meters to the surfaces. The mean horizontal wind speed, surface roughness, and to some extent atmospheric stability are the key factors determining the aerodynamic resistance.

Field and laboratory data suggest that over water, calcareous soil, and short grass, surface resistance to $SO_2$ uptake is low and is often exceeded by atmospheric resistance to transfer. However, over forests, tall crops, acidic soil, and snow, surface resistance contributes substantially to the total transfer resistance. In such cases, not only are meteorological parameters important in determining deposition rates, but also the chemical and biological characteristics of the surface (e.g., wetness, degree of leaf stomatal opening) (Garland, 1978).

Table 6-3 gives an estimate of deposition velocities for $SO_2$ over various types of vegetation. Table 6-4 gives similar information for calcareous and acidic soils (ISSA Workshop, 1978). A midday maximum in $V_d$ is frequently observed, reflecting diurnal maxima in stomatal opening and in turbulent transport. A seasonal variation, with minimum values less than 0.3 cm/sec when the vegetation is dry or senescent, is also observed. The presence of water on foliage leads to larger values (1 cm/sec or greater) providing the pH of the water is greater than about 4.

TABLE 6-3. $SO_2$ DEPOSITION VELOCITIES OVER VEGETATION

| Vegetation | | Height, | Range of V, | Typical V,[a] |
|---|---|---|---|---|
| Height | Example | m | cm/sec | cm/sec |
| Short | Grass | 0.1 | 0.1-0.8 | 0.5 |
| Medium | Crops | 1.0 | 0.2-1.5 | 0.7 |
| Tall | Forest | 10.0 | 0.2-2.0 | Uncertain |

[a]These values were obtained in a humid climate. Much lower values are likely in arid climates.

Source: ISSA Workshop (1978).

TABLE 6-4. $SO_2$ DEPOSITION VELOCITIES OVER SOIL[a]

| Type of soil | pH | State | Range of V, cm/sec | Typical V, cm/sec |
|---|---|---|---|---|
| Calcareous | $\geq 7$ | Dry | 0.3 to 1.0 | 0.8 |
| Calcareous | $\geq 7$ | Wet | 0.3 to 1.0 | 0.8 |
| Acid | ~4 | Dry | 0.1 to 0.5 | 0.4 |
| Acid | ~4 | Wet | 0.1 to 0.8 | 0.6 |

[a]As yet, no information is available to assess $v_g$ on desert sand or lateritic soils.

Source: ISSA Workshop (1978).

Several other types of surface should be mentioned. Sparse experimental evidence suggests that dry snow is a very poor sink for $SO_2$ ($V_d \approx 0.1$ cm/sec). Additionally, the surface is naturally smooth so that atmospheric mixing is minimal. Wet snow behaves like water. Natural water surfaces are efficient sinks for $SO_2$ ($V_d$, 0.2 to 1.5 cm/sec, typically 0.7 cm/sec) unless very acidic. Rates of deposition are determined by atmospheric mixing intensity. There are very few studies of dry deposition from plumes or of atmospheric budgets. These few studies provide estimates of $V_d$ over large areas of countryside. These estimates are generally consistent with estimates for homogeneous surfaces ($V_d$, 0.2 to 2.0 cm/sec, typically 0.8 cm/sec). Laboratory measurements show that many building materials absorb $SO_2$ at significant rates, but it is difficult to use the results to estimate deposition on built-up areas. Observations in London during a prolonged period of air stagnation suggest a deposition velocity of 0.7 cm/sec, but this may be atypical.

The dry-deposition velocity for aerosols depends primarily on their size and density, the intensity of turbulent mixing near the surfaces (the friction velocity, $u_*$), and the roughness height of the surfaces. Large particles deposit mainly by sedimentation (Figure 6-14; Slinn et al., ~~1979~~ 1978), but particles in the range 1.0 to 50 μm are also transported toward the surfaces by turbulence where sedimentation is supplemented by impaction and interception by roughness elements. Very fine particles diffuse to surfaces by Brownian motion, which is greater for smaller particles. Sehmel and Hodgson (1976) found that the deposition velocity for the accumulation-mode aerosols in the size range from 0.1 to 1.0 μm is minimal, since none of the above processes is efficient. The dry removal rate of accumulation-mode particles depends strongly on the surface roughness (Figure 6-14; Slinn et al., ~~1979~~ 1978). The roughness height ($Z_0$) in Figure 6-14

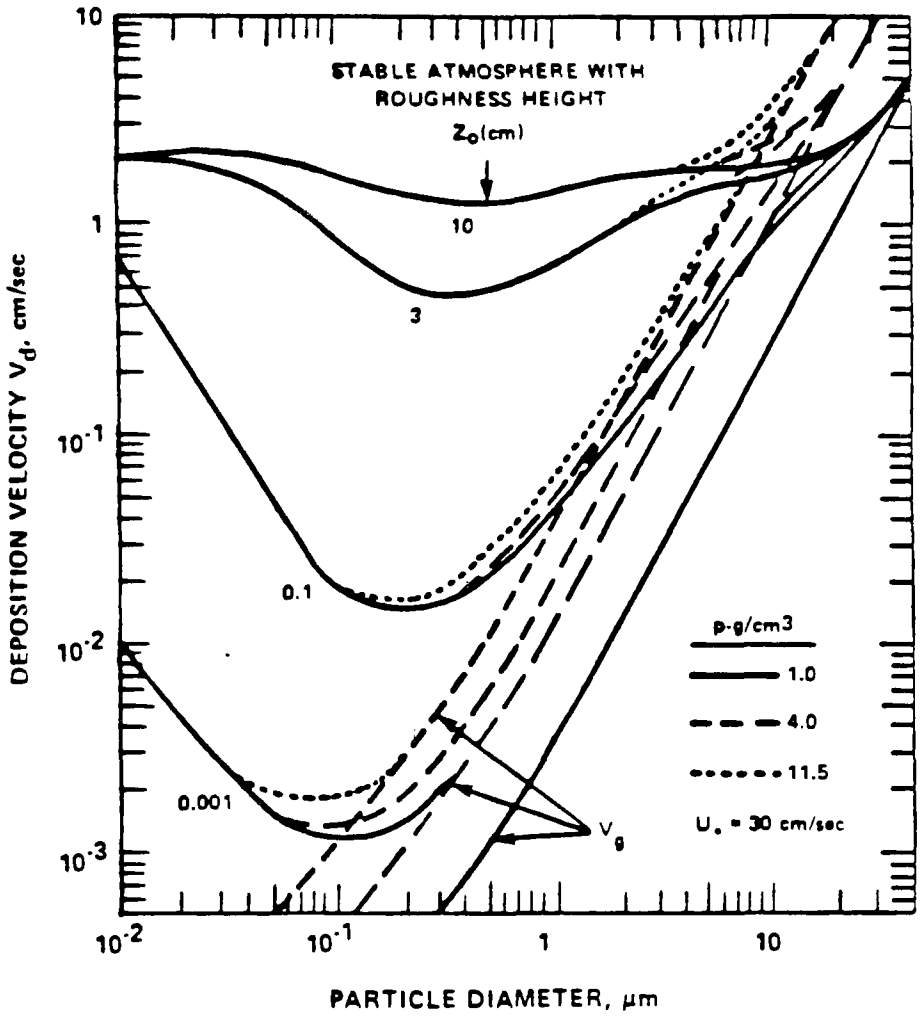



Figure 6-14. Data of Sehmel and Hodgson (1976) for dry deposition of particles on various solid surfaces was correlated by Slinn et al. (1979). The data cover 0.1 cm, and therefore the extrapolation to greater heights is tentative. The deposition velocity plotted is the flux divided by the extrapolated concentration at 1 m; $v_g$ is the gravitational settling speed for particles of indicated density; the case with $u^* = 30$ cm/sec is shown ($\bar{u} \cong 10$ cm/sec; cases with other friction velocities can be found in the referenced publication.

Source: Slinn et al. (~~1979~~ 1978).

is related to, but is not identical with, the physical roughness height. The data of Sehmel and Hodgson (1976) also indicate that the dominant resistance to particle dry deposition occurs within a few millimeters of a deposition surface. Consequently, the airborne particle concentrations vary little above the surfaces.

Since deposition velocity depends on particle size, estimation of the rate of deposition of particles requires a knowledge of aerosol size distribution. Most sulfate mass lies in the size range from 0.1 to 1.0 μm (Whitby, 1978; Stevens et al., 1978), for which the dry deposition velocity is not expected to exceed an average of 0.5 cm/sec.

The present understanding of dry deposition is such that reasonable estimates can be made for deposition rates of $SO_2$ for use in models, but not for sulfate or other aerosols. It should be emphasized that current dry deposition studies refer to uniform terrain and their appropriateness for use in cases of rough or complex terrain is not known.

6.3.2 Wet Removal

Wet deposition can be defined as the removal of material from the atmosphere by incorporation into precipitation through various scavenging mechanisms.

Mechanisms for the incorporation of pollutants into precipitation depend on the diffusion coefficient of gases, size distribution of particles, characteristics of the precipitation, and location of the pollutant within the precipitating cloud. The main attachment mechanisms include convection, impaction, interception, molecular and Brownian diffusion, turbulent transport, nucleation, thermophoresis and diffusiophoresis, and electrical effects.

The predominant attachment mechanisms for $SO_2$ are convection and diffusion, for both in- and below-cloud scavenging. According to a recent review by Hales (1978), for a known distribution of $SO_2$, the $SO_2$ scavenging rate can be calculated with reasonable confidence.

Typical sulfate concentrations and wet removal rates for sulfur compounds are summarized in Table 6-5 (ISSA Workshop, 1978). The ranges are given in order to show spatial variations in each region.

Wet deposition of sulfate formed by $SO_2$ oxidation in falling raindrops is an important removal mechanism. Modeling calculations (Overton et al., 1979; Hill and Adamowicz, 1977) suggest that sulfate from the oxidation of $SO_2$ in these droplets may range from 3 to 87 μmol/liter (and pH from 4.5 to 6.5) in the presence of $SO_2$ (10 ppb), ozone (0 to 50 ppb), ammonia (5 to 20 ppb), carbon dioxide (320 ppm), and iron ($10^{-5}$ μmol/liter).

In summary, dry and wet deposition processes are such complex phenomena that even after several decades of research our understanding is inadequate. Dry deposition has been widely investigated, but the representativeness of the results is not known. No routine monitoring of dry deposition of $SO_2$ and sulfate has been conducted. On the other hand, wet deposition of sulfate has been monitored in Europe since the late 1950's and precipitation monitoring networks have been set up in North America. Identifying the rates and mechanisms of atmospheric deposition on land and water is a key problem of atmospheric chemistry.

## 6.4 DISPERSION IN THE ATMOSPHERE

Both horizontal and vertical dispersion mechanisms contribute to the movement and dilution of pollutants in the atmosphere. Horizontal transport, characterized by wind speed and wind direction, determines long-range transport and plume trajectory. Turbulence provides vertical mixing that contributes to dilution and is a major factor in deposition. The mixing of plume material with potentially reactive background air is facilitated by both horizontal and vertical dispersion.

TABLE 6-5. REPRESENTATIVE ANNUAL AVERAGE SULFUR WET AND DRY DEPOSITION RATES

| Location | | Excess sulfate in precipitation, mg sec/liter | Wet deposition rate g sec/($m^2$/yr) | Dry deposition rate, g sec/$m^2$/yr) |
|---|---|---|---|---|
| Heavily industrialized areas | North America | 3-? | 0.1[a]-3 | ? |
| | Europe | 3-20 | 2-4 | 3-15 |
| Rural | North America | 0.5-2 | 0.1-2 | 0.2-2.6 |
| | Europe | 0.5-3 | 0.2-2 | 0.5-5.0 |
| Remote | North Atlantic | 0.2-0.6 | 0.1-0.3 | 0.04-0.4 |
| | Other oceans | 0.04 | 0.01[a]-0.2 | <0.1 |
| | Continents | 0.1 | 0.01[a]-0.5 | 0.4 |

[a]Low deposition rates result from low precipitation.

Source: ISSA Workshop (1978).

In the past there have been a number of severe air pollution episodes, when meteorological conditions have resulted in minimal atmospheric dilution over regions for extended periods. Historically, these episodes (e.g., Donora, London, Los Angeles) can be identified as resulting from stagnant air masses having light winds and limited vertical mixing heights in which pollutants accumulate.

By building tall stacks, pollutants can be injected into the faster winds of air layers at higher elevations. Often these layers are decoupled from the layers of air near the surface.

### 6.4.1 Spatial and Temporal Scales

The transmission of air pollutants in the atmosphere is a function of chemical transformation rates within the atmosphere and by removal rates, which are in turn affected by meteorological conditions. There are basically two approaches to estimating the time scales of transformation, transport, and removal processes. The most common approach is to study the atmospheric processes themselves by measurements in the atmosphere or in the laboratory, or by theoretical calculations. The other approach is to use mass conservation or "budget" calculations to estimate the space and time averages of such processes. Geochemical budgeting constitutes a systematic comparison of sources, sinks, and concentrations of a given compound averaged over reasonably large time and space scales.

The lifetime of atmospheric trace constituents emitted directly by man's activities ranges from a few seconds for large particles of tire debris to many years for fluorocarbons, methane, and carbon dioxide (Figure 6-15). The typical gaseous pollutants emitted into the lower troposphere, such as $SO_2$ and nitrogen oxides, reside in the atmosphere for days.

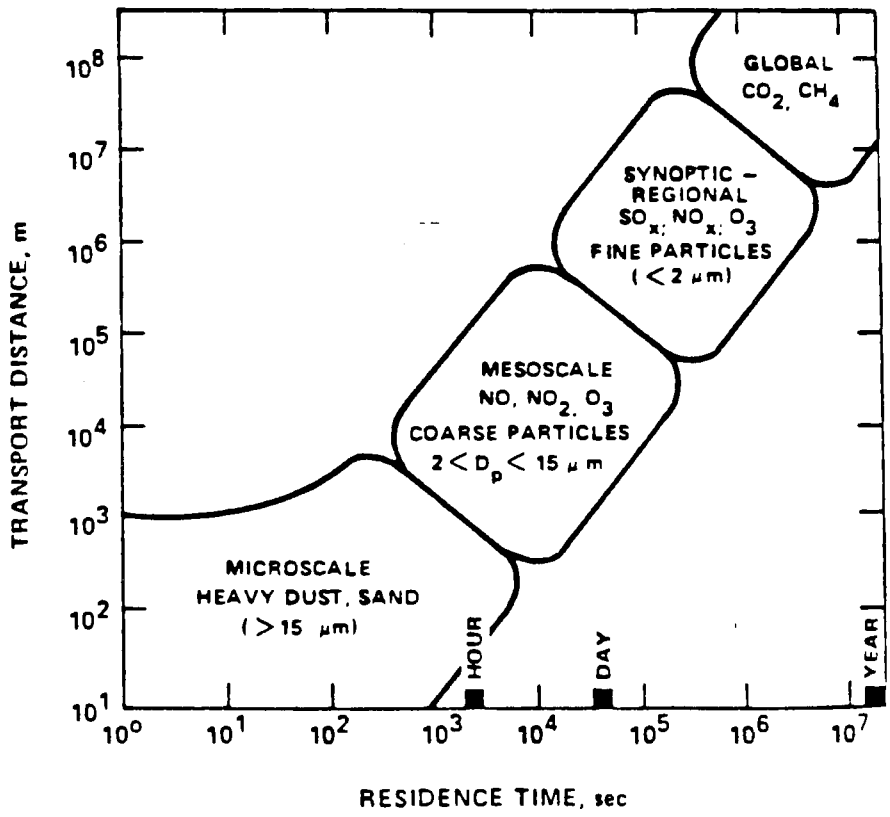



Figure 6-15. The spatial and temporal scales relevant for tropospheric air pollutants range from meters to hundreds of kilometers and from seconds to years.

The transport distance of a given compound is determined by its physical and chemical characteristics and by the mean wind speed between the source and the receptor. Thus, atmospheric processes and a pollutant's chemical and physical properties determine the residence time of a chemical compound in the atmosphere. For the description of the spatial-temporal behavior of chemical compounds in the atmosphere, it is convenient to use established meteorological terminology. The microscale is defined as a scale in which atmospheric processes occur within 1 km or less. There are only a few primary pollutants that have a mean residence time within the microscale; examples are particles from tire erosion and heavy windblown dust.

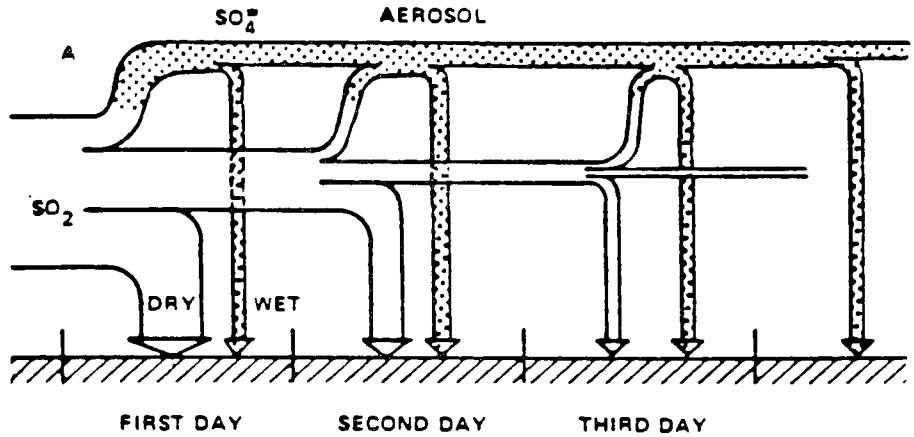
The spatial scale of one to a few hundred kilometers and the corresponding temporal scale from 15 min to a day ($10^3$ to $10^5$ sec) are referred to as the mesoscale. This scale encompasses major thunderstorms and discernible single or urban plumes. Atmospheric coarse particles in the size range of 2 to 20 μm tend to fall out within this scale. Of the gaseous primary emissions, the oxides of nitrogen, NO and $NO_2$, are typically consumed by chemical reactions or deposition within the first day after emission; a large fraction oxidize.

At a few hundred kilometers the mesoscale merges with the synoptic scale, involving migratory high- and low-pressure systems of the lower troposphere with wavelengths of 1000 to 2500 km. This scale, extending from 1 to 10 days in time, is also referred to in air pollution literature as the regional scale. Many of the primary and secondary pollutants, including $SO_2$, nitric acid, ozone, and the constituents of fine particles (sulfate, nitrate, ammonium, organics, soot) are dispersed within the synoptic or regional scale of 100 to 2500 km and 1 to 10 days.

The hemisphere scale bridges the synoptic and the global scales. The hemispheric/global scales of 2,500 to 40,000 km are limited by the circumference of the earth but unlimited in time. Meteorologically, they include the global circulation pattern, such as the westerly winds in the Northern Hemisphere, the equatorial trade winds, and the mean vertical motions of the atmosphere that rise at the equator and descend at the poles. There are numerous manmade and natural trace chemical substances whose residence times are greater than the mean circulation time around the globe of 2 weeks. These substances include carbon monoxide, carbon dioxide, freons, and methane. If fine particles or their precursors are dispersed to the upper troposphere (e.g., by thunderstorms), they may be transported on a global scale.

In the study of the overall effect of a given pollutant, the spatial/temporal scales of the effect have to be matched to the characteristic scale of pollutant lifetime in the atmosphere. In the case of the manmade sulfur compounds, for example, most of the global emissions and depositions are confined to a few regional "hot spots," such as Central Europe and portions of North America. The global budgeting of manmade and natural sulfur compounds may indicate marginal impact when assessed on a global scale. On the other hand, assessing the effect of $SO_2$ or fine particles only on a scale of tens or hundreds of kilometers may be incomplete since that scale is small compared with distance transported.

At the International Symposium on Sulfur in the Atmosphere (ISSA Workshop, 1978), it was concluded that the typical atmospheric residence time of $SO_2$ is about 1 day and that of sulfate aerosol is on the order of 3 to 5 days (Figure 6-16A) depending on precipitation patterns. A mean transport of 500 km per day is common in the Eastern United States (Pack et al., 1978); hence reasonable scales for $SO_2$ and sulfate effects are 500 and 1000 to 2000 km, respectively. The implication, as seen in Figure 6-16B, is that the ambient sulfate aerosol



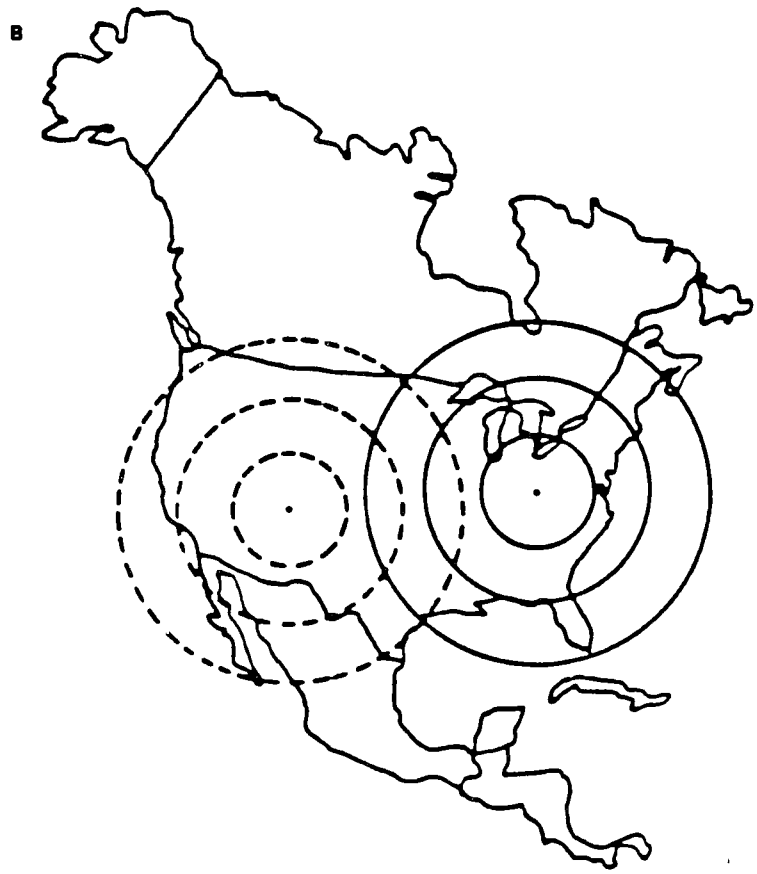




Figure 6-16. (A) This flow diagram of sulfur transmission through the atmosphere shows that over half of the $SO_2$ is removed or transformed to sulfate within the first day of its atmospheric residence. Most of the sulfate may remain beyond 4 days of residence in the atmosphere. (B) Schematic illustration shows the range of transport of fine particles. The circles have radii of 500, 1000, and 1500 km; 1500 km is considered a reasonable mean transport distance. The actual transport depends on the synoptic-scale wind field.

concentration at a receptor site can depend on the additive effects of tens or even hundreds of $SO_2$ plumes of different atmospheric ages.

### 6.4.2 Planetary Boundary Layer

The planetary boundary layer extends from the earth's surface to the geostrophic wind level; the latter marks the upper limit of frictional influence of the earth's surface. It is the layer into which heat, moisture, and air pollutants from man's activities are injected. The planetary boundary layer averages about 1.5 km in depth and varies from a few tens of meters in stable conditions to several kilometers in very unstable situations. With decreasing height, the wind speed tends to fall below the speed of the geostrophic wind found above the layer, theoretically reaching zero at the surface (Figure 6-17A; Husar et al., 1978). The decrease in wind speed with height may not be monotonic, especially in stable conditions.

The planetary boundary layer is always in a state of change; it is responding either to a change in wind velocity, temperature, moisture, or pressure field or to some change in the underlying surface. With respect to air pollution, the most important question is how the upper limit of the planetary boundary layer changes, that is, the height of the mixing layer at any given time and location. Figure 6-18, developed by Smith and Hunt (1978), shows a simple nomogram for estimating the mixing layer height for daytime conditions based on time of day, month, cloud cover, and wind speed. The time of day, month, and cloud cover determine the integrated heat input into the boundary layer. The nomogram also recognizes wind speed as another source of turbulence. Holzworth (1972) has documented the variation in mixing heights for National Weather Service rawinsonde (balloons from which temperature, wind, and humidity can be derived from on-board instruments and tracking) sites in the United States.

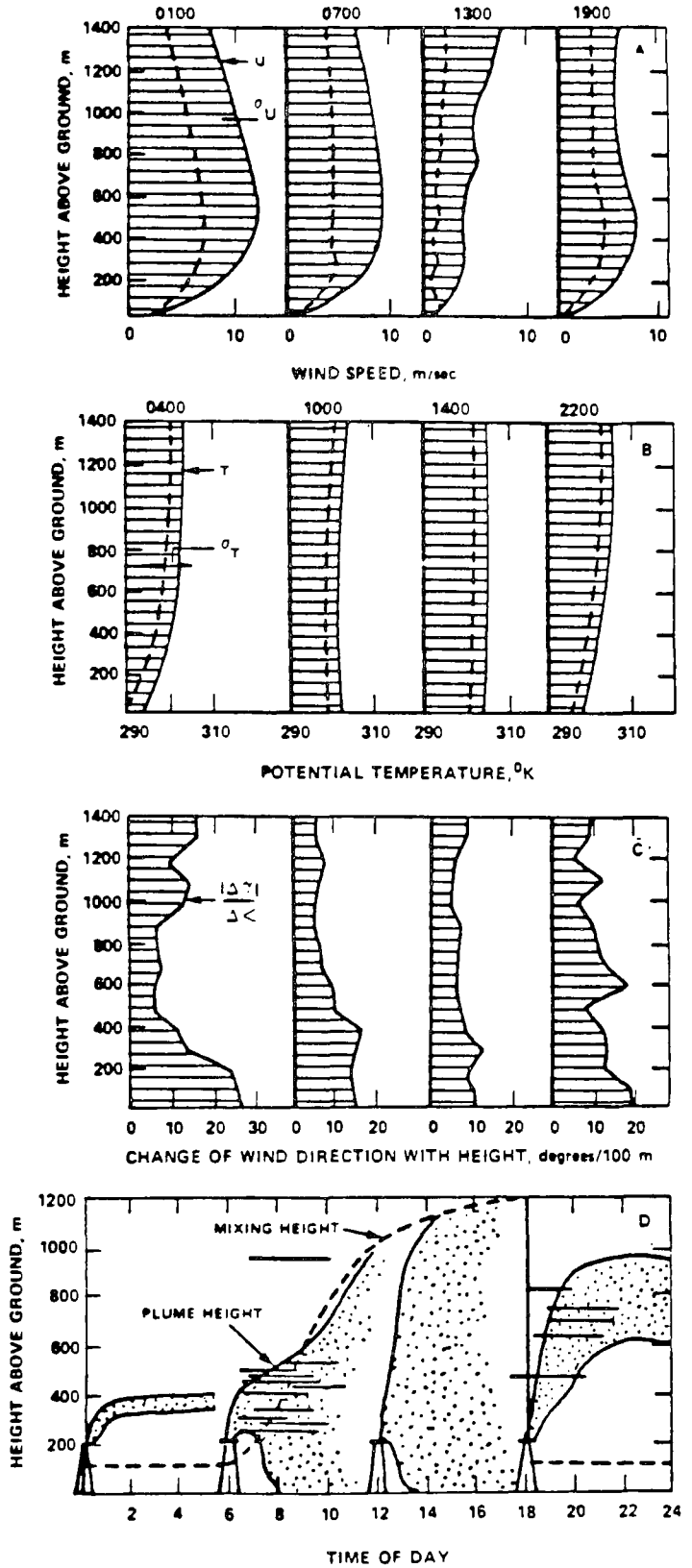



Figure 6-17. The wind data obtained from hourly releases by the RAPS balloon sounding network are averaged here for July 1976. (A) Vertical profiles of velocity for 0100, 0700, 1300, and 1900 CDT releases, (B) vertical profiles of potential temperature (referenced to 1000 mb) and its standard deviation; (C) absolute change of wind direction with height (degrees per 100 m); (D) schematics of plume geometry at four different parts of the diurnal cycle. The horizontal bars are plume height data reported by Forrest and Newman (1977) for the Labadie plume in the summer.

Source: Husar et al. (1978).

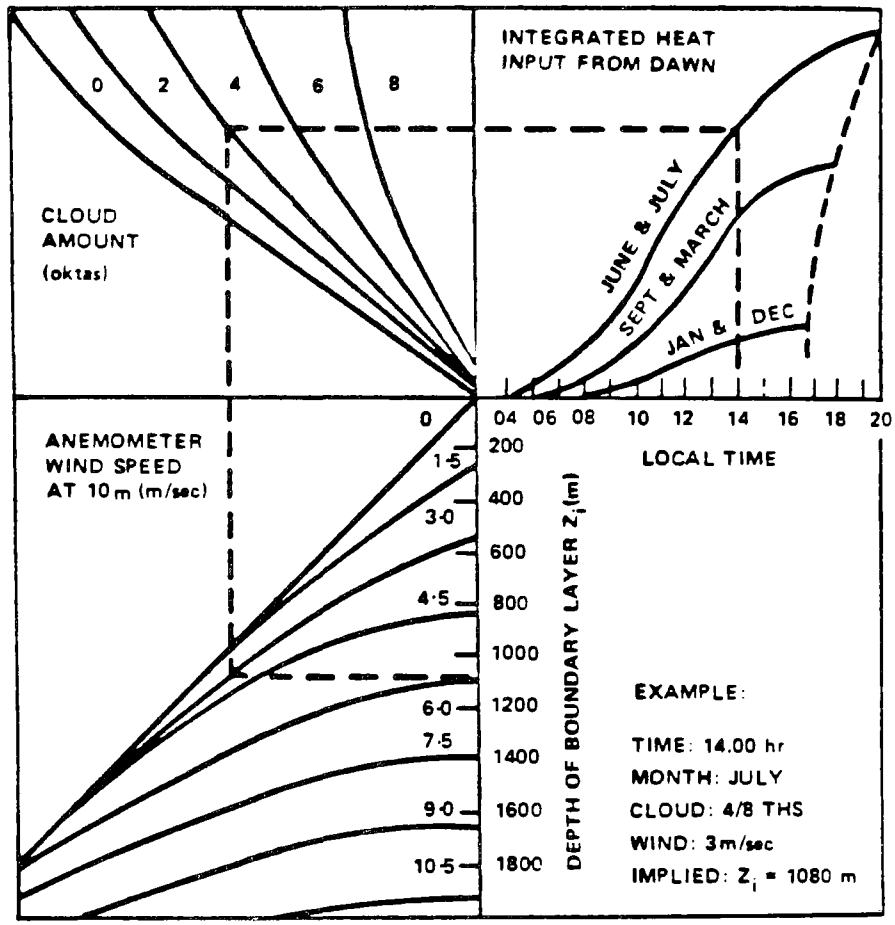



Figure 6-18. This nomogram permits estimation of the depth of the boundary layer in the absence of marked advective effects or basic changes in weather conditions. The marked example shows how the nomogram is to be used.

Source: Smith and Hunt (1978).

The dispersal of pollutants in the vertical dimension is also complex. Diurnal changes in atmospheric stability lead to the vertical dispersion of pollutants up to several kilometers during daytime mixing periods and then isolation of pollutants aloft as low-level nocturnal inversions are formed (e.g., see Hess and Hicks, 1975). Depending on wind speed, these isolated layers can be transported long distances during the night, before daytime mixing again brings the pollutant into contact with the surface. Figures 6-17A and 6-17D (Husar et al., 1978) illustrate, for example, that within the diurnal cycle in the St. Louis region, nighttime plume transport is faster than midday plume transport by a factor of nearly 2 because of variations in the vertical wind and temperature profiles of the atmosphere. Nocturnal plumes emitted from tall stacks are affected by 10- to 20-m/sec low-level jets in two ways: the effective stack height is reduced to approximately the actual stack height and the distance traveled overnight may be increased by 500 km (Smith et al., 1978). Such plumes are subject to minimal vertical mixing at night, and it is thus feasible to follow the plumes with instrumented aircraft for as much as several hundred kilometers. In the afternoon, the lower wind speed and greater instability of the atmosphere produce larger effective stack heights and greater vertical mixing of pollutants emitted into the mixed layer, resulting in greater dilution than in the nighttime regime. The large effective stack height of afternoon buoyant plumes has important consequences for sulfur transformations and removal--that is, the sulfur budget.

Daytime convective activity tends to mix pollutants uniformly within the planetary boundary layer. For problems involving long-range transport, it is usually sufficient to assume well-mixed conditions during daytime periods with respect to dispersion, although often not with respect to transformation. When

the sun sets, the surface cools, convective mixing diminishes and finally stops, and stable layers of air form. If pollutants are injected into these stable layers, concentrations can build up. After sunrise, as convection begins, these pollutants can be mixed to the surface.

This diurnal cycle plays an important role in determining the loss rate of pollutants from dry deposition at the surface. During the daytime convective period, near-surface concentrations from ground-level pollutant sources are reduced because mixing occurs through a large volume. During the night, near-surface concentrations are increased because the vertical mixing depth is very restricted. For pollutants emitted from tall stacks, the diurnal patterns of the surface concentrations are reversed: peak concentrations are observed during daytime hours, as the result of vigorous downward mixing of the plume material. At night, plumes from tall stacks are embedded in elevated stable layers that remain aloft, cut off from the ground by stable inversion layers.

Over water, conditions can differ dramatically, depending on temperature differences between water and air. During the summer, cold water creates a stable layer near the surface that prevents dry deposition of pollutants. Conversely, warm water increases mixing at night so that dry deposition is increased.

Given the importance of vertical profiles of wind and temperature in the atmosphere, it is imperative to include these factors in simulation models that account for variations in vertical mixing height. Profiles of vertical wind speed, temperature, and moisture are usually determined from rawinsondes. Typically, rawinsondes are released by the National Weather Service every 12 hr. Two releases per day are often inadequate to define the changing diurnal pattern

for a given location. In addition, the vertical resolution of the data near the surface may not be sufficient for detailed analysis or extrapolations to adjacent areas of interest.

Wind direction normally changes with height. The effect of vertical wind shear on air pollutants is to increase the horizontal dispersion about the mean flow direction; this effect usually is greater under stable nocturnal conditions than under daytime convective conditions. Under unstable or neutral conditions, typically daytime, the effect of vertical wind shear in the first 1 to 2 km above the surface is usually small. During periods of strong convection, however, pollutants could be taken to heights much greater than 5 km. Once convective activity begins cloud processes provide mechanisms for lifting polluted air to great heights and also for chemical transformations in the liquid water of cloud droplets. Once the cloud evaporates, the remaining sulfur compounds could be strongly affected by the different wind speeds and directions found at these great heights, providing greater dispersion relative to near-ground dispersion processes. The fate of pollutants injected into layers above the planetary boundary layer must be dealt with in long-range transport studies.

Topographic effects on plume dispersion also require special treatment. Mountainous terrain increases vertical mixing and causes channel flow through valleys.

Vertical dispersion is also important in determining the amount of the pollutant involved in the in-cloud condensation process above the mixing layer that leads to washout by precipitation. Vertical mixing within air masses, particularly along fronts, can permit pollutants to mix to high altitudes, thereby avoiding precipitation processes. However, such pollutants injected at high altitudes will ultimately return to the surface at greater distances.

### 6.4.3 Horizontal Transport

The main flow of manmade pollutants in the atmosphere is horizontal, whereas vertical mixing of pollutants is generally confined to the planetary boundary layer. The measurable extent of horizontal transport of $SO_2$ and fine particles from a given source is about 1000 km; thus, the dispersion of air pollutants occurs within a shallow layer (a few kilometers) of the earth's atmosphere.

The regional or synoptic-scale transport of air pollutants is most frequently assessed from computed "air parcel trajectories." The computational methods, until recently, involved manual determination of the transport wind speed and direction from synoptic weather charts. The trajectories were of two kinds: dynamic (from pressure or pressure-height charts) or kinematic (from streamline and isotach analyses of the observed winds). In the former case, the instantaneous geostrophic wind was estimated from the pressure charts. With the streamline-isotach charts, a best estimate of the existing wind was made for the desired location from the analyses.

