



Air Quality Criteria for Particulate Matter

Volume III

Notice

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



Air Quality Criteria for Particulate Matter

Volume III

Notice

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

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

Disclaimer

This document is an external review draft for review purposes only and does not constitute U.S. Environmental Protection Agency policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Preface

National Ambient Air Quality Standards (NAAQS) are promulgated by the United States Environmental Protection Agency (U.S. EPA) to meet requirements set forth in Sections 108 and 109 of the U.S. Clean Air Act (CAA). Sections 108 and 109 require the EPA Administrator: (1) to list widespread air pollutants that may reasonably be expected to endanger public health or welfare; (2) to issue air quality criteria for them which assess the latest available scientific information on nature and effects of ambient exposure to them; (3) to set “primary” NAAQS to protect human health with adequate margin of safety and to set “secondary” NAAQS to protect against welfare effects (e.g., effects on vegetation, ecosystems, visibility, climate, manmade materials, etc); and (5) to periodically (every 5-yrs) review and revise, as appropriate, the criteria and NAAQS for a given listed pollutant or class of pollutants.

The original U.S. NAAQS for particulate matter (PM), issued in 1971 as “total suspended particulate” (TSP) standards, were revised in 1987 to focus on protecting against human health effects associated with exposure to ambient PM less than 10 microns ($\leq 10 \mu\text{m}$) that are capable of being deposited in thoracic (tracheobronchial and alveolar) portions of the lower respiratory tract. Later periodic reevaluation of newly available scientific information, as presented in the last previous version of this “Air Quality Criteria for Particulate Matter” document published in 1996, provided key scientific bases for PM NAAQS decisions published in July 1997. More specifically, the PM_{10} NAAQS set in 1987 ($150 \mu\text{g}/\text{m}^3$, 24-h; $50 \mu\text{g}/\text{m}^3$, annual ave.) were retained in modified form and new standards ($65 \mu\text{g}/\text{m}^3$, 24-h; $15 \mu\text{g}/\text{m}^3$, annual ave.) for particles $\leq 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) were promulgated in July 1997.

This First External Review Draft of revised Air Quality Criteria for Particulate Matter assesses new scientific information that has become available since early 1996 through mid-1999. Extensive additional pertinent information is expected to be published during the next 6 to 9 months (including results from a vastly expanded U.S. EPA PM Research program and from other Federal and State Agencies, as well as other partners in the general scientific community) and, as such, the findings and conclusions presented in this draft document must be considered only provisional at this time. The present draft is being released for public comment and review by the Clean Air Scientific Advisory Committee (CASAC) mainly to obtain comments on the

organization and structure of the document, the issues addressed, and the approaches employed in assessing and interpreting the thus far available new information on PM exposures and effects. Public comments and CASAC review recommendations will be taken into account, along with newly available information published or accepted for peer-reviewed publication by April/May 2000, in making further revisions to this document for incorporation into a Second External Review Draft. That draft is expected to be released in June 2000 for further public comment and CASAC review (September 2000) in time for final revisions to be completed by December 2000). Evaluations contained in the present document will be drawn upon to provide inputs to associated PM Staff Paper analyses prepared by EPA's Office of Air Quality Planning and Standards (OAQPS) to pose options for consideration by the EPA Administrator with regard to proposal and, ultimately, promulgation by July 2000 of decisions on potential retention or revision of the current PM NAAQS.

This document was prepared and reviewed by experts from Federal and State government agencies, academia, industry, and NGO's for use by EPA in support of decision making on potential public health and environmental risks of ambient PM. It describes the nature, sources, distribution, measurement, and concentrations of PM in both the outdoor (ambient) and indoor environments and evaluates the latest data on the health effects in exposed human populations, as well as environmental effects on: vegetation and ecosystems; visibility and climate; manmade materials; and associated economic impacts. Although not intended to be an exhaustive literature review, this document is intended to assess all pertinent literature through mid-1999.

The National Center for Environmental Assessment – Research Triangle Park, NC (NCEA-RTP) acknowledges the contributions provided by authors, contributors, and reviewers and the diligence of its staff and contractors in the preparation of this document.

Air Quality Criteria for Particulate Matter

VOLUME I

1. EXECUTIVE SUMMARY	1-1
2. INTRODUCTION	2-1
3. PHYSICS, CHEMISTRY, AND MEASUREMENT OF PARTICULATE MATTER	3-1
4. CONCENTRATIONS, SOURCES, AND EMISSIONS OF ATMOSPHERIC PARTICLES	4-1
APPENDIX 4A: Composition of Particulate Matter Source Emissions	4A-1
5. HUMAN EXPOSURE TO AMBIENT PARTICULATE MATTER: RELATIONS TO CONCENTRATIONS OF AMBIENT AND NON-AMBIENT PARTICULATE MATTER AND OTHER AIR POLLUTANTS	5-1
APPENDIX 5A: Nomenclature	5A-1

VOLUME II

6. EPIDEMIOLOGY OF HUMAN HEALTH EFFECTS FROM AMBIENT PARTICULATE MATTER	6-1
7. DOSIMETRY AND TOXICOLOGY OF PARTICULATE MATTER	7-1
8. INTEGRATIVE SYNTHESIS OF KEY POINTS: PARTICULATE MATTER EXPOSURE, DOSIMETRY, AND HEALTH RISKS	8-1

VOLUME III

9. ENVIRONMENTAL EFFECTS OF PARTICULATE MATTER	9-1
--	-----

Table of Contents

	<u>Page</u>
List of Tables	III-ix
List of Figures	III-xi
Authors, Contributors, and Reviewers	III-xiii
U.S. Environmental Protection Agency Project Team for Development of Air Quality Criteria for Particulate Matter	III-xv
9. ENVIRONMENTAL EFFECTS OF PARTICULATE MATTER	9-1
9.1 INTRODUCTION	9-1
9.2 EFFECTS ON VEGETATION	9-1
9.2.1 Plant Response/Mode of Action	9-3
9.2.1.1 Direct Plant Response	9-4
9.3 NATURAL ECOSYSTEMS	9-12
9.3.1 Introduction	9-12
9.3.2 Ecosystem Response to Stress	9-15
9.3.3 Direct Effects of Particulate Matter	9-18
9.3.3.1 Introduction	9-18
9.3.3.2 Direct Effects	9-20
9.3.4 Indirect Effects of Particulate Matter	9-22
9.3.4.1 Introduction	9-22
9.3.4.2 Nitrogen	9-23
9.3.4.3 Sulfur	9-29
9.3.4.4 Effects of Acidic Deposition on Forest Soils	9-30
9.3.4.5 Trace Elements	9-37
9.3.4.6 Biogeochemical Cycling—the Integrated Forest Study	9-41
9.4 EFFECTS ON MATERIALS	9-57
9.4.1 Corrosive Effects of SO ₂ and Particles on Man-Made Surfaces	9-57
9.4.1.1 Metals	9-57
9.4.1.2 Painted Surfaces	9-61
9.4.1.3 Stone and Concrete	9-62
9.4.2 Soiling and Discoloration of Manmade Surfaces	9-66
9.4.2.1 Stones and Concrete	9-67
9.4.2.2 Household and Industrial Paints	9-67
9.5 EFFECTS ON VISIBILITY	9-68
9.5.1 Introduction	9-68
9.5.2 Factors Affecting Atmospheric Visibility	9-69
9.5.2.1 Anthropogenic Pollutants	9-69
9.5.2.2 Human Vision	9-69
9.5.2.3 Characteristics of the Atmosphere	9-70
9.5.3 Optical Properties of Particles	9-72
9.5.4 Effect of Relative Humidity on Particle Size and Light Scattering Properties	9-74
9.5.5 Measures of Visibility	9-75

Table of Contents
(cont'd)

	<u>Page</u>
9.5.5.1 Human Observations	9-75
9.5.5.2 Light-Extinction Coefficient and Parameters Related to the Light-Extinction Coefficient	9-75
9.5.5.3 Light-Scattering Coefficient	9-78
9.5.5.4 Fine Particulate Matter Concentrations	9-80
9.5.5.5 Discoloration	9-80
9.5.6 Visibility Monitoring Methods and Networks	9-80
9.5.7 Visibility Modeling	9-84
9.5.7.1 Regional Haze	9-84
9.5.7.2 Plume Models	9-88
9.5.7.3 Photographs	9-89
9.5.8 Trends in Visibility Impairment	9-90
9.6 THE EFFECTS OF PARTICLES ON CLIMATE AND ON THE TRANSMISSION OF SOLAR ULTRAVIOLET RADIATION	9-91
9.6.1 Effects of Particles on the Transmission of Solar Ultraviolet Radiation	9-92
9.6.2 Effects of Particles on Climate	9-95
9.7 ECONOMICS OF PM ENVIRONMENTAL EFFECTS	9-100
9.7.1 Introduction	9-100
9.7.2 Need for Defining Exposure-Effect Relationships	9-100
9.7.3 Valuation Approaches	9-101
9.7.4 Effects on Agriculture and Forestry	9-102
9.7.5 Materials Damage Effects and Valuation	9-103
9.7.5.1 Valuation Methods	9-104
9.7.5.2 Household Soiling	9-105
9.7.5.3 Materials Damage to Industrial/Commercial Structures	9-106
9.7.5.4 Materials Damage to Cultural/Historical Structures	9-106
9.7.6 Effects on Visibility	9-107
9.7.7 Effects on Ecosystems	9-108
9.8 SUMMARY	9-110
9.8.1 Particulate Matter Effects on Vegetation and Ecosystems	9-110
9.8.2 Particulate Matter-Related Effects on Materials	9-113
9.8.3 Particulate Matter-Related Effects on Visibility	9-114
9.8.4 Effects of Particulate Matter on Global Climate and the Transmission of Solar Ultraviolet Radiation	9-115
9.8.5 Economic Impact of Particulate Matter	9-116
REFERENCES	9-117

List of Tables

<u>Number</u>		<u>Page</u>
9-1	Ecosystem Services	9-14
9-2	Interaction of Air Pollution and Temperate Forest Ecosystems Under Conditions of Intermediate Air Contaminant Load	9-19
9-3	Simulated Deposition, Leaching, and Ecosystem Pools at the Duke Site with and Without Particulate Deposition Using the NuCM Model	9-52
9-4	Simulated Deposition, Leaching, and Ecosystem Pools at the Smokies Tower Site with and Without Particulate Deposition Using the NuCM Model	9-54
9-5	Effects of SO ₂ And Particulate Matter on Metals	9-59
9-6	Effects of SO ₂ and Particulate Matter on Stone	9-63
9-7	Averaged Regional PM _{2.5} Mass and Extinction Summaries for the Years 1988 to 1996	9-83

List of Figures

<u>Number</u>		<u>Page</u>
9-1	Effects of environmental stress on forest trees are presented on a hierarchical scale for the leaf, branch, tree, and stand levels of organization	9-16
9-2	Nitrogen cycle	9-26
9-3	Diagrammatic overview of N excess in North America	9-28
9-4	Schematic of sources and sinks of hydrogen ions in a forest	9-32
9-5	Relationship of plant nutrients and trace metals with vegetation	9-39
9-6	Calcium deposition in $>2 \mu\text{m}$ particles, $<2 \mu\text{m}$ particles, and wet forms and leaching in the Integrated Forest Study sites	9-43
9-7	Magnesium deposition in $>2 \mu\text{m}$ particles, $<2 \mu\text{m}$ particles, and wet forms and leaching in the Integrated Forest Study sites	9-44
9-8	Potassium deposition in $>2 \mu\text{m}$ particles, $<2 \mu\text{m}$ particles, and wet forms and leaching in the Integrated Forest Study sites	9-45
9-9	Base cation deposition in $>2 \mu\text{m}$ particles, $<2 \mu\text{m}$ particles, and wet forms and leaching in the Integrated Forest Study sites	9-46
9-10	Total cation leaching balanced by sulfate and nitrate estimated from particulate deposition and by other sources of sulfate and nitrate and by other anions in the Integrated Forest Study sites	9-47
9-11	Soil exchangeable Ca^{++} pools and net annual export of Ca^{++} in the Integrated Forest Study sites	9-48
9-12	Soil exchangeable Mg^{++} pools and net annual export of Mg^{++} in the Integrated Forest Study sites	9-49
9-13	Soil exchangeable K^{++} pools and net annual export of K^{++} in the Integrated Forest Study sites	9-50
9-14	Light reflected from a target toward an observer	9-71
9-15	Humidity effect on scattering coefficients computed for internal and external mixtures of the mixed-salt aerosol	9-76

List of Figures
(cont'd)

<u>Number</u>		<u>Page</u>
9-16	Scattering ratios for different chemical compositions as a function of relative humidity	9-77
9-17a,b	Plots of the 10th, 50th, and 90th percentile groups for PM _{2.5} and deciview at the Badlands National Park	9-79
9-18	Reduction in visual range as a function of increasing fine (sulfate) and coarse (dust) particle concentrations	9-81
9-19	Estimated global mean radiative forcing exerted by gas and particle phase species from 1850 to 1950	9-98

Authors, Contributors, and Reviewers

CHAPTER 9. ENVIRONMENTAL EFFECTS OF PARTICULATE MATTER

Principal Authors

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

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

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

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

Contributors and Reviewers

Dr. Russell R. Dickerson—University of Maryland, Department of Meteorology
Stadium Drive, College Park, MD 20742

Dr. Sagar V. Krupa—University of Minnesota, Department of Plant Pathology
495 Borlaug Hall, 1991 Upper Buford Circle, St. Paul, MN 55108

Dr. Alan J. Krupnick—Quality of the Environment Division, Resources for the Future
1616 P Street, NW, Washington, DC 20036

Mr. Paul T. Roberts—Sonoma Technology, Inc., 1360 Redwood Way - Suite C
Petaluma, CA 94954

Mr. John Spence—1206 Sturdivant Drive, Cary, NC 27511

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

Scientific Staff

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

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

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

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

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

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

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

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

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

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

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

(cont'd)

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

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

Technical Support Staff

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

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

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

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

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

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

Document Production Staff

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

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

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

(cont'd)

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

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

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

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

Technical Reference Staff

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

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

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

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

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

9. ENVIRONMENTAL EFFECTS OF PARTICULATE MATTER

9.1 INTRODUCTION

Several earlier chapters (Chapters 5-8) of this document assess the latest available information on: determinants of human exposures to particulate matter (PM); dosimetry of particle deposition, clearance, and retention in human respiratory tract; epidemiologic analyses of health effects associated with human exposures to ambient PM; and toxicologic evaluations of pathophysiologic effects of PM and underlying mechanisms of action. The human exposure and health-related findings assessed in those chapters provide key elements of the scientific bases to support upcoming decision making regarding potential retention or revision of the primary PM NAAQS. This chapter in contrast, assesses information pertinent to decision making regarding secondary standards aimed at protecting against welfare effects of PM. More specifically, this chapter assesses environmental effects of PM, including discussion of the following topics: (a) particulate matter effects on vegetation and ecosystems; (b) PM effects on visibility; (c) PM effects on man-made materials; (d) relationships of ambient PM to global climate change processes; and (e) the economics of PM environmental effects.

9.2 EFFECTS ON VEGETATION

The Particulate Matter National Ambient Air Quality Standards (NAAQS) set in 1971 were specified in terms of total suspended particulates (TSP), which included both fine and coarse mode particles (the latter ranging up to 25-40 μm in size). The 1987 revision of the TSP NAAQS to PM_{10} standards focused attention on those particles ($\leq 10 \mu\text{m}$ Mean Aerometric Diameter) capable of being deposited in lower (thoracic) portions of the human respiratory tract. The subsequent 1997 PM NAAQS revisions retained PM_{10} standards and added fine particle ($\text{PM}_{2.5}$) standards (both specified in terms of mass concentrations of particles undifferentiated in terms of their specific chemical composition). The PM effects on vegetation and ecosystems

1 evaluated in this chapter are dependent not so much just on PM size-related mass concentration,
2 but rather exposure of plants to PM components differentiated by chemical composition as well.

3 Exposure to a given mass concentration of PM₁₀ may lead to widely differing phytotoxic
4 responses, depending on the particular mix of deposited particles. The most common and useful
5 subdivision of PM, derived from the clearly bimodal distribution of atmospheric particles, is into
6 fine and coarse particles (Wilson and Suh, 1997). In the following section describing vegetation
7 and ecosystem effects, dry deposited particles are divided into: (1) “fine”, those having a mean
8 diameter <2 μm and (2) “coarse”, those whose diameter is >2 μm mean diameter. Whitby (1978)
9 recommended this size separation because it placed particles into two categories with different
10 formation, transformation, and removal characteristics.

11 Atmospheric deposition of particles to ecosystems takes place via both wet and dry
12 processes through the three major routes indicated below:

- 13 (1) Precipitation scavenging in which particles are deposited in rain and snow;
- 14 (2) Fog, cloud-water, and mist interception;
- 15 (3) Dry deposition, a much slower, yet more continuous removal to surfaces (Hicks, 1986).

16 Dry deposition is considered more effective for coarse particles of natural origin and elements
17 such as iron and manganese, whereas wet deposition generally is more effective for fine particles
18 of atmospheric origin and elements such as cadmium, chromium, lead, nickel, and vanadium
19 (Smith, 1990b). The actual importance of wet versus dry deposition, however, is highly variable,
20 depending on the type of ecosystem, location and elevation.

21 Dry deposition of particles occurs to all vegetational surfaces exposed to the atmosphere
22 (U.S. Environmental Protection Agency, 1982). The range of particle sizes, the diversity of
23 canopy surfaces, and the variety of chemical constituents in airborne PM have slowed progress in
24 both prediction and measurement of dry particulate deposition. Wet deposition generally is
25 confounded by fewer factors and has been easier to quantify (Chapter 3; U.S. Environmental
26 Protection Agency, 1999).

27 Emphasis in this and the next section is placed on discussion of PM effects on natural
28 plants and terrestrial ecosystems. Except for the deposition of nitrogen and sulfur-containing
29 compounds and their effects exerted via acidic precipitation, information concerning the effects
30 of the deposition of other specific substances as PM on crops is not readily available. The
31 NAPAP Biennial Report to Congress: An Integrated Assessment presents an extensive overall

1 discussion of the effects of acidic deposition (National Science and Technology Council, 1998).
2 The effects of gaseous sulfur oxides and nitrogen oxides on crops are discussed in detail in the
3 criteria documents for those substances (U.S. Environmental Protection Agency, 1982; 1993).
4 A detailed discussion of the ecological effects of acidic precipitation and nitrate deposition on
5 aquatic ecosystems can be found in the nitrogen oxides criteria document (U.S. Environmental
6 Protection Agency, 1993). Neither nitrate or sulfate deposition on crops is discussed in this
7 chapter, as they are frequently added in fertilizers. The document, Deposition of Air Pollutants
8 to the Great Waters (part of the hazardous air pollutant program), also presents the ecological
9 effects of deposition of nitrates and, in addition, includes the effects of metals, organic
10 compounds and pesticides deposited into the Great Lakes (U.S. Environmental Protection
11 Agency, 1997). Lastly, the effects of lead on crops, vegetation and ecosystems are discussed in
12 the document, Air Quality Criteria for Lead, Vol. II (U.S. Environmental Protection Agency,
13 1986)

14 The effects of PM may be direct or indirect. Indirect effects are chiefly nutritional
15 responses mediated through the soil and result from the effect the components of PM have on
16 soil processes. They are discussed here as ecosystem effects rather than as effects on individual
17 plants.

19 **9.2.1 Plant Response/Mode of Action**

20 Particulate matter in the atmosphere may affect vegetation directly following deposition on
21 foliar surfaces, indirectly by changing the soil chemistry, or through changes in radiation and
22 climate induced by PM. Indirect impacts, however, are usually the most significant because they
23 can alter nutrient cycling and inhibit plant nutrient uptake. Studies of the direct effects of PM
24 depositions on foliage have found little or no effects of PM on foliar processes unless exposure
25 levels were significantly higher than ambient exposures. Interpretation of the effects of
26 atmospheric chemical deposition at the level of individual plants and ecosystems is difficult
27 because of the complex interactions that exist among biological, physiochemical, and climatic
28 factors. The majority of the easily identifiable direct and indirect effects, other than climate,
29 occur in severely polluted areas around heavily industrialized point sources. Particles transferred
30 from the atmosphere to foliar surfaces may (1) reside on the leaf, twig, or bark surface for an
31 extended period; (2) be taken up through the leaf surface; or (3) be removed from the plant via

1 resuspension to the atmosphere, washing by rainfall, or litter-fall with subsequent transfer to the
2 soil (U.S. Environmental Protection Agency, 1999). Both direct and indirect effects of airborne
3 particles on vegetation are discussed in the sections that follow. The effects of particulate matter
4 on vegetation and ecosystems have been reviewed more comprehensively in U.S. Environmental
5 Protection Agency (1999).

7 **9.2.1.1 Direct Plant Response**

8 ***Introduction***

9 Particulate matter in the atmosphere may affect vegetation directly following physical
10 contact with foliar surfaces or indirectly through the soil. Indirect impacts are usually the most
11 significant because they can alter nutrient cycling and inhibit plant uptake of nutrients from the
12 soil. The majority of the easily identifiable direct and indirect effects, other than climate, occur
13 in severely polluted areas around heavily industrialized point sources such as limestone quarries,
14 cement kilns, iron, lead, and various smelting factories.

15 Particles transferred from the atmosphere to foliar surfaces may (1) reside on the leaf, twig
16 or bark surface for an extended period; (2) be taken up through the leaf surface; or (3) removed
17 from the plant via suspension to the atmosphere, washing by rainfall, or litter-fall with
18 subsequent transfer to the soil. Particulate matter deposited on above-ground plant parts can
19 have both a physical and a chemical impact. The effects of “inert” PM are mainly physical,
20 while the effects of toxic particles are both chemical and physical. The chemical effects of dust
21 deposited on plant surfaces or on soil are more likely to be associated with their chemistry than
22 with of mass deposited particles and may be more important than any physical effects (Farmer
23 1993).

24 Studies of the direct effects of chemical additions to foliage in particulate deposition have
25 found little or no effects of PM on foliar processes unless exposure levels were significantly
26 higher than would typically be experienced in the ambient environment. Interpretation of the
27 effects of atmospheric chemical deposition at the level of individual plants and ecosystems is
28 difficult because of the complex interactions that exist among biological, physicochemical, and
29 climatic factors. The diverse chemical nature, size characteristics of ambient airborne particles
30 and the lack of any clear distinction between effects attributed to phytotoxic particles and to other
31 forms of air pollutants confound the direct effects of PM on foliar surfaces. The majority of

1 documented toxic effects of particles on vegetation reflect their acidity, trace metal content,
2 nutrient content, surfactant properties, or salinity. These materials typically elicit similar
3 biological effects whether deposited as coarse or fine particles, in wet, dry, or occult form, and
4 frequently, whether deposited to foliage or to the soil. Studies of direct effects of particles on
5 vegetation have not yet advanced to the stage of reproducible exposure experiments.
6 Experimental difficulties in application of ambient particles to vegetation have been discussed by
7 Olszyk et al. (1989).

9 ***Effects of Coarse Particles***

10 Coarse particles are chemically diverse. They range in size from 2.5 to 100 μm and, in
11 general, are primary in nature having been produced and emitted from a point or area source as a
12 fully formed particle. They are dominated by local sources and the particles are deposited near
13 their source because of their sedimentation velocity. They range from road, cement kiln and
14 foundry dust, and tire particles, to soot and cooking oil droplets, plant pollen, fungal spores, and
15 abraded plant parts, to sea salt. The majority of coarse particles in rural and some urban areas are
16 composed of silicon, aluminum, calcium, and iron suggesting their source is fugitive dust from
17 disturbed land, roadways, agricultural tillage, or construction. Rapid sedimentation of these
18 particles suggests that direct effects are restricted to roadsides and forest edges (U.S.
19 Environmental Protection Agency, 1999).

21 ***Physical Effects.*** Deposition of inert PM on above-ground plant organs may result in an
22 increase in radiation received, in leaf temperature and blockage of stomata. Increased leaf
23 temperature, heat stress, reduced net photosynthesis, and leaf chlorosis, necrosis, and abscission
24 were reported by Guderian (1986). Road dust decreased the leaf temperature on *Rhododendron*
25 *catawbiense* by approximately 4° C (Eller, 1977) while foundry dust caused an 8.7° C increase in
26 leaf temperature of black poplar (*Populus nigra*) (Guderian, 1986) under the conditions of the
27 experiment. Broad-leaved plants exhibited greater temperature increases due to particle loading
28 than did the needle-like leaves of conifers. Brandt and Rhoades (1973) attributed the reduction
29 in growth of trees to crust formation on the leaves. Crust formation reduced photosynthesis and
30 formation of carbohydrate needed for normal growth, induced premature leaf-fall, destruction of
31 leaf tissues, inhibited growth of new tissue and reduced storage.

1 Dust also has been reported to physically block stomata (Krajičková and Mejstřík, 1984).
2 Stomatal clogging by particulate matter from automobiles, stone quarries and cement plants was
3 also studied by Abdullah and Iqbal (1991). The percentage of clogging was low in young leaves
4 when compared with old and mature leaves and the amount of clogging varied with species and
5 locality. The maximum clogging of stomata observed was about 25%. The authors cited no
6 evidence that stomatal clogging inhibited plant functioning. The heaviest deposit of dust is
7 usually on the upper surface of broad-leaved plants, however, while the majority of the stomata
8 are on the lower surface where stomatal clogging would be less likely.

9
10 ***Chemical Effects.*** The chemical composition of PM is usually the phytotoxic factor
11 leading to plant injury. Cement-kiln dust on hydration liberates calcium hydroxide which can
12 penetrate the epidermis and enter the mesophyll when in some cases the leaf surface alkalinity
13 may reach to pH 12. Lipid hydrolysis coagulation of the protein compounds and ultimately
14 plasmolysis of the leaf tissue results in reduction in growth and quality of plants (Guderian,
15 1986). In experimental studies, application of cement kiln dust of known composition for
16 2-3 days yielded dose-response curves between net photosynthetic inhibition or foliar injury and
17 dust application rate (Darley, 1966). Lerman and Darley (1975) determined that leaves must be
18 misted regularly to produce large effects. Alkalinity was probably the essential phytotoxic
19 property of the applied dusts.

20 Particulate matter in the form of sea salt enters the atmosphere from oceans following
21 mixing of air into the water and subsequent bursting of bubbles at the surface. This process can
22 be a significant source of sulfate, sodium chloride, and trace elements in the atmosphere over
23 coastal vegetation, resulting in the formation of the maritime forest, a specialized ecosystem.
24 Sea-salt particles can serve as nuclei for the adsorption and subsequent reaction of other gaseous
25 and particulate pollutants. Both nitrate and sulfate from the atmosphere have been found
26 associated with coarse and fine sea-salt particles (Wu and Okada, 1994). Direct effects on
27 vegetation reflect these inputs as well as classical salt injury caused by the sodium and chloride
28 that constitute the bulk of these particles.

1 *Effects of Fine Particles*

2 Fine particulate matter is generally secondary in nature having condensed from the vapor
3 phase or been formed by chemical reaction from gaseous precursors in the atmosphere and is
4 generally smaller than 1 μm , although particles up to 2.5 μm may be included in the fine fraction.
5 Nitrogen and sulfur oxides, as well as volatile organic gases, are common precursors for fine PM.
6 Condensation of volatilized metals and products of incomplete combustion also are common
7 precursors for fine PM. The conclusion reached in 1982 in the Air Quality Criteria for
8 Particulate Matter and Sulfur Oxides (U.S. Environmental Protection Agency, 1982) that
9 sufficient data were not available for adequate quantification of dose-response functions for
10 direct effects of fine aerosols on vegetation continues to be true today. Only a few studies have
11 been completed on the direct effects of acid aerosols (U. S. Environmental Protection Agency,
12 1982).

13
14 ***Nitrogen/Sulfur.*** Despite the paucity of information regarding direct effects of fine particle
15 deposition on vegetation, significant vegetation effects resulting from long-term chemical
16 deposition have been suggested. Direct foliar effects of particulate nitrogen have not been
17 documented (Martin et al., 1992). Nitrogen uptake in forests may be regulated loosely by sulfur
18 availability, but sulfate addition in excess of need does not typically lead to injury (Turner and
19 Lambert, 1980). Current levels of sulfate deposition reportedly exceed the capacity of most
20 vegetative canopies to immobilize sulfur (Johnson, 1984). There are few field demonstrations of
21 foliar sulfate uptake (Krupa and Legge, 1986). Acid sulfate aerosol (500 $\mu\text{g}/\text{m}^3$) had no effect on
22 soybean or pinto bean after a single 4-h exposure (Chevone et al., 1986). Sulfate in itself has not
23 been shown to be phytotoxic.

24
25 ***Acidic Deposition.*** The effects of acidic deposition have been given wide exposure in the
26 media and elsewhere (U. S. Environmental Protection Agency, 1984; Linthurst, 1984; Hogan
27 et al., 1998). Probably the most extensive assessment of acidic deposition processes and, effects
28 is the NAPAP Biennial Report to Congress: An Integrated Assessment (National Science and
29 Technology Council, 1998). Concern regarding the effects on crops and forest trees has resulted
30 in extensive monitoring and research. Exposures to acidic rain or clouds can be divided into
31 ‘acute’ exposures to higher ionic concentrations (several $\mu\text{mol}/\text{l}$), and ‘chronic’ long-term

1 repeated exposures to lower concentrations (Cape, 1993). Pollutant concentrations in rainfall
2 have been shown to have little capacity for producing direct effects on vegetation (U. S.
3 Environmental Protection Agency, 1984; Linthurst, 1984; Hogan et al., 1998); however, fog and
4 clouds, which may contain solute concentrations up to 10 times those found in rain, have the
5 potential for direct effects. Over 80% of the ionic composition of most cloud water is made up
6 of four major pollutant ions H^+ , NH_4^+ , NO_3^- , and SO_4^{2-} . Ratios of hydrogen to ammonium, and
7 sulphate to nitrate, vary from site to site with all four ions usually present in approximately equal
8 concentrations. Available data from plant effect studies suggests that hydrogen and sulphate ions
9 are more likely to cause injury than nitrogen containing ions (Cape, 1993).

10 Based on his review of the many studies on field and controlled laboratory experiments on
11 crops in the literature, Cape (1993) drew a number of conclusions concerning the direct effects of
12 acidic precipitation on crops:

- 13 (1) foliar injury and growth reduction occurs below pH 3;
- 14 (2) allocation of photosynthate is altered, with increased shoot to root ratios;
- 15 (3) expanded and recently expanded leaves are most susceptible, and injury occurs first to
16 epidermal cells;
- 17 (4) leaf surface characteristics such as wettability, buffering capacity, and transport of
18 material across the leaf surface contribute to susceptibility and differ among species;
- 19 (5) data obtained from experiments in greenhouses or controlled environmental chambers
20 cannot be used to predict effects on plants grown in the field;
- 21 (6) quantitative data from experimental exposures cannot be extrapolated to field
22 exposures because of differences and fluctuations in concentrations, durations and
23 frequency of exposure;
- 24 (7) there are large differences in response within species;
- 25 (8) timing of exposure in relation to phenology is of utmost importance;
- 26 (9) plants may be able to recover from or adapt to injurious exposures;
- 27 (10) sequential exposure to acidic precipitation and gaseous pollutants is unlikely to be
28 more injurious than exposure to individual pollutants.

29 Most of the above conclusions are likely to apply equally to experiments performed on
30 trees to evaluate the potential effects of acidic precipitation” (Cape, 1993). The size of mature

1 trees makes experimental exposures difficult, therefore, extrapolations have to be made from
2 experiments using seedlings or saplings.

3 Studies by Chevone et al. (1986), Krupa and Legge (1986) and Blaschke (1990) differ with
4 conclusion #10 of Cape listed above. Their studies indicate that interactions between acidic
5 deposition and gaseous pollutants does occur. Acidity affects plant responses to both O₃ and
6 SO₂. Chevone et al. (1986) observed increased visible injury on soybean and pinto bean when
7 acid aerosol exposure preceded O₃ exposure, while linear decreases in dry root weight of yellow
8 poplar as acidity increased when exposures were to O₃ and simulated acid rain at the same time.
9 Krupa and Legge (1986) also noted increased visible injury to pinto bean when aerosol exposure
10 preceded O₃ exposure. In none of the studies cited above did acid rain in itself produce
11 significant growth changes. Blaschke (1990) observed a decrease in ectomycorrhizal frequency
12 and short root distribution as result of exposure to acid rain in combination with either SO₂ or O₃.

13
14 ***Trace Elements.*** All but 10 of the 90 elements that comprise the inorganic fraction of the
15 soil occur at concentrations of less than 0.1% (1,000 μg·g⁻¹). These are termed “trace” elements.
16 Trace elements with a density greater than 6g·cm⁻³ are of particular interest because of their
17 potential toxicity for plant and animals. Although some trace metals are essential for vegetative
18 growth or animal health, in large quantities, they are all toxic. Combustion processes produce
19 metal chlorides which tend to be volatile, and metal oxides which tend to be nonvolatile in the
20 vapor phase (McGowan et al., 1993) Most trace elements exist in the atmosphere in particulate
21 form as metal oxides (Ormrod, 1984). Aerosols containing trace elements result predominantly
22 from industrial activities (Ormrod, 1984). Generally, only cadmium, chromium, nickel, and
23 mercury are released from stacks in the vapor phase (McGowan et al., 1993). The concentrations
24 of heavy metals in incinerator fly ash increase with decreasing particle size.

25 The dominant impact of trace metals on vegetative systems involve foliar and
26 above-ground plant parts. Vegetational surfaces, especially the foliage, present a major reaction
27 and filtration surface to the atmosphere and act to accumulate particles deposited via wet and dry
28 processes described in Chapter 3 (Tong, 1991; Youngs et al., 1993). Particles deposited upon
29 foliar surfaces may be taken up through the leaf surface. The greatest particle loading is usually
30 on the adaxial (upper) leaf surface where particles accumulate in the mid-vein, center portion of

1 the leaves. The mycelium of fungi becomes particularly abundant on leaf surfaces as the growing
2 season progresses and is in intimate association with deposited particles (Smith, 1990c).

3 Investigations of trace elements present along roadsides and in industrial and urban
4 environments have indicated that impressive burdens of particulate heavy metal can accumulate
5 on vegetative surfaces. Foliar uptake of available metals could result in metabolic impact in
6 above-ground tissues. Only a few metals, however, have been documented to cause direct
7 phytotoxicity in field conditions. Copper, zinc and nickel toxicities have been most frequently
8 observed. Low solubility, however, limits foliar uptake and direct heavy metal toxicity. Trace
9 metals in mixtures may interact to cause a different plant response when compared with a single
10 element, however, there has been little research on this aspect (Ormrod, 1984). In a study by
11 Marchińska and Kucharski (1987) the combined effect of SO₂ and heavy metal containing PM on
12 beans, carrots, and parsley produced little effect.