With the advent of computers in the meteorological services, programs have been devised to compute trajectories. Computer methods are still based, however, on two types of information: observed pressures or observed winds. Some techniques analyze these fields and interpolate from the irregular observing network into a regularly spaced grid system from which, by further interpolation, the transport vectors at any arbitrary point can be evaluated. Other methods interpolate the observed data directly to the desired trajectory location.

The early work of Durst et al. (1959) is an example of geostrophic computations for the upper atmosphere. A more recent article by Sykes and Hatton (1976) provides a comprehensive discussion of the two alternative approaches and

describes an advanced geostrophic computational technique (using recorded surface pressure observations) applied to the surface boundary layer.

The kinematic approach has been used in the OECD Long Range Transport of Atmospheric Pollutants (LRTAP) (Ottar, 1976; Eliassen, 1976) employing winds at the surface and at the 850-mb level (approximately 1.5 km).

Recently, work by Meyers et al. (1977) has extended interpolation as a means for determining regional flow fields. Their technique uses variational analysis as a basis for further adjusting the interpolated values in order to force consistency of the data sets with additional constraints. The constraint used by Meyers et al. (1977) is conservation of energy and momentum.

Data from which a comparison of calculated trajectories with "real" trajectories can be made are not numerous for the regional scale. The ideal would be a continuous point source of a unique material with a known emission rate. Pack et al. (1978) discuss specific data sets available for verification studies over the short, intermediate, and long ranges.

In a recent experiment in Oklahoma City, Angell et al. (1973) attempted to determine the accuracy of various approaches to trajectory determination over the relatively flat Midwestern terrain. Of 55 tetroon flights, return tags were received from 27, 13 of which traveled a distance considered suitable for analysis (Hoecker, 1977). Twelve of the recoveries were from more than 500 km from the launch site, and three were from more than 1000 km.

The Oklahoma City tetroon trajectories, while few, agree qualitatively with other, more numerous observations and illustrate the systematic differences in trajectory directions created by different synoptic situations. Taken together, it is evident that in many cases trajectory estimates perform well. They are at their best in relating air quality data at isolated locations to pollution transported from large area sources.

A second general approach, especially for anticyclone-induced stagnation episodes, can be inferred from a series of recent reports (e.g., Ferber et al., 1976; Husar et al., 1976a, 1976b). These reports show the coherence of dew point, visibility, and ozone respectively, within well-defined regions, generally when under the influence of high-pressure areas. Vukovich et al. (1977) have calculated the "residence time" within (admittedly idealized) anticyclones of different shapes and moving with different speeds. Reconstruction of the paths of anticyclones is easier than the reconstruction of multiple trajectories from the various pollutant sources. Further, prediction of the movement of these systems is one of the more accurate aspects of modern weather forecasting. When large-area estimates are needed, especially for secondary pollutants, this use of the trajectory of a large, easily indentifiable entity as a moving, changing, but calculable air mass should be investigated and the technique tested on actual weather systems.

Finally, the best approach would be the quantitative study of known amounts of material placed into the atmosphere specifically to study transport and diffusion. However, no tracer currently meets the criteria for a long-range transport tracer. Particles and reactive gases are nonconservative. Many other candidates, such as sulfur hexafluoride, already are present in the air in concentrations high enough to impose very high release amounts to overcome the background and dilution over long travel distances. Radioactive gases present environmental difficulties.

## 6.5 SOURCE-RECEPTOR RELATIONSHIPS

The relationship between emission sources and ambient concentrations at receptor sites is determined by transmission processes in the atmosphere: horizontal and vertical transport, transformation, and removal. Transformation

and removal rates for a given pollutant are competitive, and both depend on horizontal and vertical transport. Hence, to completely understand the source-receptor relationship, the specific role and interaction of each of the three processes must be quantitatively evaluated.

In this section, five different approaches to source-impact identification are discussed. The first three are receptor-oriented empirical methods. They use existing monitoring data on aerosol or $SO_2$ concentrations at various receptor sites in conjunction with other relevant data such as the aerosol chemical composition (section 6.5.1), historical trends of emissions and ambient concentrations (section 6.5.2), or the direction from which the pollutants are coming (section 6.5.3) as clues for their probable origin. The remaining two methods begin at the source and examine the pollutant transmission processes through the atmosphere and their impact at a receptor by: (1) field observations (section 6.5.4) and (2) diagnostic modeling, that is, the use of source data, ambient concentration data, and a model to clarify what happen between source and receptor (section 6.5.5). Several of these methods can only provide circumstantial evidence for the source-receptor relationships. Other approaches may provide causal evidence but may impose heavy demands on sparse or nonexistent data. Hence, it is evident that establishing the source-emission relationships for aerosols over the various regions of the United States requires prudent use of all the available source resolution techniques as well as new ones as they are developed.

### 6.5.1 Aerosol Chemical Composition

A knowledge of the chemical composition of aerosols is essential to understanding their effects. The chemical composition serves also as a tracer of their probable origin.

In the chemical mass balance method, the chemical composition of an ambient aerosol is used to trace its origin (Friedlander, 1973; Miller et al., 1972; Heisler et al., 1973; Gartrell and Friedlander, 1975). Characteristic tracer elements (e.g., vanadium, which comes primarily from residual oil) can be used to estimate the contribution of specific sources.

The first comprehensive study of the chemical composition of various size fractions of the haze aerosol was conducted in the Los Angeles air basin as part of the 1969 Pasadena Aerosol Study (Hidy, 1972). This was followed by project ACHEX (Hidy, 1975). For measured aerosol concentrations at seven locations in the Los Angeles basin, White and Roberts (~~1975~~ 1980) constructed a chemical mass balance (Figure 6-19; White and Roberts, ~~1975~~ 1980). The key contributing species for the total aerosol mass concentration were nitrates, sulfates, organics, and unidentified substances. On the basis of statistical analysis of $b_{scat}$ and chemical composition data, they concluded that sulfates are the most efficient scatterers among the measured chemical species (see chapter 9). Oil and gasoline combustion products, and their oxidation products, appear to dominate the Los Angeles aerosol.

A separate chemical-mass balance for fine and coarse particles collected in Charleston, WV, was reported by Lewis and Macias (1980) and is shown in Figure 6-20. Of the fine-particle mass concentration (33 $\mu g/m^3$) about 30 percent was sulfate, about 13 percent was ammonium ion, 18 percent was carbonaceous material; the rest consisted of trace constituents and undetermined chemical species. The coarse-particle mass concentration of 27 $\mu g/m^3$ was found to be largely associated with elements that occur in the earth's crust. Lewis and Macias concluded that some elements were found mainly in the fine fraction; other elements were found in the coarse fraction. Carbon was the only major element that was almost equally distributed between the two size fractions.

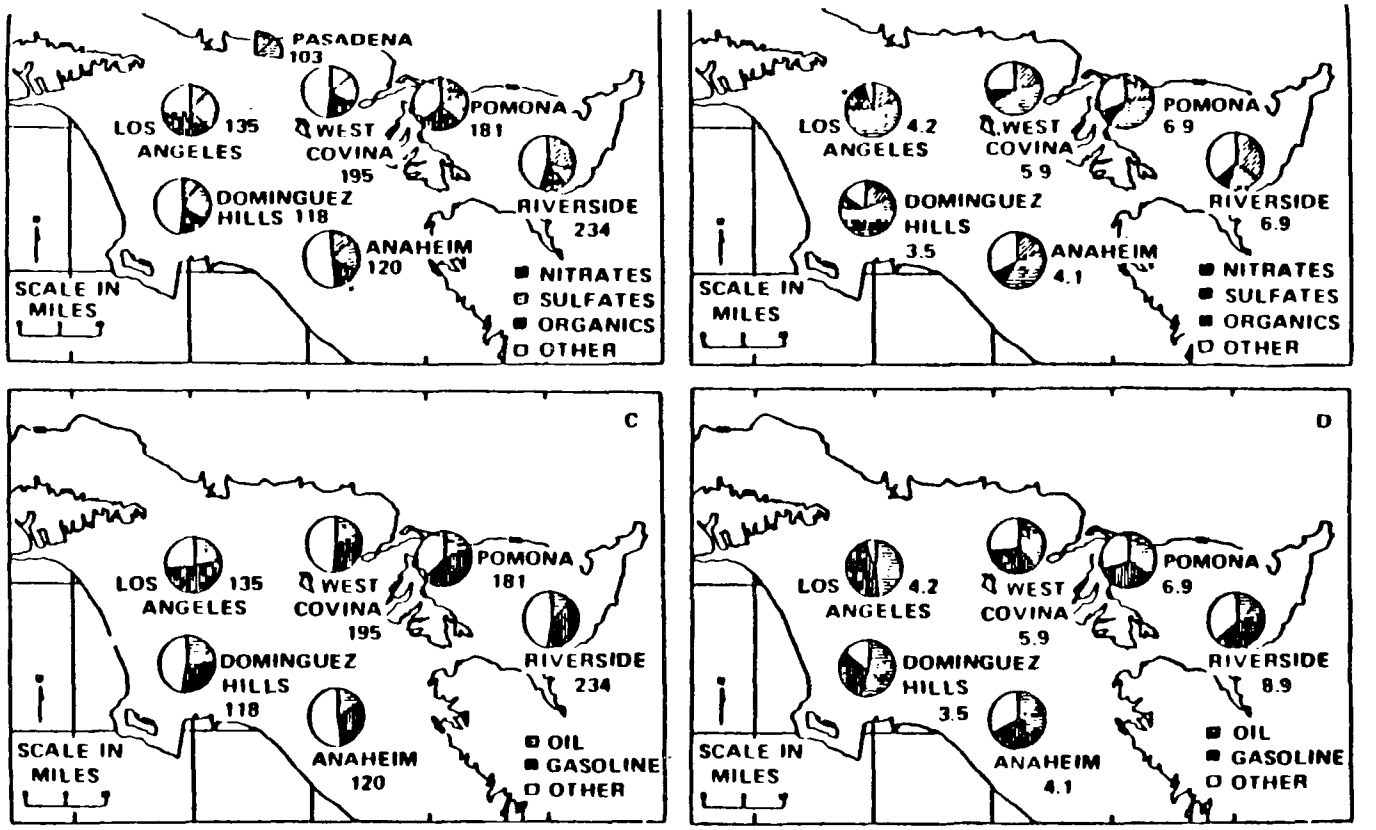



Figure 6-19. **Sulfates evidently contribute only about 25 percent of the total mass but cause about half of the light scattering, as shown in these maps of mass concentration (A) and light-scattering coefficient (B) in the Los Angeles basin. The pie diagrams show the relative contributions of nitrates, sulfates, organics, and other compounds. The contributions of source types (oil, gasoline, and other) to the mass concentration (C) and light-scattering coefficient (D) are also shown.**

**Source: White and Roberts (~~1975~~ 1980).**

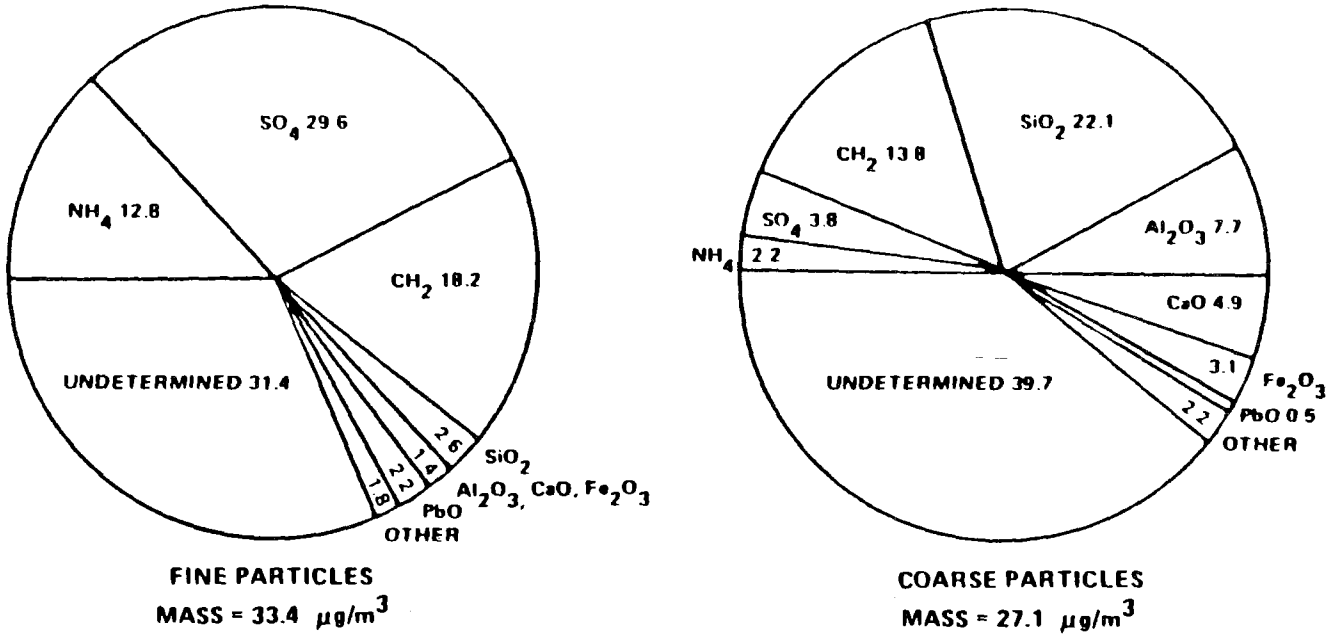



Figure 6-20. **Compositions of fine and coarse particles collected in Charleston, WV, are shown in these pie diagrams.**

**Source: Lewis and Macias (~~1979~~ 1980).**

For several years an extensive air pollution monitoring program was conducted in St. Louis as part of project RAPS (Regional Air Pollution Study). Size-segregated aerosol samples (Stevens et al., 1978) were collected automatically with dichotomous samplers and analyzed for elemental composition and mass concentration of fine and coarse particles.

The results from the 10-station monitoring network (Figure 6-21; Dzubay, 1979), analyzed by Dzubay (1979), show the distribution of the aerosol species within the St. Louis metropolitan area. Here again, sulfur compounds were the dominant species in the fine-aerosol fraction, contributing about 60 percent of the mass. For stations 103 through 112, within the central city, primary motor vehicle contribution was estimated to be about 10 percent of the fine-particle mass. For the peripheral stations, 25 km away from the city center (stations 122 and 124), the sulfate concentrations were comparable to those within the city, but motor vehicles accounted for only a few percent of the fine-particle mass. It is thus concluded that the automobile contributions were of local origin while the sulfate is distributed regionally, and the addition of the sulfate by the St. Louis metropolitan area is only 10 to 20 percent over the "regional background." In his mass balance analysis, Dzubay (1979) was able to account for practically all the coarse-particle mass as crustal shale and limestone. Figures 6-21A and 6-21B (Dzubay, 1979) also contain mass and chemical composition data for a Smoky Mountain site at Elkmount, Tenn. The fine-particle mass concentration there was about 25 $\mu g/m^3$, comparable to the values in the St. Louis region outside the city. There again, about 60 percent of the fine-particle mass was contributed by sulfur compounds. The unknown compounds may have included carbonaceous compounds, nitrates, and water. The coarse-particle mass concentration at the Smoky Mountain site was only 6 $\mu g/m^3$, substantially below that in the St. Louis region.

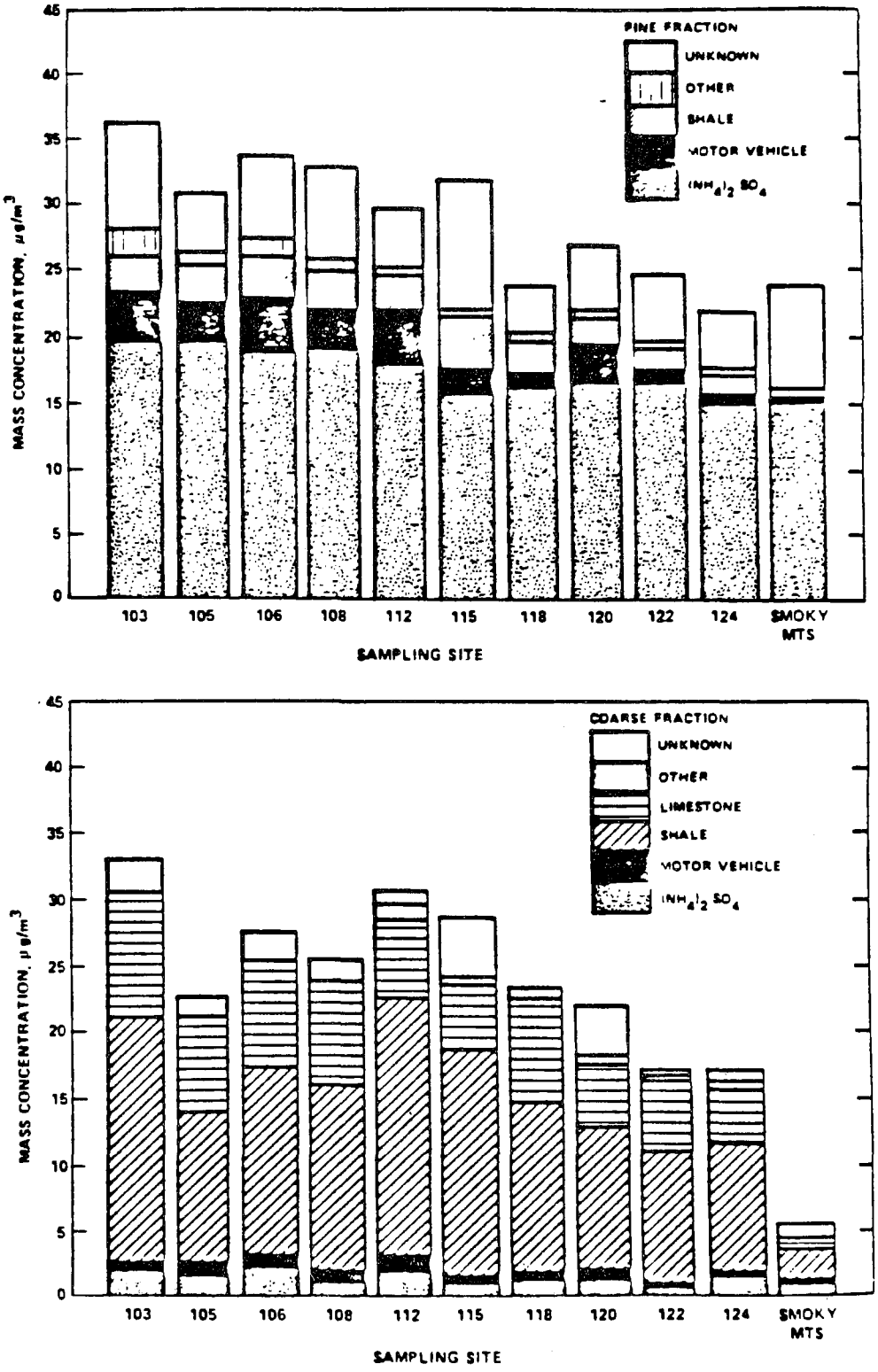



Figure 6-21. Source resolution of the St. Louis aerosol shows that less than 10 percent of the fine-particle mass is due to primary automobile emissions; about 60 percent is from sulfur oxide sources. Almost all of the coarse-particle mass is accounted for by dust from the earth's crust.

Source: Dzubay (1979).

Sulfur compounds constitute the most significant chemical component of the fine-particle mass over the Eastern United States. Statistical evidence for the importance of sulfates in the fine-particle mass was found from the analysis of RAPS data by Loo et al. (1978) (Figure 6-22). The particulate sulfur was consistently about 10 to 15 percent of the fine-particle mass for a sampling period of 2 months. Similar observations were made by Lewis and Macias (1980) for Charleston, WV, and by numerous other investigators over the past decade.

There is great concern over the origin of the fine-particle haze in the lightly populated areas of the Western and Southwestern United States and the potential impact of future emissions in that region. Reporting the results of project VISTTA, Macias et al. (1979) have presented size-chemical composition data for size-segregated aerosol collected in the Four Corners area during aircraft flights (Figure 6-23; Macias et al., 1979). As anticipated, the coarse-particle fraction could be accounted for by the crustal element contributions. In the fine-particle mass balance, about 40 percent of the 5.3 $\mu g/m^3$ was sulfate, another 10 percent was trace constituents, and 22 percent could not be accounted for. However, Macias et al. (1979) have also reported a 29 percent contribution of silica to the fine-particle mass. This is unusual because the crustal elements normally accompanying silicon were not present in the fine-particle samples. Macias et al. (1979) argued, therefore, that the fine-particle silicon may be due to direct emissions from combustion sources.

More detailed size distribution data for sulfur, silicon, and other compounds were reported by Winchester et al. (1979) for sites in New Mexico, Colorado, St. Louis, and New Hampshire. Invariably, the particulate sulfur concentration was highest for impactor stages between 0.25 and 1.0 $\mu m$. The size distribution of silicon, on the other hand, was consistently the highest for

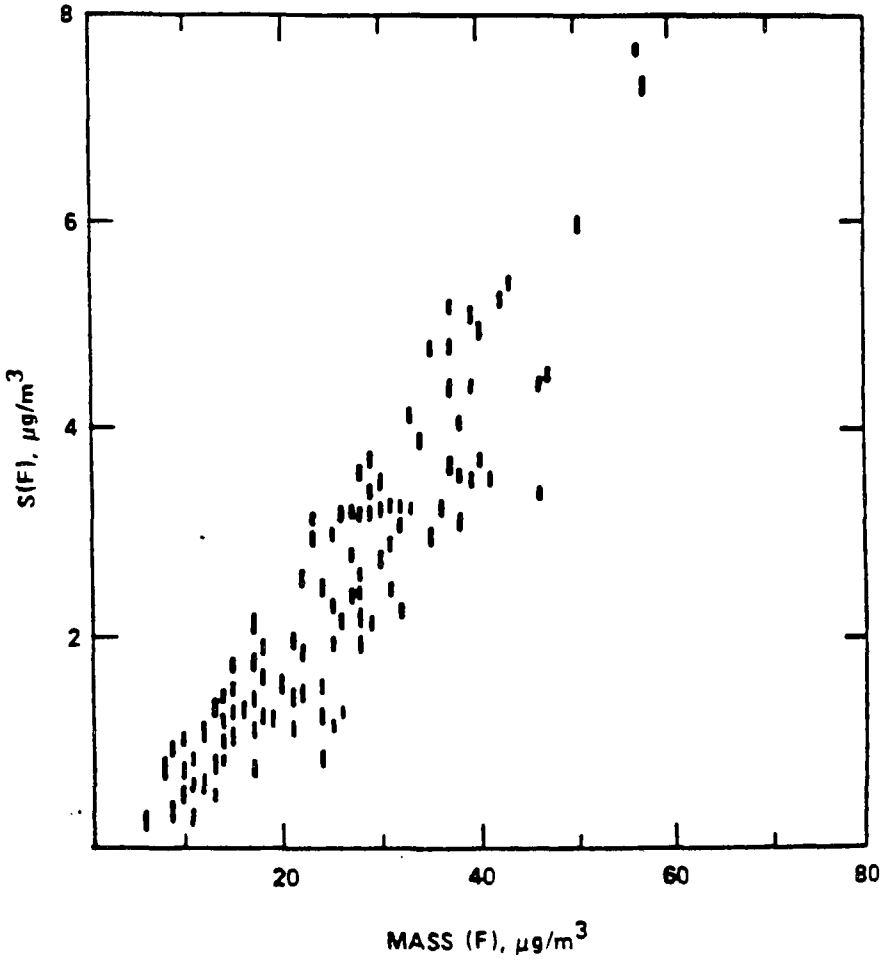



Figure 6-22. In the St. Louis area, monitoring data for about a 2-month period shows that sulfur was about 10 to 12 percent (calculated as elemental sulfur) of the fine-particle mass.

Source: Loo et al. (1978).

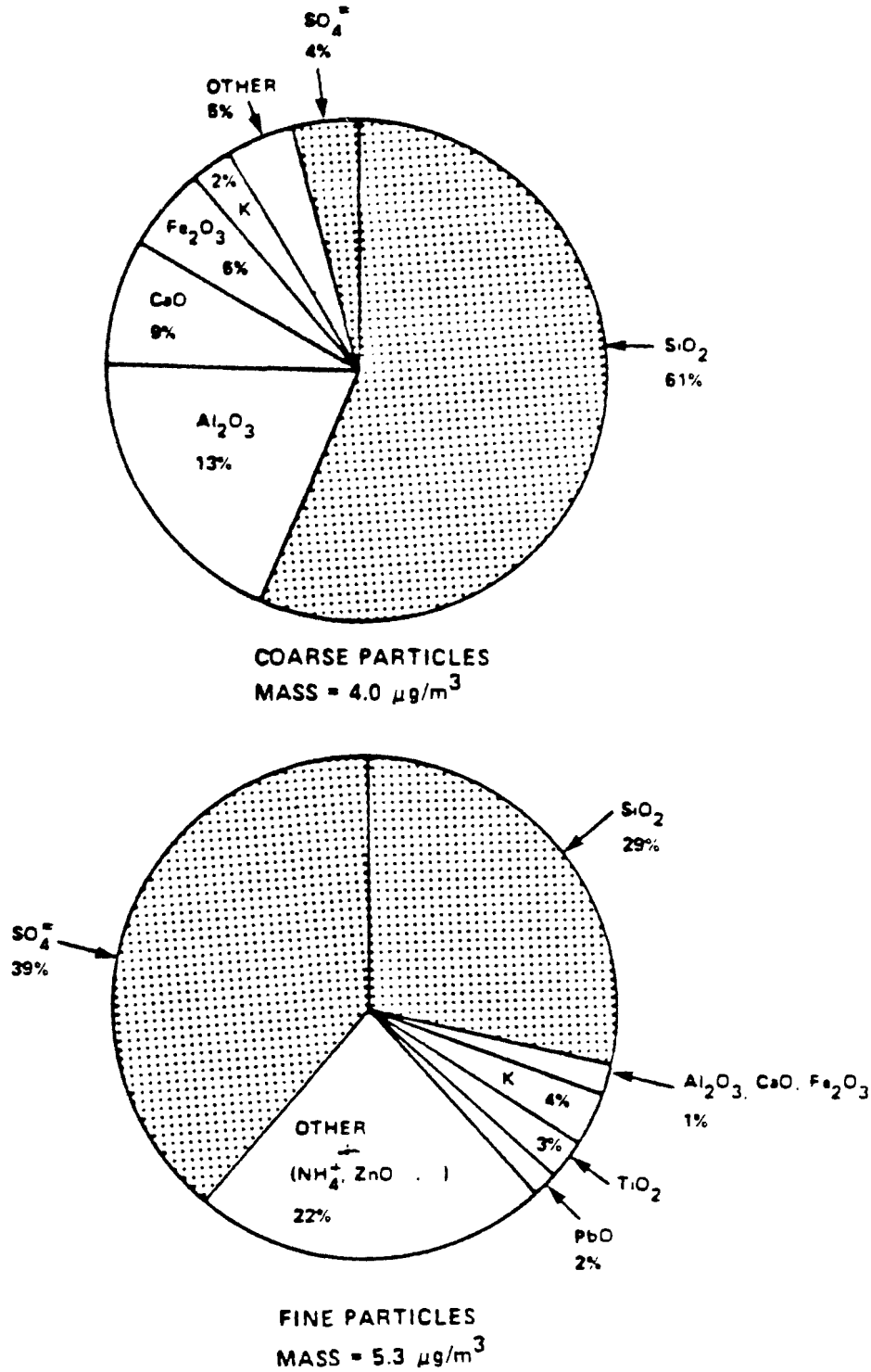



Figure 6-23. Composition of fine and coarse particles collected during flights in the Four Corners region is presented in pie diagrams. The total aerosol mass was estimated from in situ size distribution measurements. In this data set, silica accounted for an estimated 29 percent of the fine-particle mass.

Source: Macias et al. (1979).

impactor stages above 2 μm and lowest for the stages below 1 μm. Hence, in the Winchester et al. (1979) data set, the fine-particle silicon content was practically negligible, even at the New Mexico and the Colorado sampling sites. The resolution of the difference between the data reported by Macias et al. (1979) and Winchester et al. (1979) requires further data from the western States.

Factor analysis has been applied recently to data on the chemical composition of aerosols to determine which clusters of elements have high temporal correlations. The high correlation of a set of elements may indicate a common source.

In summary, the chemical composition of light-scattering aerosols provides a valuable, if not the most important, currently available clue to their sources. Sulfur compounds contribute about half of the fine-particle mass over most of the continental United States; they occur generally in the most effective light-scattering size range, 0.4 to 0.7 μm.

### 6.5.2 Historical Analysis of Trends in Emission Concentrations

The relationship between sources and their effects on ambient concentrations can also be inferred from historical trend analysis of both. If the 10- to 20-year trend of concentrations exhibits the same patterns as does the emission of some pollutant, then a possible cause-effect relationship may be inferred. On a shorter time scale, such as during the 1967-68 copper smelter strike in the Southwest, the complete shutdown of a major source can yield valuable clues to that source's role in the deterioration of air quality.

### 6.5.3 Pollution Roses and Sector Analysis

The estimation of source-receptor relationships by means of "pollution roses" has been used successfully for decades in the case of primary pollutants, such as carbon monoxide. In its simplest form, the method consists of classifying each pollutant measurement according to the corresponding wind direction and

computing the average pollutant concentration for each wind direction class. The plot of average concentration versus wind direction is referred to as a pollutant rose; with careful selection of the wind direction classes, it is possible to infer the individual effect of local sources. The major assumption required in such analysis is that the plume arrives at the receptor from the direction in which the source lies.

Wind rose analysis was applied by Latimer et al. (1978) to historical visibility data from Farmington, N.M. (Figure 6-24; Latimer et al., 1978). The percentage of daylight observations for which RH < 60 percent and visual range > 121 km was chosen rather than the mean. The visual range was significantly improved for the south-southeast to west wind direction classes during the shutdown of the copper smelter, lying in the same directions at distances of more than 400 km. Thus it may be inferred that the smelters cause up to 85 percent of the reduction of visual range below 121 km associated with south-southeast winds.

As noted by Altshuller (1976), long-range transport in the Eastern United States accounts for at least 50 to 75 percent of the measured sulfate. Since sulfate appears to cause more than its mass share of light scattering, most of the observed haziness may be unrelated to local sources. During long-range transport, the plume may meander and arrive at the receptor from almost any direction. Thus, in the Eastern United States, the traditional pollution rose may be inadequate for determining the sources of haziness.

The utility of the sulfate rose in determining the source-receptor relationship may be improved by the more sophisticated approach of trajectory sector analysis. Backward air parcel trajectories are calculated to determine the source region that most strongly contributes to the measured concentration. The

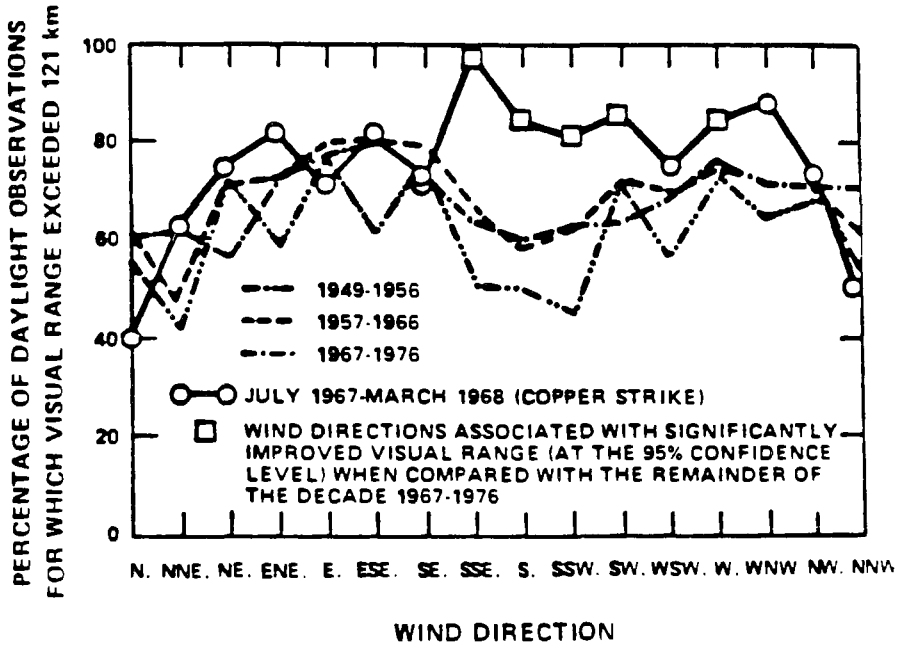



Figure 6-24. This plot of the percentage of daylight observations with RH < 60 percent for which visual range was > 121 km as a function of wind direction shows that during the period of the copper strike, there was a significant improvement of visual range from the direction of copper smelters, SSW. to W., implicating these $SO_2$ sources. Data are from Farmington, NM.

Source: Latimer et al. (1978).

direction from the receptor to the source may then be used in place of the local wind direction in constructing the pollution rose. Samson (1978) used this approach to establish the importance of the Ohio River Valley sources of sulfate at nonurban sites in New York State. Galvin et al. (1978) showed that in New York State the elevated sulfate concentrations were consistently associated with trajectories that originated in the Ohio River Valley region (Figure 6-25; Galvin et al., 1978). Chung (1978) used trajectory analysis to implicate the same region as an important source of sulfate in southwestern Canada. Rodhe et al. (1972), Brosset et al. (1975), and others established the importance of continental European sources by this technique. The OECD Program on the Long Range Transport of Air Pollutants (LRTAP) included trajectory sector analysis of sites across Europe (Figure 6-26; OECD, 1977). Thus, the relative contribution of each region to any site is clearly established. For example, it appears that most of the sulfate (and thus, probably, most of the haze) received in southern Sweden is from sources in Central Europe.

The more elaborate trajectory analysis techniques are easily adapted to include simple gas-particle conversion and removal kinetics along the trajectory. Such models are used to extract the regional-average rate constants from source emissions and measured concentrations, as in the OECD project. Such empirical approaches to data analysis are known as diagnostic models and are discussed further in section 6.5.5.

In summary, observed measurements of aerosol and haziness can be attributed to sources or source regions when the meteorological transport between source and receptor is known. For conditions in which long-range transport and unsteady winds are significant, the utility of pollution roses may be increased by receptor-back-to-source trajectory computations.