13 Trace metal toxicity of lichens has been demonstrated in relatively few cases. Nash (1975)
14 documented zinc toxicity in the vicinity of a zinc smelter near Palmerton, PA. Lichen species
15 richness and abundance were reduced by approximately 90% in lichen communities at Lehigh
16 Water Gap near the zinc smelter when compared with those at Delaware Water Gap. Zinc,
17 cadmium, and sulfur dioxide were present in concentrations toxic to some species near the
18 smelter, however, toxic zinc extended beyond the detectable limits of sulfur dioxide (Nash,
19 1975). Experimental data suggests that lichen tolerance to Zn and Cd fall between 200 and
20 600 ppm (Nash, 1975).

21 A potential direct impact of heavy metal is on the activity of arthropods and
22 microorganisms resident on and in the leaf surface ecosystem. The fungi and bacteria living on
23 and in the surfaces of leaves play an important role in the microbial succession that prepares
24 leaves for decay and litter decomposition after their fall (U.S. Environmental Protection Agency,
25 1996a).

26 Numerous fungi were consistently isolated from foliar surfaces, at various crown positions,
27 from London plane trees growing in roadside environments in New Haven, CT. Those existing
28 primarily as saprophytes included *Aureobasidium pullulans*, *Chaetomium sp.*, *Cladosporium sp.*,
29 *Epicoccum sp.*, and *Philaphora verrucosa*. Those existing primarily as parasitices included
30 *Gnomonia platani*, *Pestalotiposis sp.*, and *Pleurophomella sp.* The following cations were tested
31 in vitro for their ability to influence the growth of these fungi: cadmium, copper, manganese,

1 aluminum, chromium, nickel, iron, lead, sodium, and zinc. Results indicated variable fungal
2 response with no correlation between saprophytic or parasitic activity and sensitivity to heavy
3 metals. Both linear extension and dry weight data indicated that the saprophytic *Chaetomum sp.*
4 was very sensitive to numerous metals. *Aureobasidium pullulans*, *Epicoccum sp.*, and especially
5 *P. verrucosa*, on the other hand, appeared to be much more tolerant. Of the parasites, *G. platani*
6 appeared to be more tolerant than *Pestalotiopsis sp.* and *Pleurophomella sp.* Metals exhibiting
7 the broadest spectrum growth suppression were iron, aluminum, nickel, zinc, manganese, and
8 lead (Smith and Staskawicz, 1973; Smith, 1990d). These in vitro studies employed soluble
9 compounds containing heavy metals. In nature, trace metals probably occur on leaf surfaces as
10 low-solubility oxides, halides, sulfates, sulfides, or phosphates (Clevenger et al., 1991; Koslow
11 et al., 1977). In the event of sufficient solubility and dose, however, changes in microbial
12 community structure on leaf surfaces because of heavy metal accumulation are possible.

13
14 **Organics.** Fine particles distributed over regional- and global-scale distances are
15 contaminated preferentially with a variety of organic materials and trace metals. Henry's Law
16 constants indicate that many organic xenobiotics are present in the troposphere in the vapor
17 phase (Gaggi et al., 1985). During transport, however, organics attach to particles in the
18 atmosphere and are transferred back to earth via wet and dry deposition. Materials as diverse as
19 DDT, polychlorinated biphenyls (PCBs), and polynuclear aromatic hydrocarbons (PAHs) are
20 being deposited from the atmosphere on rural as well as urban landscapes (Kylin et al., 1994).
21 Motor vehicles emit particles to the atmosphere from several sources in addition to the tailpipe.
22 Rogge et al. (1993b) inventoried the organic contaminants associated with fine particles
23 (diameter $\leq 2.0 \mu\text{m}$) in road dust, brake lining wear particles, and tire tread debris. In excess of
24 100 organic compounds were identified in these samples, including n-alkanols, benzoic acids,
25 benaldehydes, polyalkylene glycol ethers, PAHs, oxy-PAH, steranes, hopanes, natural resins, and
26 other compound classes. A large number of PAHs, ranging from naphthalene (C_{10}H_8) to 5- and
27 6-ring and higher PAHs; their alkyl-substituted analogues; and their oxygen- and nitrogen-
28 containing derivatives are emitted from motor vehicle sources (Seinfeld, 1989).

29 Carbonaceous aerosol is an important component of urban fine PM. Aerosol carbon
30 represents 40% of the fine particle mass in Los Angeles. Black graphitic (elemental) carbon is
31 the predominant light-absorbing particle in the urban atmosphere. The carbon fraction consists

1 of both primary and secondary components. The former may be emitted directly from
2 combustion sources, whereas the latter may be formed in the atmosphere from the low-vapor-
3 pressure products of reactions involving hydrocarbons containing approximately seven or more
4 carbon atoms (Seinfeld, 1989).

5 Vegetation itself is an important source of hydrocarbon aerosols. Terpenes, particularly
6 α -pinene, β -pinene, and limonene released from tree foliage may react in the atmosphere to form
7 submicron particles. These naturally generated organic particles contribute significantly to the
8 blue haze aerosols formed naturally over forested areas (Smith, 1990e).

9 The low water solubility with high lipoaffinity of many of these organic xenobiotics
10 strongly control their interaction with the vegetative components of natural ecosystems. The
11 cuticles of foliar surfaces are covered with a wax layer that helps protect plants from moisture
12 and short-wave radiation stress. This epicuticular wax, consisting mainly of long-chain esters,
13 polyesters, and paraffins, has been demonstrated to accumulate lipophilic compounds. Organic
14 air contaminants, in the particulate or vapor phase, are absorbed to and accumulate in the
15 epicuticular wax of vegetative surfaces (Gaggi et al., 1985; Kylin et al., 1994). Direct uptake of
16 organic contaminants through the cuticle or the vapor-phase uptake through the stomates are
17 poorly characterized for most trace organics.

18 The phytotoxicity and soil microbial toxicity of organic contaminants is not well studied
19 (Foster, 1991). At regional scales with contemporary deposition levels and in the absence of
20 significant biological magnification, it is not likely that trace organics are causing direct toxicity
21 to vegetative systems at current exposure levels.

22 The most important interaction between particulate trace organics and natural ecosystems
23 may be sequestration coupled with some degree of detoxification (Lamar et al., 1992; Katayama
24 and Matsumura, 1993; Smith, 1995).

27 **9.3 NATURAL ECOSYSTEMS**

28 **9.3.1 Introduction**

29 Ecosystems are structurally complex biotic communities consisting of populations of
30 plants, animals, insects, and microorganisms interacting with one another and with their abiotic

1 environment (Odum, 1993). They are dynamic, self-adjusting, self-maintaining complex
2 adaptive systems in which patterns at higher levels of organization emerge from localized
3 interactions and selection processes. Macroscopic ecosystem properties such as structure,
4 diversity-productivity relationships and patterns of nutrient flux emerge from the interactions
5 among components and may feed back to influence subsequent development of those
6 interactions. The relationship between structure and function is a fundamental one in ecosystem
7 science (Levin, 1998). Structure refers to the species, their biodiversity, abundance, mass and
8 arrangement within an ecosystem. Ecosystem functions, energy flow, nutrient flux, and water
9 and material flow, are characterized by the way in which ecosystem components interact.
10 Elucidating these interactions across scales is fundamental to understanding the relationships
11 between biodiversity and ecosystem functioning (Levin, 1998). To function properly and
12 maintain themselves, ecosystem components must have an adequate supply of energy, chemical
13 nutrients and water. It is the flows of nutrients, energy, materials and information that provide
14 the interconnectedness between ecosystem parts and transforms the community from a random
15 collection of species into an integrated whole, an ecosystem in which the biotic and abiotic parts
16 are interrelated (Levin, 1998).

17 Growth of new trees and other vegetation requires energy in the form of carbon
18 compounds. Plants accumulate, store, and use carbon compounds to build their structures and
19 maintain physiological processes. Plants, using energy from sunlight, in their leaves combine
20 carbon dioxide from the atmosphere and water from the soil to produce the carbon compounds
21 (sugars) that provide the energy require by vegetation for growth and maintenance (Waring and
22 Schlesinger, 1985). Energy is transferred through an ecosystem from organism to organism in
23 food webs and finally is dissipated into the atmosphere as heat (Odum, 1993). Chemical
24 nutrients, such as nitrogen, phosphorus or sulfur, on the other hand, are taken up from the soil by
25 plants and when eaten by consumers move through an ecosystem in the food webs. Eventually
26 when the consumer dies, or a plant or any of its parts falls to the ground and is decomposed they
27 are return to the soil in a pattern referred to as biogeochemical cycling (Odum, 1993). The
28 biogeochemistry of an ecosystem is influenced by vegetation growth characteristics (Herbert
29 et al., 1999).

30 Human existence on this planet depends on nature and the life-support services ecosystems
31 provide. Ecosystem services (Table 9-1) are the conditions and processes through which natural

TABLE 9-1. ECOSYSTEM SERVICES

-
- purification of air and water
 - mitigation of floods and droughts
 - detoxification and decomposition of wastes
 - generation and renewal of soil and soil fertility
 - pollination of crops and natural vegetation
 - control of the vast majority of potential agricultural pests
 - dispersal of seeds and translocation of nutrients
 - maintenance of biodiversity, from which humanity has derived key elements of its agricultural, medicinal, and industrial enterprises
 - protection from the sun's harmful rays
 - partial stabilization of climate
 - moderation of temperature extremes and the force of winds and waves
 - support of diverse human cultures
 - providing of aesthetic beauty and intellectual stimulation that lift the human spirit
-

Source: Daily (1997).

1 ecosystems, and the species of which they are comprised, sustain and fulfill human life (Daily,
2 1997. Both ecosystem structure and function play an essential role in providing societal benefits.
3 Society derives two types of benefits from the structural aspects of an ecosystem: (1) products
4 with market value such as fish, minerals, forage, forest products, biomass fuels, natural fiber, and
5 many pharmaceuticals, and the genetic resources of valuable species (e.g., plants for crops and
6 timber and animals for domestication); and (2) the use and appreciation of ecosystem for
7 recreation, aesthetic enjoyment, and study (Westman,1978; Daily, 1997). The economic benefits
8 and values associated with ecosystem functions and services and the need to preserve them
9 because of their value to human life are discussed by Constanza et al. (1997) and (Pimentel et al.,
10 1997).

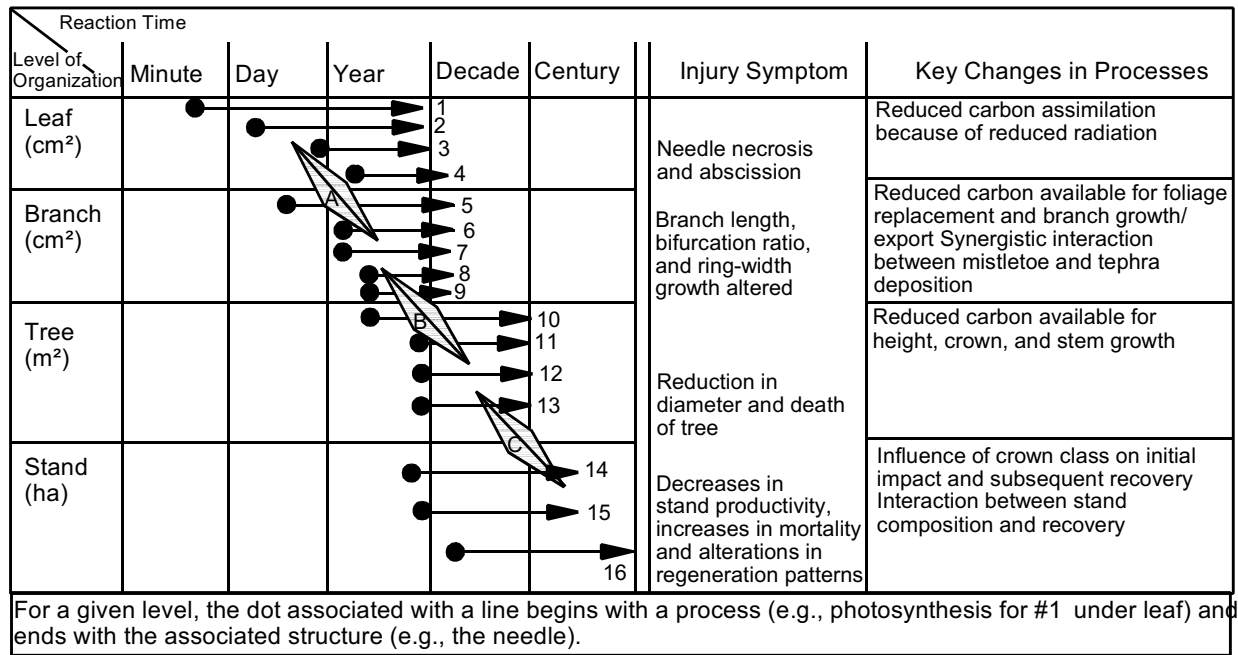
11 Ecosystem functions are characterized by the way components interact. These are the
12 functions that maintain clean water, pure air, a green earth, and a balance of creatures, the

1 functions that enable humans to survive. They are the dynamics of ecosystems. The benefits
2 they impart include absorption and breakdown of pollutants, cycling of nutrients, binding of soil,
3 degradation of organic waste, maintenance of a balance of gases in the air, regulation of radiation
4 balance, climate, and the fixation of solar energy (Table 9-1; Westman, 1978; Daily, 1997).

5 Concern has risen in recent years concerning the integrity of ecosystems (Harwell
6 et al.,1999). There are few ecosystems on planet earth today that are not influenced by humans
7 (Freudenburg and Alario, 1999; Vitousek et. al., 1997; Matson et al. 1997; Noble and Dirzo,
8 1997). The scientific literature is filled with references discussing the importance of ecosystem
9 structure and function. Ecorisk, complexity, stability, biodiversity, resilience, sustainability,
10 managing earth's ecosystems, and ecosystem health are frequently discussed topics. The
11 concerns arise because human activities are creating disturbances that are altering the complexity
12 and stability of ecosystems and producing changes in biodiversity and nutrient cycling (structure
13 and function) (Pimm, 1984; Levin, 1999; Chapin et al., 1998; Peterson et al., 1998; Tilman,
14 1996; Tilman and Downing, 1994; Wall, 1999; Daily and Ehrlich, 1999). There is a need,
15 therefore, to understand how ecosystems respond to both natural and anthropogenic stresses.

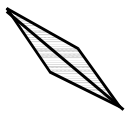
17 **9.3.2 Ecosystem Response to Stress**

18 Ecosystem responses to stresses begin at the population level. Population changes begin
19 with the response of individual plants or animals. Plant responses, both structural and functional,
20 must be propagated from the individual to the more complex levels of community interaction to
21 produce observable changes in an ecosystem (Figure 9-1). At least three levels of biological
22 interaction are involved: (1) the individual plant and its environment, (2) the population and its
23 environment, and (3) the biological community composed of many species and its environment
24 (Billings, 1978). The response of individual organisms within a population based on their
25 genetic constitution (genotype), stage of growth at time of exposure, and the microhabitats in
26 which they are growing vary in their ability to withstand the stress of environmental changes
27 (Levin, 1998). The range of variability within which the species of a population can exist and
28 function determines the ability of a population to survive. Individual organisms within a
29 population vary in their ability to withstand the stress of environmental changes. The range
30 within which these organisms can exist and function determines the ability of the population to
31 survive. Those able to cope with the stresses survive and reproduce. Competition among the



Evaluating Impacts Within a Level of Organization			
Leaf Level	Carbon exchange-1 Carbon pools-2 Needle number and size-3 Needle retention/abscission-4	Tree Level	Height and diameter growth-10 Crown shape and size-11 Tree vigor-12 Mortality-13
Branch Level	Carbon allocation-5 Branch growth-6 Branch morphology-7 Branch vigor-8 Branch retention-9	Stand Level	Productivity-14 Mortality-15 Species composition-16

Evaluating Interactions Between Different Levels of Organization



The diagonal arrow indicates the interaction between any two levels of organization. The types of interaction are due to the properties of variability and compensation.

A - Refers to the interaction between the leaf and branch levels, where, for example, variability at the branch level determines leaf quantity, and compensation at the leaf level in photosynthesis may compensate for the reduction in foliage amount.

B - Refers to the interaction between the branch and the tree, where variability in branches determines initial interception, branch vigor, and branch location in the crown; compensation may be related to increased radiation reaching lower branches.

C - Refers to the interaction between the tree and the stand. Both genetic and environmental variability, inter- and intraspecific compensations, and tree historical and competitive synergisms are involved.

Figure 9-1. Effects of environmental stress on forest trees are presented on a hierarchical scale for the leaf, branch, tree, and stand levels of organization. The evaluation of impacts within a level of organization are indicated by horizontal arrows. The evaluation of interactions between different levels of organization are indicated by diagonal arrows.

Source: Hinckley et al. (1992).

1 different species results in succession (community change over time) and ultimately produces
2 ecosystems composed of populations of plant species that have the capability to tolerate the
3 stresses (Refort and Whitford, 1999; Guderian, 1985).

4 The number of species in a community usually increases during succession in unpolluted
5 atmospheres. Productivity, biomass, community height, and structural complexity increase.
6 Severe stresses, on the other hand, divert energy from growth and reproduction to maintenance,
7 and return succession to an earlier stage (Waring and Schlesinger, 1985). Ecosystems are subject
8 to natural periodic stresses, such as drought, flooding, fire, and attacks by biotic pathogens (e.g.,
9 fungi and insects). If these natural disturbances are extremely severe, ecosystems of great
10 complexity can be rapidly transformed to an earlier successional stage of simpler structure and
11 with few or no symbiotic interactions (Rapport and Whitford, 1999). Ecosystem perturbation by
12 natural stresses can be only a temporary setback, and recovery is generally rapid. Anthropogenic
13 stresses, on the other hand, are debilitating. Stressed ecosystems do not readily recover, but may
14 be further degraded ((Odum, 1969); Rapport and Whitford, 1999). Severe stresses may
15 succession to an earlier stage reduces ecosystem structure and function, disrupts the plant
16 processes of photosynthesis, nutrient uptake, carbon allocation and transformation that are
17 directly related to energy flow and nutrient cycling, shortens food chains and reduces the total
18 nutrient inventory (Odum, 1993). Areas denuded of vegetation can lead to nutrient leaching and
19 runoff into aquatic ecosystems (Materna, 1984). The possible effects of air pollutants on
20 ecosystems have been categorized by Guderian (1977) as follows:

- 21 (1) Accumulation of pollutants in the plant and other ecosystem components (such as soil
22 and surface- and ground-water).
- 23 (2) Damage to consumers as a result of pollutant accumulation.
- 24 (3) Changes in species diversity due to shifts in competition.
- 25 (4) Disruption of biogeochemical cycles.
- 26 (5) Disruption of stability and reduction in the ability of self-regulation.
- 27 (6) Breakdown of stands and associations.
- 28 (7) Expanses of denuded zones.

29 How changes in these functions can result from PM deposition and influence ecosystems is
30 discussed in the following text. It should be remembered that, although the effects of PM are

1 being emphasized, the vegetational components of ecosystems also are responding to multiple
2 stresses from other sources.

4 **9.3.3 Direct Effects of Particulate Matter**

5 **9.3.3.1 Introduction**

6 Particulate matter, as considered in this chapter (See 9.1), is a heterogeneous mixture of
7 particles differing in size, origin, and chemical constituents. The effects of PM on ecosystems,
8 therefore, may be direct or indirect and the impact varies depending on the chemical nature of the
9 PM being deposited on vegetation or the soil.

10 The majority of the studies dealing with the direct effects of particularly dust and metals on
11 vegetation have been concerned with the responses of individual plant species and conducted in
12 the laboratory or in controlled environments (Saunders and Godzik, 1986). A few studies have
13 considered the effects of particles on populations, communities, and ecosystems. Most of these
14 focused on ecosystems in industrialized areas heavily polluted by deposits of both chemically
15 inert and active dusts. Effects can result from direct deposition or indirectly by deposition onto
16 the soil. Reductions in growth, yield, flowering, and reproduction of plants from particulate
17 deposition have been reported (Saunders and Godzik, 1986). The sensitivities of individual
18 species have been associated with changes in composition and structure of natural ecosystems.

19 Evidence from studies of effects of PM deposition, specifically chemically inert and active
20 dusts indicates that, within a population, plants exhibit a wide range of sensitivity, which is the
21 basis for the natural selection of tolerant individuals (Saunders and Godzik, 1986). Rapid
22 evolution of certain populations of tolerant species at sites with heavy trace element and nitrate
23 deposition has been observed. Tolerant individuals present in low frequencies in populations
24 when growing in unpolluted areas have been selected for tolerance at both the seedling and adult
25 stages when exposed to trace metal or nitrate deposition (Ormrod, 1984; U.S. Environmental
26 Protection Agency, 1993). Chronic pollutant injury to a forest community may result in the loss
27 of sensitive species, loss of tree canopy, and maintenance of a residual cover of pollutant-tolerant
28 herbs or shrubs that are recognized as successional species (Table 9-2; Smith, 1990). Frequently,
29 trace metals that penetrate the above-ground plant parts are less injurious than when taken up
30 through the roots (Guderian, 1986).

TABLE 9-2. INTERACTION OF AIR POLLUTION AND TEMPERATE FOREST ECOSYSTEMS UNDER CONDITIONS OF INTERMEDIATE AIR CONTAMINANT LOAD

Forest Soil and Vegetation: Activity and Response	Ecosystem Consequence and Impact
1. Forest tree reproduction, alteration, or inhibition	1. Altered species composition
2. Forest nutrient cycling, alteration <ul style="list-style-type: none"> a. Reduced litter decomposition b. Increased plant and soil leaching and soil weathering c. Disturbance of microbial symbioses 	2. Reduced growth, less biomass
3. Forest metabolism <ul style="list-style-type: none"> a. Decreased photosynthesis b. Increased respiration c. Altered carbon allocation 	3. Reduced growth, less biomass
4. Forest stress, alteration <ul style="list-style-type: none"> a. Phytophagous insects, increased or decreased activity b. Microbial pathogens, increased or decreased activity c. Foliar damage increased by direct air pollution influence 	4. Altered ecosystem stress: increased or decreased insect infestations; increased or decreased disease epidemics; reduced growth, less biomass, altered species composition

Source: Smith (1990).

1 Responses of ecosystems to stresses unless severe or catastrophic are difficult to determine
 2 because the changes are subtle (Garner, 1991). This is particularly true of responses to particles,
 3 except in the severely polluted areas around heavily industrialized point sources. Changes in the
 4 soil may not be observed until accumulation of the pollutant has occurred for 20 or more years
 5 (Saunders and Godzik, 1986). In addition, the presence of other co-occurring pollutants makes it
 6 difficult to attribute the effects to PM alone. In other words, the potential for alteration of
 7 ecosystem function and structure exists, but it is difficult to quantify, especially when there are
 8 other pollutants present in the ambient air which may produce additive or synergistic responses
 9 even through PM concentrations may not be elevated.
 10

1 9.3.3.2 Direct Effects

2 The direct effects of limestone dust on plants and ecosystems has been known for many
3 years. Long-term changes in the structure and composition of the seedling-shrub and sapling
4 strata of an experimental site near limestone quarries and processing plants in Giles County in
5 southwestern Virginia were reported by Brandt and Rhoades (1972, 1973). Dominant trees in the
6 control area, a part of the oak-chestnut association of the eastern deciduous forests of eastern
7 North America, were *Quercus prinus*, *Q. rubra*, and *Acer rubrum*. An abundance of uniformly
8 distributed saplings and seedlings were visible under the tree canopy, and herbs appeared in
9 localized areas in the canopy openings. *Q. prinus* dominated the area, and the larger trees were
10 60 to 80 years old.

11 The dusty site was dominated by *Q. alba*, whereas *Q. rubra* and *Liriodendron tulipifera*
12 were subcodominants. The largest trees were 100 years old and had necrotic leaves, peeling
13 bark, and appeared to be in generally poor condition with the exception of *L. tulipifera*, which
14 thrived in localized areas. The site contained a tangled growth of seedlings and shrubs, a few
15 saplings, and a prevalence of *Smilax spp.* and *Vitis spp.* The sapling strata in the area was
16 represented by *Acer rubrum*, *Carya spp.*, *Cornus florida*, and *Ostrya virginiana*. Saplings of
17 none of the leading dominant trees were of importance in this stratum. The most obvious form of
18 vegetation in the seedling-shrub stratum, due to their tangled appearance, were *C. florida*, *Ostrya*
19 *virginiana*, *Cercis canadensis*, and *Acer saccharum*.

20 The authors (Brandt and Rhoades, 1972), citing Odum (1969), stated that a result of the
21 accumulation of toxic pollutants in the biosphere is the simplification of both plant and animal
22 communities. In plant communities, structure is determined by sampling various strata within
23 the community. Each stratum comprises a particular life form (e.g., herbs, seedlings, saplings,
24 trees). Dust accumulation favored some species and limited others. For example, *Acer*
25 *saccharum* was more abundant in all strata of the dusty site when compared with the control site
26 where it was present only as a seedling. The growth of *L. tulipifera*, *C. florida*, *O. virginiana*,
27 *Viburnum prunifolium*, and *C. canadensis* appeared to be favored by the dust. Growth of
28 conifers and acidophiles such as *Rhododendron maximum*, however, was limited. Although dust
29 accumulation began in 1945, the heaviest accumulation occurred between 1967 and 1972 during
30 the time of the study.

1 Reduction in growth of trees was related to crust formation on leaves (Brandt and
2 Rhoades, 1973). Crust formation reduced photosynthesis, induced premature leaf fall,
3 destruction of leaf tissues, inhibited growth of new tissue and reduced the formation of
4 carbohydrate needed for normal growth and storage (Brandt and Rhoades, 1973).

5 Changes in community composition were associated closely with changes in the growth of
6 the dominant trees. Decrease in density of seedlings and saplings and in mean basal area as well
7 as lateral growth of *A. rubrum*, *Q. prinus*, and *Q. rubra* occurred in all strata. On the other hand,
8 all of these characteristics increased in *L. tulipifera*, which was a subordinate species before dust
9 accumulation began but had assumed dominance at the time of the study. Reduction in growth of
10 the dominant trees had apparently given *L. tulipifera* competitive advantage because of its ability
11 to tolerate dust. Changes in soil alkalinity occurred because of the heavy deposition of limestone
12 dust; however, the facilities necessary for critical analysis of the soils were not available.

13 The effects of acidic deposition have been discussed in several previous reports. The 1982
14 *Air Quality Criteria for Particulate Matter and Sulfur Oxides* devoted a chapter to the effects of
15 acidic deposition (U.S. Environmental Protection Agency, 1982). In 1984, EPA published *The*
16 *Acidic Deposition Phenomenon and Its Effects* (Altshuller and Linthurst, 1984), and, in 1991, the
17 U.S. National Acid Precipitation Assessment Program published the result of its extensive study,
18 *Acidic Deposition: State of Science and Technology* (Irving, 1991). The major effects of acidic
19 deposition occurs through the soil and will be discussed under Indirect Effects.

20 Included among the direct responses of forest trees to acidic deposition are increased
21 leaching of nutrients from foliage; accelerated weathering of leaf cuticular surfaces; increased
22 permeability of leaf surfaces to toxic materials, water, and disease agents; and altered
23 reproductive processes (Altshuller and Linthurst, 1984).

24 Possible direct responses of trace elements on vegetation result from their deposition and
25 residence on the phyllosphere (i.e., leaf surfaces). Fungi and other microorganisms living on the
26 leaves of trees and other vegetation play an important role in leaf decomposition after litterfall
27 (Miller and McBride, 1998; Jensen, 1974; Millar, 1974). Early needle senescence and abscission
28 in the San Bernardino Forest changed fungal microflora successional and decomposition patterns
29 by altering the taxonomic diversity and population density of the microflora that normally
30 develop on needles while they are on the tree. Changing the fungal community on the needles
31 weakened the decomposer community, decreasing the rate of decomposition, and altered nutrient

1 cycling (Bruhn, 1980). Nutrient availability was influenced by the accumulation of
2 carbohydrates and mineral nutrients in the heavy litter under the stands which had the most
3 severe needle injury and defoliation (U.S. Environmental Protection Agency, 1996a). The
4 possible impact of heavy metals on nutrient cycling and their effects on leaf microflora appear
5 not to have been studied.

6 A trace metal must be brought into solution before it can enter into the leaves or bark of
7 vascular plants. Low solubility limits entry. In those instances when trace metals are absorbed,
8 they are frequently bound in the leaf tissue and are lost when the leaf drops off (Hughes, 1981).
9 Information dealing with ecosystem effects resulting from direct deposition of trace metals is
10 sparse.

11 Trace metals, particularly heavy metals, such as cadmium, copper, lead, chromium,
12 mercury, nickel, and zinc, have the greatest potential for influencing forest growth (Smith, 1991).
13 Experimental data indicate that the broadest spectrum of growth suppression of foliar microflora
14 resulted from iron, aluminum, and zinc. These three metals also inhibited spore formation, as did
15 cadmium, chromium, manganese, and nickel (see Smith, 1990a). In the field, the greatest injury
16 occurs from pollution near mining, smelting, and other industrial sources (Ormrod, 1984). Direct
17 metal phytotoxicity will occur only if the metal can move from the surface into the leaf or
18 directly from the soil into the root.

20 **9.3.4 Indirect Effects of Particulate Matter**

21 **9.3.4.1 Introduction**

22 Indirect plant responses are chiefly soil mediated and depend primarily on the chemical
23 composition of the individual elements deposited in PM. The individual elements must be
24 bioavailable to have an effect. The soil environment, composed of mineral and organic matter,
25 water, air, and a vast array of bacteria, fungi, algae, actinomycetes, protozoa, nematodes and
26 arthropods, is one of the most dynamic sites of biological interactions in nature (Alexander,
27 1977). The quantity of organisms in soils varies by locality. Bacteria and fungi are usually most
28 abundant in the rhizosphere, the soil around plant roots that all mineral nutrients must pass
29 through. Bacteria and fungi benefit from the nutrients in the root exudates (chiefly sugars) in the
30 soil and, in turn, they play an essential role by making mineral nutrients available for plant
31 uptake (Rovira and Davey, 1974). Their activities create chemical and biological changes in the

1 rhizosphere by decomposing organic matter and making inorganic minerals available for plant
2 uptake. Bacteria are essential in the nitrogen and sulfur cycles and make these elements available
3 for plant uptake and growth (see Section 9.3.3). Fungi are directly essential to plant growth.
4 Attracted to the roots by the exudates, they develop mycorrhizae, a mutualistic, symbiotic
5 relationship, that is integral in the uptake of the mineral nutrients (Allen, 1991). The impact in
6 ecosystems of PM, particularly nitrates, sulfates, and metals, is determined by their affect on the
7 growth of the bacteria involved in nutrient cycling and the fungi involved in plant nutrient
8 uptake.

10 **9.3.4.2 Nitrogen**

11 Nitrogen has long been recognized as the nutrient most important for plant growth. Plants
12 usually absorb nitrogen through their roots by absorbing NH_4^+ or NO_3^- or by symbiotic
13 organisms. Plants, however, vary in their ability to absorb ammonium and nitrate (Chapin et al.,
14 1987). Nitrogen is of overriding importance in plant metabolism and, to a large extent, governs
15 the utilization of phosphorus, potassium and other nutrients. Most of the nitrogen in soils is
16 associated with organic matter. Typically, the availability of nitrogen via the nitrogen cycle
17 controls net primary productivity and the possibly decomposition rate. Photosynthesis is
18 influence by nitrogen uptake in that approximately 75% of the nitrogen in a plant leaf is used
19 during the process of photosynthesis. The nitrogen-photosynthesis relationship is, therefore,
20 critical to the growth of trees and other plants (Chapin et al., (1987).

21 Because nitrogen is not readily available and is usually in shortest supply, it is the chief
22 element in agricultural fertilizers. Atmospherically deposited nitrogen can also act as a fertilizer
23 in soil low in nitrogen. Not all plants, however, are capable of utilizing extra nitrogen. Inputs of
24 nitrogen to natural ecosystems that alleviate deficiencies and increase growth of some plants can
25 impact competitive relationships and alter species composition and diversity (U.S.
26 Environmental Protection Agency, 1993; Ellenberg, 1987; Kenk and Fischer, 1988).

27 The impact of increasing nitrogen deposition on the nitrogen cycle in forests, wetlands, and
28 aquatic ecosystems is discussed in detail in the oxides of nitrogen criteria document (U.S.
29 Environmental Protection Agency, 1993, 1997; Garner, 1994; World Health Organization, 1997).
30 A major concern is “nitrogen saturation”, the result of the deposition of large amounts of nitrates
31 PM. Nitrogen saturation results when additions to soil background nitrogen (nitrogen loading)

1 exceed the capacity of plants and soil microorganisms to utilize and retain nitrogen (Aber, 1989;
2 1998; Garner, 1994; US. Environmental Protection Agency, 1993). Under these circumstances
3 an ecosystem no longer functions as a nitrogen sink (Aber, 1989).

4 Growth of most forests in the United States is limited by the nitrogen supply. Severe
5 symptoms of nitrogen saturation, however, have been observed in high-elevation, nonaggrading
6 spruce-fir ecosystems in the Appalachian Mountains, as well as in the eastern hardwood
7 watersheds at Fernow Experimental Forest near Parsons, West Virginia. Mixed conifer forests
8 and chaparral watersheds with high smog exposure in the Los Angeles Air Basin also are
9 nitrogen saturated and exhibit the highest stream water NO_3^- concentrations for wildlands in
10 North America (Fenn et al., 1998). Not all forest ecosystems react in the same manner to
11 nitrogen deposition. High-elevation alpine watersheds in the Colorado Front Range and a
12 deciduous forest in Ontario, Canada, also are natural saturated even though nitrogen deposition
13 has been moderate ($\sim 8 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$). The Harvard Forest hardwood stand in Massachusetts,
14 however, has absorbed $>900 \text{ kg N/ha}$ without significant NO_3^- leaching during an nitrogen
15 amendment study of 8 years (Fenn et al., 1998). Johnson et al. (1991) reported that measurements
16 showing the leaching of nitrates and aluminum (Al^{3+}) from high elevation forests in the Great
17 Smoky Mountains indicates that these forests have reached saturation.

18 Possible ecosystem responses to nitrate saturation, as postulated by Aber and his coworkers
19 (Aber et al., 1989), include (1) a permanent increase in foliar nitrogen and reduced foliar
20 phosphorus, and lignin due to the lower availability of carbon, phosphorus, and water;
21 (2) reduced productivity in conifer stands due to disruptions of physiological function;
22 (3) decreased root biomass and increased nitrification and nitrate leaching; (4) reduced soil
23 fertility, the results of increased cation leaching, increased nitrate and aluminum concentrations
24 in streams, and decreased water quality. Saturation implies that some resource other than
25 nitrogen is limiting biotic function.

26 Water and phosphorus for plants and carbon for microorganisms are the resources most
27 likely to be the secondary limiting factors. The appearance of nitrogen in soil solution is an early
28 symptom of excess nitrogen. In the final stage, disruption of forest structure becomes visible
29 (Garner, 1994).

30 Changes in nitrogen supply can have a considerable impact on an ecosystems nutrient
31 balance (Waring, 1987). Large chronic additions of nitrogen influence normal nutrient cycling

1 and alter many plant and soil processes involved in nitrogen cycling (Aber et al., 1989). Among
2 the processes affected are (1) plant uptake and allocation, (2) litter production,
3 (3) immobilization, (includes ammonification [the release of ammonia] and nitrification
4 [conversion of ammonia to nitrate during decay of litter and soil organic matter]), (4) nitrate
5 leaching and trace gas emissions (Figure 9-2; Aber et al., 1989).