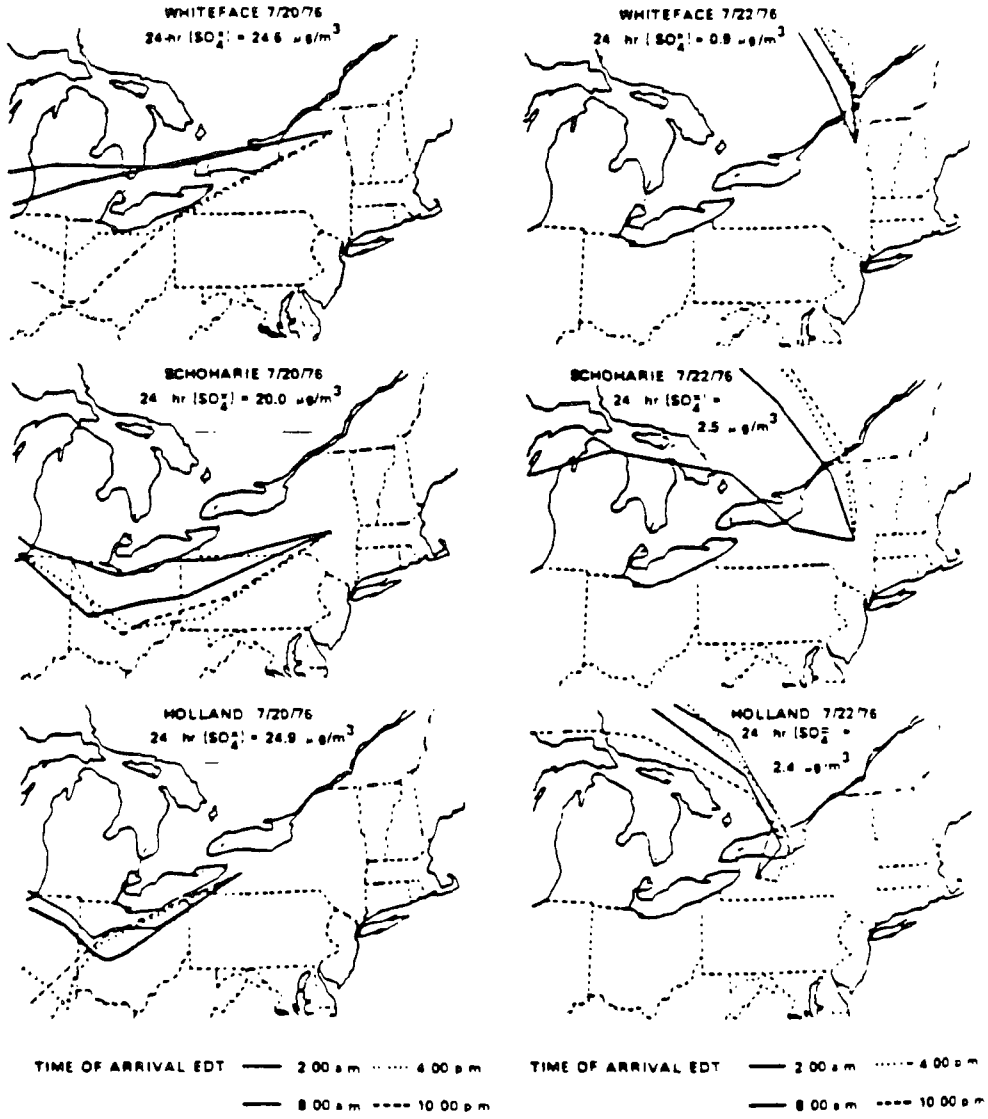



Figure 6-25. Air mass trajectories to Whiteface, Schoharie, and Holland on July 10 and 22, 1976, indicate that elevated sulfate at nonurban New York sites originated in the Ohio River Valley

Source: Galvin et al. (1978).

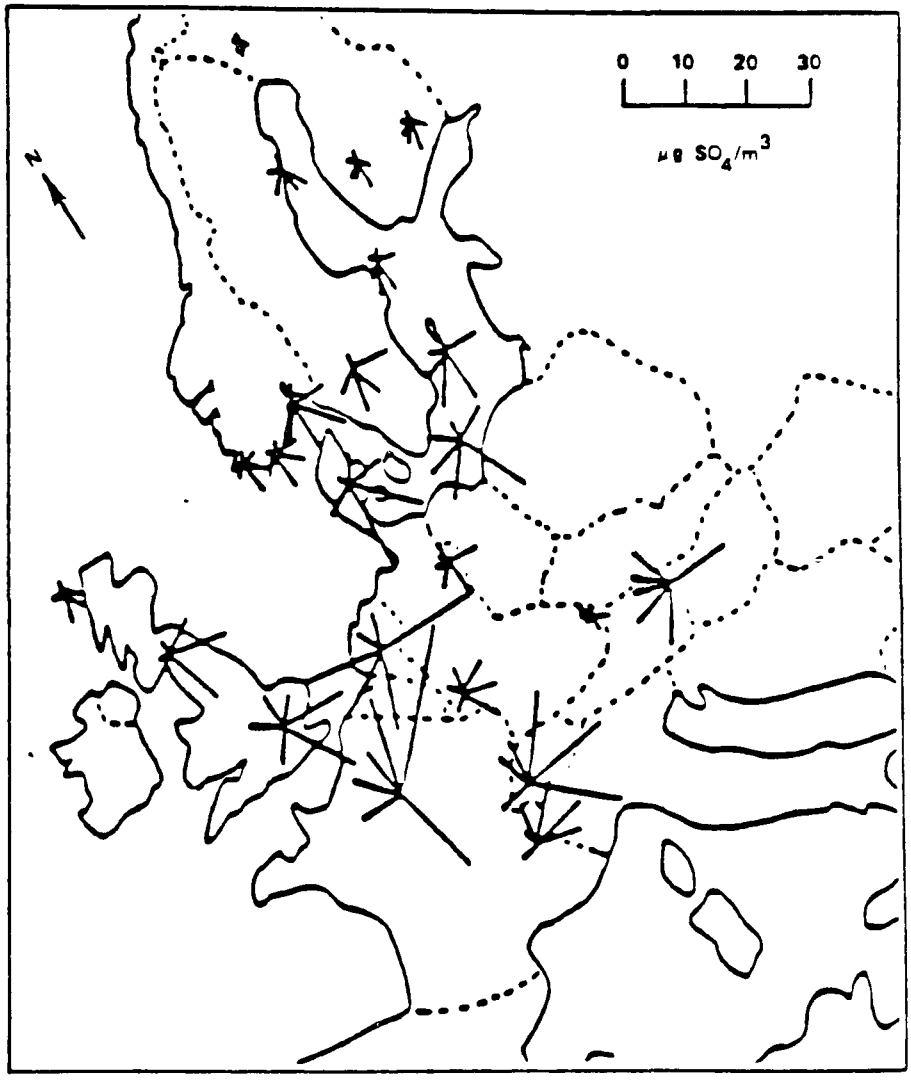



Figure 6-26. Sulfate trajectory roses in Europe reveal that most of the sulfate in southern Scandinavia is from emissions in other countries lying to the south, rather than from local contributions.

Source: OECD (1977).

### 6.5.4 Direct Measurements of Source Impacts: Plumes and Regional Hazes

In the previous three sections, the source-receptor relationships were examined from the point of view of the receptor. The approach was to determine what source types contributed and how much they contributed to the total burden at a given site. An alternative approach discussed in this section is that of starting at the source and following the transmission of the air pollutants through the atmosphere until they are ultimately removed. This more fundamental approach requires a rather detailed understanding of the chemical transformation processes, the removal processes, and the horizontal and vertical transport of matter in the atmosphere. In this approach, the specific roles of transport, transformation, and removal processes are identified. This approach facilitates consideration of these processes in the appropriate control strategies.

This section focuses almost exclusively on the transmission of sulfur compounds through the atmosphere. The empirical source-receptor methods of the preceding sections have clearly implicated sulfates as the principal components of the fine-particle aerosol population, contributing perhaps half or more of the fine-particle mass over a large part of the continental United States. The second reason for focusing on sulfur compounds is that the origin of the nonsulfur compounds in the aerosol phase, such as nitrates and organics, is not as well understood.

6.5.4.1 Power Plant Plume Studies--The actual rates and mechanisms of conversion as well as the creation of light-scattering aerosols must be studied in field experiments. In recent years, a number of power plant plume conversion studies were specifically designed to study the $SO_2$ oxidation rate and the formation of sulfate and light-scattering aerosols.

Since the late 1960's, an increasing fraction of total $SO_2$ emission has resulted from coal combustion in electric power plants equipped with stacks 150 to 200 m high.

The atmospheric transmission of tall-stack effluents has been studied extensively during the past decade, most recently in project MISTT (Midwest Interstate Sulfur Transformation and Transport) (Wilson, 1978) and STATE (Sulfur Transport and Transformation in the Environment) (~~Schurmeier~~ Schiermeier, 1980), where the transport, chemical transformation, removal, and the interaction of these processes in determining the sulfur budget of large plumes were assessed. One set of results and conclusions of these studies is given in Figures 6-1 (Husar et al., 1978) and 6-27.

It is also important to examine the long-distance effects of the Labadie power plant plume. Figure 6-28 illustrates the plume geometry and the measured $SO_2$ concentrations attributed to the Labadie plume for two long-range sampling days, July 9 and July 18, 1976 (Gillani et al., 1978). On both days the plumes were tracked to about 300 km from the source. The properties of the aging plume are shown in Figure 6-29 (Gillani et al., 1978).

6.5.4.2 Urban Plumes--Urban plumes aggregate from various sources within a metropolitan area. The best-studied urban plume is that of metropolitan St. Louis. The individual sources include coal-fired power plants with a combined capacity of 4600 MWe, oil refineries with a combined capacity of $4.4 \times 10^5$ barrels per day, various other industries, and a population of about 2 million (White et al., 1976). Because St. Louis is far from other major metropolitan areas, its impact on the surrounding ambient air quality is relatively easy to identify; air that has been modified by the aggregate emissions of the metropolitan

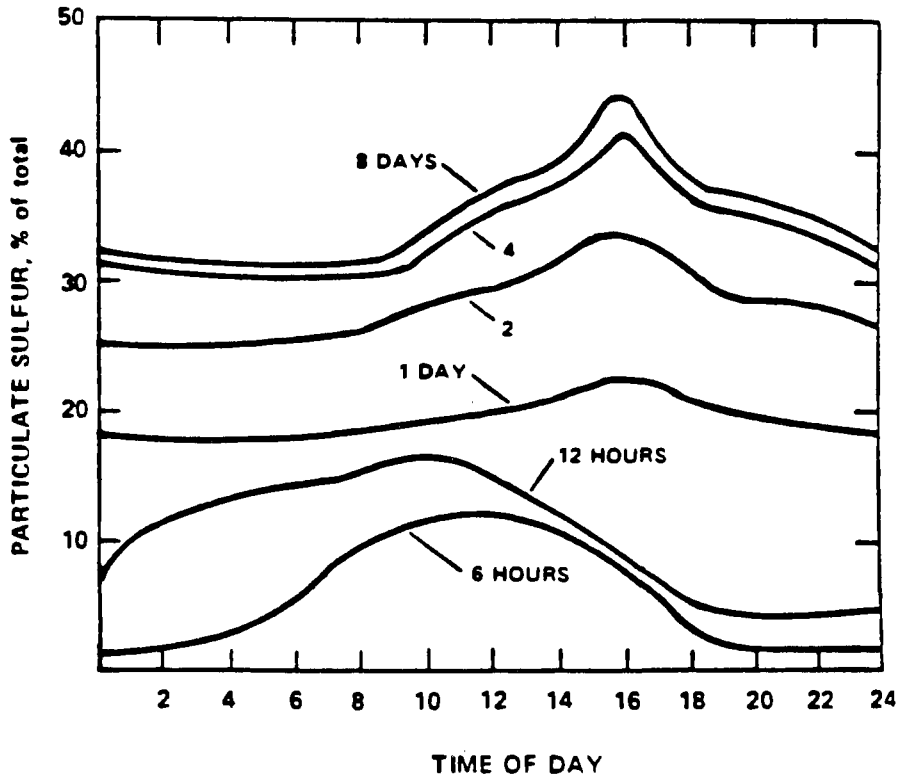



Figure 6-27. The amount of particulate sulfur formed increases when the plume is removed from the surface by dilution or by decoupling from the surface layer. Hence, daytime emissions into deeply mixed layers or elevated stable layers are expected to produce more sulfate than nighttime emissions.

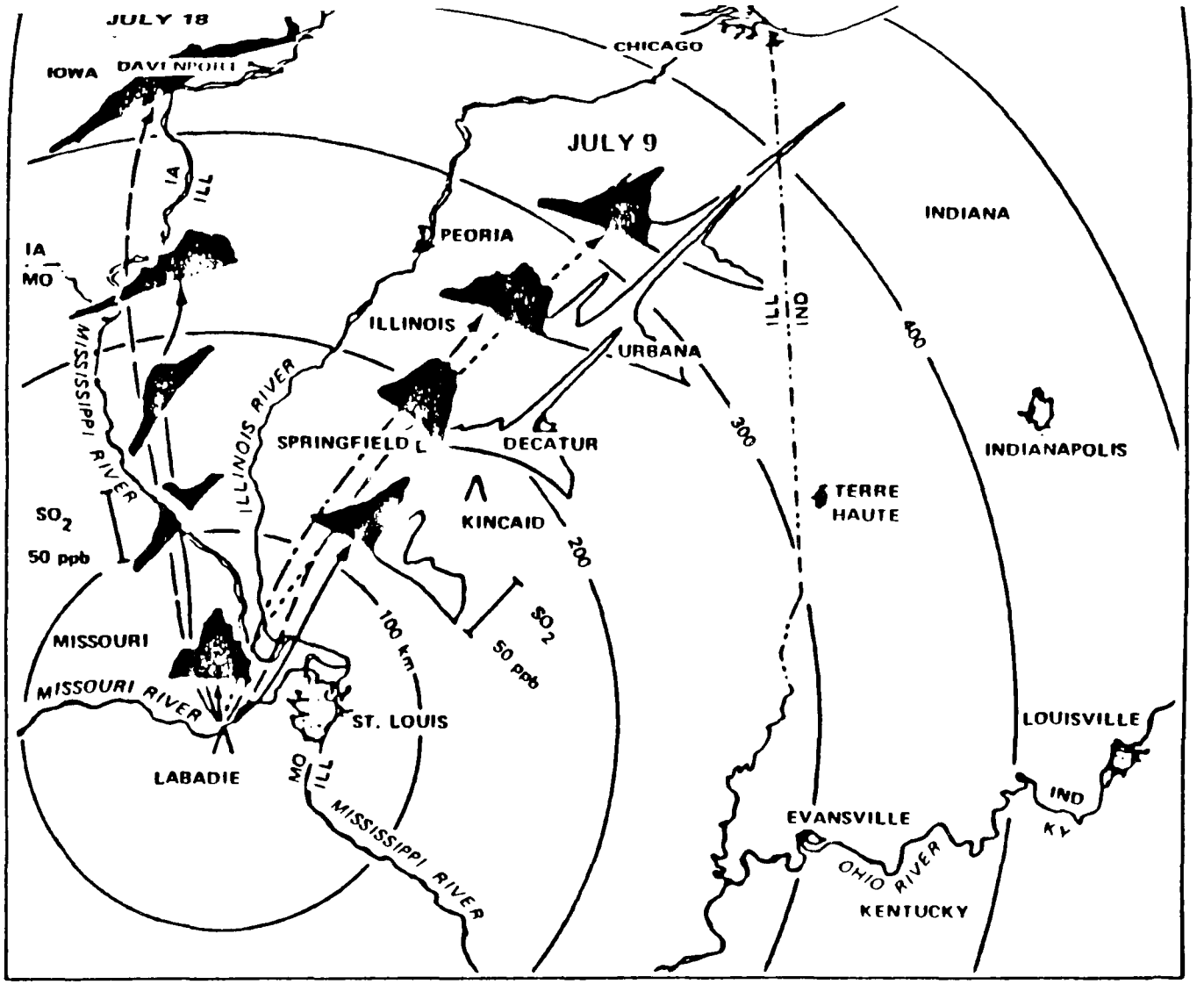



Figure 6-28. Horizontal profiles of $SO_2$ were made during selected constant-altitude traverses on July 9 and July 18, 1976. July 9 traverses are at about 450 m AGL, and July 18 traverses are at about 750 m AGL. The Labadie plume sections are shaded. Also shown are backward trajectories for the Labadie plume.

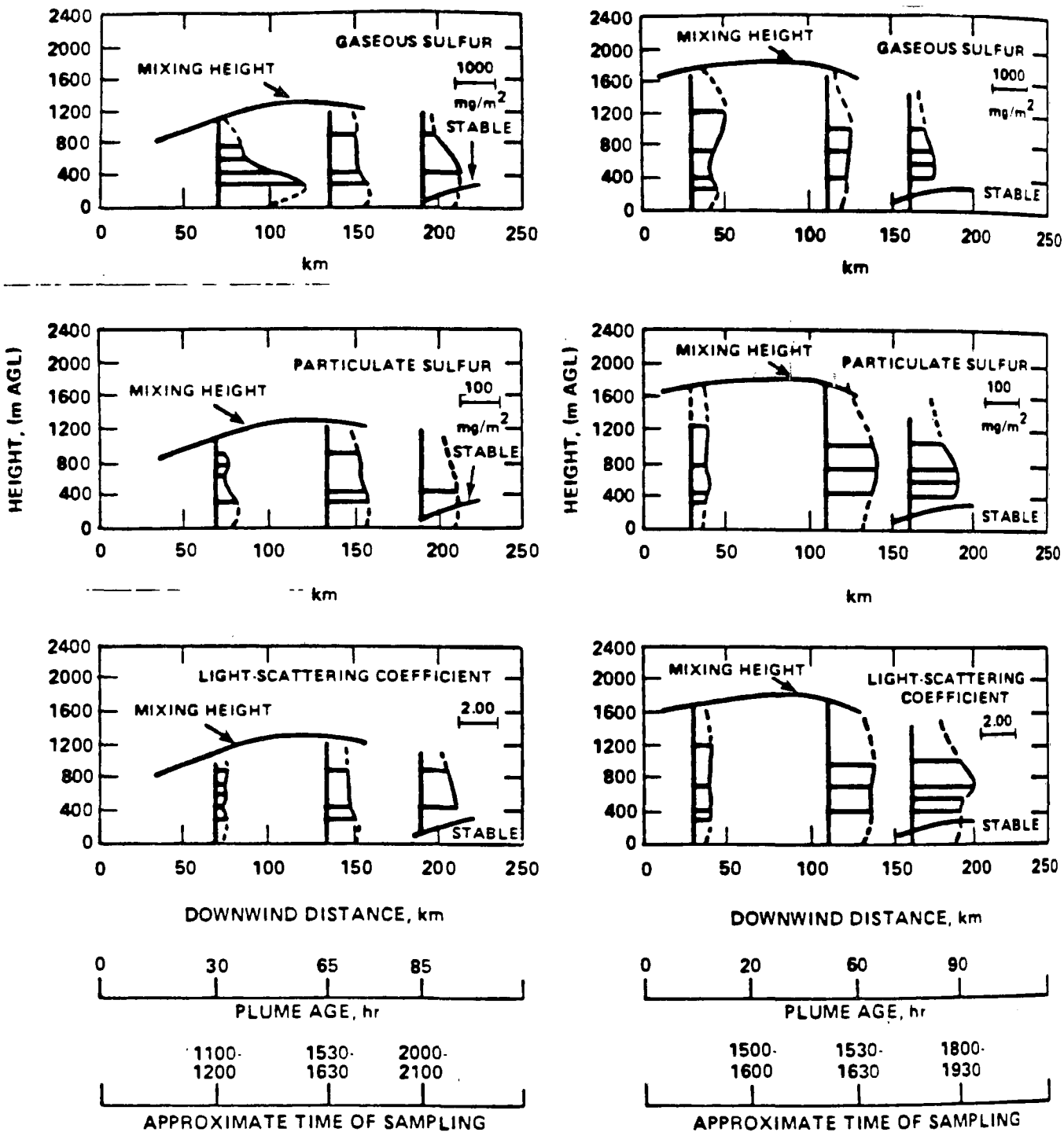



Figure 6-29. Vertical profiles show the crosswind integrals of excess plume concentrations of gaseous sulfur ($S_g$), particulate sulfur ($S_p$), and light-scattering coefficient ($b_{scat}$) for the transport of the Labadie plume of July 9 and 18, 1976. Broken portions of the vertical profiles represent extrapolations. Vertical integrals of the profiles of $S_g$ and $S_p$ denote masses $M_g$ and $M_p$, respectively, of gaseous and particulate sulfur in vertical plume slabs of unit downwind depth. The region marked "stable" represents the inversion layer forming near the ground during the evening.

Source: Gillani et al. (1978).

area forms an "urban plume downwind." The Fate of Atmospheric Pollutants Study (FAPS) (e.g., Haagenson and Morris, 1974) has shown that this plume can often be identified as far as 120 km from the city.

As part of project MISTT (Wilson, 1978), the three-dimensional flow of aerosols and trace gases in the St. Louis urban plume was studied. The plume was successfully tracked to a distance of 240 km, and it was mapped quantitatively to 160 km (Figure 6-30; Wilson, 1978). At these distances, the plume was still defined and about 50 km wide.

An increased concentration of light-scattering aerosol was a conspicuous characteristic of the St. Louis urban plume. The primary contribution of project MISTT was to quantify the flow of materials at increasing downwind distances so as to study the transformations of pollutants in the atmosphere.

The flux of ozone, $b_{scat}$, and particulate sulfur ($S_p$) all increased with distance downwind of St. Louis on July 18, 1975, reflecting the secondary origin of ozone and most of the light-scattering aerosols (White et al., 1976). Most of the increase in the $b_{scat}$ flux was observed downwind of the major increase in ozone flux, which is consistent with the finding of laboratory studies that aerosol production lags behind ozone production in a photochemical system (Wilson et al., 1973). The ratio of the flux of $b_{scat}$ to the flux of $S_p$ indicates that sulfate compounds accounted for most of the newly formed aerosol in the urban plume. This case study illustrates the fact that emissions in urban plumes from a metropolitan area such as St. Louis cause reduced visibility and elevated ozone concentrations long after the primary precursors have been diluted to low concentrations.

The visibility reduction in the St. Louis urban plume was also studied as part of project METROMEX. Komp and Auer (1978) have made direct observations of

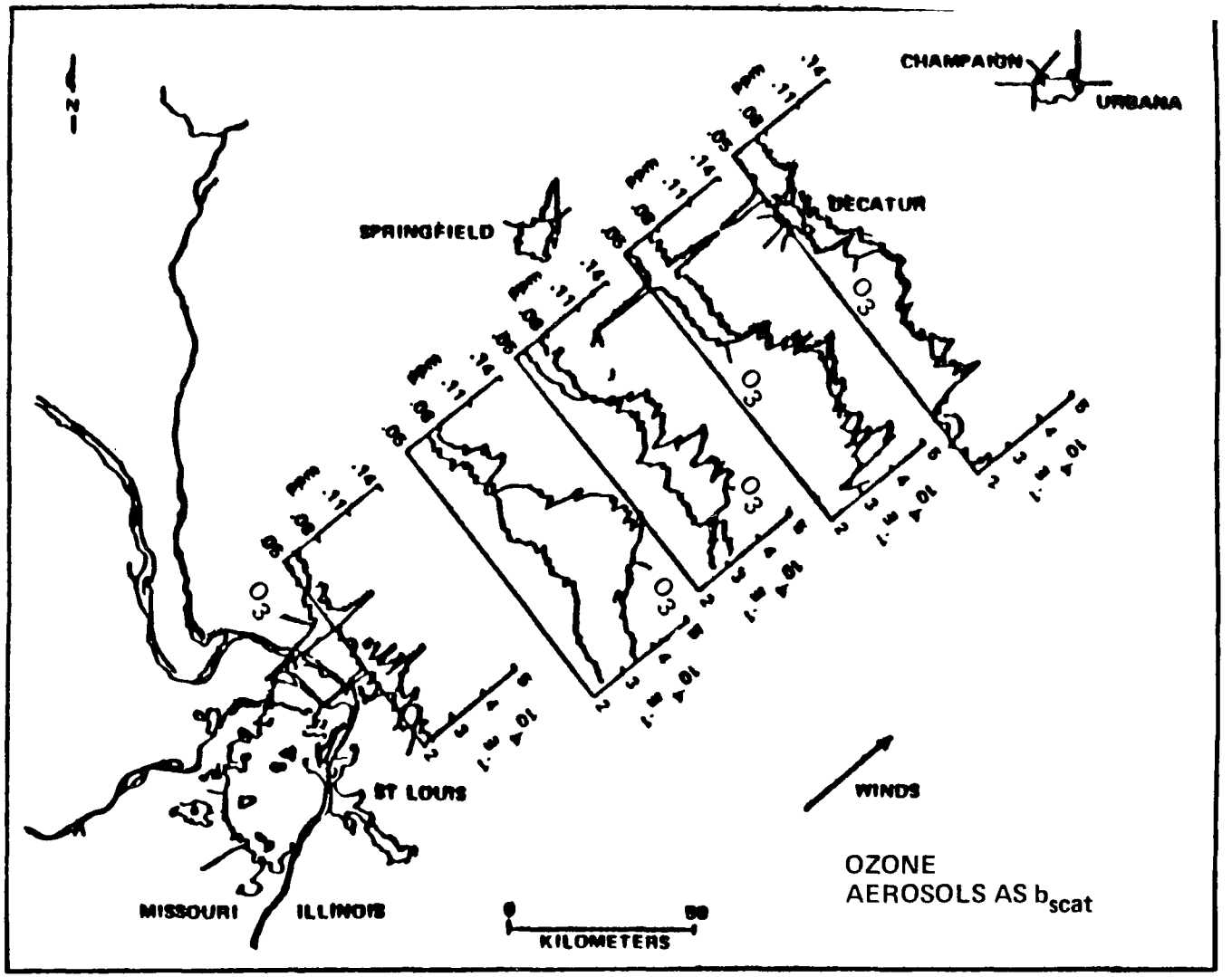



Figure 6-30. The three-dimensional flow of aerosols and ozone in the St. Louis plume is plotted for a distance of 240 km.

Source: Wilson (1978).

visual range from aircraft downwind of St. Louis and presented the data as contour maps of aging in the urban plume. The visual range was reduced by a factor of 2.

These direct measurements of the impact of a single major source area on its surrounding region show that the urban plume of one metropolitan area may become a "background haziness" for another. It is therefore reasonable to assume that the pollutant backgrounds in nonurban regions of the Eastern United States are probably the result of the combined emissions of metropolitan and industrial areas as well as of power plants far upwind. Regrettably, direct measurements of plume impacts have not been made beyond a few hundred kilometers from their sources. Beyond those distances, aircraft mapping of single plumes and even urban plumes tends to become difficult; furthermore, plumes are likely to be superimposed. It has been suggested that the observed large-scale haziness over a large part of the Eastern United States during stagnation is in fact the result of the superimposition of numerous urban, industrial, and power-plant plumes, as discussed in the next section.

6.5.4.3 Regional-Scale Episodes of Haziness--The past several decades have seen a shift in the spatial scale of particulate matter distribution. The scale has expanded from areas immediately surrounding each emission source to entire metropolitan areas, and to multistate regions. One reason for the lessening of local high concentrations has been the control of primary particulate emissions. However, the emission of precursor gases such as $SO_2$, hydrocarbons, and $NO_x$ has increased over this period.

Early work on the potential for air pollution episodes focused on local inversion situations rather than stagnation of a regional-scale air mass. Hosler (1961) found that the southeast coast of the United States and the Smoky

Mountain region had the highest incidence of surface inversions nationally. Holzworth (1967) evaluated the pollution potential of several U.S. urban areas on the basis of mean mixing heights and wind speeds. Korshover (1967) constructed a climatology of stagnating anticyclones in the Eastern United States from 1936 to 1965. He found the highest potential for large-scale stagnation east of the Rocky Mountains to be in the southern Appalachian and Smoky Mountain regions.

One of the earliest examinations of a regional-scale episode detailed the evolution and impact of the Thanksgiving 1966 episode over the eastern seaboard, in which a stagnating high-pressure system caused prolonged elevated regional concentrations of primary pollutants.

In the past decade, several investigators have presented evidence for long-range transport of visibility-reducing fine particles. Rodhe et al. (1972), Brosset et al. (1975), Eliassen and Saltbones (1975), Smith and Jeffrey (1975), and Szepesi (1978) are among those who have confirmed the existence of long-range transport of sulfates in Europe. Chung (1978) found evidence of the transport of sulfate from the northeastern Midwest of the United States into southeastern Canada.

In the United States, Altshuller (1976) noted the anomaly of decreasing urban $SO_2$ concentrations with increasing rural sulfate trends (Table 6-6) and proposed long-range transport as the cause of the increase in regional sulfate levels. Wilson et al. (1976) also proposed long-range transport as the cause of the increased regional sulfate concentrations on the basis of field studies of plume transmission. Gage et al. (1977) demonstrated that a high sulfate-episode potential occurs when multiple $SO_2$ sources lie along a given wind direction.

One of the earliest case studies of transport of large-scale hazy air masses was that of Hall (1973). Since about 1975, the evolution and transport

TABLE 6-6. THREE-YEAR RUNNING AVERAGE OF SULFATE BY GEOGRAPHICAL REGION FOR NONURBAN SITES IN THE UNITED STATES

| Region | 1965-67 | 1966-68 | 1967-69 | 1968-70 | 1969-71 | 1970-72 | 1971-73 |
|---|---|---|---|---|---|---|---|
| East Coast | 8.1 | 8.2 | 8.4 | (7.0)[a] | (7.1)[a] | (7.7)[a] | (8.9)[a] |
| Southeast | 5.4 | 6.1 | 7.2 | | 8.4 | | 8.1 |
| Eastern Midwest | 7.3 | 7.8 | 8.3 | 9.5 | 9.8 | 10.4 | 10.9 |
| Western Midwest | 3.1 | 2.7 | 3.2 | | 3.7 | | 3.6 |
| Southwest | 3.5 | 3.3 | 4.2 | 5.2 | 5.8 | 5.6 | 5.0 |
| Rocky Mountain | 1.7 | 1.2 | 1.5 | 1.8 | 2.1 | | 2.1 |
| West coast | 3.0 | 3.0 | 3.2 | 3.7 | 3.8 | | |

[a]Computations based on smaller number of sites.

of regional-scale hazy air masses has received increasing attention from many research groups: Tong et al. (1976), Husar et al. (1976a), Lyons and Husar (1976), Wolff et al. (1977), Samson and Ragland (1977), Vukovich et al. (1977), Galvin et al. (1978), and Hidy et al. (1978).

A common finding in recent studies is that formation of regional-scale haziness is usually associated with the presence of slow-moving high-pressure systems. Since precipitation is relatively infrequent in anticyclonic systems, the residence time of fine particles may be increased to a week or more.

An example of one such episode over a 2-week period in June-July 1975 is presented in Figure 6-31 (Husar et al., 1976a). Inspection of the sequence of contour maps reveals that multistate regions are covered by a hazy layer in which noon visual range is less than 10 km ($b_{ext} = 4 \times 10^{-4}\ m^{-1}$), indicated by the outer contours.

The apparent motion of the haze was confirmed by geostationary satellite photographs. The region of haziness on July 30 is clearly seen in Figure 6-32 (Lyons and Husar, 1976), which shows the hazy air mass over Arkansas, Missouri, Kansas, Iowa, and Minnesota.

Two passages of the hazy air mass over St. Louis resulted in sharp increases of $b_{scat}$ over the entire metropolitan region (Figure 6-33A; Husar et al., 1976a). Sulfate concentrations also increased during the haze episode, from about 9 to 33 $\mu g/m^3$. The spatial coherence of the haziness is seen in the correspondence between the extinction coefficient at St. Louis and that at Springfield (Figure 6-33B; Husar et al., 1976a), again confirming that the observed haziness was primarily due to inflow into the polluted "background" material of the hazy air mass rather than local contributions.

Sufficient sulfate data were available from the National Aerometric Data Bank for comparison with visibility on 2 days during the episode period.

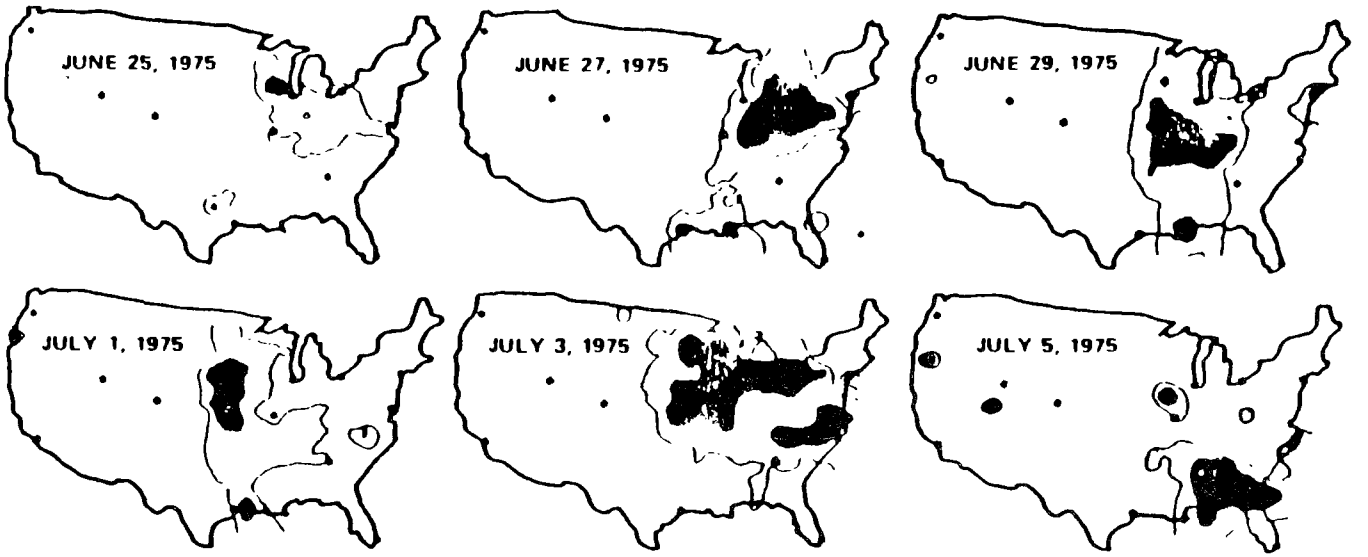



Figure 6-31. **Sequential contour maps of noon visibility for the period June 25 to July 5, 1975, illustrate the evolution and transport of a large-scale hazy air mass.**

**Source: Husar et al. (~~1976~~ 1976a).**

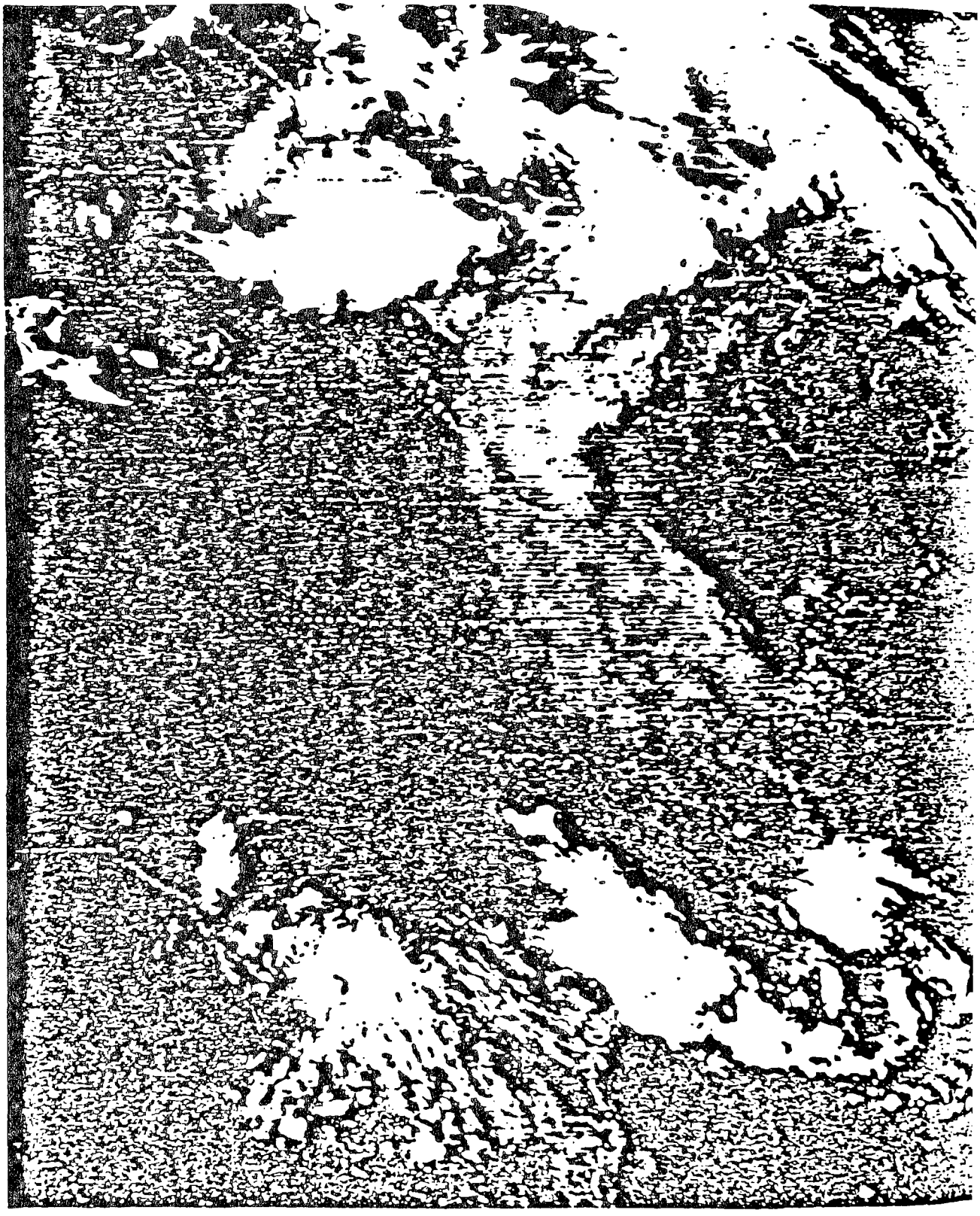


Figure 6-32. On June 30, 1975, the hazy air mass covered large parts of Arkansas, Missouri, Kansas, Iowa, and Minnesota, as seen in this geostationary satellite photograph.