6 Subsequent studies have shown that though initially there was an increase in nitrogen
7 mineralization (conversion of soil organic matter to nitrogen in available form (see #3 above),
8 under nitrogen enriched conditions rates were reduced. In addition, studies suggest that during
9 saturation soil microbial communities change from predominantly fungal (mycorrhizal)
10 communities to those dominated by bacteria (Aber et al., 1998).

11 Trees and other vegetation growing on soil low in nitrogen have become adapted over time.
12 All plant growing in low resource environments (e.g., fertile soil, shaded understory, deserts, and
13 tundra) have been observed to have certain similar characteristics: (1) a slow growth rate,
14 (2) low photosynthetic rate, and (3) low capacity for nutrient uptake. An important feature to
15 plants adapted to low-resource environments is that they grow slowly and tend to respond less
16 even when provided with an optimal supply and balance of resources (Percy et al., 1987;
17 Chapin, 1991). Plants adapted to cold moist environments grow more leaves than roots as the
18 relative availability to nitrogen increases; however, other nutrients may soon be limiting. The
19 capacity of gymnosperms in general, and subalpine and boreal species in particular, to reduce
20 nitrates in either roots or leaves appears to be limited. In addition, the ability of trees to use
21 nitrogen varies with the age of the tree and the density of the stand (Waring, 1987).

22 Since the competitive equilibrium of plants in any community is finely balanced, the
23 alteration of one of a number of environmental parameters, (e.g., continued nitrogen additions),
24 can change the vegetation structure of an ecosystem (Skeffington and Wilson, 1987). Increases
25 in soil nitrogen plays a selective role. When nitrogen become readily available, plants adapted to
26 living in an environment of low nitrogen availability will be replaced by plants capable of using
27 increased nitrogen because they have a competitive advantage. Excess nitrogen inputs to
28 unmanaged heathlands in the Netherlands has resulted in nitrophilous grass species replacing
29 slower growing heath species (Roelofs et al., 1987; Garner, 1994). Van Breeman and Van Dijk
30 (1988) noted that over the past several decades the composition of plants in the forest herb layers

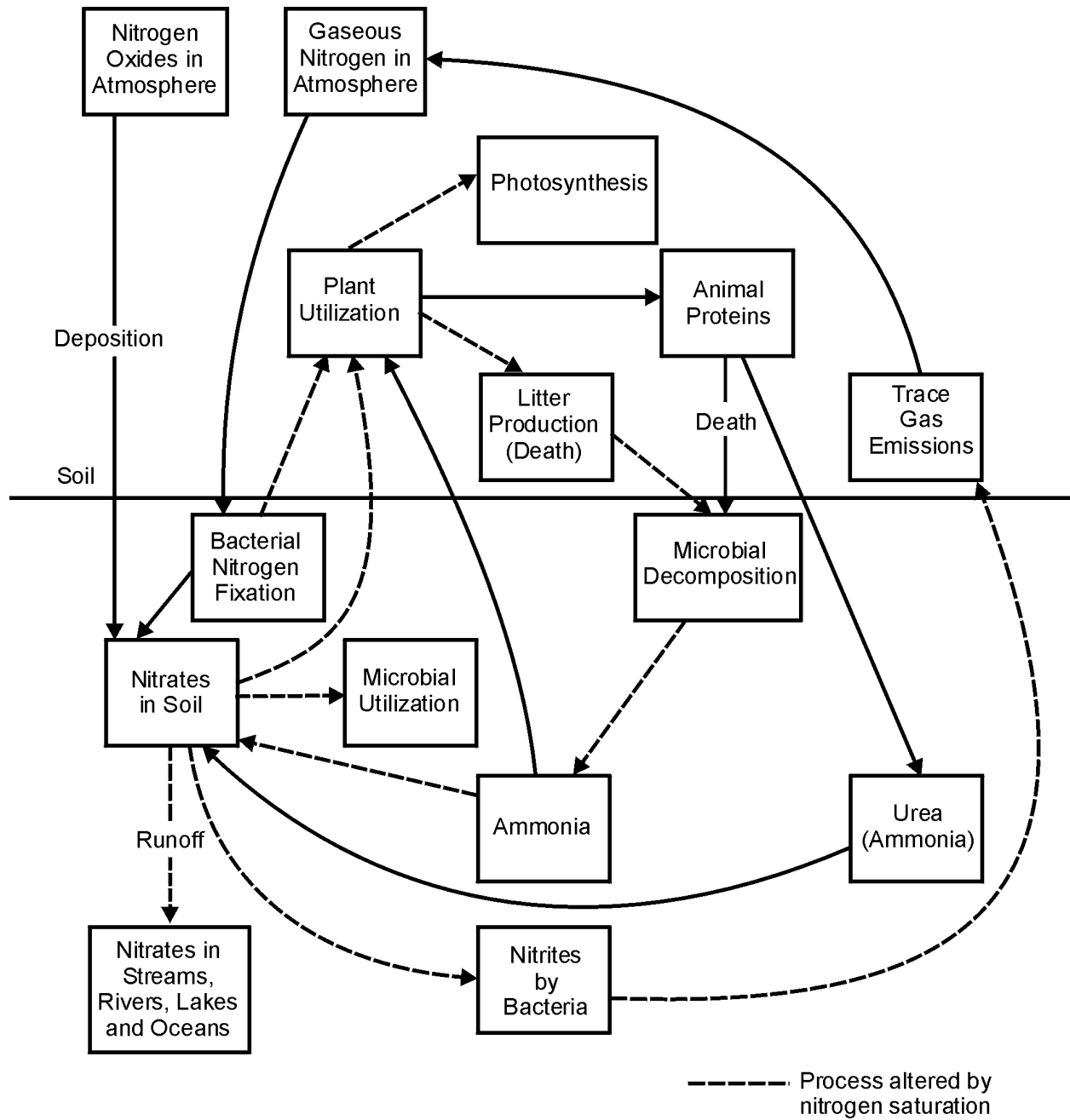


Figure 9-2. Nitrogen Cycle (dotted lines indicate processes altered by nitrogen saturation).

Source: Garner (1994).

- 1 have been shifting toward species commonly found on nitrogen-rich areas. It also was observed
- 2 that the fruiting bodies of mycorrhizal fungi had decreased in number.

1 Other studies in Europe point out the effects of excessive nitrogen deposition. The
2 influence of atmospheric nitrogen deposition on mixed-oak forest vegetation along a deposition
3 gradient largely controlled by soil acidity, nitrogen supply, canopy composition and location of
4 sample plots was studied using multivariate methods. Results of the study suggest that nitrogen
5 deposition has affected the field layer vegetation directly by increased nitrogen availability and
6 indirectly by accelerating soil acidity. Time series studies indicate that 20 of the 30 field layer
7 species (non-woody plants) that were most closely associated with high nitrogen deposition
8 increased in frequency in areas with high nitrogen deposition during the past decades. Included
9 in the field layer species were many generally considered nitrophilous, however, there were
10 several acid tolerant species (Brunet et al, 1998). Falkengren-Grerup (1998) in an experimental
11 study involving 15 herbs and 13 grasses observed that species with a high nitrogen demand and a
12 lesser demand for other nutrients were particularly competitive in areas with acidic soils and high
13 nitrogen deposition. The grasses grew better than herbs with the addition of nitrogen. It was
14 concluded that at the highest nitrogen deposition, growth was limited for most species by the
15 supply of other nutrients. At the intermediate nitrogen concentration the grasses were more
16 efficient than the herbs in utilizing nitrogen.

17 Nihlgård (1985) suggested that excessive nitrogen deposition may contribute to forest
18 decline in other specific regions of Europe. Schulze (1989), Heinsdorf (1993), and Lamersdorf
19 and Meyer (1993) attribute magnesium deficiencies in German forests in part to excessive
20 nitrogen deposition.

21 Plant succession patterns and biodiversity are significantly affected by chronic nitrogen
22 additions in some ecosystems (Figure 9-3). Fenn et al., (1998) report that long-term nitrogen
23 fertilization studies in both New England and Europe suggest that some forests receiving chronic
24 inputs of nitrogen may decline in productivity and experience greater mortality. Long-term
25 fertilization experiments at Mount Ascutney, Vermont, suggest that declining coniferous forest
26 stands with slow nitrogen cycling may be replaced by deciduous fast-growing forests that cycle
27 nitrogen rapidly.

28 In experimental studies of nitrogen deposition by Wedin and Tilman (1996) on Minnesota
29 grasslands, plots dominated by native warm-season grasses shifted to low-diversity mixtures
30 dominated by cool-season grasses at all but the lowest rates of nitrogen addition. Grasslands
31 with high nitrogen retention and carbon storage rates were the most vulnerable to loss of species

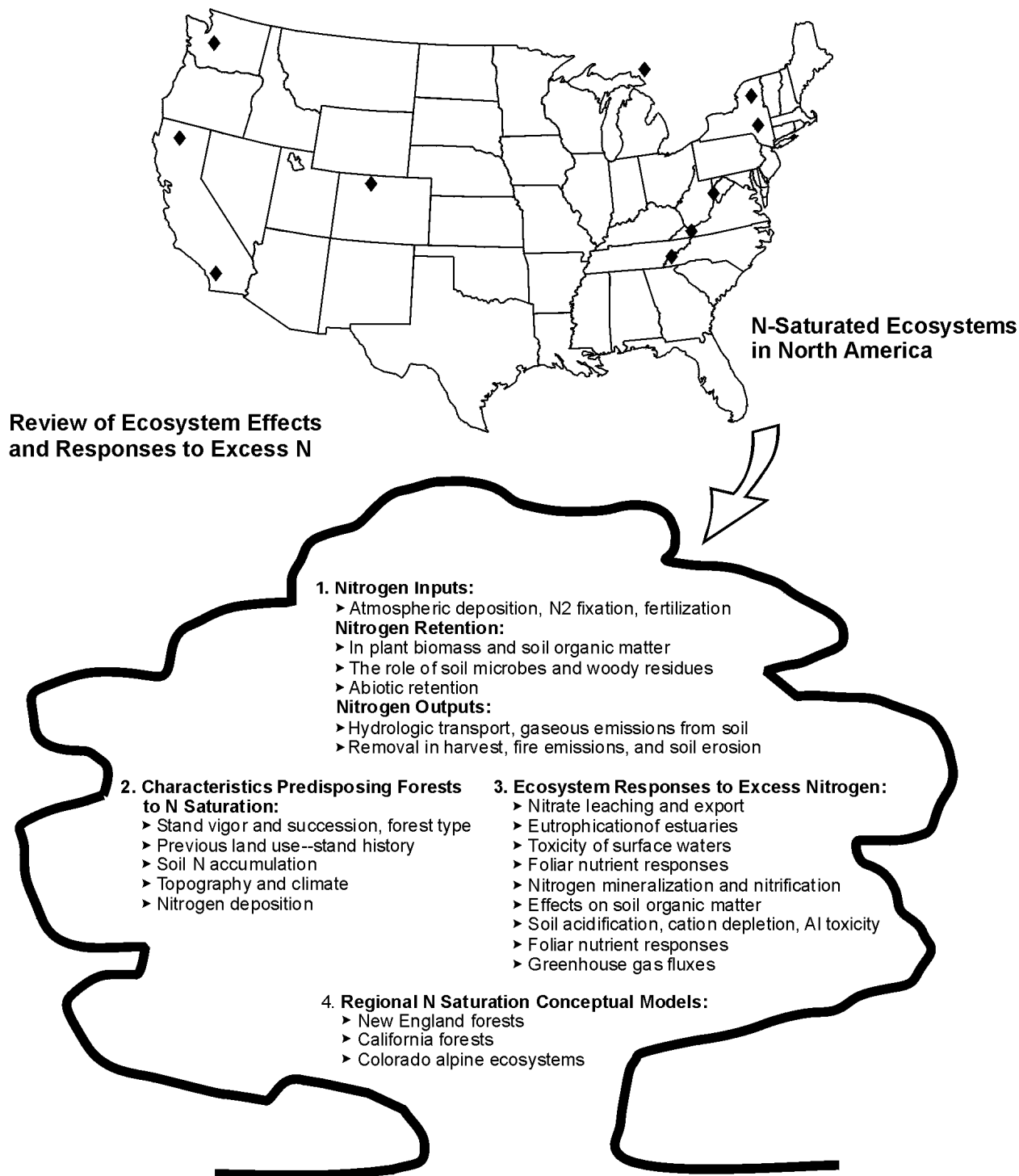


Figure 9-3. Diagrammatic overview of N excess in North America.

Source: Finn et al. (1998).

1 and major shifts in nitrogen cycling. The shift to low-diversity mixtures was associated with the
2 decrease in biomass carbon to nitrogen (C:N) ratios, increased nitrogen mineralization, increased
3 soil nitrate, high nitrogen losses, and low carbon storage (Wedin and Tilman, 1996). Naeem
4 et al. (1994) demonstrated experimentally under controlled environmental conditions that loss of
5 biodiversity, in addition to loss of genetic resources, loss of productivity, loss of ecosystem
6 buffering against ecological perturbation, and loss of aesthetic and commercially valuable
7 resources, may also alter or impair the services that ecosystems provide.

9 **9.3.4.3 Sulfur**

10 Sulfur is an essential plant nutrient and as such is a major component of plant proteins.
11 The most important source of sulfur is sulfate taken up from the soil by plant roots even though
12 plants can utilize atmospheric SO_2 (Marschner, 1995). The availability of organically bound
13 sulfur in soils depends largely on microbial decomposition, a relatively slow process. The major
14 factor controlling the movement of sulfur from the soil into vegetation is the rate of release from
15 the organic to the inorganic compartment (May et al., 1972; U. S. Environmental Protection
16 Agency, 1982; Marschner, 1995). Sulfur plays a critical role in agriculture as an essential
17 component of the balanced fertilizers needed to grow and increase worldwide food production
18 (Ceccotti and Messick, 1997). Atmospheric deposition is an important component of the sulfur
19 cycle. This is true not only in polluted areas where atmospheric deposition is very high, but also
20 in areas of low sulfur input. Additions of sulfur into the soil in the form of SO_4^{2-} could alter the
21 important organic-sulfur organic-nitrogen relationship involved in protein formation in plants.
22 The biochemical relationship between sulfur and nitrogen in plant proteins indicates that neither
23 element can be adequately assessed without reference to the other. There is a regulatory coupling
24 of sulfur and nitrogen metabolism. Sulfur deficiency reduces nitrate reductase and to a similar
25 extent also glutamine synthetase activity. Nitrogen uptake in forests, therefore, may be loosely
26 regulated by sulfur availability, but sulfate additions in excess of needs do not necessarily lead to
27 injury (Turner and Lambert, 1980; Hogan et al., 1998).

28 Only two decades ago, there was little information comparing sulfur cycling in forests with
29 nutrients, especially nitrogen. With the discovery of deficiencies in some unpolluted regions
30 (Kelly and Lambert, 1972; Humphreys et al., 1975; Turner et al., 1977; Schnug, 1997) and
31 excesses associated with acidic deposition in other regions of the world (Meiwes and Khanna,

1 1981 Shriner and Henderson, 1978; Johnson et al., 1982a,b) interest in sulfur nutrition and
2 cycling in forests has heightened. General reviews of sulfur cycling in forests have been written
3 by Turner and Lambert, (1980), Johnson (1984), and Mitchell et al. (1992a,b) Hogan, (1998).
4 The salient elements of the sulfur cycle as it may be affected by changing atmospheric deposition
5 are summarized by Johnson and Mitchell (1988) and U.S. Environmental Protection Agency,
6 (1999). Sulfur has become the most important limiting factor in European agriculture due to the
7 desulfurization of industrial emissions (Schnug, 1997).

8 Most of the studies dealing with the impacts of sulfur on plant communities have been
9 conducted in the vicinity of point sources and have investigated the above-ground effects of
10 SO_4^{2-} exposures, not the effects of sulfate deposition onto the soil (Krupa and Legge, 1998;
11 Dreisinger and McGovern, 1970; Legge, 1980; Winner and Bewley, 1997a,b; Lauenroth and
12 Milchunas, 1984; U.S. Environmental Protection Agency, 1982).

14 **9.3.4.4 Effects of Acidic Deposition on Forest Soils**

15 Substantial and previously unsuspected changes in soils are occurring both in polluted areas
16 of eastern North America, Central Europe, Sweden and the United Kingdom and in less polluted
17 regions of Australia and western North America (Johnson et al., 1991b).

18 Significant changes have occurred at many sites in the eastern United States during recent
19 decades. Temporal trends in tree ring chemistry were examined as indicators of historical
20 changes in the chemical environment of red spruce. Chemical changes in tree ring chemistry
21 reflect changing inputs of regional pollutants to forests. If significant base cation mobilization
22 and depletion of base cations from eastern forest soils has occurred, a temporal sequence of
23 changes in uptake patterns and possibly in tree growth would be expected. Patterns of tree ring
24 chemistry principally at high-elevation sites in the eastern United States, leads to the conclusion
25 that significant changes in soil chemistry have occurred in many of these sites during recent
26 decades leading to changes in growth (Bondietti and McLaughlin, 1992).

27 These changes are spatially and temporally consistent within emissions of SO_2 and NO_2
28 across the region, suggesting that increased acidification of forest soils has occurred. Increases in
29 the levels of Al and Fe typically occur as base cations are removed from soils by tree uptake.
30 A region-wide Ca increase above expected levels followed by a decrease suggests that increased
31 mobilization began perhaps 30 to 40 years ago (Bondietti and McLaughlin, 1992). The period of

1 Ca mobilization coincides with a region-wide increase in growth rate of red spruce, while the
2 period of decreasing levels of Ca in wood corresponds temporally with patterns of decreasing
3 radial growth at high elevation sites throughout the region during the past 20 to 30 years. The
4 decline in wood Ca suggests that Ca loss may have been increased to the point at which base
5 saturation of soils has been reduced (Bondietti and McLaughlin, 1992).

6 Acidic deposition has played a major role in recent soil acidification in some areas of
7 Europe and, to a more limited extent, in Sweden and eastern North America. Examples include
8 the study by Hauhs (1989) at Lange Bramke, Germany, which indicated that leaching was of
9 major importance in causing substantial reduction in soil-exchangeable base cations over a
10 10-year period (1974-1984). Soil acidification and its effects result from the deposition of nitrate
11 (NO_3^-) and sulfate (SO_4^{2-}) and the associated hydrogen (H^+) ion. The effects of excessive
12 nitrogen deposition on soil acidification and nutrient imbalances have been well established in
13 Dutch forests (Van Breemen et al., 1982; Roelofs et al., 1985; Van Dijk and Roelofs, 1988).
14 For example, Roelofs et al. (1987) proposed that $\text{NH}_3/\text{NH}_4^+$ deposition leads to heathland
15 changes via two modes: (1) acidification of the soil and the loss of cations K^+ , Ca^{2+} , and Mg^{2+} ;
16 and (2) nitrogen enrichment which results in “abnormal” plant growth rates and altered
17 competitive relationships. Nihlgård (1985) suggested that excessive nitrogen deposition may
18 contribute to forest decline in other specific regions of Europe. Falkengren-Grerup (1987) noted
19 that over approximately 50 years unexpectedly large increases in growth of beech (*Fagus*
20 *sylvatica* L.) were associated with decreases in pH and exchangeable cations in some sites in
21 southernmost Sweden.

22 Likens et al. (1996) suggested that soils are changing at the Hubbard Brook Watershed,
23 NH, because of a combination of acidic deposition and reduced base cation deposition. They
24 surmised, based on long-term trends in stream-water data, that large amounts of Ca and Mg have
25 been lost from the soil-exchange complex over a 30-year period from approximately 1960 to
26 1990. The authors speculate that the declines in base cations in soils may be the cause of recent
27 slowdowns in forest growth at Hubbard Brook.

28 Hydrogen ions entering a forest ecosystem first encounter the forest canopy where they are
29 often exchanged for base cations that then appear in throughfall (Figure 9-4 depicts a model of
30 H^+ sources and sinks). Base cations leached from the foliage must be replaced through uptake
31 from the soil, or foliage cations will be reduced by the amounts leached. In the former case, the

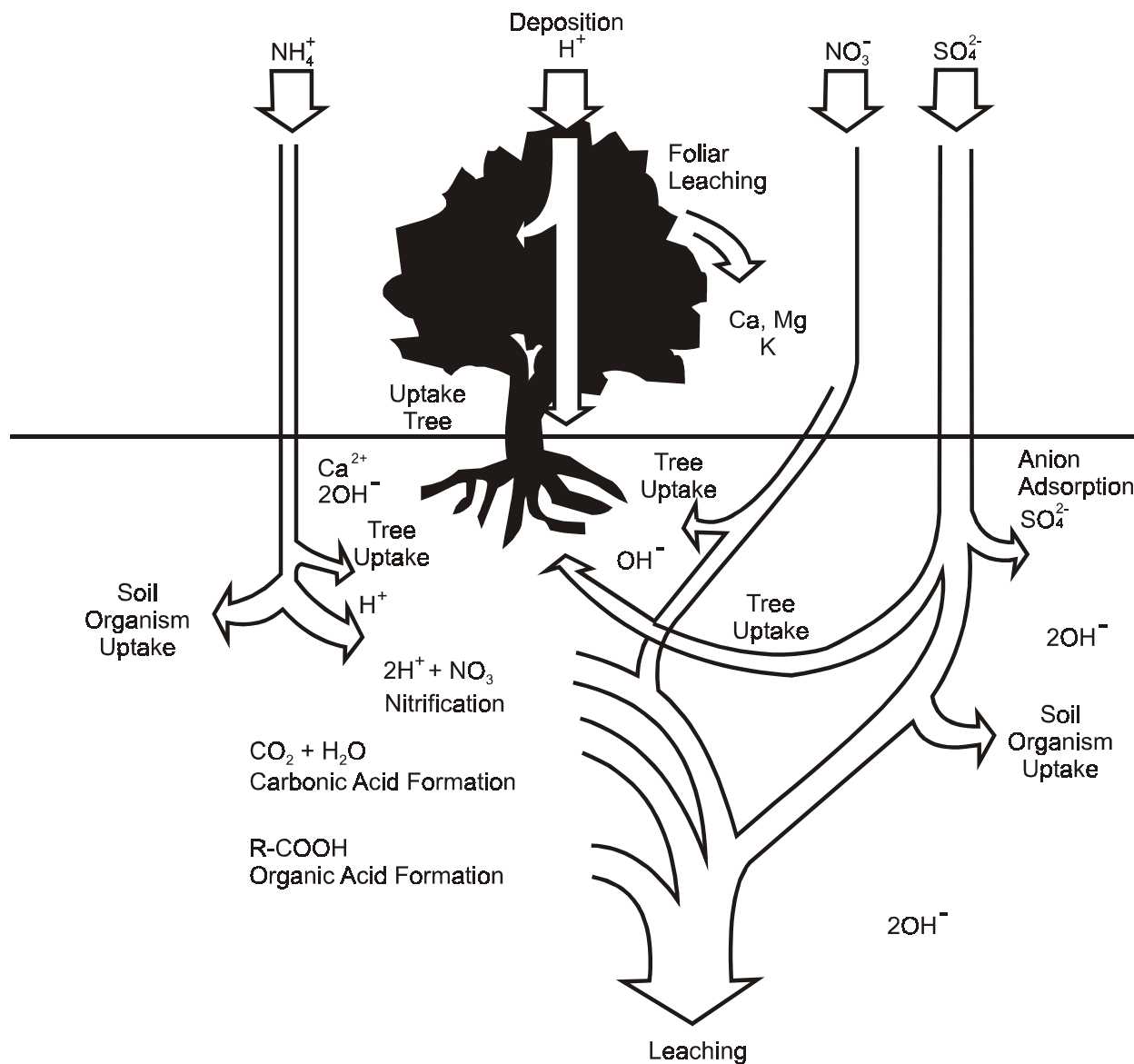


Figure 9-4. Schematic of sources and sinks of hydrogen ions in a forest (from Taylor et al., 1994).

- 1 acidification effect is transferred to the soil where H⁺ is exchanged for a base cation at the
- 2 root-soil interface. Uptake of base cations or NH₄⁺ by vegetation or soil microorganisms causes
- 3 the release of H⁺ in order to maintain charge balance. Uptake of nutrients in anionic form (NO₃⁻;
- 4 SO₄²⁻, PO₄³⁻) causes the release of OH⁻ in order to maintain charge balance. Thus the net

1 acidifying effect of uptake is the difference between cation and anion uptake (U.S.
2 Environmental Protection Agency, 1999).

3 The cycles of base cations differ from those of N, P, and S in several respects. The fact that
4 Ca, K, and Mg exist primarily as cations in solution whereas N, P, and S exist primarily as anions
5 has major implications for the cycling of the nutrients and the effects of acid deposition on these
6 cycles. The most commonly accepted model of base cation cycling in soils is one in which base
7 cations are released by weathering of primary minerals to cation exchange sites where they are
8 then available for either plant uptake or leaching (Figure 9-4). The introduction of H⁺ by
9 atmospheric deposition or by internal processes, will directly impact the fluxes of Ca, K, and
10 Mg via cation exchange or weathering processes. Therefore, soil leaching is often of major
11 importance in cation cycles, and many forest ecosystems show a net loss of base cations
12 (U.S. Environmental Protection Agency, 1999).

13 Two basic types of soil change are involved: (1) a short-term intensity type change
14 resulting from the chemicals in soil water, and (2) a long-term capacity change based on the total
15 content of bases, aluminum and iron stored in the soil (Van Breeman, 1983). Changes of the
16 intensity type can be easily induced or reversed with the introduction or removal of mineral acid
17 anions from soil solution and need not be accompanied by any change of the capacity type
18 (National Science and Technology Council, 1998; U.S. Environmental Protection Agency, 1999).

19 Rapid changes in intensity resulting from the addition of increased amounts of nitrogen or
20 sulfur in acidic deposition can have a rapid impact on the chemistry of soil solutions by
21 increasing the acidity and mobilizing aluminum. Increased concentrations of aluminum and an
22 increase in the ratio of calcium-to-aluminum in soil solution have been linked to significantly
23 reduced plant availability to essential cations.

24 Capacity changes are the result of many factors acting over long time periods. The content
25 of base cations (calcium, magnesium, sodium, potassium) in soils result from additions from the
26 atmospheric deposition, decomposition of vegetation, geologic weathering. Loss of base cations
27 may occur through plant uptake and leaching. Increased leaching of base cations may result in
28 nutrient deficiencies in soils as has been happening in some sensitive forest ecosystems
29 (National Science and Technology Council, 1998).

30 A major concern has been that soil acidity would lead to nutrient deficiency. Tree species
31 may be adversely affected if high Al to nutrient ratios limit uptake of Ca and Mg and create a

1 nutrient deficiency (Shortle and Smith, 1988; Garner, 1994). Calcium is essential in the
2 formation of wood and the maintenance of cells, the primary plant tissues necessary for tree
3 growth. Trees obtain Ca from the soil, but to be taken up by roots, the Ca (a positively charged
4 ion) must be dissolved in soil water (Lawrence and Huntington, 1999). Acid deposition by
5 lowering the pH of aluminum-rich soil can increase aluminum concentrations in soil water
6 through dissolution and ion-exchange processes. When in solution, aluminum can be taken up
7 by roots, transported through the tree and eventually deposited on the forest floor in leaves and
8 branches. Aluminum is more readily taken up than Ca because it has a higher affinity for
9 negatively charged surfaces than Ca. When present in the forest floor, Al tends to displace
10 adsorbed Ca and causes it to be more readily leached. The continued buildup of Al in the forest
11 floor layer where nutrient uptake is greatest can (1) decrease the availability of Ca to the roots
12 (Lawrence et al., 1995), (2) lower the efficiency of Ca uptake because Al is more readily taken up
13 than Ca²⁺ when the ratio of Ca to Al in soil water is less than one (Lawrence and Huntington,
14 1999). A Swedish report to the United Nations in 1968 postulated a decrease in forest growth of
15 approximately 1.5 % year⁻¹ as result of Ca²⁺ loss by leaching (Johnson and Taylor, 1989). The
16 concern that soil acidification and nutrient deficiency may result in forest decline remains extant
17 today. Cronan and Grigal (1995) suggest that calcium to aluminum ratios may be used as
18 indicators of stress in forest ecosystems.

19 Aluminum toxicity is a possibility in acidified soils. Atmospheric deposition (or any other
20 source of mineral anions) can increase the concentration of Al, especially Al³⁺, in soil solution
21 without causing significant soil acidification (Johnson and Taylor, 1989). Aluminum can be
22 brought into soil solution in two ways: (1) by acidification of the soil and (2) by an increase in
23 the total anion and cation concentration of the soil solution. The introduction of mobile, mineral
24 acid anions to an acid soil will cause increases in the concentration of aluminum in the soil
25 solution, but extremely acid soils in the absence of mineral acid anions will not produce a
26 solution high in aluminum. Reuss (1983) provides an excellent review of the relationships
27 among the most widely used cation-exchange equations and their implications for the
28 mobilization of aluminum into soil solution.

29 Aluminum toxicity may influence forest tree growth where acid deposition and natural
30 acidifying processes increase soil acidity. Aluminum concentrations have been observed to
31 exhibit a strongly descending gradient from bulk soil through the rhizosphere to the root (Smith,

1 1990a). Once it enters the forest tree roots, aluminum accumulates in root tissue (Thornton et al.,
2 1987; Vogt et al., 1987a,b). There is abundant evidence that aluminum is toxic to plants.
3 Reductions in calcium uptake by roots has been associated with increases in aluminum uptake
4 (Clarkson and Sanderson, 1971). Calcium plays a major role in cell membrane integrity and cell
5 wall structure. A number of studies have suggested that the toxic effect of aluminum on forest
6 trees could be due to Ca^{2+} deficiency (Shortle and Smith, 1988; Smith, 1990a). Mature trees
7 have a high Ca^{2+} requirement relative to agricultural crops (Rennie, 1955).

8 Shortle and Smith (1988) attributed the decline of red spruce in eight stands across northern
9 New England from Vermont to Maine to an imbalance of Al^{3+} and Ca^{2+} in the fine root
10 environment. Aluminum in the soil solution reduces calcium uptake by competing for binding
11 sites in the cortex of fine roots. Reduction in calcium uptake suppresses cambial growth and
12 reduces the rate of wood formation (annual ring formation), decreases the amount of functional
13 sapwood and live crown and predisposes trees to disease and injury from stress agents when the
14 functional sapwood becomes less than 25% of cross sectional stem area (Smith, 1990a).

15 Air pollution is not the sole cause of soil change. High rates of acidification are occurring
16 in less polluted regions of the western United States and Australia due to internal soil processes
17 such as tree uptake of nitrate and nitrification associated with excessive nitrogen fixation
18 (Johnson et al., 1991a). Many studies have shown that acidic deposition is not a necessary
19 condition for the presence of extremely acid soils, as evidenced by their presence in unpolluted,
20 even pristine forests of the northwestern United States and Alaska (Johnson et al., 1991b). The
21 soil becomes acidic when H^+ ions attached to NH_4^+ or HNO_3 remain in the soil after nitrogen is
22 taken up by plants. For example, Johnson et al. (1982b) found significant reductions in
23 exchangeable K^+ over a period of only 14 years in a relatively unpolluted Douglas fir Integrated
24 Forest Study (IFS) site in the Washington Cascades. The effects of acid deposition at this site
25 were negligible relative to the effects of natural leaching (primarily carbonic acid) and nitrogen
26 tree uptake (Cole and Johnson, 1977). Even in polluted regions, numerous studies have shown
27 the importance of tree uptake of NH_4^+ and NO_3^- in soil acidification. Binkley et al. (1989)
28 attributed the marked acidification (pH decline of 0.3 to 0.8 units and base saturation declines of
29 30 to 80%) of abandoned agricultural soil in South Carolina over a 20-year period to NH_4^+ and
30 NO_3^- uptake by a loblolly pine plantation.

1 An interesting example of uptake effects on soil acidification is that of aluminum uptake
2 and cycling (Johnson et al., 1991b). Aluminum accumulation in the leaves of coachwood
3 (*Ceratopetalum apetalum*) in Australia has been found to have a major impact on the distribution
4 and cycling of base cations (Turner and Kelly, 1981). The presence of *C. apetalum* as a
5 secondary tree layer beneath bus cox (*Lophostemon confertus*) was found to lead to increased soil
6 exchangeable Al^{3+} and decreased soil exchangeable Ca^{2+} (Turner and Kelly, 1981). The
7 constant addition of aluminum-rich litter fall obviously has had a substantial effect on soil
8 acidification, even if base cation uptake is not involved directly.

9 Given the potential importance of particulate deposition for base cation status of forest
10 ecosystems, the findings of Driscoll et al. (1989) and Hedin et al. (1994) are especially relevant.
11 Driscoll et al. (1989) noted a decline in both SO_4^{2-} and base cations in both atmospheric
12 deposition and stream water over the past two decades at Hubbard Brook Watershed, NH. The
13 decline in SO_4^{2-} deposition was attributed to a decline in emissions and the decline in stream
14 water SO_4^{2-} was attributed to the decline in sulfur deposition.

15 Hedin et al. (1994) reported a steep decline in atmospheric base cation concentrations in
16 both Europe and North America over the past 10 to 20 years. The reductions in SO_2 emissions
17 in Europe and North America in recent years have not been accompanied by equivalent declines
18 in net acidity related to sulphate in precipitation. These current declines in sulfur deposition have
19 in varying degrees been offset by declines in base cations and may be contributing “to the
20 increased sensitivity of poorly buffered systems.” Analysis of the data from Integrated Forest
21 Studies (IFS) supports the authors’ contention that atmospheric base cation inputs may seriously
22 affect ecosystem processes. Johnson et al. (1994a) analyzed base cation cycles at the Whiteface
23 Mountain IFS site in detail and concluded that losses in calcium from the forest floor were much
24 greater than historical losses, based on historical changes in forest floor calcium observed in an
25 earlier study (Johnson et al., 1994b). Further, the authors suggest that “the difference between
26 historical and current net loss rates of forest floor calcium may be caused by sharply reduced
27 atmospheric inputs of calcium after about 1970, and exacerbated by sulfate leaching” (U.S.
28 Environmental Protection Agency, 1999).

1 **9.3.4.5 Trace Elements**

2 Trace metals are natural elements that are ubiquitous in small (trace) amounts in soils,
3 ground water and vegetation. Many are essential elements required for growth by plants and
4 animals as micronutrients. Naturally occurring surface mineralizations can produce metal
5 concentrations in soils and vegetation that are as high, or higher, than those in the air and
6 deposited near man-made sources (Freedman and Hutchinson, 1981). The occurrence and
7 concentration of trace metals in any ecosystem component depend on the sources of the metal via
8 the soil or as particulate. Even when air pollution is the primary source, continued deposition
9 can result in the accumulation of trace metals in the soil (Martin and Coughtrey, 1981). Many
10 metals deposited into soils by chemical processes and are not available to plants (Saunders and
11 Godzik, 1986).