Source: Lyons and Husar (1976).

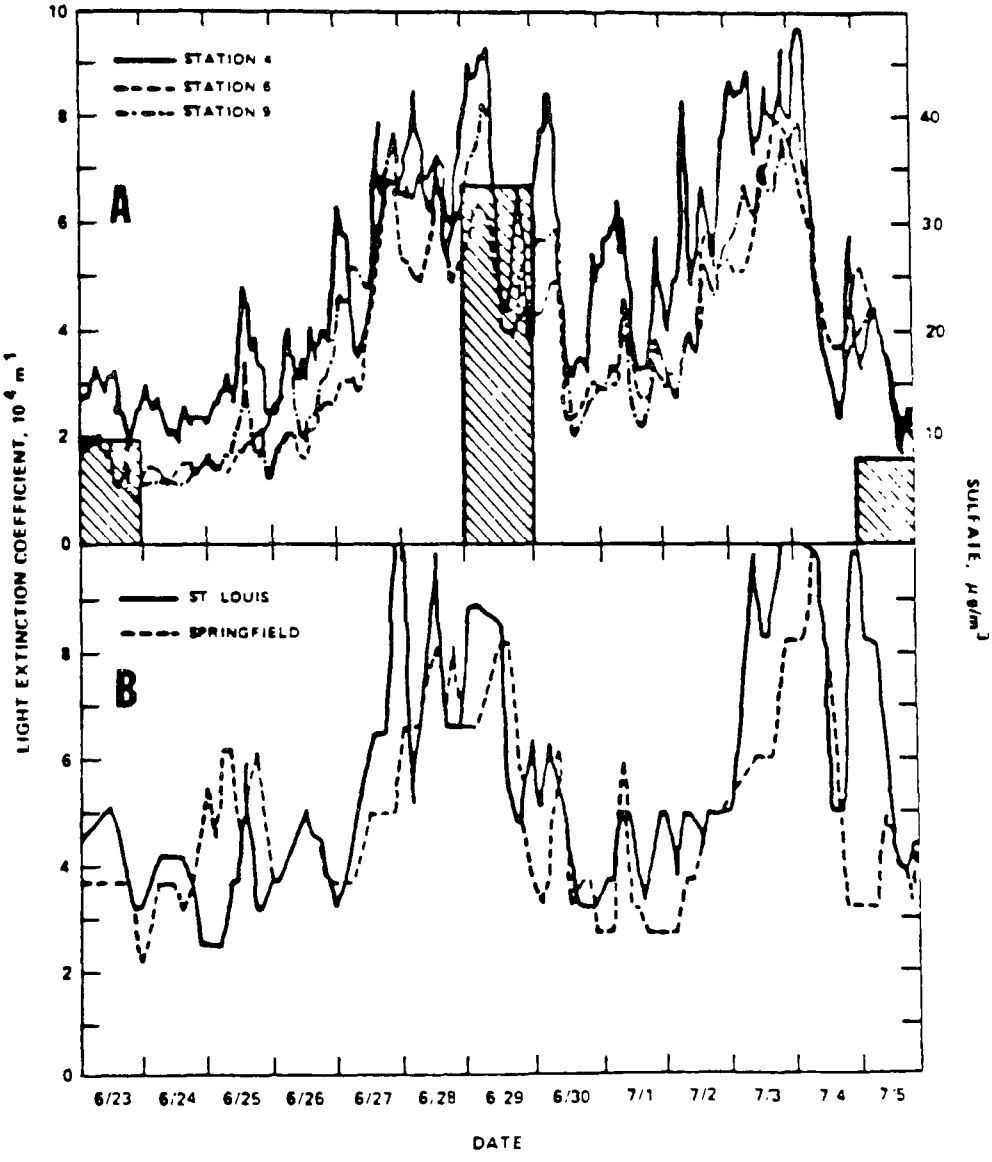



Figure 6-33. Local monitoring data in the St. Louis, MO, area during the June-July 1975 haziness episode (A) Light-scattering coefficient ($b_{scat}$) recorded at three widely spaced locations in the St Louis metropolitan area and daily average sulfate concentrations, (B) extinction coefficients ($b_{ext}$) obtained from visibility observations at St. Louis, MO, and Springfield, IL, 150 km apart

Source: Husar et al. (1976).

Figure 6-34 (Husar et al., 1976a) indicates the substantial correspondence between highest sulfate and lowest visibility.

During this period, the visual air quality was beyond the control of any local jurisdiction. The Alabama Air Pollution Control Commission reported the following (Bulletin of the AAPCC, 1975):

> During the weekend of July 5, 1975, a heavy haze layer enveloped the state of Alabama and much of the Southeastern United States. At that time, the AAPCC technical staff received many comments from the public concerning the origin and composition of the haze.
>
> The National Weather Service in Birmingham did issue an air stagnation advisory (ASA) for Alabama for this same time period; however, the traditional pollutant measurements made by the AAPCC and local programs did not show excessive levels. In fact, the measured local levels were lower than had been measured under previous ASA's making the dramatic decrease in visibility more intriguing.

Husar et al. (1976b) reported that in June-August 1975 there were at least six episodes similar to the one above. The work of other investigators confirms that episodes of regional-scale hazy air masses are not rare in the Eastern United States. At present, however, only the qualitative features of such episodes are understood: the observed effect on visibility, secondary sulfate and ozone composition, and the apparent motion of the haze.

Important questions remain to be answered about regional-scale episodes of haziness, including the following:

(1) Do the hazy air mass and the meteorologically defined anticyclone completely coincide?

(2) What are the quantitative effects of superimposing multiple $SO_2$ plumes and urban reactive plumes?

(3) What are the effects (and possible feedback mechanisms) of high pollutant concentrations on dry and wet deposition and cloudiness?

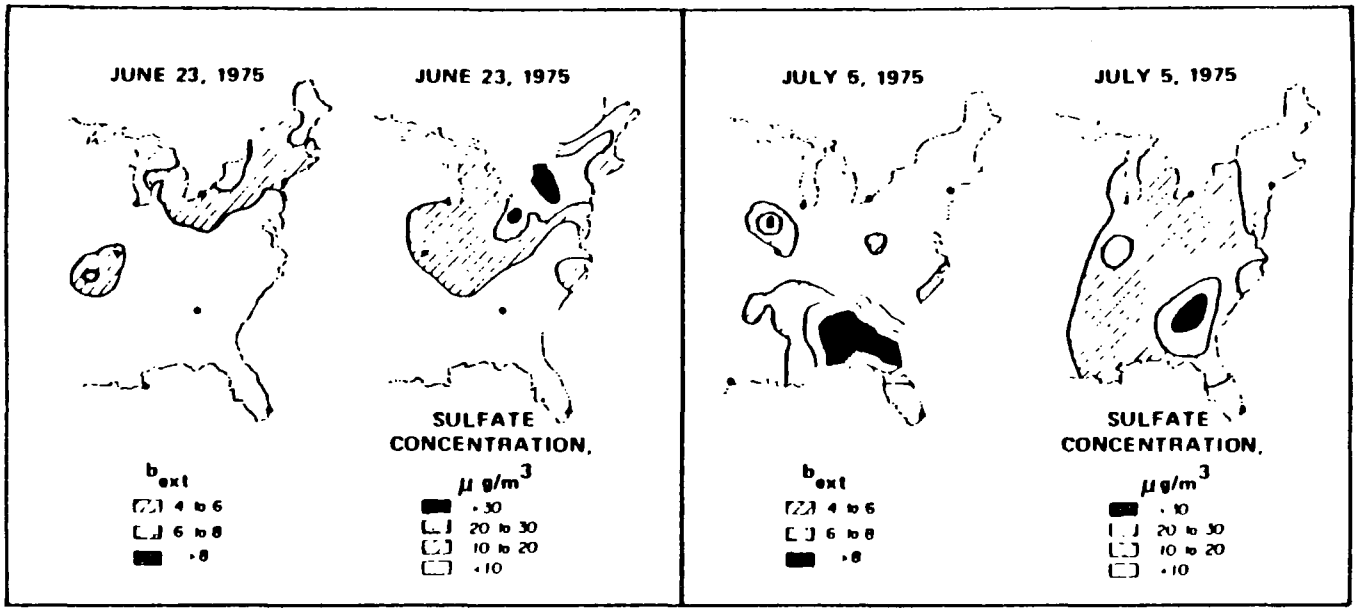



Figure 6-34. **Noon extinction coefficient and daily mean sulfate concentrations are compared for June 23 and July 5, 1975. The regions of highest sulfate concentrations coincide with areas of lowest visibility.**

**Source: Husar et al. (1976).**

(4) What is the exact residence time of the fine particles in the atmosphere during such episodes? It may be, for example, that lack of precipitation leads to extremely long sulfate lifetime.

The current Sulfate Regional Experiment (SURE), sponsored by the Electric Power Research Institute, is yielding valuable information about sulfur transmission in the Eastern United States. The U.S. Environmental Protection Agency's Sulfur Transformation and Transport in the Environment (STATE) is directed toward the complicated source-receptor relationship. The upcoming Prolonged Elevated Pollution Episode (PEPE) project of STATE is specifically designed to sample such regional-scale episodes of haziness from their inception throughout their residence over the Eastern United States.

The Eastern United States has experienced the most severe episodes of manmade haziness to date because the sources of precursor gases are concentrated in that area. Empirical evidence indicates that manmade sulfate and nitrate are also important factors in the visual air quality of the Western and Southwestern United States. Figure 6-35 (Holzworth, 1972) reveals that the meteorological potential for air pollution or haziness for the Western United States is as high or higher than that for the Eastern United States. Since the frequency of precipitation is low in the western regions, the residence time and the overall visual impact of the same emissions could be greater there than in the East.

It is not currently known whether regional haze occurs in the Western and Southwestern United States. Extinction coefficients for remote western areas may be as low as $0.2 \times 10^{-4}$ $m^{-1}$; a haze episode thus may require very little mass to cause a significant deterioration of visibility. For example, only about 4 $\mu g/m^3$ of fine-particle mass is needed to produce an increase in the

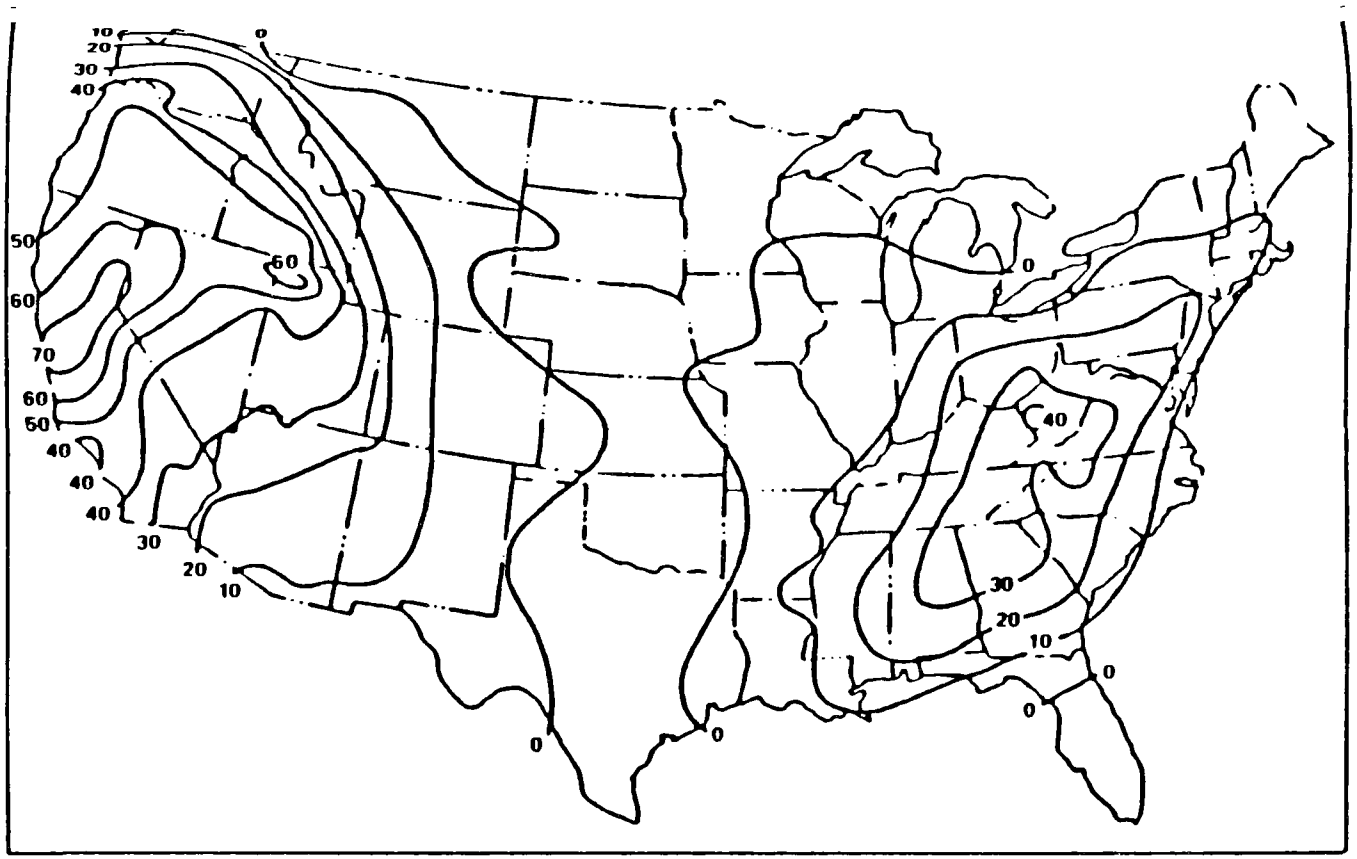



Figure 6-35. Isopleths of total number of forecast days of high meteorological potential for air pollution in a 5-year period demonstrate that the potential for regional-scale manmade haziness is at least as high in the Western United States as in the Eastern.

Source: Holzworth (1972).

extinction coefficient of $0.2 \times 10^{-4}$ $m^{-1}$. In pristine Western areas, this mass could double the extinction coefficient and reduce the visual range by half, from about 240 km to 120 km (Bachman, 1979).

### 6.5.5 Diagnostic Models

Knowledge of the transmission from source to receptor completes quantification of the source-receptor relationship (see chapter 5). Atmospheric transformations and removal during transport are the key processes involving $SO_x$ and particles, particularly for the secondary fine-particle species (i.e., sulfate, nitrate, and organics). These processes entirely determine the impact of a source.

The kinetics of atmospheric transmission cannot in general be measured directly because of the interference caused by removal. However, the available data on emissions, trajectories, and resulting concentrations can be processed through a model incorporating the key processes. The unknown rate constants are then extracted by adjusting the rate constants until a good fit is obtained between the model and the observed data. The mathematical formulation used for this purpose is referred to as a diagnostic model.

One of the best-known applications of a diagnostic model is the analysis of the OECD monitoring data (OECD, 1977). An emission inventory and transmission conditions for Europe were used in the model. The rates of gas-to-particle conversion and of removal were then extracted by tuning these parameters until the best fit between calculated and observed concentrations was achieved. The results for sulfur transmission from the OECD study are listed in Table 6-7.

The year-round average conversion rate of 1-2 percent per hour and the overall average dry-removal rate of 3-4 percent per hour were major new results of the OECD program. Studies being conducted in the United States with similar scope and objectives include the Sulfate Regional Experiment (SURE) of the

TABLE 6-7. VALUES APPLIED IN CALCULATIONS WITH THE LAGRANGIAN DISPERSION MODEL IN THE OECD PROJECT[a]

| Characteristic | Value |
|---|---|
| Fraction of emitted sulfur deposited locally | 0.15 |
| Fraction of emitted sulfur transformed directly to sulfate | 0.05 |
| Decay rate of sulfur dioxide, $sec^{-1}$ | |
| Rain | $4 \cdot 10^{-5}$ (14.4% $hr^{-1}$) |
| Dry | $1 \cdot 10^{-5}$ (3.6% $hr^{-1}$) |
| Transformation rate $SO_2$ to $SO_4^{2-}$, $sec^{-1}$ | $3.5 \cdot 10^{-6}$ (1.26% $hr^{-1}$) |
| Loss rate of $SO_4^{2-}$, $sec^{-1}$ | $4 \cdot 10^{-6}$ (1.44% $hr^{-1}$) |
| Mixing height, m | 1000 |

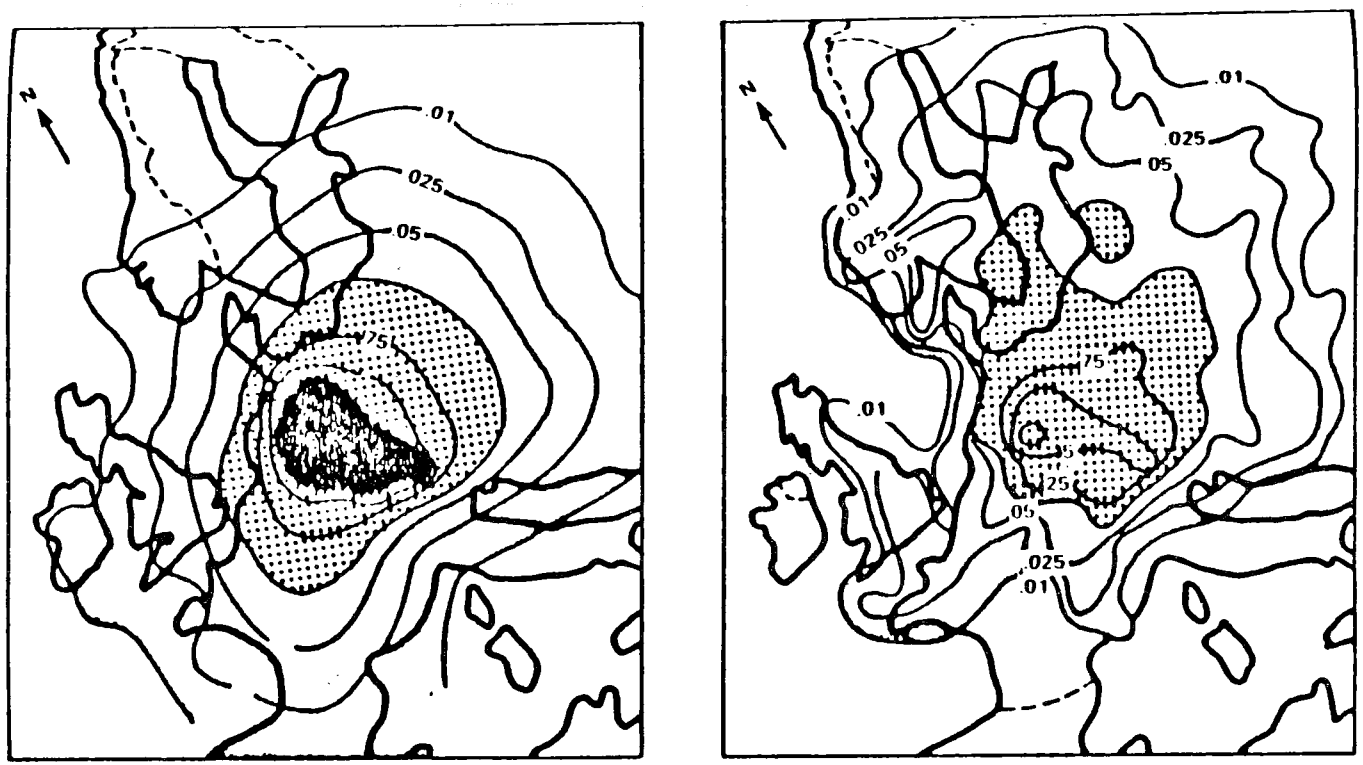
[a]Data from OECD, 1977.

Electric Power Research Institute (Perhac, 1978), the Multistate Atmospheric Power Production Pollutant Study (MAP3S) of the Department of Energy and EPA (MacCracken, 1978), and the Sulfur Transport and Transformation in the Environment (STATE) project of EPA. Similar models have been developed by Eliassen and Saltbones (1975), Fisher (1978), and Johnson et al. (1978).

The main advantage of the regional approach is that the rate constants represent averages over all sources and spatial-temporal scales of interest. The OECD estimates of the dry and wet deposition of sulfur compounds emitted from the Federal Republic of Germany (Figure 6-36; OECD, 1977), which is the size of a Midwestern State, indicate that 30 percent is dry deposited and 5 percent is wet deposited within the country and 65 percent is transported. Nevertheless, the impact on air quality is greater within the state or country than without.

Isaksen et al. (1978) applied a diagnostic model of free-radical conversion chemistry to the urban plume of St. Louis, Mo., on July 18, 1975. Inputs to the model included aircraft measurements of ozone, nitric oxide, nitrogen dioxide, sulfur dioxide, sulfate, and transport information. By tuning the chemical rate constants to fit both ozone and sulfate at a series of plume ages, the magnitude of the conversion rate of sulfur dioxide to sulfate was extracted as a function of plume age (Figure 6-37; Isaksen et al., 1978). The highest conversion rate occurred at 2 p.m. at a plume age of about 6 hr. Of the peak 5 percent per hour rate computed, about 1 percent per hour was attributed to oxidation by the hydroxyl radical.

Gillani et al. (1978) have applied a model with diurnally varying parameters of mixing height, mixing intensity (turbulence), conversion rate, and removal rate to three-dimensional aircraft measurements of a power plant plume. With




DRY DEPOSITION

WET DEPOSITION

Figure 6-36. **Maps of dry and wet deposition of sulfur compounds from the Federal Republic of Germany show that about 5 percent of Germany's emissions are wet deposited and 30 percent are dry deposited within the country.**

**Source: OECD (1977).**

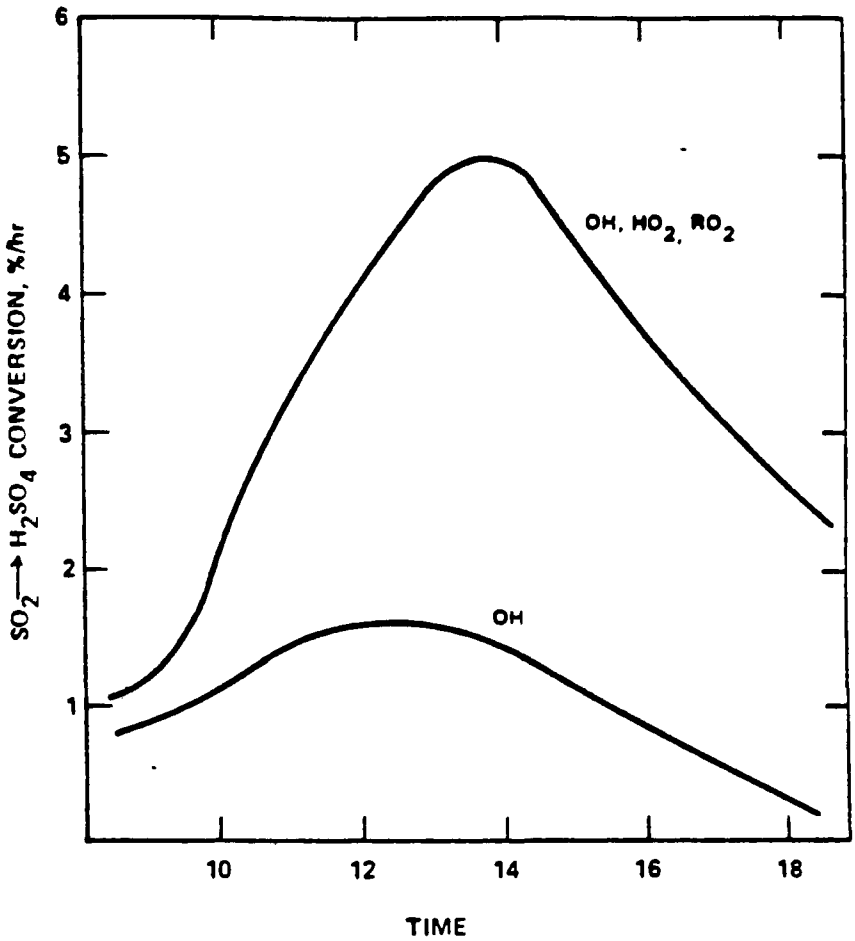



Figure 6-37. Extracted conversion rates of $SO_2$ to sulfate in the St. Louis urban plume show a peak at about 5 percent per hour at 2 p.m. The rates due to the OH radical alone are also derived.

Source: Isakson et al. (1978).

aircraft concentration measurements and trajectory data, simultaneous rates of conversion and removal were estimated at 200 km. Once tuned, the model was applied to estimate the effect of $SO_2$ emission height and time of day of release on the total sulfate formation.

In summary, the determination of the source-effect relationship of secondary fine particles requires the filtering of measurable data (emissions, transport path, and concentrations) through a diagnostic model. The impact of individual sources can be estimated once the model is properly tuned.

## 6.6 SUMMARY

The relationship of emissions of sulfur oxides and particulate matter to resulting ambient concentrations of these substances and their derivatives depends on the process of transmission, which includes the transport, diffusion, transformation, and deposition of atmospheric pollutants. Since each of these component processes is a function of numerous physiochemical and meteorological variables, source-receptor relationships are necessarily complex. Despite the difficulty in analyzing the transmission process, certain findings have been substantiated.

Atmospheric particulate matter tends to be bimodally distributed in terms of size; thus, fine particles are less than 2 μm in diameter and coarse particles are 2 μm or more in diameter. Fine and coarse particles also tend to differ in their sources and chemical composition, with much of the fine particulate matter being derived in the atmosphere from the transformation of gases (notably sulfur dioxide, nitrogen oxides, and organics) vis-a-vis coarse particles generally being emitted directly from industrial sources or combustion processes, or simply consisting of various types of suspended dust. Nevertheless, it is clear that certain chemical reactions do occur, most notably the transformation of sulfur dioxide in the atmosphere to various sulfates, including sulfuric acid.

Although comparable masses of find and coarse particles are measured in urban areas, coarse particles settle out more readily during transport than fine particles. Thus, with increasing distance downwind from urban areas, the fine particle fraction exceeds the coarse, except perhaps for fugitive dust from soil. Fine particles may be trasnported 1000 km or more from their origin before being deposited. During this long-range transport additional

fine particles may be formed from gaseous precursors of aerosols. Moreover, other downwind sources may be superimposed and further contribute to the fine particulate mass.

## 6.7 REFERENCES


Altshuller, A. P. Model Predictions of the Rates of Homogeneous Oxidation of Sulfur Dioxide to Sulfate in the Troposphere. Atmos. Environ. 13:1653-1662, 1980.

Altshuller, A. P. Regional transport and transformation of sulfur dioxide to sulfates in the United States. J. Air Pollut. Control Assoc. 26:318-324, 1976.

Angell, J. K., W. H. Hoecker, C. R. Dickinson, and S. H. Pack. Urban influence on a strong daytime air flow as determined from tetroon flights. J. Appl. Meteoral. 12:924-936, 1973.

Appel B. R., S. M. Wall, Y. Tokiwa, and M. Haik. Interference effects in sampling particulate nitrate in ambient air. Atmos. Environ. 13:319-325, 1979.

Bachman, J., ed. Protecting Visibility: An EPA Report to Congress. EPA-450/5-79-008, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1979.

Backstrom, H. L. J. The chain mechanism in the auto-oxidation of sodium sulfite solutions. Z. Phys. Chem. B25:122-128, 1934.

Bigelow, J. Z., 1898.

Boulaud, D., J. Bricard, and G. Madelaine. Aerosol growth kinetics during $SO_2$ oxidation. Atmos. Environ. 12:171-177, 1978.

Brosset, C., K. Andreasson, and M. Ferm. The nature and possible origin of acid particles observed at the Swedish west coast. Atmos. Environ. 9:631-642, 1975.

Bull. Alabama Air Pollut. Control Comm., 1975.

Calvert, J. G., F. Su, J. W. Bottenheim, and O. P. Strausz. Mechanism of the homogeneous oxidation of sulfur dioxide in the troposphere. Atmos. Environ. 12:197-226, 1978.

Chamberlain, A. C. Movement of particles in plant communities. In: Vegetation in the Atmosphere. J. L. Monteith, ed., Academic Press Inc., New York. 1975. pp. 155-201.

Chang, S. G., et al., 1978.

Chang, S. G., R. Brodzinsky, R. Toossi, S. Markowitz, and T. Novakov. Catalytic oxidation of $SO_2$ on carbon in aqueous solutions. In: Proceedings of Carbonaceous Particles in the Atmosphere, Lawrence Berkeley Laboratory, Berkeley, Calif., 1979.

## 6.7 REFERENCES


Altshuller, A. P. Model Predictions of the Rates of Homogeneous Oxidation of Sulfur Dioxide to Sulfate in the Troposphere. Atmos. Environ. 13:1653-1662, 1980.

Altshuller, A. P. Regional transport and transformation of sulfur dioxide to sulfates in the United States. J. Air Pollut. Control Assoc. 26:318-324, 1976.

Angell, J. K., W. H. Hoecker, C. R. Dickinson, and S. H. Pack. Urban influence on a strong daytime air flow as determined from tetroon flights. J. Appl. Meteoral. 12:924-936, 1973.

Appel B. R., S. M. Wall, Y. Tokiwa, and M. Haik. Interference effects in sampling particulate nitrate in ambient air. Atmos. Environ. 13:319-325, 1979.

Appel, B. R., E. L. Kothny, S. Wall, M. Haik, and R. L. Knights. Diurnal and spatial variations of organic aerosol constituents in the Los Angeles basin. In: Proceedings of the Conference on Carbonaceous Particles in the Atmosphere, Lawrence Berkley Laboratory, Berkley, CA, March 20-22, 1978.

Bachman, J., ed. Protecting Visibility: An EPA Report to Congress. EPA-450/5-79-008, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1979.

Backstrom, H. L. J. The chain mechanism in the auto-oxidation of sodium sulfite solutions. Z. Phys. Chem. B25:122-128, 1934.

Bigelow, J. Z., 1898.

Boulaud, D., J. Bricard, and G. Madelaine. Aerosol growth kinetics during $SO_2$ oxidation. Atmos. Environ. 12:171-177, 1978.

Brosset, C., K. Andreasson, and M. Ferm. The nature and possible origin of acid particles observed at the Swedish west coast. Atmos. Environ. 9:631-642, 1975.

Bull. Alabama Air Pollut. Control Comm., 1975.

Calvert, J. G., F. Su, J. W. Bottenheim, and O. P. Strausz. Mechanism of the homogeneous oxidation of sulfur dioxide in the troposphere. Atmos. Environ. 12:197-226, 1978.

Chamberlain, A. C. Movement of particles in plant communities. In: Vegetation in the Atmosphere. J. L. Monteith, ed., Academic Press Inc., New York. 1975. pp. 155-201.

Chang, S. G., R. Brodzinsky, R. Toossi, S. Markowitz, and T. Novakov. Catalytic oxidation of $SO_2$ on carbon in aqueous solutions. In: Proceedings of Carbonaceous Particles in the Atmosphere, Lawrence Berkeley Laboratory, Berkeley, Calif., 1978.

Charlson, R. J., A. H. Vanderpol, D. S. Covert, A. P. Waggoner, and N. C. Ahlquist. $H_2SO_4/(NH_4)_2SO_4$ background aerosol: optical detection in the St. Louis region. Atmos. Environ. 8:1257-1267, 1974.

Charlson, R. J., D. S. Covert, T. V. Larson, and A. P. Waggoner. Chemical properties of tropospheric sulfur aerosols. Atmos. Environ. 12:39-53, 1978.

Chun, K. C., and J. E. Quon. Capacity of ferric oxide particles to oxidize sulfur dioxide in air. Environ. Sci. Technol. 7:532-538, 1973.

Chung, Y. C. The distribution of atmospheric sulfates in Canada and its relationship to long range transport of air pollutants. Atmos. Environ. 12:1471-1480, 1978.

Clark, W. E., D. A. Landis, and A. B. Harker. Measurements of the photochemical production of aerosols in ambient air near a freeway for a range of $SO_2$ concentrations. Atmos. Environ. 10:637-644, 1976.

Clark, W. E. and K. T. Whitby. Concentration and size distribution measurement of atmospheric aerosols and a test of the theory of self-preserving size distributions. J. Atmos. Sci. 24:677-687, 1967.

Coordinating Research Council. Handbook of Chemistry and Physics 49:D-180, E-37, Chemical Rubber Co., Cleveland, OH, 1968.

Coughanowr, D. R., and F. E. Krause. The reaction of $SO_2$ and $O_2$ in aqueous solution of $MnSO_4$. Ind. Eng. Fund. 4:61-66, 1965.

Covert, D. W. A study of the relationship of chemical composition and humidity to light scattering by aerosols. Ph.D. Thesis, University of Washington, Seattle, 1974.

Cronn D. R., R. J. Charlson, R. L. Knights, A. L. Crittenden, and B. R. Appel. A survey of the molecular nature of primary and secondary components of particles in urban air by high-resolution mass spectrometry. Atmos. Environ. 11:929-937, 1977.

Demerjian K., J. A. Kerr, and J. Calvert. Mechanism of photochemical smog formation. In: Advances in Environmental Science and Technology, Vol. 4. (Edited by J. N. Pitts, and R. J. Metcalf). John Wiley, NY, 1974.

Draftz, R. G., and K. Severin. Microscopical Analysis of Aerosols Collected in St. Louis, Missouri. EPA-600/3-80-27, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1980.

Draftz, R. G. Aerosol Source Characterization Study in Miami, Florida: Microscopical Analysis. EPA-600/3-79-097, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1979.

Durham, J. L., R. K. Patterson, and R. G. Draftz. Carbon in Denver's Urban Plume. Proceedings: Carbonaceous Particles in the Atmosphere, Lawrence Berkeley Laboratory, Rep. No. LBL-9037, March 20-22, 1978. pp. 102-106.

Durst, C. S., A. F. Crossley, and N. E. Davis. Horizontal diffusion in the atmosphere as determined by geostrophic trajectories. J. Fluid Mech. 6:401-422, 1959.

Dzubay, T. G. Chemical element balance method applied to dichotomous sampler data. In: Proceedings of Symposium on Aerosols, Anthropogenic and Natural Sources and Transport, Annals of the New York Acad. of Sci., New York, 1979.

Easter, R. C., D. F. Miller, and W. E. Wilson. Kinetic simulation of the diurnal rates of $SO_2$ oxidation in a power plant plume. Atmos. Environ. vol. 14, 1980.

Eatough, D. J., T. Major, J. Ryder, M. Hill, N. F. Mangelson, N. L. Eatough, L. D. Hansen, R. G. Meisenheimer, and J. W. Fischer. The formation and stability of sulfite species in aerosols. Atmos. Environ. 12:262-271, 1978.

Eatough, D. J., W. P. Green, and L. D. Hansen. Oxidation of sulfite by activated charcoal. In: Proceedings of the Conference on Carbonaceous Particles in the Atmosphere, Lawrence Berkley Laboratory, Berkley, CA, 1978a.

Eliassen, A. The Trajectory Model: A Technical Description. Norwegian Institute for Air Research, Kjeller, Norway, 1976.

Eliassen, A., and J. Saltbones. Decay and transformation rates of $SO_2$ as estimated from emission data, trajectories and measured air concentrations. Atmos. Environ. 12:489-501, 1975.

Erickson, R. E., L. M. Yates, R. L. Clark, and C. M. McEwen. The reaction of sulfur dioxide with ozone in water and its possible atmospheric significance. Atmos. Environ. 11:813-817, 1977.

Ferber, G. J., K. Telegada, J. L. Heffter, and A. E. Smith. Air concentrations of krypton-85 in the mid-west United States during January-May, 1974. Atmos. Environ. 10:379-385, 1976.

Fisher, B. E. A. The calculation of long term sulphur deposition in Europe. Atmos. Environ. 12:489-501, 1978.

Forrest and Newman, 1977.

Fowler, D., and M. H. Unsworth. Dry deposition of sulfur dioxide on wheat. Nature 249:389-290, 1974.

Friedlander, S. K. A review of the dynamics of sulfate containing aerosols. Atmos. Environ. 12:187-195, 1978.

Friedlander, S. K. Chemical element balances and identification of air pollution sources. Environ. Sci. Technol. 7:235-240, 1973.

Gage, S. J., L. F. Smith, P. M. Cukor, and B. L. Nieman. Long-range transport of $SO_x/MSO_4$ from the U.S. Environmental Protection Agency/Teknekron integrated technology assessment of electric utility energy systems. In: Proceedings of the International Symposium on Sulfur in the Atmosphere (ISSA), Dubrovnik, Yugoslavia, 1977.

Galvin, P. J., P. J. Samson, P. E. Coffey, and D. Ramano. Transport of sulfate in New York state. Environ. Sci. Technol. 12:580-584, 1978.

Garland, J. A. Dry and wet removal of sulphur from the atmosphere. Atmos. Environ. 12:349-362, 1978.

Gartrell, G., Jr., and S. K. Friedlander. Relating particulate pollution to sources: the 1972 California aerosol characterization study. Atmos. Environ. 9:279-299, 1975.

Gelbard F., and J. H. Seinfeld. The general dynamic equation for areosols--Theory and application to aerosol formation and growth. J. Colloid Interface Sci. 68:363- , 1979.

Gillani, N. V., R. B. Husar, J. D. Husar, D. E. Patterson, and W. E. Wilson. Project MISTT: kinetics of particulate sulfur formation in a power plant plume out to 300 km. Atmos. Environ. 12:589-598, 1978.

Graf, J., R. H. Snow, and R. G. Draftz. Aerosol Sampling and Analysis - Phoenix, Arizona. EPA-600/3-77-015, U.S. Environmental Protection Agency, Research Triangle Park, 1977.

Graham, R. Rate constants for the reaction of $HO_2$ with $HO_2$,$SO_2$,CO,$N_2O$, trans-2-butene, and 2,3-dimethyl-2-butene at 300°K. J. Phys. Chem., vol. 83, 1979.

Grosjean D. Chapters, Aerosols. In: Ozone and Other Photochemical Oxidants. National Academy of Sciences, Washington, DC, 1977. pp. 45-125.

Grosjean D., and S. K. Friedlander. Gas-particle distribution factors for organic and other pollutants in the Los Angeles atmosphere. J. Air Pollut. Control Assoc. 25:1038:1044, 1975.

Haagenson, P. L., and A. L. Morris. Forecasting the behavior of the St. Louis, Missouri pollutant plume. J. Appl. Meteoro. 13:901-909, 1974.

Hardy, K. A. Aerosol Source Characterization Study in Miami, Florida: Trace Element Analysis. EPA-600/7-79-197, September, 1979.

Hales, J. M. Wet removal of sulfur compounds from the atmosphere. Atmos. Environ. 12:389-399, 1978.

Hall, F. P., Jr., C. E. Duchon, L. G. Lee, and R. R. Hagan. Long-range transport of air pollution, a case study, August 1970. Mon. Weather Rev. 101:404, 1973.

Harker A. B., L. W. Richards, and W. E. Clark. The effect of atmosperhic $SO_2$ photochemistry upon observed nitrate concentrations in aerosols. Atmos. Environ. 11:87-91, 1977.

Harrison, P. R., R. G. Draftz, and W. H. Murphy. Identification and Impact of Chicago's Ambient Suspended Dust. In: Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants (1974), pp 540-560.

Haury, G., S. Jordan, and C. Hofmann. Experimental investigation of aerosol-catalyzed oxidation of $SO_2$ under atmospheric conditions. Atmos. Environ. 12:281-287, 1978.

Hegg, D. A., and P. V. Hobbs. Oxidation of sulfur dioxide in aqueous systems with particular reference to the atmosphere. Atmos. Environ. 12:241-253, 1978.

Heisler, N. L., S. K. Friedlander, and R. B. Husar. Atmos. Environ. 7:633, 1973.

Hess, G. D., and B. B. Hicks. A study of PBL structure: the Sangamon experiment of 1975. Argonne National Laboratory Report ANL 75-60, Part IV, 1975. pp. 1-4.

Hidy G. M., and J. R. Brock. The Dynamics of Aerocolloidal Systems. Pergamon Press, NY, 1970.

Hidy, G. M. Summary of the California aerosol characterization experiment. J. Air Pollut. Control Assoc. 25:1106-1114, 1975.

Hidy, G. M., ed. Aerosols and Atmospheric Chemistry. Kendall Award Symposium. Academic Press Inc., New York. 1972.

Hidy, G. M., P. K. Mueller, and E. Y. Tong. Spatial and temporal distributions of airborne sulfate in parts of the United States. Atmos. Environ. 12: 735-752, 1978.

Hill, F. B., and R. F. Adamowicz. A model for rain composition and the washout of sulfur dioxide. Atmos. Environ. 11:917-927, 1977.

Hoather, R. C., and C. F. Goodeve. The oxidation of sulphmous acid. III. Catalysis of mangenous sulphate. Trans. Faraday Soc. 30:1149-1156, 1934.

Hoecker, W. H. Accuracy of various techniques for estimating boundary layer trajectories. J. Appl. Meteorol. 16:374-383, 1977.

Holt, B. D., P. T. Cunningham, and R. Kumar. Use of oxygen isotopy in the study of transformations of $SO_2$ to sulfates in the atmosphere. Presented at WMO Symposium, Sofia, Bulgaria, Oct. 1-5, 1970.

Holzworth, G. C. Mixing depths, wind speeds and air pollution potential for selected locations in the United States. J. Appl. Meteorol. 6:1039-1044, 1967.

Holzworth, G. C. Mixing Heights, Wind Speeds and Potential for Urban Air Pollution Throughout Contiguous United States. Environmental Protection Agency, Office of Air Programs Publication No. AP-101. U.S. Environmental Protection Agency, Research Triangle Park, NC, 1972. p. 35.

Hosler, C. R. Low level inversion frequency in the contiguous United States. Mon. Weather Rev. 89:319-339, 1961.

Husar, R. B., and K. T. Whitby. Growth mechanisms and size spectra of photochemical aerosols. Environ. Sci. Technol. 7:214, 1973.

Husar, R. B., D. E. Patterson, C. C. Paley, and N. V. Gillani. Ozone in hazy air masses. In: Proceedings of the International Conference on Photochemical Oxidants and Its Control, Research Triangle Park, NC, Sept. 12-20, 1976b.

Husar, R. B., D. E. Patterson, J. D. Husar, N. V. Gillani, and W. E. Wilson. Sulfur budget of a power plant plume. Atmos. Environ. 12:549-568, 1978.

Husar, R. B., N. V. Gillani, J. D. Husar, C. C. Paley, and P. N. Turcu. Long range transport of pollutants observed through visibility contour maps, weather maps, and trajectory analysis. Presented at the Third Symposium on Atmospheric Turbulence, Diffusion, and Air Quality, Raleigh, NC, Oct. 19-22, 1976a.

International Symposium on Sulfur in the Atmosphere (ISSA) Proceedings. Atmos. Environ. 12:1-769, 1978.

Isaksen, I. S. A., E. Hesstved, and O. Hov. A chemical model for urban plumes: test for ozone and particulate sulfur formation in St. Louis urban plume. Atmos. Environ. 12:599-604, 1978.

Johnson, W. B., D. E. Wolf, and R. L. Mancuso. Long term regional patterns and transfrontier exchanges of airborne sulfur pollution in Europe. Atmos. Environ. 12:511-527, 1978.

Judeikis, H. S. The Role of Solid-Gas Interactions in Air Pollution. EPA-650/3-74-007, U.S. Environmental Protection Agency, August 1974.

Judeikis, H. S., and S. Siegel. Particle-catalyzed oxidation of atmospheric pollutants. Atmos. Environ. 7:619-631, 1973.

Junge, C. E. Air Chemistry and Radioactivity. Academic Press Inc., New York, 1963.

Junge, C. E. Die Konstitution der atmospheuschen Aerosols. Ann. Meteorol. Hamburg 5:1-55, 1952.

Junge, C. E. Die rolle der aerosole und der gasformingen beimengungen der luft in spurenstoffhaushalt der troposphere. Tellus 5:1-26, 1953.

Kapustin, V. N., Yu. S. Lynbortseva, and G. V. Rozenberg. Variability of aerosols under the influence of cloud modulation of the radiation field. Izv. Atmos. Oceanic Phys. 10:1327-1331, 1974.

Karraker, D. G. The kinetics of the reaction between sulphurous acid and ferric ion. J. Phys. Chem. 67:871-874, 1963.

Komp, M. J., and A. H. Auer, Jr. Visibility reduction and accompanying aerosol evolution downwind of St. Louis. J. Appl. Meteorol. 17:1357-1367, 1978.

Korshover, J. Climatology of stagnating anticyclones east of the Rocky Mountains 1936-1965. Public Health Service Publication No. 999-AP-34, Cincinnati, OH, 1967. 15 pp.

Kuhlman, M. R., D. L. Fox, and H. E. Jeffries. The effect of CO on sulfate aerosol formation. Atmos. Environ. 12:2415-2423, 1978.

Latimer, D. A., R. W. Bergstrom, S. R. Hayes, M. K. Liw, J. H. Seinfeld, G. Z. Whitten, M. A. Wojcik, and M. J. Hillyar. The Development of mathematical models for the prediction of anthropogenic visibility impairment. EPA-450/3-78-110 a, U.S. Environmental Protection Agency, 1978.

Lee, R. E. Jr. The Size of Suspended Particulate Matter in Air. Science 178:567-575, 1972.

Lewis, C. W., and E. S. Macias. Composition of size fractioned aerosol in Charleston, West Virginia. Submitted for publication. Atmos. Environ. 14:185-194, 1980.

Liberti, A., D. Brocco, and M. Possanzini. Adsorption and oxidation of sulfur dioxide on particles. Atmos. Environ. 12:255-261, 1978.

Lipeles M., C. S. Burton, H. H. Wang, E. P. Parry, and G. M. Hidy. Mechanisms of Formation and Composition of Photochemical Aerosols. EPA-650/73-036. Thousand Oaks, CA: Rockwell International Science Center, 1973. 98 pp.

Loo, B. W., W. R. French, R. C. Gatti, F. S. Goulding, J. M. Jaklevic, J. Llacer, and A. C. Thompson. Large-scale measurement of airborne particulate sulfur. Atmos. Environ. 12:759-771, 1978.

Low, R. D. H. A theoretical study of nineteen condensation nuclei. J. Rech. Atmos. 4:65-78, 1969.

Lyons, W. A., and R. B. Husar. SMS/GOES visible images detect a synoptic-scale air pollution episode. Mon. Weather Rev. 104:1623-1626, 1976.

MacCracken, M. C. MAP3S: an investigation of atmospheric energy related pollutants in the northeastern United States. Atmos. Environ. 12:649-659, 1978.

Macias, E. S., D. L. Blumenthal, J. A. Anderson, and B. K. Cantrell. Characterization of Visibility Reducing Aerosols in the Southwestern United States. Interim report on Project VISTTA. MRI Report 78 1R, 15-85, 1979.

McMurry, P. H., and S. K. Friedlander. Aerosol formation in reacting gases: relation of surface area to rate of gas-to-particle conversion. J. Colloid Interface Sci. 64:248-257, 1978.

McNelis, D. N., L. A. Ripperton, W. E. Wilson, P. L. Hanst, and B. W. Gay. Gas Phase Reactions of Ozone and Olifin in the Presence of Sulfur Dioxide. In: Removal of Trace Contaminants from Air, B.R. Dietz, ed., A.C.S. Symposium Series 17:187-200, 1975.

Meyers, R. E., R. T. Cederwall, W. D. Ohmstede, and J. Kampe. Transport and diffusion using a diagnostic meso-scale model employing mass and total energy conservation constraints. In: Proceedings of the Third Symposium on Atmospheric Turbulence, Diffusion and Air Quality, American Meteorological Society, Boston, MA, 1977. pp. 90-97.

Middleton P. B., and J. R. Brock. Simulation of aerosol kinetics. J. Colloid Interface Sci. 54:249- , 1976.

Middleton P. B, S. H. Suck, and J. R. Brock. On the multimodality of density functions of pollutant aerosols. Atmos. Environ. 11:251-255, 1977.

Middleton, P., and C. S. Kiang. Experimental and theoretical examination of the formation of sulfuric acid particles. Atmos. Environ. 12:179-185, 1978.

Miller, D. F. Precursor effects on $SO_2$ oxidation. Atmos. Environ. 12:273-280, 1978.

Miller, F. J., D. E. Gradner, J. A. Grahm, R. E. Lu, Jr., W. E. Wilson, and J. D. Bachman. Size Considerations for Establishing a Standard for Inhalable Particles. J. Air Pollut. Control Assoc. 29:610-615, 1979.

Miller, M. S., S. K. Friedlander, and G. M. Hidy. A chemical element balance for the Pasadena aerosol. J. Colloid Interface Sci. 39:165-176, 1972.

Mueller, P. K., G. M. Hidy, K. Warren, T. F. Lavery, and R. L. Baskett. The occurrence of atmospheric aerosols in the northeastern United States. Annals of the New York Academy of Sciences 338:462-482, 1980.

Newman, J. E., M. D. Abel, P. R. Harrison, and K. J. Yost. Wind as Related to Critical Flushing Speed Versus Reflotation Speed by High-Volume Sampler Particulate Loading, 466-496. In: Atmospheric-Surface Exchange of Particulate and Gaseous Pollutants (1974). Englemann, R. J., ed. Energy Research and Development Administration symposium series, CONF-740921, 1976.

Neytzell-de Wilde, F. G., and L. Taverner. Experiments relating to the possible production of an oxidizing acid leach liquor by auto-oxidation for the extraction of uranium. In: Proceedings of the Second U.N. Conference Peaceful Uses of Atomic Energy, vol. 3, 1958. pp. 303-317.

Novakov, T. Conference on Carbonoceous Particles in the Atmosphere. Lawrence Berkley Laboratory, Berkley, CA, March 20-22, 1978.

OECD. The OECD Program on Long-Range Transport of Air Pollutants--Measurements and Findings. Organization for Economic Cooperation and Development, Paris, 1977.

Orel A. E., and J. H. Seinfeld. Nitrate formation in atmospheric aerosols. Environ. Sci. Technol. 11:1000-1007, 1977.

Orr, C., F. K. Hurd, and W. J. Corbert. Aerosol size and relative humidity. J. Colloid Interface Sci. 13:472-482, 1958.

Ottar, B. Monitoring long-range transport of air pollutants: the OECD study. Ambio 6:203-206, 1976.

Overton, J. H., V. P. Aneja, and J. L. Durham. Production of sulfate in rain and raindrops in polluted atmospheres. Atmos. Environ. 13:355-367, 1979.

Pack, D. H., G. J. Ferber, J. L. Hefter, K. Telegadas, J. K. Angell, W. H. Hoecker, and L. Machta. Meteorology of long-range transport. Atmos. Environ. 12:425-444, 1978.

Penkett, S. A., B. M. R. Jones, K. A. Brice, and A. E. J. Eggleton. The importance of atmospheric ozone and hydrogen peroxide in oxidizing sulphur dioxide in cloud and rainwater. Atmos. Environ. 13:123-137, 1979.

Perhac, R. M. Sulfate regional experiment in northeastern United States: the 'SURE' program. Atmos. Environ. 12:641-647, 1978.

Pierson, W. R., and P. A. Russell. Aerosol carbon in the Denver area in November 1973. Atmos. Environ. 13:1623-1628, 1979.

Roberts, P. T., and S. K. Friedlander. Photochemical aerosol formation--$SO_2$, 1-heptene, and $NO_x$ in ambient air. Environ. Sci. Technol. 10:573, 1976.

Rodhe, H. Budgets and turn-over times of atmospheric sulfur compounds. Atmos. Environ. 12:671-680, 1978.

Rodhe, H., C. Persson, and O. Akesson. An investigation into regional transport of soot and sulfate aerosols. Atmos. Environ. 6:675-693, 1972.

Ross, D. S. Comments on Arel and Seinfeld. Environ. Sci. Technol. 11:1000, 1977; 12:726, 1978.

Samson, P. J. Ensemble trajectory analysis of summertime sulfate concentrations in New York. Atmos. Environ. 12:1889-1893, 1978.

Samson, P. J., and K. W. Ragland. Ozone and visibility reduction in the Midwest: evidence for large scale transport. J. Appl. Meteorol. 16:1101-1106, 1977.

Schuetzle D., D. Cronn, A. L. Crittenden, and R. J. Charlson. Molecular composition of secondary aerosol and its possible origin. Environ. Sci. Technol. 9:838-845, 1975.

Schiermeier, F. A., F. Pooler, N. V. Gillani, J. F. Clarke, J. K. S. Ching, and W. E. Wilson. Experimental investigation of atmospheric sulfur transport and transformation in the STATE program. In: Proceedings of the 10th International Technical Meeting on Air Pollution Modeling and its Application. NATO/CCMS, Rome, Italy. Oct. 23-26, 1979.

Schwartz W. Chemical Characterization of Model Aerosols. EPA-650/3-74-011. Columbus, Ohio: Battelle Memorial Institute, 1974. pp. 124

Sehmel, G. A., and W. H. Hodgson. Particle dry deposition velocities. In: Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants. 1974 Proceedings of ERDA Symposium Series 38, Richland, WA, Publication No. CONF-740921 from NTIS, Springfield, VA, 1976.

Sinclair, D., R. J. Countess, and G. S. Hoopes. Effect of relative humidity on the size of atmospheric aerosol particles. Atmos. Environ. 8:1111-1118, 1974.

Slinn, W. G. N. Dry Deposition and Resuspension of Aerosol Particles - A New Look at Lome Old Problems. In: Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants (1974). Englemann, R. J. ed. Energy Research and Development Administration symposium series, CONF-740921, 1976. pp. 1-40.

Slinn, W. G. N., L. Hasse, B. B. Hicks, A. W. Hogan, D. Lal, P. S. Liss, K. O. Munnich, G. A. Sehmel, and O. Vittori. Some aspects of the transfer of atmospheric trace constituents past the air-sea interface. Atmos. Environ. 12:2055-2087, 1978.

Smith, B. M., J. Wagman, and B. R. Fish. Interaction of airborne particles with gases. Environ. Sci. Technol. 9:558-562, 1969.

Smith, F. B., and G. H. Jeffrey. Airborne transport of sulfur dioxide from the United Kingdom. Atmos. Environ. 9:643-659, 1975.

Smith, F. B., and R. D. Hunt. Meteorological aspects of the transport of pollution over long distances. Atmos. Environ. 12:461-477, 1978.

Smith, T. B., D. L. Blumenthal, J. A. Anderson, and A. H. Vanderpol. Transport of $SO_2$ in Power Plant Plumes: Day and Night. Atmos. Environ. 12:605-611, 1978.

Spicer C. W., and P. M. Schumacher. Particulate nitrate: Laboratory and field studies of major sampling interferences. Atmos. Environ. 13:543-552, 1979.

Spicer, C. W. The Fate of Nitrogen Oxides in the Atmosphere. EPA 600/3-76-030, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1976.

Stelson A. W., S. K. Friedlander, and J. H. Seinfeld. A note on the equilibrium realtionship between ammonia and nitric acid and particulate ammonium nitrate. Atmos. Environ. 13:369-371, 1979.

Stevens, R. K., T. G. Dzubay, G. Russwurm, and D. Rickel. Sampling and analysis of atmospheric sulfates and related species. Atmos. Environ. 12:55-68, 1978.

Stevens, R. K., editor. Current Methods to Measure Atmosperhic Nitric Acid and Nitrate Artifacts. EPA-600/2-79-051, U.S. Environmental Protection Agency, Research Triangle Park, N.C. 99 pp. (1979).

Suck, S. H., E. C. Upchurch, and J. R. Brock. Dust transport in Maricopa County, Arizona. Atmos. Environ. 12:2265-2271, 1978.

Sykes, R. I., and L. Hatton. Computation of horizontal trajectory based on the surface geostrophic wind. Atmos. Environ. 10:925-934, 1976.

Szepesi, D. J. Transmission of sulfur dioxide on local, regional and continental scale. Atmos. Environ. 12:529-535, 1978.

Tang, I. N. Phase transformation and growth of aerosol particles composed of mixed salts. J. Aerosol Sci. 7:361-371, 1976.

Tang, I. N., and H. R. Munkelwitz. Aerosol growth studies. III. Ammonium bisulfate aerosol in a moist atmosphere. J. Aerosol Sci. 8:321-330, 1977.

Tang, I. N. On the Equilibrium Partial Pressures of Nitric Acid and Ammonia in the Atmosphere. Atmos. Environ. (accepted for publication) 1980.

Tartarelli, R., P. Davine, F. Morelli, and P. Corsi. Interactions between $SO_2$ and carbonaceous particulates. Atmos. Environ. 12:289-293, 1978.

Titoff, A. Beitrage zur Kaentnis der negativen Katalyze im homogenen System. Z. Phys. Chem. 45:641-683, 1903.

Tong, E. Y., G. M. Hidy, T. F. Lavery, and F. Berlandi. Regional and local aspects of atmospheric sulfates in the northeast quadrant of the United States. In: Proceedings Third Symposium of Turbulence, Diffusion and Air Quality, American Meteorological Society, 1976.

Urone, P., H. Lutsep, C. M. Noyes, and J. F. Parcher. Static studies of sulfur dioxide reactions in air. Environ. Sci. Technol. 8:611-618, 1968.

Vukovich, F. M., W. D. Bach, Jr., B. W. Cressman, and W. J. King. On the relationships between high ozone in the rural boundary layer and high pressure systems. Atmos. Environ. 11:967-983, 1977.

Wagman, J., R. E. Lee, and C. J. Axt. Influence of Some Atmospheric Variables on the Concentration and Particle Size Distribution of Sulfate in Urban Air. Atmospheric Environ 1:479-489, 1967.

Whitby, K. T. The physical characteristics of sulfur aerosols. Atmos. Environ. 12:135-159, 1978.

Whitby, K. T. and G. M. Sverdrup. California Aerosols: Their Physical and Chemical Characteristics. In: The Characters and Origin of Smog Aerosols. G. M. Hidy et al., eds. John Wiley, New York, 1980.

Whitby, K. T., R. B. Hausar, and B. Y. H. Lui. The Aerosol Size Distribution of Los Angeles Smog. J. Colloid Interfrace Sci. 39:177-204, 1972.

Whitby, K. T., R. E. Charlson, W. E. Wilson, and R. K. Stevens. The Size of Suspended Particle Matter in Air. Science 183:1098-1199, 1974.

White, W. H., and P. T. Roberts. On the nature and origins of visibility-reducing aerosols in the Los Angeles air basin. In: The Character and Origins of Smog Aerosols. Advances in Environ. Sci. and Technol. 10:715-753, 1980.

White, W. H., J. A. Anderson, D. L. Blumenthal, R. B. Husar, N. V. Gillani, J. D. Husar, and W. E. Wilson. Formation and transport of secondary air pollutants: ozone and aerosols in the St. Louis urban plume. Science 194:187-189, 1976.

Wilson, W. E. Sulfates in the atmosphere: a progress report on Project MISTT. Atmos. Environ. 12:537-548, 1978.

Wilson, W. E. Transformation during transport: a state of the art survey of the conversion of $SO_2$ to sulfate. Presented at WMO Symposium, Sofia, Bulgaria, Oct. 1-5, 1979.

Wilson, W. E., D. F. Miller, A. Levy, and R. K. Stone. The effect of Fuel Composition on Atmospheric Aerosol Due to Auto Exhaust. J. Air Pollut. Control Assoc. 23:949-956, 1973.

Wilson, W. E., et al., 1979.

Wilson, W. E., L. L. Spiller, T. G. Ellestad, P. L. J. Lamothe, T. G. Dzuby, R. K. Stevens, E. S. Macias, R. A. Fletcher, J. D. Jusar, R. B. Husar, K. T. Whitby, D. B. Kittelson, and B. K. Cantrell. General Motors Sulfate Dispersion Experiment: Summary of EPA Measurements. J. Air Pollut. Control Assoc. 27:46-51, 1977.

Wilson, W. E., R. J. Charlson, R. B. Hasar, K. T. Whitby, and D. L. Blumenthal. Sulfates in the atmosphere. Presented at the 69th Annual Meeting of Air Pollution Control Assoc., Portland, OR, June 27-July 1, 1976.

Winchester, J. W., R. J. Ferek, D. R. Lawson, J. O. Pilotte, M. A. Thiemens, and L. E. Wagon. Comparison of aerosol sulfur and crystal element concentrations in particle size fractions from continental United States locations. Submitted for publication, 1979.

Winkler, P. The growth of atmospheric aerosol particles as a function of the relative humidity. II. An improved concept of mixed nuclei. Aerosol Sci. 4:373-387, 1973.

Winkler, P., and C. Junge. The growth of atmospheric aerosol particles as a function of the relative humidity. I. Methods and measurements of different locations. J. Rech. Atmos. 6:617-638, 1972.

Wolff, G. T., P. J. Lioy, R. E. Meyers, and R. T. Cederwall. An investigation of long-range transport of ozone across the Midwestern and Eastern United States. Atmos. Environ. 11:797-802, 1977.

Charlson, R. J., A. H. Vanderpol, D. S. Covert, A. P. Waggoner, and N. C. Ahlquist. $H_2SO_4/(NH_4)_2SO_4$ background aerosol: optical detection in the St. Louis region. Atmos. Environ. 8:1257-1267, 1974.

Charlson, R. J., D. S. Covert, T. V. Larson, and A. P. Waggoner. Chemical properties of tropospheric sulfur aerosols. Atmos. Environ. 12:39-53, 1978.

Chun, K. C., and J. E. Quon. Capacity of ferric oxide particles to oxidize sulfur dioxide in air. Environ. Sci. Technol. 7:532-538, 1973.

Chung, Y. C. The distribution of atmospheric sulfates in Canada and its relationship to long range transport of air pollutants. Atmos. Environ. 12:1471-1480, 1978.

Clark, W. E., D. A. Landis, and A. B. Harker. Measurements of the photochemical production of aerosols in ambient air near a freeway for a range of $SO_2$ concentrations. Atmos. Environ. 10:637-644, 1976.

Clark, W. E. and K. T. Whitby. Concentration and size distribution measurement of atmospheric aerosols and a test of the theory of self-preserving size distributions. J. Atmos. Sci. 24:677-687, 1967.

Coordinating Research Council, 1968.

Coughanowr, D. R., and F. E. Krause. The reaction of $SO_2$ and $O_2$ in aqueous solution of $MnSO_4$. Ind. Eng. Fund. 4:61-66, 1965.

Covert, D. W. A study of the relationship of chemical composition and humidity to light scattering by aerosols. Ph.D. Thesis, University of Washington, Seattle, 1974.

Cronn D. R., R. J. Charlson, R. L. Knights, A. L. Crittenden, and B. R. Appel. A survey of the molecular nature of primary and secondary components of particles in urban air by high-resolution mass spectrometry. Atmos. Environ. 11:929-937, 1977.

Demerjian K., J. A. Kerr, and J. Calvert. Mechanism of photochemical smog formation. In: Advances in Environmental Science and Technology, Vol. 4. (Edited by J. N. Pitts, and R. J. Metcalf). John Wiley, NY, 1974.

Draftz, R. G., and K. Severin. Microscopical Analysis of Aerosols Collected in St. Louis, Missouri. EPA-600/3-80-27, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1980.

Draftz, R. G. Aerosol Source Characterization Study in Miami, Florida: Microscopical Analysis. EPA-600/3-79-097, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1979.

Durham, et al., 1979.

Durst, C. S., A. F. Crossley, and N. E. Davis. Horizontal diffusion in the atmosphere as determined by geostrophic trajectories. J. Fluid Mech. 6:401-422, 1959.

Dzubay, T. G. Chemical element balance method applied to dichotomous sampler data. In: Proceedings of Symposium on Aerosols, Anthropogenic and Natural Sources and Transport, Annals of the New York Acad. of Sci., New York, 1979.

Easter, R. C., D. F. Miller, and W. E. Wilson. Kinetic simulation of the diurnal rates of $SO_2$ oxidation in a power plant plume. Atmos. Environ. vol. 14, 1980.

Eatough, D. J., et al., 1979.

Eatough, D. J., T. Major, J. Ryder, M. Hill, N. F. Mangelson, N. L. Eatough, L. D. Hansen, R. G. Meisenheimer, and J. W. Fischer. The formation and stability of sulfite species in aerosols. Atmos. Environ. 12:262-271, 1978.

Eliassen, A. The Trajectory Model: A Technical Description. Norwegian Institute for Air Research, Kjeller, Norway, 1976.

Eliassen, A., and J. Saltbones. Decay and transformation rates of $SO_2$ as estimated from emission data, trajectories and measured air concentrations. Atmos. Environ. 12:489-501, 1975.

Erickson, R. E., L. M. Yates, R. L. Clark, and C. M. McEwen. The reaction of sulfur dioxide with ozone in water and its possible atmospheric significance. Atmos. Environ. 11:813-817, 1977.

Ferber, G. J., K. Telegada, J. L. Heffter, and A. E. Smith. Air concentrations of krypton-85 in the mid-west United States during January-May, 1974. Atmos. Environ. 10:379-385, 1976.

Fisher, B. E. A. The calculation of long term sulphur deposition in Europe. Atmos. Environ. 12:489-501, 1978.

Forrest and Newman, 1977.

Fowler, D., and M. H. Unsworth. Dry deposition of sulfur dioxide on wheat. Nature 249:389-290, 1974.

Friedlander, S. K. A review of the dynamics of sulfate containing aerosols. Atmos. Environ. 12:187-195, 1978.

Friedlander, S. K. Chemical element balances and identification of air pollution sources. Environ. Sci. Technol. 7:235-240, 1973.

Gage, S. J., L. F. Smith, P. M. Cukor, and B. L. Nieman. Long-range transport of $SO_x/MSO_4$ from the U.S. Environmental Protection Agency/Teknekron integrated technology assessment of electric utility energy systems. In: Proceedings of the International Symposium on Sulfur in the Atmosphere (ISSA), Dubrovnik, Yugoslavia, 1977.

Galvin, P. J., P. J. Samson, P. E. Coffey, and D. Ramano. Transport of sulfate in New York state. Environ. Sci. Technol. 12:580-584, 1978.

Garland, J. A. Dry and wet removal of sulphur from the atmosphere. Atmos. Environ. 12:349-362, 1978.

Gartrell, G., Jr., and S. K. Friedlander. Relating particulate pollution to sources: the 1972 California aerosol characterization study. Atmos. Environ. 9:279-299, 1975.

Gelbard F., and J. H. Seinfeld. The general dynamic equation for areosols--Theory and application to aerosol formation and growth. J. Colloid Interface Sci. 68:363- , 1979.

Gillani, N. V., R. B. Husar, J. D. Husar, D. E. Patterson, and W. E. Wilson. Project MISTT: kinetics of particulate sulfur formation in a power plant plume out to 300 km. Atmos. Environ. 12:589-598, 1978.

Graf, J., R. H. Snow, and R. G. Draftz. Aerosol Sampling and Analysis - Phoenix, Arizona. EPA-600/3-77-015, U.S. Environmental Protection Agency, Research Triangle Park, 1977.

Graham, R. Rate constants for the reaction of $HO_2$ with $HO_2$,$SO_2$,CO,$N_2O$, trans-2-butene, and 2,3-dimethyl-2-butene at 300°K. J. Phys. Chem., vol. 83, 1979.

Grosjean D. Chapters, Aerosols. In: Ozone and Other Photochemical Oxidants. National Academy of Sciences, Washington, DC, 1977. pp. 45-125.

Grosjean D., and S. K. Friedlander. Gas-particle distribution factors for organic and other pollutants in the Los Angeles atmosphere. J. Air Pollut. Control Assoc. 25:1038:1044, 1975.

Haagenson, P. L., and A. L. Morris. Forecasting the behavior of the St. Louis, Missouri pollutant plume. J. Appl. Meteoro. 13:901-909, 1974.

Hales, J. M. Wet removal of sulfur compounds from the atmosphere. Atmos. Environ. 12:389-399, 1978.

Hall, F. P., Jr., C. E. Duchon, L. G. Lee, and R. R. Hagan. Long-range transport of air pollution, a case study, August 1970. Mon. Weather Rev. 101:404, 1973.

Harker A. B., L. W. Richards, and W. E. Clark. The effect of atmosperhic $SO_2$ photochemistry upon observed nitrate concentrations in aerosols. Atmos. Environ. 11:87-91, 1977.

Harker, A. B., et al., 1979.

Haury, G., S. Jordan, and C. Hofmann. Experimental investigation of aerosol-catalyzed oxidation of $SO_2$ under atmospheric conditions. Atmos. Environ. 12:281-287, 1978.

Hegg, D. A., and P. V. Hobbs. Oxidation of sulfur dioxide in aqueous systems with particular reference to the atmosphere. Atmos. Environ. 12:241-253, 1978.

Heisler, N. L., S. K. Friedlander, and R. B. Husar. Atmos. Environ. 7:633, 1973.

Hess, G. D., and B. B. Hicks. A study of PBL structure: the Sangamon experiment of 1975. Argonne National Laboratory Report ANL 75-60, Part IV, 1975. pp. 1-4.

Hidy G. M., and J. R. Brock. The Dynamics of Aerocolloidal Systems. Pergamon Press, NY, 1970.

Hidy, G. M. Summary of the California aerosol characterization experiment. J. Air Pollut. Control Assoc. 25:1106-1114, 1975.

Hidy, G. M., ed. Aerosols and Atmospheric Chemistry. Kendall Award Symposium. Academic Press Inc., New York. 1972.

Hidy, G. M., P. K. Mueller, and E. Y. Tong. Spatial and temporal distributions of airborne sulfate in parts of the United States. Atmos. Environ. 12: 735-752, 1978.

Hill, F. B., and R. F. Adamowicz. A model for rain composition and the washout of sulfur dioxide. Atmos. Environ. 11:917-927, 1977.

Hoather, R. C., and C. F. Goodeve. The oxidation of sulphmous acid. III. Catalysis of mangenous sulphate. Trans. Faraday Soc. 30:1149-1156, 1934.

Hoecker, W. H. Accuracy of various techniques for estimating boundary layer trajectories. J. Appl. Meteorol. 16:374-383, 1977.

Holt, B. D., P. T. Cunningham, and R. Kumar. Use of oxygen isotopy in the study of transformations of $SO_2$ to sulfates in the atmosphere. Presented at WMO Symposium, Sofia, Bulgaria, Oct. 1-5, 1979.

Holzworth, G. C. Mixing depths, wind speeds and air pollution potential for selected locations in the United States. J. Appl. Meteorol. 6:1039-1044, 1967.

Holzworth, G. C. Mixing Heights, Wind Speeds and Potential for Urban Air Pollution Throughout Contiguous United States. Environmental Protection Agency, Office of Air Programs Publication No. AP-101. U.S. Environmental Protection Agency, Research Triangle Park, NC, 1972. p. 35.

Hosler, C. R. Low level inversion frequency in the contiguous United States. Mon. Weather Rev. 89:319-339, 1961.

Husar, R. B., and K. T. Whitby. Growth mechanisms and size spectra of photochemical aerosols. Environ. Sci. Technol. 7:214, 1973.