12 When aerial deposition is the primary source of metal particles, both the chemical form and
13 particle size deposited determine the heavy metal concentration in the various ecosystem
14 components (Martin and Coughtrey, 1981). Human activities introduce heavy metals into the
15 atmosphere and have resulted in the deposition of antimony, cadmium, chromium, copper, lead,
16 molybdenum, nickel, silver, tin, vanadium, and zinc (Smith, 1990b). Extensive evidence
17 indicates that heavy metals deposited from the atmosphere to forests accumulate either in the
18 richly organic forest floor or in the soil layers immediately below, areas where the activity of
19 roots and soil is greatest. The greater the depth of soil, the lower the metal concentration. The
20 accumulation of metal in the soil layers where the biological activity is greatest, therefore, has the
21 potential for being toxic to roots and soil organisms and interfering with nutrient cycling (Smith,
22 1990a). Though all metals can be directly toxic at high levels, only copper, nickel and zinc have
23 been frequently documented. Toxicity of cadmium, cobalt, and lead has been seen only under
24 unusual conditions (Smith, 1990a). Exposures at lower concentrations have the potential, over
25 the long-term, for interfering with the nutrient-cycling processes when they affect mycorrhizal
26 function.

27 Accumulation of heavy metals in litter presents the greatest potential for interference with
28 nutrient cycling. Accumulation of metals in the litter occurs chiefly around brass works and lead
29 and zinc smelters. There is some evidence that invertebrates inhabiting soil litter do accumulate
30 metals. Earthworms from roadsides were shown to contain elevated concentrations of cadmium,
31 nickel lead and zinc, however, interference with earthworm activity was not cited (Martin and

1 Coughtrey, 1981). Studies by Babich and Stotsky (1978) support the concept that increased
2 accumulation of litter in metal-contaminated areas is the result of effects on the microorganismal
3 populations. Cadmium toxicity to microbial populations was observed to decrease and prolong
4 logarithmic rates of microbial increase, to reduce microbial respiration and fungal spore
5 formation and germination, to inhibit bacterial transformation, and to induce abnormal
6 morphologies. Additionally, the effects on symbiotic activity of fungi, bacteria and
7 actinomycetes were reported by Smith (1990a). The formation of mycorrhizae of *Glomus*
8 *musseae* with onions was reduced when additions of zinc, copper, nickel or cadmium was added
9 to the soil.

10 The potential pathways of accumulation of trace metals in terrestrial ecosystems, as well as
11 the possible consequences of trace metal deposition on ecosystem functions is summarized in
12 Figure 9-5. Indicated in the figure are the generalized trophic levels found in an ecosystem and
13 the various physiological and biological processes that could be affected by trace metals.
14 Reduction in physiological processes can affect productivity, fecundity and mortality (Martin and
15 Coughtrey, 1981). Therefore, any effects on structure and function of an ecosystem are likely to
16 occur through the soil and litter (Tyler, 1972).

17 Trace metals deposited from the atmosphere to forests accumulate either in the richly
18 organic forest floor or in the soil layers immediately below, layers where greatest biological
19 activity occurs. The shallow-rooted species plant species are those most likely to take up metals
20 from the soil (Martin and Coughtrey, 1981). Though all metals can be toxic at high levels, only
21 copper, nickel, and zinc have been frequently documented. Toxicity from cadmium, cobalt, and
22 lead has been seen only under unusual conditions (Smith, 1991g). Exposure at lower
23 concentrations have the potential over the long term, for interfering with nutrient-cycling
24 processes.

25 Certain species of plants are tolerant of metal contaminated soils (e.g., soils from mining
26 activities) (Antonovics et al., 1971). Certain species of plants have also been used as
27 bioindicators of metals. The sources of both macroelements and trace metals in the soil of the
28 Botanical Garden of the town of Wroclow, Poland were determined by measuring the
29 concentrations of the metals in *Rhododendron catawbiense*, *Ilex aquifolium* and *Mahonia*
30 *aquifolium* growing in the garden and comparing the results with the same plant species growing

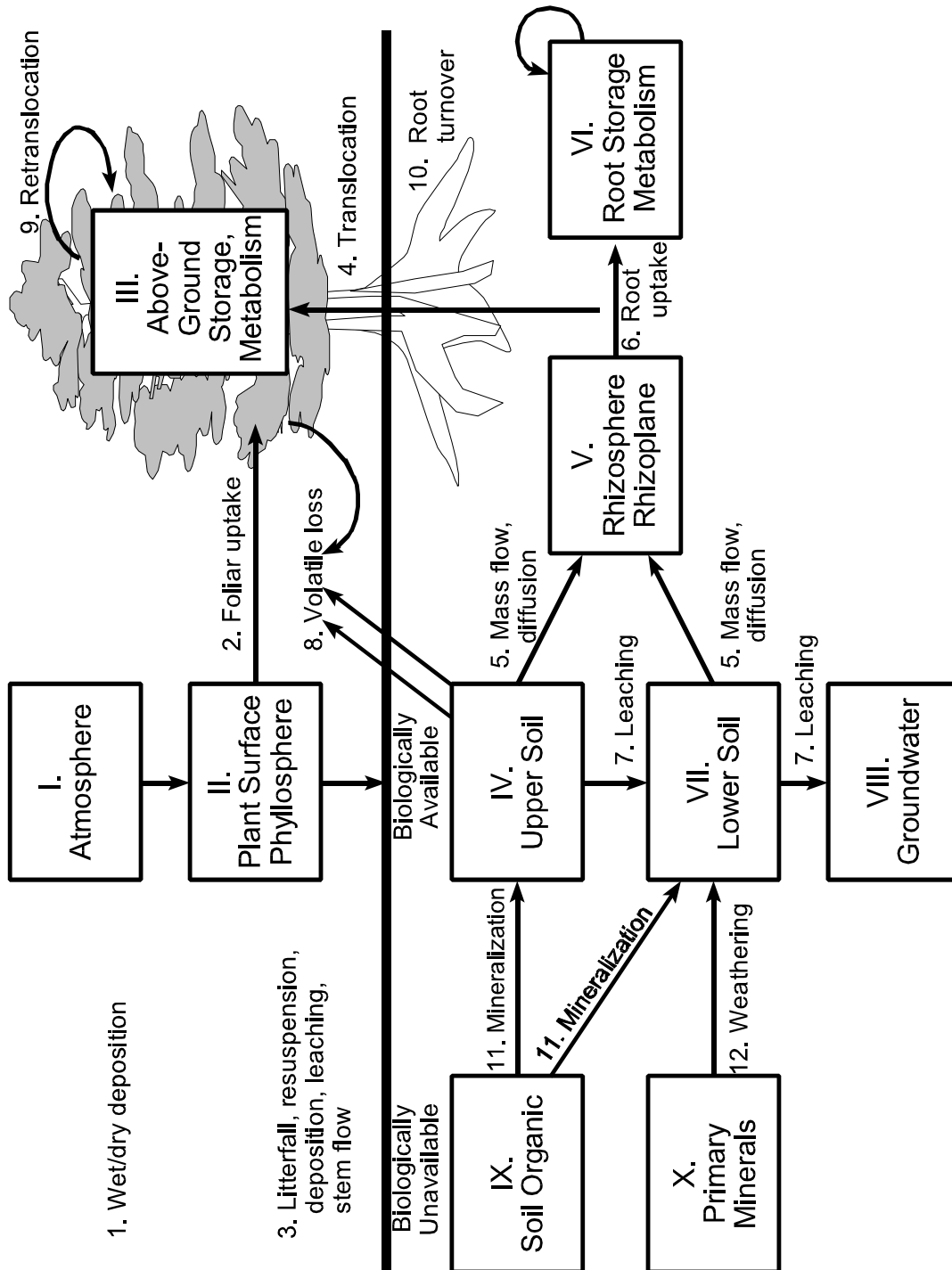


Figure 9-5. Relationship of plant nutrients and trace metals with vegetation. Compartments (Roman numerals) represent potential storage sites, whereas arrows (Arabic numerals) represent potential transfer routes.

1 in two other botanical gardens in non-polluted areas. Air pollution was determined as the source
2 rather than the soil (Samecka-Cymerman and Kempers, 1999).

3 Biological accumulation of metals through the plant-herbivore and litter-detrivore chains
4 can occur. A study of the accumulation of cadmium, lead, and zinc concentrations in
5 earthworms suggested that cadmium and zinc were concentrated, but not lead. Studies indicate
6 that heavy metal deposition onto the soil, via food chain accumulation, can cause excessive
7 levels and toxic effects in certain animals. Cadmium appears to be relatively mobile within
8 terrestrial food chains; however, the subsequent mobility of any metal after it is ingested by a
9 herbivorous animal depends on the site of accumulation within body tissues. Although food
10 chain accumulation may not in itself cause death, it can reduce the breeding potential in a
11 population (Martin and Coughtrey, 1981).

12 There is evidence that some invertebrates inhabiting soil litter do accumulate metal
13 concentrations of cadmium, nickel, lead, and zinc. Organisms that feed on earthworms in the
14 elevated concentrations of Cd, Ni, Pb, and Z for extended periods could accumulate lead and zinc
15 to toxic levels (Martin and Coughtrey, 1981). Increased concentrations of heavy metals have
16 been found in a variety of small mammals living in areas with elevated heavy metal
17 concentrations in the soils.

18 In actual case studies, it was observed that copper and zinc pollution around a brassworks
19 resulted in an accumulation of incompletely decomposed litter. In one study, litter accumulation
20 was reported up to 7.4 km from the stack of a primary smelter in southeastern Missouri. Similar
21 results were reported around a metal smelter at Avonmouth, England. In the latter case, litter
22 accumulation was associated closely with concentrations specifically of cadmium, as well as
23 with those of lead, copper, and zinc (Martin and Coughtrey, 1981). Experimental data (using
24 mesh bags containing litter) supports the hypothesis that reduced decomposition occurs close to
25 heavy metal sources.

26 In addition, litter accumulations of metals were reported in soil close to a metal smelter at
27 Palmerton, PA, in both 1975 and 1978. The continued presence of cadmium, lead, zinc, and
28 copper in the upper soil horizons (layers) were observed 6 years after the smelter terminated
29 operation in 1980. Metal levels were highest near the smelter. The relationship of decreasing
30 amounts of metal in body tissues also held true for amphibians and mammals. Levels of
31 cadmium in kidneys and liver of white-tailed deer (*Odocoileus virginianus*) were five times higher

1 at Palmerton than in those collected 180 km southwest downwind. The abnormal amounts of
2 metal in the tissues of terrestrial vertebrates and the absence or low abundance of wildlife at
3 Palmerton indicated that ecological processes within 5 km of the smelters continued to be
4 markedly influenced even 6 years after the closing of the zinc smelter (Storm et al., 1994).

5 Increased amounts of litter in metal-contaminated areas appear to result from the reduced
6 activity of the microorganismal populations Babich and Stotzky (1978). Cadmium toxicity to
7 microbial populations was observed to decrease and prolong rates of microbial increase, to
8 reduce microbial respiration and fungal spore germination, to inhibit bacterial transformation and
9 formation of fungal spores. Additionally, the effects on the symbiotic activity of cadmium,
10 copper, nickel, and zinc on fungi, bacteria, and actinomycetes were reported by Smith (1991).
11 The formation of mycorrhizae by *Glomus mosseae* with onions was reduced when zinc, copper,
12 nickel, or cadmium was added to the soil. The relationship of the fungus with white clover,
13 however, was not changed. It was suggested that the effect of heavy metals on
14 vesicular-arbuscular mycorrhizal fungi will vary from host to host (Gildon and Tinker, 1983).
15 Studies with ericoid plants indicated that, in addition to *Calluna vulgaris*, mycorrhizae also
16 protect *Vaccinium macrocarpa* and *Rhodendron ponticum* from heavy metals (Bradley et al.,
17 1981). Heavy metals tend to accumulate in the roots, and shoot toxicity is prevented.

18 The effects of lead in ecosystems are discussed in the *Air Quality Criteria for Lead*
19 (U.S. Environmental Protection Agency, 1986b). Studies have shown that there is cause for
20 concern in three areas where ecosystems may be extremely sensitive to lead: (1) delay of
21 decomposition because the activity of some decomposer microorganisms and invertebrates is
22 inhibited by lead, (2) subtle shifts toward plant populations tolerant of lead, and (3) lead in the
23 soil and on the surfaces of vegetation circumvent the processes of biopurification. The problems
24 cited above arise because lead is deposited on the surface of vegetation, accumulates in the soil,
25 and is not removed by the surface and ground water of the ecosystem (U.S. Environmental
26 Protection Agency, 1986b).

27 28 **9.3.4.6 Biogeochemical Cycling—the Integrated Forest Study**

29 The Integrated Forest Study (IFS) (Johnson and Lindberg, 1992a) has provided the most
30 extensive data set available on wet and dry deposition and the effects of deposition on the cycling
31 of elements in forest ecosystems. The overall patterns of deposition and cycling have been

1 summarized by Johnson and Lindberg (1992a), and the reader is referred to that reference for
2 details. The following is a summary of particulate deposition, total deposition, and leaching in
3 the IFS sites.

4 Particulate deposition in the IFS was separated at the 2- μm level; a decision was made to
5 include total particulate deposition in this analysis, and may include the deposition of particles
6 larger than 10 μm .

7 Particulate deposition contributes considerably to the total impact of base cations to most of
8 the IFS sites. On average, particulate deposition contributes 47% to total calcium deposition
9 (range: 4 to 88%), 49% of total potassium deposition (range: 7 to 77%), 41% to total magnesium
10 deposition (range: 20 to 88%), 36% to total sodium deposition (range: 11 to 63%), and 43% to
11 total base cation deposition (range: 16 to 62%). Of the total particulate deposition, the vast
12 majority (>90%) is >2 μm .

13 Figures 9-6 through 9-9 summarize the deposition and leaching of calcium, magnesium,
14 potassium, and some of the base cations for the IFS sites. As noted in the original synthesis
15 (Johnson and Lindberg, 1992a), some sites show net annual gains of base cations (i.e., total
16 deposition > leaching), some show losses (total deposition < leaching), and some are
17 approximately in balance. Not all cations follow the same pattern at each site. For example,
18 calcium shows net accumulation at the Coweeta, Duke, and Florida sites (Figure 9-5), potassium
19 shows accumulation at the Duke, Florida, Douglas-fir, red alder, Huntington Forest, and
20 Whiteface Mountain sites (Figure 9-7), and magnesium accumulated only at the Florida sites
21 (Figure 9-8). Only at the Florida site is there a clear net accumulation of total base cations
22 (Figure 9-9).

23 The factors affecting net calcium accumulation or loss include the soil-exchangeable cation
24 composition, as noted previously; base cation deposition rate; the total leaching pressure due to
25 atmospheric sulfur and nitrogen inputs, as well as natural (carbonic and organic) acids; and
26 biological demand (especially for potassium). In the Florida site, which has a very cation-poor,
27 sandy soil (an Ultic Haploquod derived from marine sand), the combination of all these factors
28 leads to net base cation accumulation from atmospheric deposition (Johnson and Lindberg,
29 1992a). The site showing the greatest net base cation losses, the red alder stand in Washington
30 state, is one that is under extreme leaching pressure by nitrate produced because of excessive
31 fixation by that species (Van Miegroet and Cole, 1984). In the red spruce site in the Smokies,

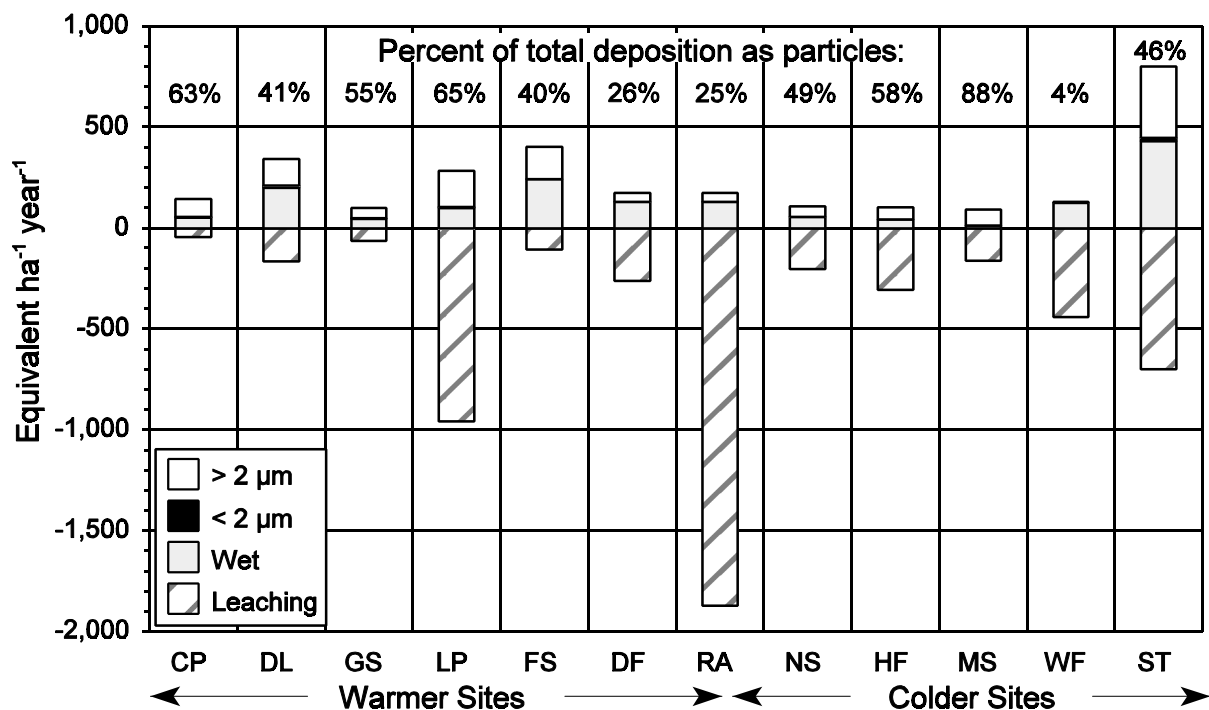


Figure 9-6. Calcium deposition in >2 μm particles, <2 μm particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. CP = *Pinus strobus*, Coweeta, NC; DL = *Pinus taeda*, Durham (Duke), NC; GS = *Pinus taeda*, B. F. Grant Forest, GA; LP = *Pinus taeda*, Oak Ridge, TN; FS = *Pinus eliottii*, Bradford Forest, FL; DF = *Pseudotsuga menziesii*, Thompson, WA; RA = *Alnus rubra*; NS = *Picea abies*, Nordmoen, Norway; HF = northern hardwood, Huntington Forest, NY; MS = *Picea rubens*, Howland, ME; WF = *Picea rubens*, Whiteface Mountain, NY; and ST = *Picea rubens*, Clingman's Dome, NC.