Husar, R. B., D. E. Patterson, C. C. Paley, and N. V. Gillani. Ozone in hazy air masses. In: Proceedings of the International Conference on Photochemical Oxidants and Its Control, Research Triangle Park, NC, Sept. 12-20, 1976b.

Husar, R. B., D. E. Patterson, J. D. Husar, N. V. Gillani, and W. E. Wilson. Sulfur budget of a power plant plume. Atmos. Environ. 12:549-568, 1978.

Husar, R. B., et al., 1976.

Husar, R. B., N. V. Gillani, J. D. Husar, C. C. Paley, and P. N. Turcu. Long range transport of pollutants observed through visibility contour maps, weather maps, and trajectory analysis. Presented at the Third Symposium on Atmospheric Turbulence, Diffusion, and Air Quality, Raleigh, NC, Oct. 19-22, 1976a.

International Symposium on Sulfur in the Atmosphere (ISSA) Proceedings. Atmos. Environ. 12:1-769, 1978.

Isaksen, I. S. A., E. Hesstved, and O. Hov. A chemical model for urban plumes test for ozone and particulate sulfur formation in St. Louis urban plume. Atmos. Environ. 12:599-604, 1978.

Johnson, W. B., D. E. Wolf, and R. L. Mancuso. Long term regional patterns and transfrontier exchanges of airborne sulfur pollution in Europe. Atmos. Environ. 12:511-527, 1978.

Judeikis, H. S. The Role of Solid-Gas Interactions in Air Pollution. EPA-650/3-74-007, U.S. Environmental Protection Agency, August 1974.

Judeikis, H. S., and S. Siegel. Particle-catalyzed oxidation of atmospheric pollutants. Atmos. Environ. 7:619-631, 1973.

Junge, C. E. Air Chemistry and Radioactivity. Academic Press Inc., New York, 1963.

Junge, C. E. Die Konstitution der atmospheuschen Aerosols. Ann. Meteorol. Hamburg 5:1-55, 1952.

Junge, C. E. Die rolle der aerosole und der gasformingen beimengungen der luft in spurenstoffhaushalt der troposphere. Tellus 5:1-26, 1953.

Kapustin, V. N., Yu. S. Lynbortseva, and G. V. Rozenberg. Variability of aerosols under the influence of cloud modulation of the radiation field. Izv. Atmos. Oceanic Phys. 10:1327-1331, 1974.

Karraker, D. G. The kinetics of the reaction between sulphurous acid and ferric ion. J. Phys. Chem. 67:871-874, 1963.

Komp, M. J., and A. H. Auer, Jr. Visibility reduction and accompanying aerosol evolution downwind of St. Louis. J. Appl. Meteorol. 17:1357-1367, 1978.

Korshover, J. Climatology of stagnating anticyclones east of the Rocky Mountains 1936-1965. Public Health Service Publication No. 999-AP-34, Cincinnati, OH, 1967. 15 pp.

Kuhlman, M. R., D. L. Fox, and H. E. Jeffries. The effect of CO on sulfate aerosol formation. Atmos. Environ. 12:2415-2423, 1978.

Latimer, D. A., R. W. Bergstrom, S. R. Hayes, M. K. Liw, J. H. Seinfeld, G. Z. Whitten, M. A. Wojcik, and M. J. Hillyar. The Development of mathematical models for the prediction of anthropogenic visibility impairment. EPA-450/3-78-110 a, U.S. Environmental Protection Agency, 1978.

Lee, R. E. Jr. The Size of Suspended Particulate Matter in Air. Science 178:567-575, 1972.

Lewis, C. W., and E. S. Macias, 1979.

Lewis, C. W., and E. S. Macias. Composition of size fractioned aerosol in Charleston, West Virginia. Submitted for publication, Atmos. Environ., 1980.

Liberti, A., D. Brocco, and M. Possanzini. Adsorption and oxidation of sulfur dioxide on particles. Atmos. Environ. 12:255-261, 1978.

Lipeles M., C. S. Burton, H. H. Wang, E. P. Parry, and G. M. Hidy. Mechanisms of Formation and Composition of Photochemical Aerosols. EPA-650/73-036. Thousand Oaks, CA: Rockwell International Science Center, 1973. 98 pp.

Loo, B. W., W. R. French, R. C. Gatti, F. S. Goulding, J. M. Jaklevic, J. Llacer, and A. C. Thompson. Large-scale measurement of airborne particulate sulfur. Atmos. Environ. 12:759-771, 1978.

Low, R. D. H., 1971.

Lyons, W. A., and R. B. Husar. SMS/GOES visible images detect a synoptic-scale air pollution episode. Mon. Weather Rev. 104:1623-1626, 1976.

MacCracken, M. C. MAP3S: an investigation of atmospheric energy related pollutants in the northeastern United States. Atmos. Environ. 12:649-659, 1978.

Macias, E. S., D. L. Blumenthal, J. A. Anderson, and B. K. Cantrell. Characterization of Visibility Reducing Aerosols in the Southwestern United States. Interim report on Project VISTTA. MRI Report 78 1R, 15-85, 1979.

McNelis, D. N., L. A. Ripperton, W. E. Wilson, P. L. Hanst, and B. W. Gay. Gas Phase Reactions of Ozone and Olifin in the Presence of Sulfur Dioxide. In: Removal of Trace Contaminants from Air, B.R. Dietz, ed., A.C.S. Symposium Series 17:187-200, 1975.

McMurry, P. H., and S. K. Friedlander. Aerosol formation in reacting gases: relation of surface area to rate of gas-to-particle conversion. J. Colloid Interface Sci. 64:248-257, 1978.

Meyers, R. E., R. T. Cederwall, W. D. Ohmstede, and J. Kampe. Transport and diffusion using a diagnostic meso-scale model employing mass and total energy conservation constraints. In: Proceedings of the Third Symposium on Atmospheric Turbulence, Diffusion and Air Quality, American Meteorological Society, Boston, MA, 1977. pp. 90-97.

Middleton P. B., and J. R. Brock. Simulation of aerosol kinetics. J. Colloid Interface Sci. 54:249- , 1976.

Middleton P. B, S. H. Suck, and J. R. Brock. On the multimodality of density functions of pollutant aerosols. Atmos. Environ. 11:251-255, 1977.

Middleton, P., and C. S. Kiang. Experimental and theoretical examination of the formation of sulfuric acid particles. Atmos. Environ. 12:179-185, 1978.

Miller, D. F. Precursor effects on $SO_2$ oxidation. Atmos. Environ. 12:273-280, 1978.

Miller, F. J., D. E. Gradner, J. A. Grahm, R. E. Lu, Jr., W. E. Wilson, and J. D. Bachman. Size Considerations for Establishing a Standard for Inhalable Particles. J. Air Pollut. Control Assoc. 29:610-615, 1979.

Miller, M. S., S. K. Friedlander, and G. M. Hidy. A chemical element balance for the Pasadena aerosol. J. Colloid Interface Sci. 39:165-176, 1972.

Mueller, P. K., et al., 1979.

Newman, J. E., M. D. Abel, P. R. Harrison, and K. J. Yost. Wind as Related to Critical Flushing Speed Versus Reflotation Speed by High-Volume Sampler Particulate Loading, 466-496. In: Atmospheric-Surface Exchange of Particulate and Gaseous Pollutants (1974). Englemann, R. J., ed. Energy Research and Development Administration symposium series, CONF-740921, 1976.

Neytzell-de Wilde, F. G., and L. Taverner. Experiments relating to the possible production of an oxidizing acid leach liquor by auto-oxidation for the extraction of uranium. In: Proceedings of the Second U.N. Conference Peaceful Uses of Atomic Energy, vol. 3, 1958. pp. 303-317.

Novakov, 1979.

OECD. The OECD Program on Long-Range Transport of Air Pollutants--Measurements and Findings. Organization for Economic Cooperation and Development, Paris, 1977.

Orel A. E., and J. H. Seinfeld. Nitrate formation in atmospheric aerosols. Environ. Sci. Technol. 11:1000-1007, 1977.

Orr, C., F. K. Hurd, and W. J. Corbert. Aerosol size and relative humidity. J. Colloid Interface Sci. 13:472-482, 1958.

Ottar, B. Monitoring long-range transport of air pollutants: the OECD study. Ambio 6:203-206, 1976.

Overton, J. H., V. P. Aneja, and J. L. Durham. Production of sulfate in rain and raindrops in polluted atmospheres. Atmos. Environ. 13:355-367, 1979.

Pack, D. H., G. J. Ferber, J. L. Hefter, K. Telegadas, J. K. Angell, W. H. Hoecker, and L. Machta. Meteorology of long-range transport. Atmos. Environ. 12:425-444, 1978.

Penkett, S. A., B. M. R. Jones, K. A. Brice, and A. E. J. Eggleton. The importance of atmospheric ozone and hydrogen peroxide in oxidizing sulphur dioxide in cloud and rainwater. Atmos. Environ. 13:123-137, 1979.

Perhac, R. M. Sulfate regional experiment in northeastern United States: the 'SURE' program. Atmos. Environ. 12:641-647, 1978.

Pierson and Russell, 1979.

Roberts, P. T., and S. K. Friedlander. Photochemical aerosol formation--$SO_2$, 1-heptene, and $NO_x$ in ambient air. Environ. Sci. Technol. 10:573, 1976.

Rodhe, H. Budgets and turn-over times of atmospheric sulfur compounds. Atmos. Environ. 12:671-680, 1978.

Rodhe, H., C. Persson, and O. Akesson. An investigation into regional transport of soot and sulfate aerosols. Atmos. Environ. 6:675-693, 1972.

Ross, D. S. Comments on Arel and Seinfeld. Environ. Sci. Technol. 11:1000, 1977; 12:726, 1978.

Samson, P. J. Ensemble trajectory analysis of summertime sulfate concentrations in New York. Atmos. Environ. 12:1889-1893, 1978.

Samson, P. J., and K. W. Ragland. Ozone and visibility reduction in the Midwest: evidence for large scale transport. J. Appl. Meteorol. 16:1101-1106, 1977.

Schuetzle D., D. Cronn, A. L. Crittenden, and R. J. Charlson. Molecular composition of secondary aerosol and its possible origin. Environ. Sci. Technol. 9:838-845, 1975.

Schurmeier, 1980.

Schwartz W. Chemical Characterization of Model Aerosols. EPA-650/3-74-011. Columbus, Ohio: Battelle Memorial Institute, 1974. pp. 124

Sehmel, G. A., and W. H. Hodgson. Particle dry deposition velocities. In: Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants. 1974 Proceedings of ERDA Symposium Series 38, Richland, WA, Publication No. CONF-740921 from NTIS, Springfield, VA, 1976.

Sinclair, D., R. J. Countess, and G. S. Hoopes. Effect of relative humidity on the size of atmospheric aerosol particles. Atmos. Environ. 8:1111-1118, 1974.

Slinn, W. G. N., 1974.

Slinn, W. G. N. Dry Deposition and Resuspension of Aerosol Particles - A New Look at Lome Old Problems. In: Atmosphere-Sufrace Exchange of Particulate and Gaseous Pollutants (1974). Englemann, R. J. ed. Energy Research and Development Administration symposium series, CONF-740921, 1976.

Slinn, W. G. N., L. Hasse, B. B. Hicks, A. W. Hogan, D. Lal, P. S. Liss, K. O. Munnich, G. A. Sehmel, and O. Vittori. Some aspects of the transfer of atmospheric trace constituents past the air-sea interface. Atmos. Environ. 12:2055-2087, 1978.

Slinn, W. G., et al., 1979.

Smith, B. M., J. Wagman, and B. R. Fish. Interaction of airborne particles with gases. Environ. Sci. Technol. 9:558-562, 1969.

Smith, F. B., and G. H. Jeffrey. Airborne transport of sulfur dioxide from the United Kingdom. Atmos. Environ. 9:643-659, 1975.

Smith, F. B., and R. D. Hunt. Meteorological aspects of the transport of pollution over long distances. Atmos. Environ. 12:461-477, 1978.

Smith, T. B., D. L. Blumenthal, J. A. Anderson, and A. H. Vanderpol. Transport of $SO_2$ in Power Plant Plumes: Day and Night. Atmos. Environ. 12:605-611, 1978.

Spicer C. W., and P. M. Schumacher. Particulate nitrate: Laboratory and field studies of major sampling interferences. Atmos. Environ. 13:543-552, 1979.

Spicer, C. W. The Fate of Nitrogen Oxides in the Atmosphere. EPA 600/3-76-030, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1976.

Stelson A. W., S. K. Friedlander, and J. H. Seinfeld. A note on the equilibrium realtionship between ammonia and nitric acid and particulate ammonium nitrate. Atmos. Environ. 13:369-371, 1979.

Stevens, R. K., T. G. Dzubay, G. Russwurm, and D. Rickel. Sampling and analysis of atmospheric sulfates and related species. Atmos. Environ. 12:55-68, 1978.

Stevens, R. K., 1979.

Suck, S. H., E. C. Upchurch, and J. R. Brock. Dust transport in Maricopa County, Arizona. Atmos. Environ. 12:2265- , 1978.

Sykes, R. I., and L. Hatton. Computation of horizontal trajectory based on the surface geostrophic wind. Atmos. Environ. 10:925-934, 1976.

Szepesi, D. J. Transmission of sulfur dioxide on local, regional and continental scale. Atmos. Environ. 12:529-535, 1978.

Tang, I. N. Phase transformation and growth of aerosol particles composed of mixed salts. J. Aerosol Sci. 7:361-371, 1976.

Tang, I. N., and H. R. Munkelwitz. Aerosol growth studies. III. Ammonium bisulfate aerosol in a moist atmosphere. J. Aerosol Sci. 8:321-330, 1977.

Tang, I. N., 1979.

Tartarelli, R., P. Davine, F. Morelli, and P. Corsi. Interactions between $SO_2$ and carbonaceous particulates. Atmos. Environ. 12:289-293, 1978.

Titoff, A. Beitrage zur Kaentnis der negativen Katalyze im homogenen System. Z. Phys. Chem. 45:641-683, 1903.

Tong, E. Y., G. M. Hidy, T. F. Lavery, and F. Berlandi. Regional and local aspects of atmospheric sulfates in the northeast quadrant of the United States. In: Proceedings Third Symposium of Turbulence, Diffusion and Air Quality, American Meteorological Society, 1976.

Urone, P., H. Lutsep, C. M. Noyes, and J. F. Parcher. Static studies of sulfur dioxide reactions in air. Environ. Sci. Technol. 8:611-618, 1968.

Vukovich, F. M., W. D. Bach, Jr., B. W. Cressman, and W. J. King. On the relationships between high ozone in the rural boundary layer and high pressure systems. Atmos. Environ. 11:967-983, 1977.

Wagman, J., R. E. Lee, and C. J. Axt. Influence of Some Atmospheric Variables on the Concentration and Particle Size Distribution of Sulfate in Urban Air. Atmospheric Environ 1:479-489, 1967.

Whitby, K. T. The physical characteristics of sulfur aerosols. Atmos. Environ. 12:135-159, 1978.

Whitby, K. T. and G. M. Sverdrup. California Aerosols: Their Physical and Chemical Characteristics. In: The Characters and Origin of Smog Aerosols. G. M. Hidy et al., eds. John Wiley, New York, 1980.

Whitby, K. T., R. B. Hausar, and B. Y. H. Lui. The Aerosol Size Distribution of Los Angeles Smog. J. Colloid Interfrace Sci. 39:177-204, 1972.

Whitby, K. T., R. E. Charlson, W. E. Wilson, and R. K. Stevens. The Size of Suspended Particle Matter in Air. Science 183:1098-1199, 1974.

White, W. H., and P. T. Roberts, 1975.

White, W. H., J. A. Anderson, D. L. Blumenthal, R. B. Husar, N. V. Gillani, J. D. Husar, and W. E. Wilson. Formation and transport of secondary air pollutants: ozone and aerosols in the St. Louis urban plume. Science 194:187-189, 1976.

Wilson, W. E. Sulfates in the atmosphere: a progress report on Project MISTT. Atmos. Environ. 12:537-548, 1978.

Wilson, W. E. Transformation during transport: a state of the art survey of the conversion of $SO_2$ to sulfate. Presented at WMO Symposium, Sofia, Bulgaria, Oct. 1-5, 1979.

Wilson, W. E., D. F. Miller, A. Levy, and R. K. Stone. The effect of Fuel Composition on Atmospheric Aerosol Due to Auto Exhaust. J. Air Pollut. Control Assoc. 23:949-956, 1973.

Wilson, W. E., et al., 1979.

Wilson, W. E., Jr., D. F. Miller, A. Levy, and R. K. Stone. J. Air Pollut. Control Assoc. 23:949, 1973.

Wilson, W. E., L. L. Spiller, T. G. Ellestad, P. L. J. Lamothe, T. G. Dzuby, R. K. Stevens, E. S. Macias, R. A. Fletcher, J. D. Jusar, R. B. Husar, K. T. Whitby, D. B. Kittelson, and B. K. Cantrell. General Motors Sulfate Dispersion Experiment: Summary of EPA Measurements. J. Air Pollut. Control Assoc. 27:46-51, 1977.

Wilson, W. E., R. J. Charlson, R. B. Hasar, K. T. Whitby, and D. L. Blumenthal Sulfates in the atmosphere. Presented at the 69th Annual Meeting of Air Pollution Control Assoc., Portland, OR, June 27-July 1, 1976.

Winchester, J. W., R. J. Ferek, D. R. Lawson, J. O. Pilotte, M. A. Thiemens, and L. E. Wagon. Comparison of aerosol sulfur and crystal element concentrations in particle size fractions from continental United States locations. Submitted for publication, 1979.

Winkler, P. The growth of atmospheric aerosol particles as a function of the relative humidity. II. An improved concept of mixed nuclei. Aerosol Sci. 4:373-387, 1973.

Winkler, P., and C. Junge. The growth of atmospheric aerosol particles as a function of the relative humidity. I. Methods and measurements of different locations. J. Rech. Atmos. 6:617-638, 1972.

Wolff, G. T., P. J. Lioy, R. E. Meyers, and R. T. Cederwall. An investigation of long-range transport of ozone across the Midwestern and Eastern United States. Atmos. Environ. 11:797-802, 1977.

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## 6.8 STATUS OF SOURCE APPORTIONMENT RESEARCH

Federal, state, and local agencies generally use atmospheric dispersion models to provide guidelines in the control of particulate loadings in the atmosphere. These source oriented dispersion models based on emission inventories and meteorological parameters were developed to predict the impact of a particulate emission source on a receptor site.

An alternative to the predictive dispersion models to assist in air quality management is the application of receptor oriented models. The Chemical Element Balance (CEB) Model is one type of receptor model that has been widely used over the past ten years to measure the impact of particulate sources on air quality (1-3).

These CEB models assume that the elemental composition of ambient particles collected at a receptor site is a linear combination of the components of the particulate matter originating from various sources. In theory, knowledge of the elemental composition of the ambient air particles and the emissions of all important sources permits the solution of a set of simultaneous equations which will provide quantitatively the contributions of each source of the aerosol to a selected receptor.

In practice, the information is never as complete or reliable as desired, so the assumptions that go into the model must be simplified. Typically, rather than use all the emission data from each source, a set of marker elements is used to characterize a few prominent sources. The marker elements are normally those that are strongly associated with specified sources.

Examples are lead and bromine with motor vehicles, sodium with sea salt, and Vanadium or nickel with combustion of fuel oil.

Kowalczyk, et al.[4], Watson[5], and Dzubay[6] have reported results from CEB analysis on filters collected from networks of samples in the three cities, Washington, DC, Portland, OR, and St. Louis, MO, respectively. Watson and Dzubay analyzed aerosol that was fractionated into two size ranges to separate primary from secondary aerosols. Figure 1 is a figure from the work of Dzubay[6] which shows a comparison of the average mass concentration in the coarse fraction (particles >2.5 μm) and the components deduced in the chemical element balance. The corresponding fine fraction was mainly composed of sulfate.

These previous applications of CEB to source apportionment studies suffer from the following shortcomings (1) all major sources contributing to the ambient aerosols at the time of the study were not well characterized, (2) the computational methods used had not been verified nor their sensitivities to variations in input parameters established, and (3) ambient and source aerosol characterization was incomplete.

Whereas CEB methods apply knowledge about source characterization to a relatively small set of filters to derive a source contribution, multi variate analysis methods, such as factor analysis pattern recognition methods extract information about a source contribution on the basis of the variability of elements measured on large numbers of filters. In factor analysis, data on the concentrations of each element in each sample of the data set are manipulated to find groupings of variables (common factors) that best explain the variations of elemental composition from their average values.

Factor analysis has been applied by Hopke et al.[7] to a set of 18 elements in 90 samples from the Boston area. From this data set, 77.5 percent of the

variance could be accounted for by six common factors. From the composition of the factors, primary airborne particles could be attributed to several sources: soil mixed with emission from coal fired power plants, sea salt, combusion of fuel oil, auto emissions, and incineration of refuse. A sixth factor, with large loadings for only manganese and selenium could not be identified with a particular source.

Factor analysis has several advantages over CEB in that no a priori assumptions need to be made about either the number or composition of the sources. Thus, secondary particles that become associated with primary particulates between release and collection can be incorporated in the analysis. For example, Gaarenstroom[8] found that sulfate, ammonium, and nitrate ions in the ambient aerosol can be included in factor analysis.

The major weaknesses in factor analysis is that it requires a data set where there are large variation in the concentration of the elements from sample to sample. In addition, factor analysis can only provide information on the number of source contributing to a receptor but not the magnitude of their contribution.

The source of aerosols can also be determined by microscopic methods[9]. These methods have high resolving capabilities for sources with characteristic morphological features such as wood fiber, pollen,quartz, mica, and tire dust. To be quantitative, however, one must estimate the number of particles, their density and volume and must analyze enough particles to be representative of the total sample.

Microscopic methods can be divided into two categories: optical, which is generally limited to particles greater than 1 μm, and scanning electron microscopy (SEM) which is applicable to smaller particles.

Recently, Lee et al.[10] coupled an SEM with an energy dispersive x-ray fluorescence system and automated the instrument to scan and analyze a large number of particles. The system promises to extend the general applicability of microscopic methods.

Davis[11] has applied x-ray transmission and diffraction techniques to the analysis of hi-volume filters collected in Rapid City, SD. These analyses revealed that a majority of the aerosol pollution in Rapid City was a result of emissions from quarrying activities near the city. These x-ray diffraction techniques show promise of being able to quantitatively measure the source of aerosol pollution in variety of urban locations where reentrained dust is a major aerosol pollution problem.

REFERENCES FOR SECTION 6.8


1. Miller, M. S., S. K. Friedlander, and G. M. Hidy. A chemical element balance for Pasedena aerosol. J. Colloid Interface Sci. 39:165, 1972.

2. Friedlander, S. K. Chemical element balances and identification of air pollution sources. Environ. Sci. Technol. 7:235-240, 1973.

3. Gatz, D. F. Relative contributions of different sources of urban aerosols: Application of new estimation method to multiple sites in Chicago. Atmos. Environ. 9:1-18, 1975.

4. Kowalczyk, G. S., C. E. Choquette, and G. E. Gordon. Chemical element balances and identification of air pollution sources in Washington, D.C. Atmos. Environ. 12:1143-1153, 1978.

5. Watson, J. G., Jr. Chemical Element Balance Receptor Methodology for Assessing the Sources of Fine and Total Suspended Particulate Matter in Portland, Oregon. Ph.D. Thesis, Department of Chemistry, Oregon Graduate Center, Beaverton, OR, 1979.

6. Dzubay, T. G. Chemical element balance method applied to dichotomous sampler data. In: Proceedings of the Conference on Aerosol: Anthropogenic and Natural -- Sources and Transport. New York Academy of Sciences, in press, 1979.

7. Hopke, P. K., E. S. Gladney, G. E. Gordon, W. H. Zoller, and A. G. Jones. The use of multivariate analysis to identify sources of selected elements in the Boston urban aerosol. Atmos. Environ. 10:1015-1025, 1976.

8. Gaarenstroom, P. D., S. P. Perone, and J. L. Moyers. Application of pattern recognition and factor analysis for characterization of atmospheric particulate composition in the Southwest Desert atmosphere. Environ. Sci. Technol. 11:795-800, 1977.

9. Graf, J., R. H. Snow, and R. G. Draftz. Aerosol Sampling and Analysis - Phoenix, Arizona. EPA-600/2-77-015, U.S. Environmental Protection Agency, Washington, DC, 1977.

10. Lee, R. J., E. J. Fasiska, P. Jonocko, D. McFarland, and S. Penicala. Electron beam particle analysis. Ind. Res. Dev. 21:105, 1979.

11. Davis, B. L. Additional suggestions for x-ray quantitative analysis of high volume filter samples. Atmos. Environ. 12:1403-1406, 1978.

## GLOSSARY

$AaDO_2$: Alveolar-arterial difference or gradient of the partial pressure of oxygen. An overall measure of the efficiency of the lung as a gas exchanger. In healthy subjects, the gradient is 5 to 15 mm Hg (torr).

A/PR/8 virus: A type of virus capable of causing influenza in laboratory animals; also, A/PR/8/34.

Abscission: The process whereby leaves, leaflets, fruits, or other plant parts become detached from the plant.

Absorption coefficient: A quantity which characterizes the attenuation with distance of a beam of electromagnetic radiation (like light) in a substance.

Absorption spectrum: The spectrum that results after any radiation has passed through an absorbing substance.

Abstraction: Removal of some constituent of a substance or molecule.

Acetaldehyde: $CH_3CHO$; an intermediate in yeast fermentation of carbohydrate and in alcohol metabolism; also called acetic aldehyde, ethaldehyde, ethanal.

Acetate rayon: A staple or filament fiber made by extrusion of cellulose acetate. It is saponified by dilute alkali whereas viscose rayon remains unchanged.

Acetylcholine: A naturally-occurring substance in the body which can cause constriction of the bronchi in the lungs.

Acid: A substance that can donate hydrogen ions.

Acid dyes: A large group of synthetic coal tar-derived dyes which produce bright shades in a wide color range. Low cost and ease of application are features which make them the most widely used dyes for wool. Also used on nylon. The term acid dye is derived from their precipitation in an acid bath.

Acid mucopolysaccharide: A class of compounds composed of protein and polysaccharide. Mucopolysaccharides comprise much of the substance of connective tissue.

Acid phosphatase: An enzyme (EC 3.1.3.2) which catalyzes the disassociation of phosphate ($PO_4$) from a wide range of monoesters of orthophosphoric acid. Acid phosphatase is active in an acidic pH range.

Acid rain: Rain having a pH less than 5.6, the minimum expected from atmospheric $CO_2$.

Acrolein: $CH_2$=CHCHO; a volatile, flammable, oily liquid, giving off irritant vapor. Strong irritant of skin and mucuous membranes. Also called acrylic aldehyde, 2-propenal.

Acrylics (plastics): Plastics which are made from acrylic acid and are light in weight, have great breakage resistance, and a lack of odor and taste. Not resistant to scratching, burns, hot water, alcohol or cleaning fluids. Examples include Lucite and Plexiglass. Acrylics are thermoplastics and are softened by heat and hardened into definite shapes by cooling.

Acrylic fiber: The generic name of man-made fibers derived from acrylic resins (minimum of 85 percent acrylonitrite units).

Actinic: A term applied to wavelengths of light too small to affect one's sense of sight, such as ultraviolet.

Actinomycetes: Members of the genus Actinomyces; nonmotile, nonspore-forming, anaerobic bacteria, including both soil-dwelling saprophytes and disease-producing parasites.

Activation energy: The energy required to bring about a chemical reaction.

Acute respiratory disease: Respiratory infection, usually with rapid onset and of short duration.

Acute toxicity: Any poisonous effect produced by a single short-term exposure, that results in severe biological harm or death.

Acyl: Any organic radical or group that remains intact when an organic acid forms an ester.

Adenoma: An ordinarily benign neoplasm (tumor) of epithelial tissue; usually well circumscribed, tending to compress adjacent tissue rather than infiltrating or invading.

Adenosine monophosphate (AMP): A nucleotide found amoung the hydrolysis products of all nucleic acids; also called adenylic acid.

Adenosine triphosphatase (ATPase): An enzyme (EC 3.6.1.3) in muscle and elsewhere that catalyzes the release of the high-energy, terminal phosphate group of adenosine triphosphate.

Adrenalectomy: Removal of an adrenal gland. This gland is located near or upon the kidney and is the site of origin of a number of hormones.

Adsorption: Adhesion of a thin layer of molecules to a liquid or solid surface.

Advection: Horizontal flow of air at the surface or aloft; one of the means by which heat is transferred from one region of the earth to another.

Aerodynamic diameter: Expression of aerodynamic behavior of an irregularly shaped particle in terms of the diameter of a sphere of unit density having identical aerodynamic behavior to the particle in question.

Aerosol: Solid particles or liquid droplets which are dispersed or suspended in a gas.

Agglutination: The process by which suspended bacteria, cells or similar particles adhere and form into clumps.

Airborne pathogen: A disease-causing microorganism which travels in the air or on particles in the air.

Air pollutant: A substance present in the ambient atmosphere, resulting from the activity of man or from natural processes, which may cause damage to human health or welfare, the natural environment, or materials or objects.

Airway conductance: Inverse of airway resistance.

Airway resistance ($R_{aw}$): The pressure difference between the alveoli and the mouth required to produce an air flow of 1 liter per second.

Alanine aminotransferase: An enzyme (EC 2.6.1.2) transferring amino groups from L-alanine to 2-ketoglutarate. Also known as alanine transaminase.

Albumin: A type of simple, water-soluble protein widely distributed throughout animal tissues and fluids, particularly serum.

Aldehyde: An organic compound characterized by the group $-\overset{\overset{\displaystyle O}{\|}}{C}-H$.

Aldolase: An enzyme (EC 4.1.2.7) involved in metabolism of fructose which catalyzes the formation of two 3-carbon intermediates in the major pathway of carbohydrate metabolism.

Algal bloom: Sudden spurt in growth of algae which can affect water quality adversely.

Alkali: A salt of sodium or potassium capable of neutralizing acids.

Alkaline phosphatase: A phosphatase (EC 3.1.3.1) with an optimum pH of 8.6, present ubiquitously.

Allergen: A material that, as a result of coming into contact with appropriate tissues of an animal body, induces a state of sensitivity resulting in various reactions; generally associated with idiosyncratic hypersensitivities.

Alpha-hydroxybutyrate dehydrogenase: An enzyme (EC 1.1.1.30), present mainly in mitochondria, which catalyzes the conversion of hydroxybutyrate to acetoacetate in intermediate biochemical pathways.

Alpha rhythm: A rhythmic pulsation obtained in brain waves exhibited in the sleeping state of an individual.

Alveolar capillary membrane: Finest portion of alveolar capillaries, where gas transfer to and from blood takes place.

Alveolar macrophages (AM): Large, mononuclear, phagocytic cells found on the alveolar surface, responsible for the sterility of the lung.

Alveolar oxygen partial pressure ($PAO_2$): Partial pressure of oxygen in the air contained in the air sacs of the lungs.

Alveolar septa: The tissue between two adjacent pulmonary alveoli, consisting of a close-meshed capillary network covered on both surfaces by thin alveolar epithelial cells.

Alveolus: An air cell; a terminal, sac-like dilation in the lung. Gas exchange ($O_2/CO_2$) occurs here.

Ambient: The atmosphere to which the general population may be exposed. Construed here <u>not</u> to include atmospheric conditions indoors, or in the workplace.

Amine: A substance that may be derived from ammonia ($NH_3$) by the replacement of one, two or three of the hydrogen (H) atoms by hydrocarbons or other radicals (primary, secondary or tertiary amines, respectively).

Amino acids: Molecules consisting of a carboxyl group, a basic amino group, and a residue group attached to a central carbon atom. Serve as the building blocks of proteins.

p-Aminohippuric acid (PAH): A compound used to determine renal plasma flow.

Aminotriazole: A systemic herbicide, $C_2H_4N_4$, used in areas other than croplands, that also possesses some antithyroid activity; also called amitrole.

Ammonification: Decomposition with production of ammonia or ammonium compounds, esp. by the action of bacteria on nitrogenous organic matter.

Ammonium: Anion ($NH_4^+$) or radical ($NH_4$) derived from ammonia by combination with hydrogen. Present in rainwater, soils and many commercial fertilizers.

Amnestic: Pertains to immunologic memory: upon receiving a second dose of antigen, the host "remembers" the first dose and responds faster to the challenge.

Anaerobic: Living, active or occurring in the absence of free oxygen.

Anaerobic bacteria: A type of microscopic organism which can live in an environment not containing free oxygen.

Anaphylactic dyspneic attack: Difficulty in breathing associated with a systemic allergic response.

Anaphylaxis: A term commonly used to denote the immediate, transient kind of immunological (allergic) reaction characterized by contraction of smooth muscle and dilation of capillaries due to release of pharmacologically active substances.

Angiosperm: A plant having seeds enclosed in an ovary; a flowering plant.

Angina pectoris: Severe constricting pain in the chest which may be caused by depletion of oxygen delivery to the heart muscle; usually caused by coronary disease.

Angstrom Å: A unit ($10^{-8}$ cm) used in the measurement of the wavelength of light.

Anhydride: A compound resulting from removal of water from two molecules of a carboxylic (-COOH) acid. Also, may refer to those substances (anhydrous) which do not contain water in chemical combination.

Anion: A negatively charged atom or radical.

Anorexia: Diminished appetite; aversion to food.

Anoxic: Without or deprived of oxygen.

Anthraquinone: A yellow crystalline ketone, $C_{14}H_8O_2$, derived from anthracene and used in the manufacture of dyes.

Anthropogenic: Of, relating to or influenced by man. An anthropogenic source of pollution is one caused by man's actions.

Antibody: Any body or substance evoked by the stimulus of an antigen and which reacts specifically with antigen in some demonstrable way.

Antigen: A material such as a foreign protein that, as a result of coming in contact with appropriate tissues of an animal, after a latent period, induces a state of sensitivity and/or the production of antibody.

Antistatic agent: A chemical compound applied to fabrics to reduce or eliminate accumulation of static electricity.

Arachidonic acid: Long-chain fatty-acid which serves as a precursor of prostaglandins.

Area source: In air pollution, any small individual fuel combustion or other pollutant source; also, all such sources grouped over a specific area.

Aromatic: Belonging to that series of carbon-hydrogen compounds in which the carbon atoms form closed rings containing unsaturated bonds (as in benzene).

Arterial partial pressure of oxygen ($PaO_2$): Portion of total pressure of dissolved gases in arterial blood as measured directly from arterial blood.

Arterialized partial pressure of oxygen: The portion of total pressure of dissolved gases in arterial blood attributed to oxygen, as measured from non-arterial (e.g., ear-prick) blood.

Arteriosclerosis: Commonly called hardening of the arteries. A condition that exists when the walls of the blood vessels thicken and become infiltrated with excessive amounts of minerals and fatty materials.

Artifact: A spurious measurement produced by the sampling or analysis process.

Ascorbic acid: Vitamin C, a strong reducing agent with antioxidant properties.

Aspartate transaminase: Also known as aspartate aminotransferase (EC 2.6.1.1). An enzyme catalyzing the transfer of an amine group from glutamic acid to oxaloacetic, forming aspartic acid in the process. Serum level of the enzyme is increased in myocardial infarction and in diseases involving destruction of liver cells.

Asphyxia: Impaired exchange of oxygen and carbon dioxide, excess of carbon dioxide and/or lack of oxygen, usually caused by ventilatory problems.

Asthma: A term currently used in the context of bronchial asthma in which there is widespread narrowing of the airways of the lung. It may be aggravated by inhalation of pollutants and lead to "wheezing" and shortness of breath.

Asymptomatic: Presenting no subjective evidence of disease.

Atmosphere: The body of air surrounding the earth. Also, a measure of pressure (atm.) equal to the pressure of air at sea level, 14.7 pounds per square inch.

Atmospheric deposition: Removal of pollutants from the atmosphere onto land, vegetation, water bodies or other objects, by absorption, sedimentation, Brownian diffusion, impaction, or precipitation in rain.

Atomic absorption spectrometry: A measurement method based on the absorption of radiant energy by gaseous ground-state atoms. The amount of absorption depends on the population of the ground state which is related to the concentration of the sample being analyzed.

Atropine: A poisonous white crystalline alkaloid, $C_{17}H_{23}NO_3$, from belladonna and related plants, used to relieve spasms and to dilate the pupil of the eye.

Autocorrelation: Statistical interdependence of variables being analyzed; produces problems, for example, when observations may be related to previous measurements or other conditions.

Autoimmune disease: A condition in which antibodies are produced against the subject's own tissues.

Autologous: A term referring to cellular elements, such as red blood cells and alveolar macrophage, from the same organism; also, something natually and normally ocurring in some part of the body.

Autotrophic: A term applied to those microorganisms which are able to maintain life without an exogenous organic supply of energy, or which only need carbon dioxide or carbonates and simple inorganic nitrogen.

Autotrophic bacteria: A class of microorganisms which require only carbon dioxide or carbonates and a simple inorganic nitrogen compound for carrying on life processes.

Auxin: An organic substance that causes lengthening of the stem when applied in low concentrations to shoots of growing plants.

Awn: One of the slender bristles that terminate the glumes of the spikelet in some cereals and other grasses.

Azo dye: Dyes in which the azo group is the chromophore and joins benzene or napthalene rings.

Background measurement: A measurement of pollutants in ambient air due to natural sources; usually taken in remote areas.

Bactericidal activity: The process of killing bacteria.

Barre: Bars or stripes in a fabric, caused by uneven weaving, irregular yarn or uneven dye distribution.

Basal cell: One of the innermost cells of the deeper epidermis of the skin.

Benzenethiol: A compound of benzene and a hydrosulfide group.

Beta (b)-lipoprotein: A biochemical complex or compound containing both lipid and protein and characterized by having a large molecular weight, rich in cholesterol. Found in certain fractions of human plasma.

Bilateral renal sclerosis: A hardening of both kidneys of chronic inflammatory origin.

Biomass: That part of a given habitat consisting of living matter.

Biosphere: The part of the earth's crust, waters and atmosphere where living organisms can subsist.

Biphasic: Having two distinct successive stages.

Bleb: A collection of fluid beneath the skin; usually smaller than bullae or blisters.

Blood urea: The chief end product of nitrogen metabolism in mammals, excreted in human urine in the amount of about 32 grams (1 oz.) a day.

Bloom: A greenish-gray appearance imparted to silk and pile fabrics either by nature of the weave or by the finish; also, the creamy white color observed on some good cottons.

Blue-green algae: A group of simple plants which are the only $N_2$-fixing organisms which photosynthesize as do higher plants.

Brightener: A compound such as a dye, which adheres to fabrics in order to provide better brightness or whiteness by converting ultraviolet radiation to visible light. Sometimes called optical bleach or whitening agent. The dyes used are of the florescent type.

Broad bean: The large flat edible seed of an Old World upright vetch (*Vicia faba*), or the plant itself, widely grown for its seeds and for fodder.

Bronchi: The first subdivisions of the trachea which conduct air to and from the bronchioles of the lungs.

Bronchiole: One of the finer subdivisions of the bronchial (trachea) tubes, less than 1 mm in diameter, and having no cartilage in its wall.

Bronchiolitis: Inflammation of the smallest bronchial tubes.

Bronchiolitis fibrosa obliterans syndrome: Obstruction of the bronchioles by fibrous granulation arising from an ulcerated mucosa; the condition may follow inhalation of irritant gases.

Bronchitis: Inflammation of the mucous membrane of the bronchial tubes. It may aggravate an existing asthmatic condition.

Bronchoconstrictor: An agent that causes a reduction in the caliber (diameter) of a bronchial tube.

Bronchodilator: An agent which causes an increase in the caliber (diameter) of a bronchus or bronchial tube.

Bronchopneumonia: Acute inflammation of the walls of the smaller bronchial tubes, with irregular area of consolidation due to spread of the inflammation into peribronchiolar alveoli and the alveolar ducts.

Brownian diffusion: Diffusion by random movement of particles suspended in liquid or gas, resulting from the impact of molecules of the fluid surrounding the particles.

Buffer: A substance in solution capable of neutralizing both acids and bases and thereby maintaining the original pH of the solution.

Buffering capacity: Ability of a body of water and its watershed to neutralize introduced acid.

Butanol: A four-carbon, straight-chain alcohol, $C_4H_9OH$, also known as butyl alcohol.

Butylated hydroxytoluene (BHT): A crystalline phenolic antioxidant.

Butylated hydroxyanisol (BHA): An antioxidant.

$^{14}C$ labeling: Use of a radioactive form of carbon as a tracer, often in metabolic studies.

$^{14}C$-proline: An amino acid which has been labeled with radioactive carbon.

Calcareous: Resembling or consisting of calcium carbonate (lime), or growing on limestone or lime-containing soils.

Calorie: Amount of heat required to raise temperature of 1 gram of water at $15^{o}C$ by 1 degree.

Cannula: A tube that is inserted into a body cavity, or other tube or vessel, usually to remove fluid.

Capillary: The smallest type of vessel; resembles a hair. Usually in reference to a blood or lymphatic capillary vessel.

Carbachol: A chemical compound (carbamoylcholine chloride, $C_6H_{15}ClN_2O_2$) that produces a constriction of the bronchi; a parasympathetic stimulant used in veterinary medicine and topically in glaucoma.

Carbon monoxide: An odorless, colorless, toxic gas with a strong affinity for hemoglobin and cytochrome; it reduces oxygen absorption capacity, transport and utilization.

Carboxyhemoglobin: A fairly stable union of carbon monoxide with hemoglobin which interferes with the normal transfer of carbon dioxide and oxygen during circulation of blood. Increasing levels of carboxyhemoglobin result in various degrees of asphyxiation, including death.

Carcinogen: Any agent producing or playing a stimulatory role in the formation of a malignancy.

Carcinoma: Malignant new growth made up of epithelial cells tending to infiltrate the surrounding tissues and giving rise to metastases.

Cardiac output: The volume of blood passing through the heart per unit time.

Cardiovascular: Relating to the heart and the blood vessels or the circulation.

Carotene: Lipid-soluble yellow-to-orange-red pigments universally present the photosynthetic tissues of higher plants, algae, and the photosynthetic bacteria.

Cascade impactor: A device for measuring the size distribution of particulates and/or aerosols, consisting of a series of plates with orifices of graduated size which separate the sample into a number of fractions of decreasing aerodynamic diameter.

Catabolism: Destructive metabolism involving the release of energy and resulting in breakdown of complex materials in the organism.

Catalase: An enzyme (EC 1.11.1.6) catalyzing the decomposition of hydrogen peroxide to water and oxygen.

Catalysis: A modification of the rate of a chemical reaction by some material which is unchanged at the end of the reaction.

Catalytic converter: An air pollution abatement device that removes organic contaminants by oxidizing them into carbon dioxide and water.

Catecholamine: A pyrocatechol with an alkalamine side chain, functioning as a hormone or neurotransmitter, such as epinephrine, morepinephrine, or dopamine.

Cathepsins: Enzymes which have the ability to hydrolyze certain proteins and peptides; occur in cellular structures known as lysosomes.

Cation: A positively charged ion.

Cellular permeability: Ability of gases to enter and leave cells; a sensitive indicator of injury to deep-lung cells.

Cellulose: The basic substance which is contained in all vegetable fibers and in certain man-made fibers. It is a carbohydrate and constitutes the major substance in plant life. Used to make cellulose acetate and rayon.

Cellulose acetate: Commonly refers to fibers or fabrics in which the cellulose is only partially acetylated with acetate groups. An ester made by reacting cellulose with acetic anhydride with $SO_4$ as a catalyst.

Cellulose rayon: A regenerated cellulose which is chemically the same as cellulose except for physical differences in molecular weight and crystallinity.

Cellulose triacetate: A cellulose fiber which is completely acetylated. Fabrics of triacetate have higher heat resistance than acetate and may be safely ironed at higher temperature. Such fabrics have improved ease-of-care characteristics because after heat treatment during manufacture, a change in the crystalline structure of the fiber occurs.

Cellulosics: Cotton, viscose rayon and other fibers made of natural fiber raw materials.

Celsius scale: The thermometric scale in which freezing point of water is 0 and boiling point is 100.

Central hepatic necrosis: The pathologic death of one or more cells, or of a portion of the liver, involving the cells adjacent to the central veins.

Central nervous system (CNS): The brain and the spinal cord.

Centroacinar area: The center portion of a grape-shaped gland.

Cerebellum: The large posterior brain mass lying above the pons and medulla and beneath the posterior portion of the cerebrum.

Cerebral cortex: The layer of gray matter covering the entire surface of the cerebral hemisphere of mammals.

Chain reaction: A reaction that stimulates its own repetition.

Challenge: Exposure of a test organism to a virus, bacteria, or other stress-causing agent, used in conjunction with exposure to a pollutant of interest, to explore possible susceptibility brought on by the pollutant.

Chamber study: Research conducted using a closed vessel in which pollutants are reacted or substances exposed to pollutants.

Chemiluminescence: A measurement technique in which radiation is produced as a result of chemical reaction.

Chemotactic: Relating to attraction or repulsion of living protoplasm by chemical stimuli.

Chlorophyll: A group of closely related green photosynthetic pigments occurring in leaves, bacteria, and organisms.

Chloroplast: A plant cell inclusion body containing chlorophyll.

Chlorosis: Discoloration of normally green plant parts that can be caused by disease, lack of nutrients, or various air pollutants, resulting in the failure of chlorophyll to develop.

Cholesterol: A steroid alcohol $C_{27}H_{45}OH$; the most abundant steroid in animal cells and body fluids.

Cholinesterase (CHE): One (EC 3.1.1.8) of a family of enzymes capable of catalyzing the hydrolysis of acylcholines.

Chondrosarcoma: A malignant neoplasm derived from cartilage cells, occurring most frequently near the ends of long bones.

Chromatid: Each of the two strands formed by longitudinal duplication of a chromosome that becomes visible during an early stage of cell division.

Chromophore: A chemical group that produces color in a molecule by absorbing near ultraviolet or visible radiation when bonded to a nonabsorbing, saturated residue which possesses no unshared, nonbonding valence electrons.

Chromosome: One of the bodies (46 in man) in the cell nucleus that is the bearer and carrier of genetic information.

Chronic respiratory disease (CRD): A persistent or long-lasting intermittent disease of the respiratory tract.

Cilia: Motile, often hairlike extensions of a cell surface.

Ciliary action: Movements of cilia in the upper respiratory tract, which move mucus and foreign material upward.

Ciliogenesis: The formation of cilia.

Citric acid (Krebs) cycle: A major biochemical pathway in cells, involving terminal oxidation of fatty acids and carbohydrates. It yields a major portion of energy needed for essential body functions and is the major source of $CO_2$. It couples the glycolytic breakdown of sugar in the cytoplasm with those reactions producing ATP in the mitochondria. It also serves to regulate the synthesis of a number of compounds required by a cell.

Clara cell: A nonciliated mammalian cell.

Closing volume (CV): The lung volume at which the flow from the lower parts of the lungs becomes severely reduced or stops during expiration presumably because of airway closure.

Codon: A sequence of three nucleotides which encodes information required to direct the synthesis of one or more amino acids.

Coefficient of haze (COH): A measurement of visibility interference in the atmosphere.

Cohort: A group of subjects included in a test or experiment; usually characterized by age, class or other characteristic.

Collagen: The major protein of the white fibers of connective tissue, cartilage, and bond. Comprises over half the protein of the mammal.

Collisional deactivation: Reduction in energy of excited molecules caused by collision with other molecules or other objects such as the walls of a container.

Colorimetric: A chemical analysis method relying on measurement of the degree of color produced in a solution by reaction with the pollutant of interest.

Community exposure: A situation in which people in a sizeable area are subjected to ambient pollutant concentrations.

Compliance: A measure of the change in volume of an internal organ (e.g. lung, bladder) produced by a unit of pressure.

Complement: Thermolabile substance present in serum that is destructive to certain bacteria and other cells which have been sensitized by specific complement-fixing antibody.

Compound: A substance with its own distinct properties, formed by the chemical combination of two or more elements in fixed proportion.

Concanavalin-A: One of two crystalline globulins occurring in the jack bean; a potent hemagglutinin.

Conifer: A plant, generally evergreen, needle-leafed, bearing naked seeds singly or in cones.

Converter: See catalytic converter.

Coordination number: The number of bonds formed by the central atom in a complex.

Copolymer: The product of the process of polymerization in which two or more monomeric substances are mixed prior to polymerization. Nylon is a copolymer.

Coproporphyrin: One of two porphyrin compounds found normally in feces as a decomposition product of bilirubin (a bile pigment). Porphyrin is a widely-distributed pigment consisting of four pyrrole nuclei joined in a ring.

Cordage: A general term which includes banding, cable, cord, rope, string, and twine made from fibers. Synthetic fibers used in making cordage include nylon and dacron.

Corrosion: Destruction or deterioration of a material because of reaction with its environment.

Corticosterone: A steroid obtained from the adrenal cortex. It induces some deposition of glycogen in the liver, sodium conservation, and potassium excretion.

Cosmopolitan: In the biological sciences, a term denoting worldwide distribution.

Coulometric: Chemical analysis performed by determining the amount of a substance released in electrolysis by measuring the number of coulombs used.

Coumarin: A toxic white crystalline lactone ($C_9H_6O_2$) found in plants.

Coupler: A chemical used to combine two others in a reaction, e.g. to produce the azo dye in the Griess-Saltzman method for $NO_2$.

Crevice corrosion: Localized corrosion occurring within crevices on metal surfaces exposed to corrosives.

Crosslink: To connect, by an atom or molecule, parallel chains in a complex chemical molecule, such as a polymer.

Cryogenic trap: A pollutant sampling method in which a gaseous pollutant is condensed out of sampled air by cooling (e.g. traps in one method for nitrosamines are maintained below -79°C, using solvents maintained at their freezing points).

Cuboidal: Resembling a cube in shape.

Cultivar: An organism produced by parents belonging to different species or to different strains of the same species, originating and persisting under cultivation.

Cuticle: A thin outer layer, such as the thin continuous fatty film on the surface of many higher plants.

Cyanosis: A dark bluish or purplish coloration of the skin and mucous membrane due to deficient oxygenation of the blood.

Cyclic GMP: Guanosine 5'-phosphoric acid.

Cytochrome: A class of hemoprotein whose principal biological function is electron and/or hydrogen transport.

Cytology: The anatomy, physiology, pathology and chemistry of the cell.

Cytoplasm: The substance of a cell exclusive of the nucleus.

Dacron: The trade name for polyester fibers made by E.I. du Pont de Nemours and Co., Inc., made from dimethyl terephthalate and ethylene glycol.

Dark adaptation: The process by which the eye adjusts under reduced illumination and the sensitivity of the eye to light is greatly increased.

Dark respiration: Metabolic activity of plants at night; consuming oxygen to use stored sugars and releasing carbon dioxide.

Deciduous plants: Plants which drop their leaves at the end of the growing season.

Degradation (textiles): The decomposition of fabric or its components or characteristics (color, strength, elasticity) by means of light, heat, or air pollution.

Denitrification: A bacterial process occurring in soils, or water, in which nitrate is used as the terminal electron acceptor and is reduced primarily to $N_2$. It is essentially an anaerobic process; it can occur in the presence of low levels of oxygen only if the microorganisms are metabolizing in an anoxic microzone.

De novo: Over again.

Deoxyribonucleic acid (DNA): A nucleic acid considered to be the carrier of genetic information coded in the sequence of purine and pyrimidine bases (organic bases). It has the form of a double-stranded helix of a linear polymer.

Depauperate: Falling short of natural development or size.

Derivative spectrophotometer: An instrument with an increased capability for detecting overlapping spectral lines and bands and also for suppressing instrumentally scattered light.

Desorb: To release a substance which has been taken into another substance or held on its surface; the opposite of absorption or adsorption.

Desquamation: The shedding of the outer layer of any surface.

Detection limit: A level below which an element or chemical compound cannot be reliably detected by the method or measurement being used for analysis.

Detritus: Loose material that results directly from disintegration.

DeVarda alloy: An alloy of 50 percent Cu, 45 percent Al, 5 percent Zn.

Diastolic blood pressure: The blood pressure as measured during the period of filling the cavities of the heart with blood.

Diazonium salt: A chemical compound (usually colored) of the general structure $ArN_2^+Cl^-$, where Ar refers to an aromatic group.

Diazotizer: A chemical which, when reacted with amines ($RNH_2$, for example), produces a diazonium salt (usually a colored compound).

Dichotomous sampler: An air-sampling device which separates particulates into two fractions by particle size.

Differentiation: The process by which a cell, such as a fertilized egg, divides into specialized cells, such as the embryonic types that eventually develop into an entire organism.

Diffusion: The process by which molecules or other particles intermingle as a result of their random thermal motion.

Diffusing capacity: Rate at which gases move to or from the blood.

Dimer: A compound formed by the union of two like radicals or molecules.

Dimerize: Formation of dimers.

1,6-diphosphofructose aldolase: An enzyme (EC 4.1.1.13) cleaving fructose 1,6-bisphosphate to dihydroxyacetone phosphate and glyceraldehyde-3-phosphate.

D-2,3-diphosphoglycerate: A salt or ester of 2,3-diphosphoglyceric acid, a major component of certain mammalian erythrocytes involved in the release of $O_2$ from $HbO_2$. Also a postulated intermediate in the biochemical pathway involving the conversion of 3- to 2-phosphoglyceric acid.

<u>Diplococcus</u> <u>pneumoniae</u>: A species of spherical-shaped bacteria belonging to the genus Streptococcus. May be a causal agent in pneumonia.

Direct dye: A dye with an affinity for most fibers; used mainly when color resistance to washing is not important.

Disperse dyes: Also known as acetate dyes; these dyes were developed for use on acetate fabrics, and are now also used on synthetic fibers.

Distal: Far from some reference point such as median line of the body, point of attachment or origin.

Diurnal: Having a repeating pattern or cycle 24 hours long.

$DL_{CO}$: The diffusing capacity of the lungs for carbon monoxide. The ability of the lungs to transfer carbon monoxide from the alveolar air into the pulmonary capillary blood.

Dorsal hyphosis: Abnormal curvative of the spine; hunch-back.

Dose: The quantity of a substance to be taken all at one time or in fractional amounts within a given period; also the total amount of a pollutant delivered or concentration per unit time times time.

Dose-response curve: A curve on a graph based on responses occurring in a system as a result of a series of stimuli intensities or doses.

Dry deposition: The processes by which matter is transferred to ground from the atmosphere, other than precipitation; includes surface absorption of gases and sedimentation, Brownian diffusion and impaction of particles.

Dyeing: A process of coloring fibers, yarns, or fabrics with either natural or synthetic dyes.

Dynamic calibration: Testing of a monitoring system using a continuous sample stream of known concentration.

Dynamic compliance ($C_{L_{dyn}}$): Volume change per unit of transpulmonary pressure minus the pressure of pulmonary resistance during airflow.

Dynel: A trademark for a modacrylic staple fiber spun from a copolymer of acrylonitrile and vinyl chloride. It has high strength, quick-drying properties, and resistance to alkalies and acids.

Dyspepsia: Indigestion, upset stomach.

Dyspnea: Shortness of breath; difficulty or distress in breathing; rapid breathing.

Ecosystem: The interacting system of a biological community and its environment.

Eddy: A current of water or air running contrary to the main current.

Edema: Pressure of excess fluid in cells, intercellular tissue or cavities of the body.

Elastomer: A synthetic rubber product which has the physical properties of natural rubber.

Electrocardiogram: The graphic record of the electrical currents that initiate the heart's contraction.

Electrode: One of the two extremities of an electric circuit.

Electrolyte: A non-metallic electric conductor in which current is carried by the movement of ions; also a substance which displays these qualities when dissolved in water or another solvent.

Electronegativity: Measure of affinity for negative charges or electrons.

Electron microscopy: A technique which utilizes a focused beam of electrons to produce a high-resolution image of minute objects such as particulate matter, bacteria, viruses, and DNA.

Electronic excitation energy: Energy associated in the transition of electrons from their normal low-energy orbitals or orbitals of higher energy.

Electrophilic: Having an affinity for electrons.

Electrophoresis: A technique by which compounds can be separated from a complex mixture by their attraction to the positive or negative pole of an applied electric potential.

Eluant: A liquid used in the process of elution.

Elute: To perform an elution.

Elution: Separation of one material from another by washing or by dissolving one in a solvent in which the other is not soluble.

Elutriate: To separate a coarse, insoluble powder from a finer one by suspending them in water and pouring off the finer powder from the upper part of the fluid.

Emission spectrometry: A rapid analytical technique based on measurement of the characteristic radiation emitted by thermally or electrically excited atoms or ions.

Emphysema: An anatomic alteration of the lung, characterized by abnormal enlargement of air spaces distal to the terminal bronchioles, due to dilation or destructive changes in the alveolar walls.

Emphysematous lesions: A wound or injury to the lung as a result of emphysema.

Empirical modeling: Characterization and description of a phenomena based on experience or observation.

Encephalitis: Inflammation of the brain.

Endoplasmic reticulum: An elaborate membrane structure extending from the nuclear membrane or eucaryotic cells to the cytoplasmic membrane.

Endothelium: A layer of flat cells lining especially blood and lymphatic vessels.

Entropy: A measure of disorder or randomness in a system. Low entropy is associated with highly ordered systems.

Enzyme: Any of numerous proteins produced by living cells which catalyze biological reactions.

Enzyme Commission (EC): The International Commission on Enzymes, established in 1956, developed a scheme of classification and nomenclature under which each enzyme is assigned an EC number which identifies it by function.

Eosinophils: Leukocytes (white blood cells) which stain readily with the dye, eosin.

Epidemiology: A study of the distribution and determinants of disease in human population groups.

Epidermis: The outermost living layer of cells of any organism.

Epididymal fat pads: The fatty tissue located near the epididymis. The epididymis is the first convoluted portion of the excretory duct of the testis.

Epiphyte: A plant growing on another plant but obtaining food from the atmosphere.

Epithelial: Relating to epithelium, the membranous cellular layer which covers free surfaces or lines tubes or cavities of an animal body, which encloses, protects, secretes, excretes and/or assimilates.

Erosion corrosion: Acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface. Characterized by grooves, gullies, or waves in the metal surface.

Erythrocyte: A mature red blood cell.

*Escherichia coli*: A short, gram-negative, rod-shaped bacteria common to the human intestinal tract. A frequent cause of infections in the urogenital tract.

Esophageal: Relating to the portion of the digestive tract between the pharynx and the stomach.

Estrus: That portion or phase of the sexual cycle of female animals characterized by willingness to permit coitus.

Estrus cycle: The series of physiologic uterine, ovarian and other changes that occur in higher animals.

Etiolation: Paleness and/or altered development resulting from the absence of light.

Etiology: The causes of a disease or condition; also, the study of causes.

Eucaryotic: Pertaining to those cells having a well-defined nucleus surrounded by a double-layered membrane.

Euthrophication: Elevation of the level of nutrients in a body of water, which can contribute to accelerated plant growth and filling.

Excited state: A state of higher electronic energy than the ground state, usually a less stable one.

Expiratory (maximum) flow rate: The maximum rate at which air can be expelled from the lungs.

Exposure level: Concentration of a contaminant to which an individual or a population is exposed.

Extinction coefficient: A measure of the space rate of diminution, or extinction, of any transmitted light, thus, it is the attenuation coefficient applied to visible radiation.

Extramedullary hematopoiesis: The process of formation and development of the various types of blood cells and other formed elements not including that occurring in bone marrow.

Extravasate: To exclude from or pass out of a vessel into the tissues; applies to urine, lymph, blood and similar fluids.

Far ultraviolet: Radiation in the range of wavelengths from 100 to 190 nanometers.

Federal Reference Method (FRM): For $NO_2$, the EPA-approved analyzers based on the gas-phase chemiluminescent measurement principle and associated calibration procedures; regulatory specifications prescribed in Title 40, Code of Federal Regulations, Part 50, Appendix F.

Fenestrae: Anatomical aperatures often closed by a membrane.

Fiber: A fine, threadlike piece, as of cotton, jute, or asbestos.

Fiber-reactive dye: A water-soluble dyestuff which reacts chemically with the cellulose in fibers under alkaline conditions; the dye contains two chlorine atoms which combine with the hydroxyl groups of the cellulose.

Fibrin: A white insoluble elastic filamentous protein derived from fibrinogen by the action of thrombin, especially in the clotting of blood.

Fibroadenoma: A benign neoplasm derived from glandular epithelium, involving proliferating fibroblasts, cells found in connective tissue.

Fibroblast: An elongated cell with cytoplasmic processes present in connective tissue, capable of forming collagen fibers.

Fibrosis: The formation of fibrous tissue, usually as a reparative or reactive process and not as a normal constituent of an organ or tissue.

Flocculation: Separation of material from a solution or suspension by reaction with a flocculant to create fluffy masses containing the material to be removed.

Fly ash: Fine, solid particles of noncombustible ash carried out of a bed of solid fuel by a draft.

Folded-path optical system: A long (e.g. 8-22 m) chamber with multiple mirrors at the ends which can be used to reflect an infrared beam through an ambient air sample many times; a spectrometer can be used with such a system to detect trace pollutants at very low levels.

Forced expiratory flow (FEF): The rate at which air can be expelled from the lungs; see expiratory flow rate.

Forced expiratory volume (FEV): The maximum volume of air that can be expired in a specific time interval when starting from maximal inspiration.

Forced vital capacity (FVC): The greatest volume of air that can be exhaled from the lungs under forced conditions after a maximum inspiration.

Fractional threshold concentration: The portion of the concentration at which an event or a response begins to occur, expressed as a fraction.

Free radical: Any of a variety of highly-reactive atoms or molecules characterized by having an unpaired electron.

Fritted bubbler: A porous glass device used in air pollutant sampling systems to introduce small bubbles into solution.

Functional residual capacity: The volume of gas remaining in the lungs at the end of a normal expiration. It is the sum of expiratory reserve volume and residual volume.

Gas exchange: Movement of oxygen from the alveoli into the pulmonary capillary blood as carbon dioxide enters the alveoli from the blood.

Gas chromatography (GC): A method of separating and analyzing mixtures of chemical substances. A flow of gas causes the components of a mixture to migrate differentially from a narrow starting zone in a special porous, insoluble sorptive medium. The pattern formed by zones of separated pigments and of colorless substances in this process is called a chromatogram, and can be analyzed to obtain the concentration of identified pollutants.

Gas-liquid chromatography: A method of separating and analyzing volatile organic compounds, in which a sample is vaporized and swept through a column filled with solid support material covered with a nonvolatile liquid. Components of the sample can be identified and their concentrations determined by analysis of the characteristics of their retention in the column, since compounds have varying degrees of solubility in the liquid medium.

Gastric juice: A thin watery digestive fluid secreted by glands in the mucous membrane of the stomach.

Gastroenteritis: Inflammation of the mucous membrane of stomach and intestine.

Genotype: The type of genes possessed by an organism.

Geometric mean: An estimate of the average of a distribution. Specifically, the nth root of the product of n observations.

Geometric standard deviation: A measure of variability of a distribution. It is the antilogarithm of the standard deviation of the logarithms of the observations.

Globulins (a, b, q): A family of proteins precipitated from plasma (or serum) by half-saturation with ammonium sulfate, or separable by electrophoresis. The main groups are the a, b, q fractions, differing with respect to associated lipids and carbohydrates and in their content of antibodies (immunoglobulins).

Glomular nephrotic syndrome: Dysfunction of the kidneys characterized by excessive protein loss in the urine, accumulation of body fluids and alteration in albumin/globulin ratio.

Glucose: A sugar which is a principal source of energy for man and other organisms.

Glucose-6-phosphate dehydrogenase: An enzyme (EC 1.1.1.49) catalyzing the dehydrogenation of glucose-6-phosphate to 6-phosphogluconolactone.

Glutamic-oxaloacetic transaminase (SGOT): An enzyme (EC 2.6.1.1) whose serum level increases in myocardial infarction and in diseases involving destruction of liver cells. Also known as aspartate aminotransferase.

Glutamic-pyruvic transaminase (SGPT): Now known as alanine aminotransferase (EC 2.6.1.2), the serum levels of this enzyme are used in liver function tests.

Glutathione (GSH): A tripeptide composed of glycine, cystine, and glutamic acid.

Glutathione peroxidase: An enzyme (EC 1.11.1) which catalyzes the destruction of hydroperoxides formed from fatty acids and other substances. Protects tissues from oxidative damage. It is a selenium-containing protein.

Glutathione reductase: The enzyme (EC 1.6.4.2) which reduces the oxidized form of glutathione.

Glycolytic pathway: The biochemical pathway by which glucose is converted to lactic acid in various tissues, yielding energy as a result.

Glycoside: A type of chemical compound formed from the condensation of a sugar with another chemical radical via a hemiacetal linkage.

Goblet cells: Epithelial cells that have been distended with mucin and when this is discharged as mucus, a goblet-shaped shell remains.

Golgi apparatus: A membrane system involved with secretory functions and transport in a cell. Also known as a dictyosome.

Grana: The lamellar stacks of chlorophyll-containing material in plant chloroplasts.

Griege carpet: A carpet in its unfinished state, i.e. before it has been scoured and dyed. The term also is used for woven fabrics in the unbleached and unfinished state.

Ground state: The state of minimum electronic energy of a molecule or atom.

Guanylate cyclase (GC): An enzyme (EC 4.6.2.1) catalyzing the transformation of guanosine triphosphate to guanosine 3':5'-cyclic phosphate.

H-Thymidine: Thymine deoxyribonucleoside: One of the four major nucleosides in DNA. $^{3}$H-thymidine has been uniformly labeled with tritium, a radioactive form of hydrogen.

Haze: Fine dust, smoke or fine vapor reducing transparency of air.

Hemagglutination: The agglutination of red blood cells. Can be used as as a measurement of antibody concentration.

Hematocrit: The percentage of the volume of a blood sample occupied by cells.

Hematology: The medical specialty that pertains to the blood and blood-forming tissues.

Hemochromatosis: A disease characterized by pigmentation of the skin possibly due to inherited excessive absorption of iron.

Hemoglobin (Hb): The red, respiratory protein of the red blood cells, hemoglobin transports oxygen from the lungs to the tissues as oxy-hemoglobin ($HbO_2$) and returns carbon dioxide to the lungs as hemoglobin carbamate, completing the respiratory cycle.

Hemolysis: Alteration or destruction of red blood cells, causing hemoglobin to be released into the medium in which the cells are suspended.

Hepatectomy: Complete removal of the liver in an experimental animal.

Hepatic: Relating to the liver.

Hepatocyte: A liver cell.

Heterogeneous process: A chemical reaction involving reactants of more than one phase or state, such as one in which gases are absorbed into aerosol droplets, where the reaction takes place.

Heterologous: A term referring to donor and recipient cellular elements from different organisms, such as red blood cells from sheep and alveolar macrophage from rabbits.

Hexose monophosphate shunt: Also called the phosphogluconate oxidative pathway of glucose metabolism which affords a total combustion of glucose independent of the citric acid cycle. It is the important generator of NADPH necessary for synthesis of fatty acids and the operation of various enzymes. It serves as a source of ribose and 4- and 7-carbon sugars.

High-volume sampler (Hi-vol): Device for taking a sample of the particulate content of a large amount of air, by drawing air through a fiber filter at a typical rate of 2,000 $m^3$/24 hr (1.38 $m^3$/min), or as high as 2,880 $m^3$/24 hr (2 $m^3$/min).

Histamine: An amine derived from the amino acid, histidine. It is a powerful stimulant of gastric secretion and a constrictor of bronchial smooth muscle. It is a vasodilator and causes a fall in blood pressure.

Homogenate: Commonly refers to tissue ground into a creamy consistency in which the cell structure is disintegrated.

Host defense mechanism: Inherent means by which a biologic organism protects itself against infection, such as antibody formation, macrophage action, ciliary action, etc.

Host resistance: The resistance exhibited by an organism, such as man, to an infecting agent, such as a virus or bacteria.

Humoral: Relating to the extracellular fluids of the body, blood and lymph.

Hybrid: An organism descended from parents belonging to different varieties or species.

Hydrocarbons: A vast family of compounds containing carbon and hydrogen in various combinations; found especially in fossil fuels. Some contribute to photochemical smog.

Hydrolysis: Decomposition involving splitting of a bond and addition of the H and OH parts of water to the two sides of the split bond.

Hydrometeor: A product of the condensation of atmospheric water vapor (e.g. fog, rain, hail, snow).

Hydroxyproline: An amino acid found among the hydrolysis products of collagen.

Hygroscopic: Pertaining to a marked ability to accelerate the condensation of water vapor.

Hyperplasia: Increase in the number of cells in a tissue or organ excluding tumor formation.

Hyperplastic: Relating to hyperplasia; an increase in the number of cells.

Hypertrophy: Increase in the size of a tissue element, excluding tumor formation.

Hypertension: Abnormally elevated blood pressure.

Hypolimnia: Portions of a lake below the thermocline, in which water is stagnant and uniform in temperature.

Hypoxia: A lower than normal amount of oxygen in the air, blood or tissues

Immunoglobulin (Ig): A class of structurally related proteins consisting of two pairs of polypeptide chains. Antibodies are Ig's and all Ig's probably function as antibodies.

Immunoglobulin A (IgA): A type of antibody which comprises approximately 10 to 15 percent of the total amount of antibodies present in normal serum.

Immunoglobulin G (IgG): A type of antibody which comprises approximately 80 percent of the total amount of antibodies present in normal serum. Subfractions of IgG are fractions $G_1$, and $G_2$.

Immunoglobulin M (IgM): A type of antibody which comprises approximately 5 to 10 percent of the total amount of antibodies present in normal serum.

Impaction: An impinging or striking of one object against another; also, the force transmitted by this act.

Impactor: An instrument which collects samples of suspended particulates by directing a stream of the suspension against a surface, or into a liquid or a void.

Index of proliferation: Ratio of promonocytes to polymorphic monocytes in the blood.

Infarction: Sudden insufficiency of arterial or venous blood supply due to emboli, thrombi, or pressure.

Infectivity model: A testing system in which the susceptibility of animals to airborne infectious agents with and without exposure to air pollutants is investigated to produce information related to the possible effects of the pollutant on man.

Inflorescence: The arrangement and development of flowers on an axis; also, a flower cluster or a single flower.

Influenza $A_2$/Taiwan Virus: An infectious viral disease, believed to have originated in Taiwan, characterized by sudden onset, chills, fevers, headache, and cough.

Infrared: Light invisible to the human eye, between the wavelengths of $7 \times 10^{-7}$ and $10^{-3}$ m (7000 and 10,000,000 A).

Infrared laser: A device that utilizes the natural oscillations of atoms or molecules to generate coherent electromagnetic radiation in the infrared region of the spectrum.

Infrared spectrometer: An instrument for measuring the relative amounts of radiant energy in the infrared region of the spectrum as a function of wavelength.

Ingestion: To take in for digestion.

In situ: In the natural or original position.

Instrumental averaging time: The time over which a single sample or measurement is taken, resulting in a measurement which is an average of the actual concentrations over that period.

Insult: An injury or trauma.

Intercostal: Between the ribs, especially of a leaf.

Interferant: A substance which a measurement method cannot distinguish completely from the one being measured, which therefore can cause some degree of false response or error.

Interferon: A macromolecular substance produced in response to infection with active or inactivated virus, capable of inducing a state of resistance.

Intergranular corrosion: A type of corrosion which takes place at and adjacent to grain boundaries, with relatively little corrosion of the grains.

Interstitial edema: An accumulation of an excessive amount of fluids in a space within tissues.

Interstitial pneumonia: A chronic inflammation of the interstitial tissue of the lung, resulting in compression of air cells.

Intraluminal mucus: Mucus that collects within any tubule.

Intraperitoneal injection: An injection of material into the serous sac that lines the abdominal cavity.

In utero: Within the womb; not yet born.

In vitro: Refers to experiments conducted outside the living organism.

In vivo: Refers to experiments conducted within the living organism.

Irradiation: Exposure to any form of radiation.

Ischemia: Local anemia due to mechanical obstruction (mainly arterial narrowing) of the blood supply.

Isoenzymes: Also called isozymes. One of a group of enzymes that are very similar in catalytic properties, but may be differentiated by variations in physical properties, such as isoelectric point or electrophoretic mobility. Lactic acid dehydrogenase is an example of an enzyme having many isomeric forms.

Isopleth: A line on a map or chart connecting points of equal value.

Jacobs-Hochheiser method: The original Federal Reference Method for $NO_2$, currently unacceptable for air pollution work.

Klebsiella pneumoniae: A species of rod-shaped bacteria found in soil, water, and in the intestinal tract of man and other animals. Certain types may be causative agents in pneumonia.

Kyphosis: An abnormal curvature of the spine, with convexity backward.

Lactate: A salt or ester of lactic acid.

Lactic acid (lactate) dehydrogenase (LDH): An enzyme (EC 1.1.1.27) with many isomeric forms which catalyzes the oxidation of lactate to pyruvate via transfer of H to NAD. Isomeric forms of LDH in the blood are indicators of heart damage.

Lamellar bodies: Arranged in plates or scales. One of the characteristics of Type II alveolar cells.

Lavage fluid: Any fluid used to wash out hollow organs, such as the lung.

Lecithin: Any of several waxy hygroscopic phosphatides that are widely distributed in animals and plants; they form colloidal solutions in water and have emulsifying, wetting and hygroscopic properties.

Legume: A plant with root nodules containing nitrogen fixing bacteria.

Lesion: A wound, injury or other more or less circumscribed pathologic change in the tissues.

Leukocyte: Any of the white blood cells.

Lewis base: A base, defined in the Lewis acid-base concept, is a substance that can donate an electron pair.

Lichens: Perennial plants which are a combination of two plants, an alga and a fungus, growing together in an association so intimate that they appear as one.

Ligand: Those molecules or anions attached to the central atom in a complex.

Light-fastness: The ability of a dye to maintain its original color under natural or indoor light.

Linolenic acid: An unsaturated fatty acid essential in nutrition.

Lipase: An enzyme that accelerates the hydrolysis or synthesis of fats or the breakdown of lipoproteins.

Lipids: A heterogeneous group of substances which occur widely in biological materials. They are characterized as a group by their extractability in nonpolar organic solvents.

Lipofuscin: Brown pigment granules representing lipid-containing residues of lysosomal digestion. Proposed to be an end product of lipid oxidation which accumulates in tissue.

Lipoprotein: Complex or protein containing lipid and protein.

Loading rate: The amount of a nutrient available to a unit area of body of water over a given period of time.

Locomotor activity. Movement of an organism from one place to another of its own volition.

Long-pathlength infrared absorption: A measurement technique in which a system of mirrors in a chamber is used to direct an infrared beam through a sample of air for a long distance (up to 2 km); the amount of infrared absorbed is measured to obtain the concentrations of pollutants present.

Lung compliance ($C_L$): The volume change produced by an increase in a unit change in pressure across the lung, i.e., between the pleural surface and the mouth.

Lycra: A spandex textile fiber created by E. I. du Pont de Nemours & Co., Inc., with excellent tensile strength, a long flex life and high resistance to abrasion and heat degradation. Used in brassieres, foundation garments, surgical hosiery, swim suits and military and industrial uses.

Lymphocytes: White blood cells formed in lymphoid tissue throughout the body, they comprise about 22 to 28 percent of the total number of leukocytes in the circulating blood and function in immunity.

Lymphocytogram: The ratio, in the blood, of lymphocyte with narrow cytoplasm to those with broad cytoplasm.

Lysosomes: Organelles found in cells of higher organisms that contain high concentrations of degradative enzymes and are known to destroy foreign substances that cells engulf by pinocytosis and phyocytosis. Believed to be a major site where proteins are broken down.

Lysozymes: Lytic enzymes destructive to cell walls of certain bacteria. Present in some body fluids, including tears and serum.

Macaca speciosa: A species of monkeys used in research.

Macrophage: Any large, ameboid, phagocytic cell having a nucleus without many lobes, regardless of origin.

Malaise: A feeling of general discomfort or uneasiness, often the first indication of an infection or disease.

Malate dehydrogenase: An enzyme (EC 1.1.1.37) with at least six isomeric forms that catalyze the dehydrogenation of malate to oxaloacetate or its decarboxylation (removal of a $CO_2$ group) to pyruvate. Malate, oxaloacetate, and pyruvate are intermediate components of biochemical pathways.

Mannitol: An alcohol derived from reduction of the sugar, fructose. Used in renal function testing to measure glomerular (capillary) filtration.

Manometer: An instrument for the measurement of pressure of gases or vapors.

Mass median diameter (MMD): Geometric median size of a distribution of particles based on weight.

Mass spectrometry (MS): A procedure for identifying the various kinds of particles present in a given substance, by ionizing the particles and subjecting a beam of the ionized particles to an electric or magnetic field such that the field deflects the particles in angles directly proportional to the masses of the particles.

Maximum flow ($V_{max}$): Maximum rate or expiration, usually expressed at 50 or 25 percent of vital capacity.

Maximum mid-expiratory flow rate (MMFR): The mean rate of expiratory gas flow between 25 and 75 percent of the forced expiratory vital capacity.

Mean (arithmetic): The sum of observations divided by sample size.

Median: A value in a collection of data values which is exceeded in magnitude by one-half the entries in the collection.

Mesoscale: Of or relating to meteorological phenomena from 1 to 100 kilometers in horizontal extent.

Messenger RNA: A type of RNA which conveys genetic information encoded in the DNA to direct protein synthesis.

Metaplasia: The abnormal transformation of an adult, fully differentiated tissue of one kind into a differentiated tissue of another kind.

Metaproterenol: A bronchodilator used for the treatment of bronchial asthma.

Metastases: The shifting of a disease from one part of the body to another; the appearance of neoplasms in parts of the body remote from the seat of the primary tumor.

Meteorology: The science that deals with the atmosphere and its phenomena.

Methemoglobin: A form of hemoglobin in which the normal reduced state of iron ($Fe^{2+}$) has been oxidized to $Fe^{3+}$. It contains oxygen in firm union with ferric ($Fe^{3+}$) iron and is not capable of exchanging oxygen in normal respiratory processes.

Methimazole: An anti-thyroid drug similar in action to propylthiouracil.

Methyltransferase: Any enzyme transferring methyl groups from one compound to another.

Microcoulometric: Capable of measuring millionths of coulombs used in electrolysis of a substance, to determine the amount of a substance in a sample.

Microflora: A small or strictly localized plant.

Micron: One-millionth of a meter.

Microphage: A small phagocyte; a polymorphonuclear leukocyte that is phagocytic.

Millimolar: One-thousandth of a molar solution. A solution of one-thousandth of a mole (in grams) per liter.

Minute volume: The minute volume of breathing; a product of tidal volume times the respiratory frequency in one minute.

Mitochondria: Organelles of the cell cytoplasm which contain enzymes active in the conservation of energy obtained in the aerobic part of the breakdown of carbohydrates and fats, in a process called respiration.

Mobile sources: Automobiles, trucks and other pollution sources which are not fixed in one location.

Modacrylic fiber: A manufactured fiber in which the fiber-forming substance is any long chain synthetic polymer composed of less than 85 percent but at least 35 percent by weight of acrylonitrite units.

Moeity: One of two or more parts into which something is divided.

Mole: The mass, in grams, numerically equal to the molecular weight of a substance.

Molecular correlation spectrometry: A spectrophotometric technique which is used to identify unknown absorbing materials and measure their concentrations by using preset wavelengths.

Molecular weight: The weight of one molecule of a substance obtained by adding the gram-atomic weights of each of the individual atoms in the substance.

Monocyte: A relatively large mononuclear leukocyte, normally constituting 3 to 7 percent of the leukocytes of the circulating blood.

Mordant: A substance which acts to bind dyes to a textile fiber of fabric.

Morphological: Relating to the form and structure of an organism or any of its parts.

Moving average: A procedure involving taking averages over a specific period prior to and including a year in question, so that successive averaging periods overlap; e.g. a three-year moving average would include data from 1967 through 1969 for the 1969 average and from 1968 through 1970 for 1970.

Mucociliary clearance: Removal of materials from the upper respiratory tract via ciliary action.

Mucociliary transport: The process by which mucus is transported, by ciliary action, from the lungs.

Mucosa: The mucous membrane; it consists of epithelium, lamina propria and, in the digestive tract, a layer of smooth muscle.

Mucous membrane: A membrane secreting mucus which lines passages and cavities communicating with the exterior of the body.

Murine: Relating to mice.

Mutagen: A substance capable of causing, within an organism, biological changes that affect potential offspring through genetic mutation.

Mutagenic: Having the power to cause mutations. A mutation is a change in the character of a gene (a sequence of base pairs in DNA) that is perpetuated in subsequent divisions of the cell in which it occurs.

Myocardial infarction: Infarction of any area of the heart muscle usually as a result of occlusion of a coronary artery.

Nares: The nostrils.

Nasopharyngeal: Relating to the nasal cavity and the pharynx (throat).

National Air Surveillance Network (NASN): Network of monitoring stations for sampling air to determine extent of air pollution; established jointly by federal and state governments.

Near ultraviolet: Radiation of the wavelengths 2000-4000 Angstroms.

Necrosis: Death of cells that can discolor areas of a plant or kill the entire plant.

Necrotic: Pertaining to the pathologic death of one or more cells, or of a portion of tissue or organ, resulting from irreversible damage.

Neonate: A newborn.

Neoplasm: An abnormal tissue that grows more rapidly than normal; synonymous with tumor.

Neoplasia: The pathologic process that results in the formation and growth of a tumor.

Neutrophil: A mature white blood cell formed in bone marrow and released into the circulating blood, where it normally accounts for 54 to 65 percent of the total number of leukocytes.

Ninhydrin: An organic reagent used to identify amino acids.

Nitramine: A compound consisting of a nitrogen attached to the nitrogen of amine.

Nitrate: A salt or ester of nitric acid ($NO_3^-$).

Nitrification: The principal natural source of nitrate in which ammonium ($NH_4+$) ions are oxidized to nitrites by specialized microorganisms. Other organisms oxidize nitrites to nitrates.

Nitrite: A salt or ester of nitrous acid ($NO_2^=$).

Nitrocellulose: Any of several esters of nitric acid formed by its action on cellulose, used in explosives, plastics, varnishes and rayon; also called cellulose nitrate.

Nitrogen cycle: Refers to the complex pathways by which nitrogen-containing compounds are moved from the atmosphere into organic life, into the soil, and back to the atmosphere.

Nitrogen fixation: The metabolic assimilation of atmospheric nitrogen by soil microorganisms, which becomes available for plant use when the microorganisms die; also, industrial conversion of free nitrogen into combined forms used in production of fertilizers and other products.

Nitrogen oxide: A compound composed of only nitrogen and oxygen. Components of photochemical smog.

Nitrosamine: A compound consisting of a nitrosyl group connected to the nitrogen of an amine.

Nitrosation: Addition of a nitrosyl group.

N-Nitroso compounds: Compounds carrying the functional nitrosyl group.

Nitrosyl: A group composed of one oxygen and one nitrogen atom (-N=O).

Nitrosylhemoglobin (NOHb): The red, respiratory protein of erythrocytes to which a nitrosyl group is attached.

N/P Ratio: Ratio of nitrogen to phosphorous dissolved in lake water, important due to its effect on plant growth.

Nucleolus: A small spherical mass of material within the substance of the nucleus of a cell.

Nucleophilic: Having an affinity for atomic nuclei; electron-donating.

Nucleoside: A compound that consists of a purine or pyrimidine base combined with deoxyribose or ribose and found in RNA and DNA.

5'-Nucleotidase: An enzyme (EC 3.1.3.5) which hydrolyzes nucleoside 5'-phosphates into phosphoric acid ($H_3PO_4$) and nucleosides.

Nucleotide: A compound consisting of a sugar (ribose or deoxyribose), a base (a purine or a pyrimidine), and a phosphate; a basic structural unit of RNA and DNA.

Nylon: A generic name chosen by E. I. du Pont de Nemours & Co., Inc. for a group of protein-like chemical products classed as synthetic linear polymers; two main types are Nylon 6 and Nylon 66.

Occlusion: A point which an opening is closed or obstructed.

Olefin: An open-chain hydrocarbon having at least one double bond.

Olfactory: Relating to the sense of smell.

Olfactory epithelium: The inner lining of the nose and mouth which contains neural tissue sensitive to smell.

Oligotrophic: A body of water deficient in plant nutrients; also generally having abundant dissolved oxygen and no marked stratification.

Oribitals: Areas of high electron density in an atom or molecule.

Orlon: An acrylic fiber produced by E. I. du Pont de Nemours and Co., Inc., based on a polymer of acrylonitrite; used extensively for outdoor uses, it is resistant to chemicals and withstands high temperatures.

Osteogenic osteosarcoma: The most common and malignant of bone sarcomas (tumors). It arises from bone-forming cells and affects chiefly the ends of long bones.

Ovarian primordial follicle: A spheroidal cell aggregation in the ovary in which the primordial oocyte (immature female sex cell) is surrounded by a single layer of flattened follicular cells.

Oxidant: A chemical compound which has the ability to remove electrons from another chemical species, thereby oxidizing it; also, a substance containing oxygen which reacts in air to produce a new substance, or one formed by the action of sunlight on oxides of nitrogen and hydrocarbons.

Oxidation: An ion or molecule undergoes oxidation by donating electrons.

Oxidative deamination: Removal of the $NH_2$ group from an amino compound by reaction with oxygen.

Oxidative phosphorylation: The mitochondrial process by which "high-energy" phosphate bonds form from the energy released as a result of the oxidation of various substrates. Principally occurs in the tricarboxylic acid pathway.

Oxyhemoglobin: Hemoglobin in combination with oxygen. It is the form of hemoglobin present in arterial blood.

Ozone layer: A layer of the stratosphere from 20 to 50 km above the earth's surface characterized by high ozone content produced by ultraviolet radiation.

Ozone scavenging: Removal of $O_3$ from ambient air or plumes by reaction with NO, producing $NO_2$ and $O_2$.

Paired electrons: Electrons having opposite intrinsic spins about their own axes.

Parenchyma: The essential and distinctive tissue of an organ or an abnormal growth, as distinguished from its supportive framework.

Parenchymal: Referring to the distinguishing or specific cells of a gland or organ.

Partial pressure: The pressure exerted by a single component in a mixture of gases.

Particulates: Fine liquid or solid particles such as dust, smoke, mist, fumes or smog, found in the air or in emissions.

Pascal: A unit of pressure in the International System of Units. One pascal is equal to $7.4 \times 10^{-3}$ torr. The pascal is equivalent to one newton per square meter.

Pathogen: Any virus, microorganism, or other substance causing disease.

Pathophysiological: Derangement of function seen in disease; alteration in function as distinguished from structural defects.

Peptide bond: The bond formed when two amino acids react with each other.

Percentiles: The percentage of all observations exceeding or preceding some point; thus, 90th percentile is a level below which will fall 90 percent of the observations.

Perfusate: A liquid, solution or colloidal suspension that has been passed over a special surface or through an appropriate structure.

Perfusion: Artificial passage of fluid through blood vessels.

Permanent-press fabrics: Fabrics in which applied resins contribute to the easy care and appearance of the fabric and to the crease and seam flat-
ness by reacting with the cellulose on pressing after garment manufacture.

Permeation tube: A tube which is selectively porous to specific gases.

Peroxidation: Refers to the process by which certain organic compounds are converted to peroxides.

Peroxyacetyl nitrate (PAN): Pollutant created by action of sunlight on hydrocarbons and $NO_x$ in the air; an ingredient of photochemical smog.

pH: A measure of the acidity or alkalinity of a material, liquid, or solid. pH is represented on a scale of 0 to 14 with 7 being a neutral state, 0 most acid, and 14 most alkaline.

Phagocytosis: Ingestion, by cells such as macrophages, of other cells, bacteria, foreign particles, etc.; the cell membrane engulfs solid or liquid particles which are drawn into the cytoplasm and digested.

Phenotype: The observable characteristics of an organism, resulting from the interaction between an individual genetic structure and the environment in which development takes place.

Phenylthiourea: A crystalline compound, $C_7H_8N_2S$, that is bitter or tasteless depending on a single dominant gene in the tester.

Phlegm: Viscid mucus secreted in abnormal quantity in the respiratory passages.

Phosphatase: Any of a group of enzymes that liberate inorganic phosphate from phosphoric esters (E.C. sub-subclass 3.1.3).

Phosphocreatine kinase: An enzyme (EC 2.7.3.2) catalyzing the formation of creatine and ATP, its breakdown is a source of energy in the contraction of muscle; also called creatine phosphate.

Phospholipid: A molecule consisting of lipid and phosphoric acid group(s). An example is lecithin. Serves as an important structural factor in biological membranes.

Photochemical oxidants: Primary ozone, $NO_2$, PAN with lesser amounts of other compounds formed as products of atmospheric reactions involving organic pollutants, nitrogen oxides, oxygen, and sunlight.

Photochemical smog: Air pollution caused by chemical reaction of various airborne chemicals in sunlight.

Photodissociation: The process by which a chemical compound breaks down into simpler components under the influence of sunlight or other radiant energy.

Photolysis: Decomposition upon irradiation by sunlight.

Photomultiplier tube: An electron multiplier in which electrons released by photoelectric emission are multiplied in successive stages by dynodes that produce secondary emissions.

Photon: A quantum of electromagnetic energy.

Photostationary: A substance or reaction which reaches and maintains a steady state in the presence of light.

Photosynthesis: The process in which green parts of plants, when exposed to light under suitable conditions of temperature and water supply, produce carbohydrates using atmospheric carbon dioxide and releasing oxygen.

Phytotoxic: Poisonous to plants.

Phytoplankton: Minute aquatic plant life.

Pi $\pi$ bonds: Bonds in which electron density is not symmetrical about a line joining the bonded atoms.

Pinocytotic: Refers to the cellular process (pinocytosis) in which the cytoplasmic membrane forms invaginations in the form of narrow channels leading into the cell. Liquids can flow into these channels and the membrane pinches off pockets that are incorporated into the cytoplasm and digested.

Pitting: A form of extremely localized corrosion that results in holes in the metal. One of the most destructive forms of corrosion.

Pituary: A stalk-like gland near the base of the brain which is attached to the hypothalmus. The anterior portion is a major repository for for hormones that control growth, stimulate other glands, and regulate the reproductive cycle.

Placenta: The organ in the uterus that provides metabolic interchange between the fetus and mother.

Plasmid: Replicating unit, other than a nucleus gene, that contains nucleoprotein and is involved in various aspects of metabolism in organisms; also called paragenes.

Plasmolysis: The dissolution of cellular components, or the shrinking of plant cells by osmotic loss of cytoplasmic water.

Plastic: A plastic is one of a large group of organic compounds synthesized from cellulose, hydrocarbons, proteins or resins and capable of being cast, extruded, or molded into various shapes.

Plasticizer: A chemical added to plastics to soften, increase malleability or to make more readily deformable.

Platelet (blood): An irregularly-shaped disk with no definite nucleus; about one-third to one-half the size of an erythrocyte and containing no hemoglobin. Platelets are more numerous than leukocytes, numbering from 200,000 to 300,000 per cu. mm. of blood.

Plethysmograph: A device for measuring and recording changes in volume of a part, organ or the whole body; a body plethysmograph is a chamber apparatus surrounding the entire body.

Pleura: The serous membrane enveloping the lungs and lining the walls of the chest cavity.

Plume: Emission from a flue or chimney, usually distributed stream-like downwind of the source, which can be distinguished from the surrounding air by appearance or chemical characteristics.

Pneumonia (interstitial): A chronic inflammation of the interstitial tissue of the lung, resulting in compression of the air cells. An acute, infectious disease.

Pneumonocytes: A nonspecific term sometimes used in referring to types of cells characteristic of the respiratory part of the lung.

Podzol: Any of a group of zonal soils that develop in a moist climate, especially under coniferous or mixed forest.

Point source: A single stationary location of pollutant discharge.

Polarography: A method of quantitative or qualitative analysis based on current-voltage curves obtained by electrolysis of a solution with steadily increasing voltage.

Pollution gradient: A series of exposure situations in which pollutant concentrations range from high to low.

Polyacrylonitrile: A polymer made by reacting ethylene oxide and hydrocyanic acid. Dynel and Orlon are examples.

Polyamides: Polymerization products of chemical compounds which contain amino ($-NH_2$) and carboxyl ($-COOH$) groups. Condensation reactions between the groups form amides ($-CONH_2$). Nylon is an example of a polyamide.

Polycarbonate: Any of various tough transparent thermoplastics characterized by high impact strength and high softening temperature.

Polycythemia: An increase above the normal in the number of red cells in the blood.

Polyester fiber: A man-made or manufactured fiber in which the fiber-forming substance is any long-chain synthetic polymer composed of at least 85 percent by weight of an ester of a dihydric alcohol and terephthalic acid. Dacron is an example.

Polymer: A large molecule produced by linking together many like molecules.

Polymerization: In fiber manufacture, converting a chemical monomer (simple molecule) into a fiber-forming material by joining many like molecules into a stable, long-chain structure.

Polymorphic monocyte: Type of leukocyte with a multi-lobed nucleus.

Polymorphonuclear leukocytes: Cells which represent a secondary non-specific cellular defense mechanism. They are transported to the lungs from the bloodstream when the burden handled by the alveolar macrophages is too large.

Polysaccharides: Polymers made up of sugars. An example is glycogen which consists of repeating units of glucose.

Polystyrene: A thermoplastic plastic which may be transparent, opaque, or translucent. It is light in weight, tasteless and odorless, it also is resistant to ordinary chemicals.

Polyurethane: Any of various polymers that contain NHCOO linkages and are used especially in flexible and rigid foams, elastomers and resins.

Pores of Kohn: Also known as interalveolar pores; pores between air cells. Assumed to be pathways for collateral ventilation.

Precipitation: Any of the various forms of water particles that fall from the atmosphere to the ground, rain, snow, etc.

Precursor: A substance from which another substance is formed; specifically, one of the anthropogenic or natural emissions or atmospheric constituents which reacts under sunlight to form secondary pollutants comprising photochemical smog.

Probe: In air pollution sampling, the tube or other conduit extending into the atmosphere to be sampled, through which the sample passes to treatment, storage and/or analytical equipment.

Proline: An amino acid, $C_5H_9NO_2$, that can be synthesized from glutamate by animals.

Promonocyte: An immature monocyte not normally seen in the circulating blood.

Proteinuria: The presence of more than 0.3 gm of urinary protein in a 24-hour urine collection.

Pulmonary: Relating to the lungs.

Pulmonary edema: An accumulation of excessive amounts of fluid in the lungs.

Pulmonary lumen: The spaces in the interior of the tubular elements of the lung (bronchioles and alveolar ducts).

Pulmonary resistance: Sum of airway resistance and viscous tissue resistance.

Purine bases: Organic bases which are constituents of DNA and RNA, including adenine and guanine.

Purulent: Containing or forming pus.

Pyrimidine bases: Organic bases found in DNA and RNA. Cytosine and thymine occur in DNA and cytosine and uracil are found in RNA.

QRS: Graphical representation on the electrocardiogram of a complex of three distinct waves which represent the beginning of ventricular contraction.

Rainout: Removal of particles and/or gases from the atmosphere by their involvement in cloud formation (particles act as condensation nuclei, gases are absorbed by cloud droplets), with subsequent precipitation.

Rayleigh scattering: Coherent scattering in which the intensity of the light of wavelength g, scattered in any direction making an angle with the incident direction, is directly proportional to $1 + \cos^2 r$ and inversely proportional to $g^4$.

Reactive dyes: Dyes which react chemically with cellulose in fibers under alkaline conditions. Also called fiber reactive or chemically reactive dyes.

Reduction: Acceptance of electrons by an ion or molecule.

Reference method (RM): For $NO_2$, an EPA-approved gas-phase chemiluminescent analyzer and associated calibration techniques; regulatory specifications are described in Title 40, Code of Federal Regulations, Part 50, Appendix F. Formerly, Federal Reference Method.

Residual capacity: The volume of air remaining in the lungs after a maximum expiratory effort; same as residual volume.

Residual volume (RV): The volume of air remaining in the lungs after a maximal expiration. RV = TLC - VC

Resin: Any of various solid or semi-solid amorphous natural organic substances, usually derived from plant secretions, which are soluble in organic solvents but not in water; also any of many synthetic substances with similar properties used in finishing fabrics, for permanent press shrinkage control or water repellency.

Ribosomal RNA: The most abundant RNA in a cell and an integral constituent of ribosomes.

Ribosomes: Discrete units of RNA and protein which are instrumental in the synthesis of proteins in a cell. Aggregates are called polysomes.

Runoff: Water from precipitation, irrigation or other sources that flows over the ground surface to streams.

Sclerosis: Pathological hardening of tissue, especially from overgrowth of fibrous tissue or increase in interstitial tissue.

Selective leaching: The removal of one element from a solid alloy by corrosion processes.

Septa: A thin wall dividing two cavities or masses of softer tissue.

Seromucoid: Pertaining to a mixture of watery and mucinous material such as that of certain glands.

Serum antiprotease: A substance, present in serum, that inhibits the activity of proteinases (enzymes which destroy proteins).

Sigma (s) bonds: Bonds in which electron density is symmetrical about a line joining the bonded atoms.

Silo-filler's disease: Pulmonary lesion produced by oxides of nitrogen produced by fresh silage.

Single breath nitrogen elimination rate: Percentage rise in nitrogen fraction per unit of volume expired.

Single breath nitrogen technique: A procedure in which a vital capacity inspiration of 100 percent oxygen is followed by examination of nitrogen in the vital capacity expirate.

Singlet state: The highly-reactive energy state of an atom in which certain electrons have unpaired spins.

Sink: A reactant with or absorber of a substance.

Sodium arsenite: $Na_3AsO_3$, used with sodium hydroxide in the absorbing solution of a 24-hour integrated manual method for $NO_2$.

Sodium dithionite: A strong reducing agent (a supplier of electrons).

Sodium metabisulfite: $Na_2S_2O_5$, used in absorbing solutions of $NO_2$ analysis methods.

Sorb: To take up and hold by absorption or adsorption.

Sorbent: A substance that takes up and holds another by absorption or adsorption.

Sorbitol dehydrogenase: An enzyme that interconverts the sugars, sorbitol and fructose.

Sorption: The process of being sorbed.

Spandex: A manufactured fiber in which the fiber forming substance is a long chain synthetic elastomer composed of at least 85 percent of a segmented polyurethane.

Spectrometer: An instrument used to measure radiation spectra or to determine wavelengths of the various radiations.

Spectrophotometry: A technique in which visible, UV, or infrared radiation is passed through a substance or solution and the intensity of light transmitted at various wavelengths is measured to determine the spectrum of light absorbed.

Spectroscopy: Use of the spectrometer to determine concentrations of an air pollutant.

Spermatocytes: A cell destined to give rise to spermatozoa (sperm).

Sphingomyelins: A group of phospholipids found in brain, spinal cord, kidney and egg yolk.

Sphygomenometer: An apparatus, consisting of a cuff and a pressure gauge, which is used to measure blood pressure.

Spirometry: Also called pneometry. Testing the air capacity of the lungs with a pneometer.

Spleen: A large vascular organ located on the upper left side of the abdominal cavity. It is a blood-forming organ in early life. It is a storage organ for red corpuscles and because of the large number of macrophages, acts as a blood filter.

Sputum: Expectorated matter, especially mucus or mucopurulent matter expectorated in diseases of the air passages.

Squamous: Scale-like, scaly.

Standard deviation: Measure of the dispersion of values about a mean value. It is calculated as the positive square root of the average of the squares of the individual deviations from the mean.

Standard temperature and pressure: $0^{o}C$, 760 mm mercury.

<u>Staphylococcus aureus</u>: A spherically-shaped, infectious species of bacteria found especially on nasal mucous membrane and skin.

Static lung compliance ($C_{lstat}$): Measure of lung's elastic recoil (volume change resulting from change in pressure) with no or insignificant airflow.

Steady state exposure: Exposure to air pollutants whose concentration remains constant for a period of time.

Steroids: A large family of chemical substances comprising many hormones and vitamins and having large ring structures.

Stilbene: An aromatic hydrocarbon $C_{14}H_{12}$ used as a phosphor and in making dyes.

Stoichiometric factor: Used to express the conversion efficiency of a non-quantitative reaction, such as the reaction of $NO_2$ with azo dyes in air monitoring methods.

Stoma: A minute opening or pore (plural is stomata).

Stratosphere: That region of the atmosphere extending from 11 km above the surface of the earth to 50 km. At 50 km above the earth temperature rises to a maximum of $0^oC$.

Streptococcus pyogenes: A species of bacteria found in the human mouth, throat and respiratory tract and in inflammatory exudates, blood stream, and lesions in human diseases. It causes formation of pus or even fatal septicemias.

Stress corrosion cracking: Cracking caused by simultaneous presence of tensile stress and a specific corrosive medium. The metal or alloy is virtually unattached over most of its surface, while fine cracks progress through it.

Strong interactions: Forces or bond energies holding molecules together. Thermal energy will not disrupt the formed bonds.

Sublobular hepatic necrosis: The pathologic death of one or more cells, or of a portion of the liver, beneath one or more lobes.

Succession: The progressive natural development of vegetation towards a climax, during which one community is gradually replaced by others.

Succinate: A salt of succinic acid involved in energy production in the citric acid cycle.

Sulfadiazine: One of a group of sulfa drugs. Highly effective against pneumococcal, staphlococcal, and streptococcal infections.

Sulfamethazine: An antibacterial agent of the sulfonamide group, active against homolytic streptococci, staphytococci, pneumococci and meningococci

Sulfanilimide: A crystalline sulfonamide ($C_6H_8N_2O_2S$), the amide of sulfanilic acid and parent compound of most sulfa drugs.

Sulfhydryl group: A chemical radical consisting of sulfur and hydrogen which confers reducing potential to the chemical compound to which it is attached (-SH).

Sulfur dioxide ($SO_2$): Colorless gas with pungent odor released primarily from burning of fossil fuels, such as coal, containing sulfur.

Sulfur dyes: Used only on vegetable fibers, such as cottons. They are insoluble in water and must be converted chemically in order to be soluble. They are resistant (fast) to alkalies and washing and fairly fast to sunlight.

Supernatant: The clear or partially clear liquid layer which separates from the homogenate upon centrifugation or standing.

Surfactant: A substance capable of altering the physiochemical nature of surfaces, such as one used to reduce surface tension of a liquid.

Symbiotic: A close association between two organisms of different species in which at least one of the two benefits.

Synergistic: A relationship in which the combined action or effect of two or more components is greater than that of the components acting separately.

Systolic: Relating to the rhythmical contraction of the heart.

Tachypnea: Very rapid breathing.

Terragram (Tg): One million metric tons, $10^{12}$ grams.

Teratogenesis: The disturbed growth processes resulting in a deformed fetus.

Teratogenic: Causing or relating to abnormal development of the fetus.

Threshold: The level at which a physiological or psychological effect begins to be produced.

Thylakoid: A membranous lamella of protein and lipid in plant chloroplasts where the photochemical reactions of photosynthesis take place.

Thymidine: A nucleoside ($C_{10}H_{14}N_2O_5$) that is composed of thymine and deoxyribose; occurs as a structural part of DNA.

Tidal volume ($V_T$): The volume of air that is inspired or expired in a single breath during regular breathing.

Titer: The standard of strength of a volumetric test solution. For example, the titration of a volume of antibody-containing serum with another volume containing virus.

Tocopherol: a-d-tocopherol is one form of Vitamin E prepared synthetically. The a form exhibits the most biological activity. It is an antioxidant and retards rancidity of fats.

Torr: A unit of pressure sufficient to support a 1 mm column of mercury; 760 torr = 1 atmosphere.

Total lung capacity (TLC): The sum of all the compartments of the lung, or the volume of air in the lungs at maximum inspiration.

Total suspended particulates (TSP): Solid and liquid particles present in the atmosphere.

Trachea: Commonly known as the windpipe, a cartilaginous air tube extending from the larnyx (voice box) into the thorax (chest) where it divides, serving as the entrance to each of the lungs.

Transaminase: Aminotransferase; an enzyme transferring an amino group from an a-amino acid to the carbonyl carbon atom of an a-keto acid.

Transmissivity (UV): The percent of ultraviolet radiation passing through a a medium.

Transmittance: The fraction of the radiant energy entering an absorbing layer which reaches the layer's further boundary.

Transpiration: The process of the loss of water vapor from plants.

Triethanolamine: An amine, $(HOCH_2CH_2)_3N$, used in the absorbing solution of one analytical method for $NO_2$.

Troposphere: That portion of the atmosphere in which temperature decreases rapidly with altitude, clouds form, and mixing of air masses by convection takes place. Generally extends to about 7 to 10 miles above the earth's surface.

Type 1 epithelial cells: Squamous cells which provide a continuous lining to the alveolar surface.

Type I pneumonocytes: Pulmonary surface epithelial cells.

Type II pneumonocytes: Great alveolar cells.

Ultraviolet: Light invisible to the human eye of wavelengths between $4x10^{-7}$ and $5x10^{-9}$ m (4000 to 50A).

Urea-formaldehyde resin: A compound composed of urea and formaldehyde in an arrangement that conveys thermosetting properties.

Urobilinogen: One of the products of destruction of blood cells; found in the liver, intestines and urine.

Uterus: The womb; the hollow muscular organ in which the impregnated ovum (egg) develops into the fetus.

Vacuole: A minute space in any tissue.

Vagal: Refers to the vagus nerve. This mixed nerve arises near the medulla oblongata and passes down from the cranial cavity to supply the larynx, lungs, heart, esophagus, stomach, and most of the abdominal viscera.

Valence: The number of electrons capable of being bonded or donated by an atom during bonding.

Van Slyke reactions: Reaction of primary amines, including amino acids, with nitrous acid, yielding molecular nitrogen.

Variance: A measure of dispersion or variation of a sample from its expected value; it is usually calculated as the square root a sum of squared deviations about a mean divided by the sample size.

Vat dyes: Dyes which have a high degree of resistance to fading by light, $NO_x$ and washing. Widely used on cotton and viscose rayon. Colors are brilliant and of almost any shade. The name was originally derived from their application in a vat.

Venezuelan equine encephalomyelitis: A form of equine encephalomyelitis found in parts of South America, Panama, Trinidad, and the United States, and caused by a virus. Fever, diarrhea, and depression are common. In man, there is fever and severe headache after an incubation period of 2 to 5 days.

Ventilatory volume ($V_E$): The volume of gas exchanged between the lungs and the atmosphere that occurs in breathing.

Villus: A projection from the surface, especially of a mucous membrane.

Vinyl chloride: A gaseous chemical suspected of causing at least one type of cancer. It is used primarily in the manufacture of polyvinyl chloride, a plastic.

Viscose rayon: Filaments of regenerated cellulose coagulated from a solution of cellulose xanthate. Raw materials can be cotton linters or chips of spruce, pine, or hemlock.

Visible region: Light between the wavelengths of 4000-8000 Å.

Visual range: The distance at which an object can be distinguished from background.

Vital capacity: The greatest volume of air that can be exhaled from the lungs after a maximum inspiration.

Vitamin E: Any of several fat-soluble vitamins (tocopherols), essential in nutrition of various vertibrates.

Washout: The capture of gases and particles by falling raindrops.

Weak interactions: Forces, electrostatic in nature, which bind atoms and/or molecules to each other. Thermal energy will disrupt the interaction. Also called van der Waal's forces.

Wet deposition: The process by which atmospheric substances are returned to earth in the form of rain or other precipitation.

Wheat germ lipase: An enzyme, obtained from wheat germ, which is capable of cleaving a fatty acid from a neutral fat; a lipolytic enzyme.

X-ray fluorescence spectrometry: A nondestructive technique which utilizes the principle that every element emits characteristic x-ray emissions when excited by high-energy radiation.

Zeolites: Hydrous silicates analogous to feldspars, occurring in lavas and various soils.

Zooplankton: Minute animal life floating or swimming weakly in a body of water.