1 the combined effects of SO_4^{2-} and NO_3^- leaching are even greater than in the red alder site
 2 (Figure 9-10), but a considerable proportion of the cations leached from this extremely acid soil
 3 consist of H^+ and Al^{3+} rather than of base cations (Johnson and Lindberg, 1992a). Thus the red
 4 spruce site in the Smokies is approximately in balance with respect to calcium and total base
 5 cations, despite the very high leaching pressure at this site (Figures 9-10 and 9-12).

6 The relative importance of particulate base cation deposition varies widely with site and
 7 cation and is not always related to the total deposition rate. The proportion of calcium deposition
 8 in particulate form ranges from a low of 4% at the Whiteface Mountain site to a high of 8% in

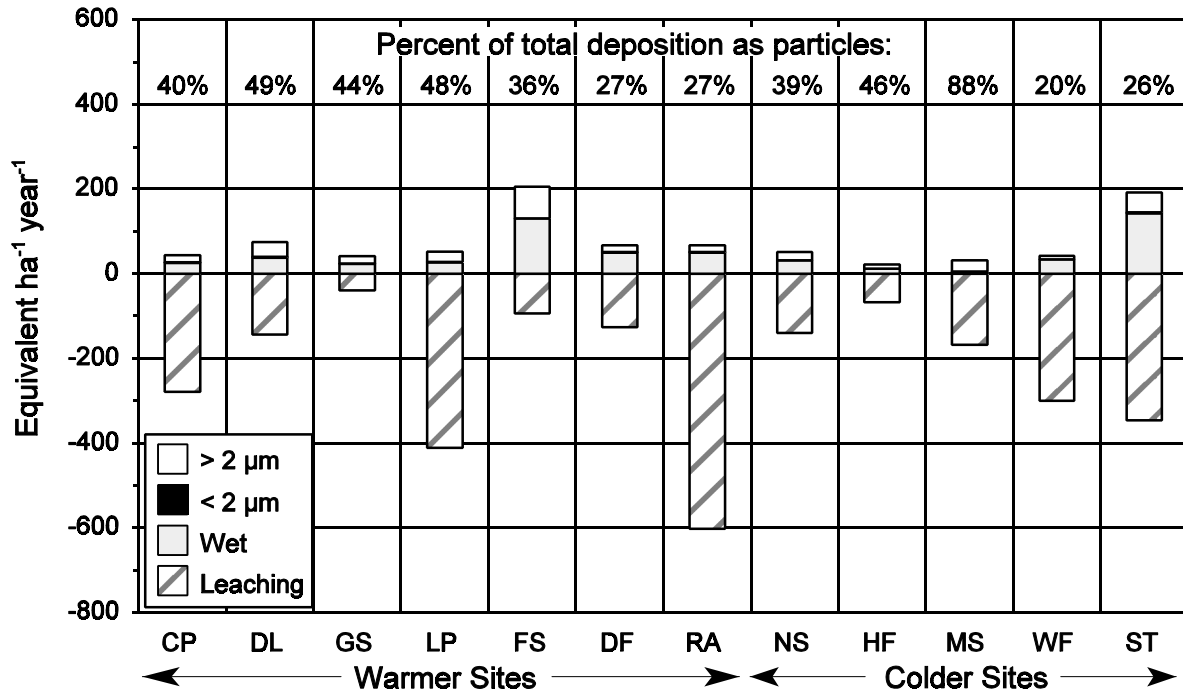


Figure 9-7. Magnesium deposition in >2 μm particles, <2 μm particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. See Figure 9-6 for legend.

1 the Maine site (Figure 9-6), and the proportion of magnesium deposition as particles ranges from
 2 >20% at the Whiteface Mountain site to 88% at the Maine site. The proportion of magnesium
 3 deposition as particles ranges from >20% at the Whiteface Mountain site to 88% at the Maine
 4 site, and the proportion of potassium deposition as particles ranges from 7% at the Smokies site
 5 to 77% at the Coweeta site (Figures 9-10 and 9-11). Overall, particulate deposition at the site in
 6 Maine accounted for the greatest proportion of calcium, potassium, magnesium, and base cation
 7 deposition (88, 57, 88, and 62%, respectively), even though total deposition was relatively low.
 8 At some sites, the relative importance of particulate deposition varies considerably by cation.
 9 At the Whiteface Mountain site, particulate deposition accounts for 4, 40, and 20% of calcium,
 10 potassium, and magnesium deposition, respectively. At the red spruce site in the Smokies,
 11 particulate deposition accounts for 46, 7, and 26% of calcium, potassium, and magnesium
 12 deposition.

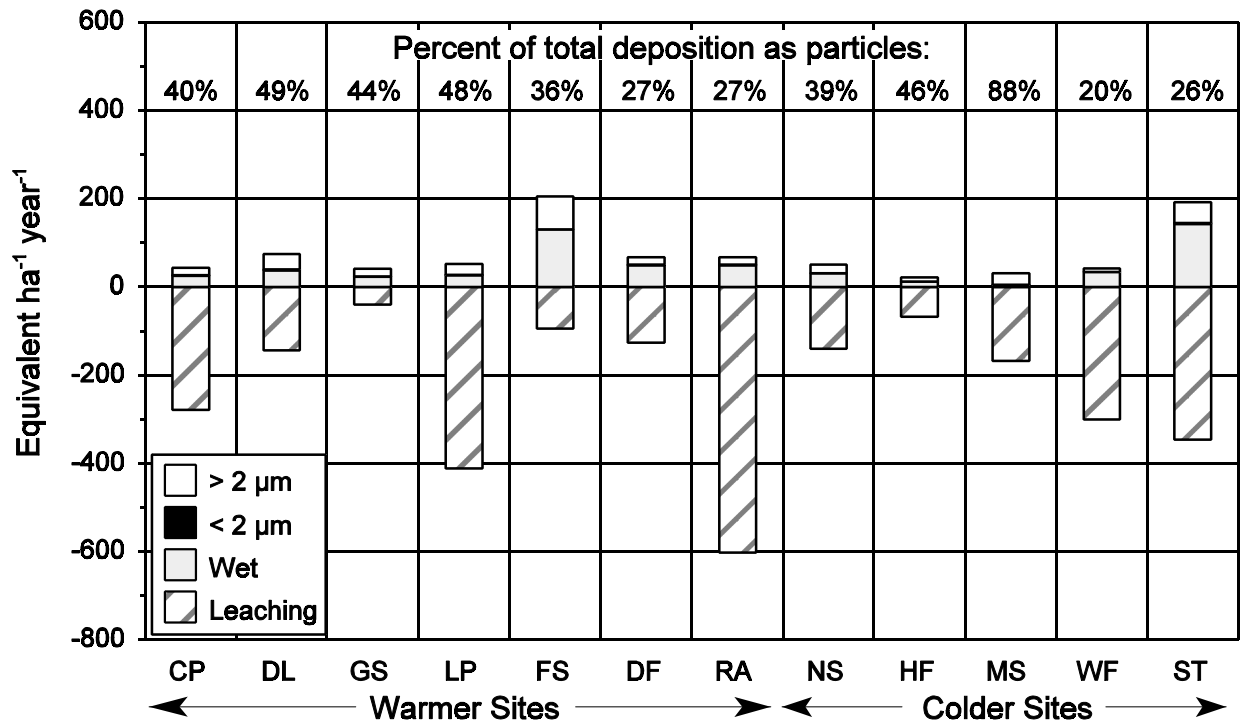


Figure 9-8. Potassium deposition in >2 μm particles, <2 μm particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. See Figure 9-6 for legend.

1 As noted in the IFS synthesis, SO_4^{2-} and NO_3^- leaching often are dominated by atmospheric
 2 sulfur and nitrogen (Johnson and Lindberg, 1992a). The exceptions to this are in cases where
 3 natural nitrogen inputs are high (i.e., the nitrogen-fixing red alder stand), as are NO_3^- leaching
 4 rates, even though nitrogen deposition is low, and where soils adsorb much of the
 5 atmospherically deposited SO_4^{2-} , thus reducing SO_4^{2-} leaching compared to atmospheric sulfur
 6 input.

7 Sulfate and NO_3^- leaching have a major effect on cation leaching in many of the IFS sites
 8 (Johnson and Lindberg, 1992a). Figure 9-11 shows the total cation leaching rates of the IFS sites
 9 and the degree to which cation leaching is balanced by $\text{SO}_4^{2-} + \text{NO}_3^-$. The SO_4^{2-} and NO_3^- fluxes
 10 are subdivided further into that proportion potentially derived from particulate sulfur and
 11 nitrogen deposition (assuming no ecosystem retention, a maximum effect) and other sulfur and
 12 nitrogen sources (wet and gaseous deposition, internal production).

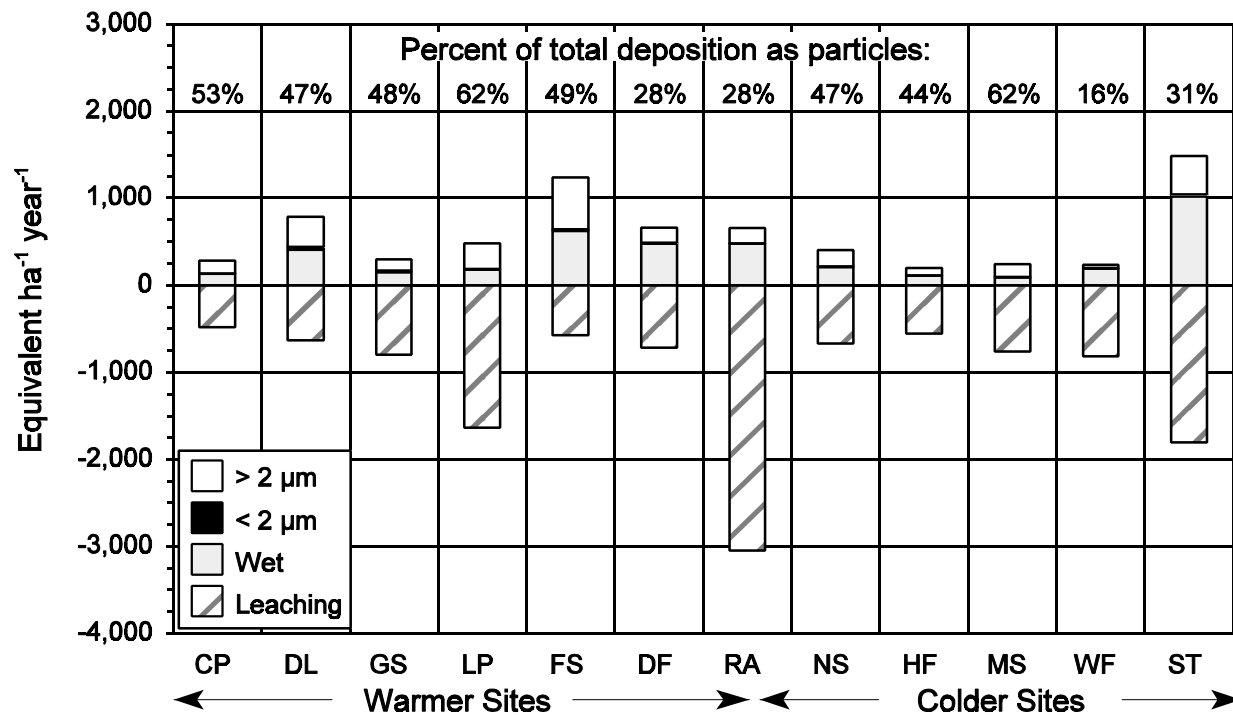


Figure 9-9. Base cation deposition in >2 μm particles, <2 μm particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. See Figure 9-6 for legend.

1 As noted in the IFS synthesis, SO_4^{2-} and NO_3^- account for a large proportion (28 to 88%)
 2 total cation leaching in most sites. The exception is the Georgia loblolly pine site where there
 3 were high rates of HCO_3^- and Cl^- leaching (Johnson and Lindberg, 1992a). The role of
 4 particulate sulfur and nitrogen deposition in this leaching is generally very small (<10%),
 5 however, even if it is assumed that there is no ecosystem sulfur or nitrogen retention.

6 As noted previously in this chapter, the contribution of particles to total deposition of
 7 nitrogen and sulfur at the IFS sites is lower than is the case for base cations. On average,
 8 particulate deposition contributes 18% to total nitrogen deposition (range: 1 to 33%) and 17%
 9 to total sulfur deposition (range: 1 to 30%). Particulate deposition contributes only a small
 10 amount to total H^+ deposition (average = 1%; range: 0 to 2%). (It should be noted, however,
 11 that particulate H^+ deposition in the >2-μm fraction was neglected.)

12 From the IFS data, then, it appears that the particulate deposition has a greater effect on
 13 base cation inputs to soils than on base cation losses associated with inputs of sulfur, nitrogen,

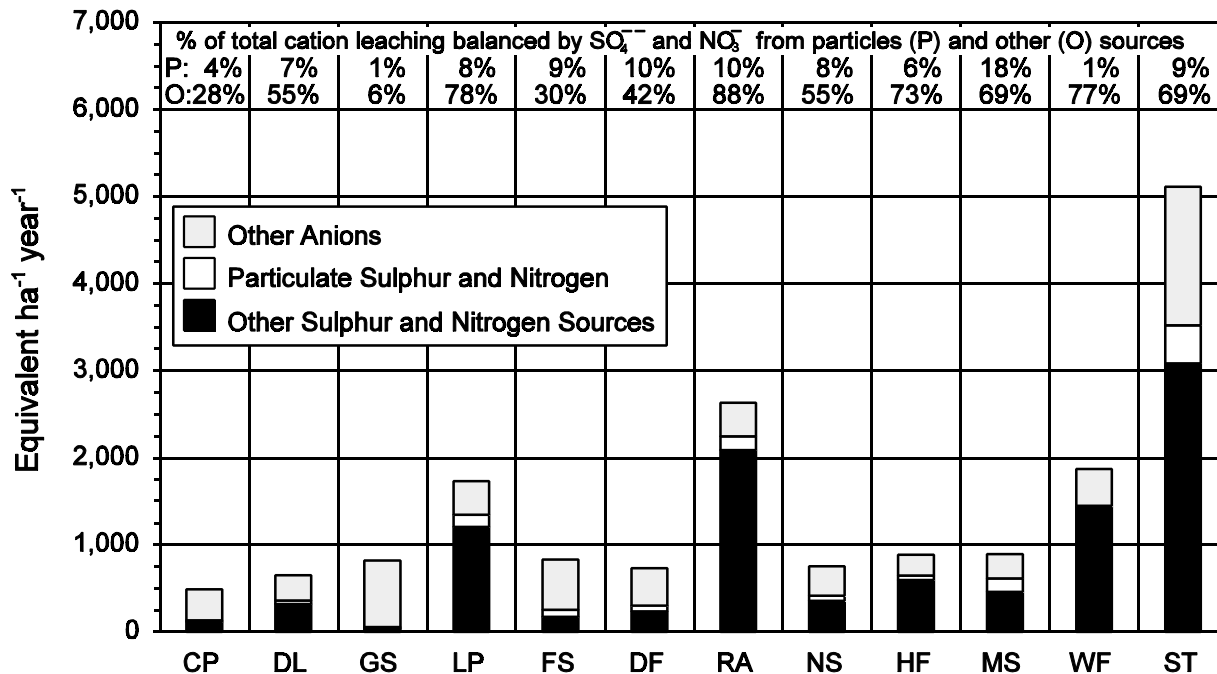


Figure 9-10. Total cation leaching (total height of bar) balanced by sulfate and nitrate estimated from particulate deposition (assuming no ecosystem retention, particulate sulfur and nitrogen) and by other sources (both deposition and internal) of sulfate and nitrate (other sulfur and nitrogen sources) and by other anions in the Integrated Forest Study sites. See Figure 9-6 for legend.

1 and H⁺. It cannot be determined what fraction of the mass of these particles are <10 μm, but only
 2 a very small fraction is <2 μm. These inputs of base cations have considerable significance, not
 3 only to the base cation status of these ecosystems but also to the potential of incoming
 4 precipitation to acidify or alkalize the soils in these ecosystems. As noted above, the potential of
 5 precipitation to acidify or alkalize soils depends on the ratio of base cations to H⁺ in deposition,
 6 rather than simply on the inputs of H⁺ alone. In the case of calcium, the term “lime potential” has
 7 been applied to describe this ratio; the principle is the same with respect to magnesium and
 8 potassium. Sodium is a rather special case, in that sodium is a poorly absorbing cation, and
 9 leaching tends to balance input over a relatively short term.

10 Net balances of base cations tell only part of the story as to potential effects on soils; these
 11 net losses or gains must be placed in the perspective of the soil pool size. One way to express
 12 this perspective is to simply compare soil pool sizes with the net balances. This comparison is

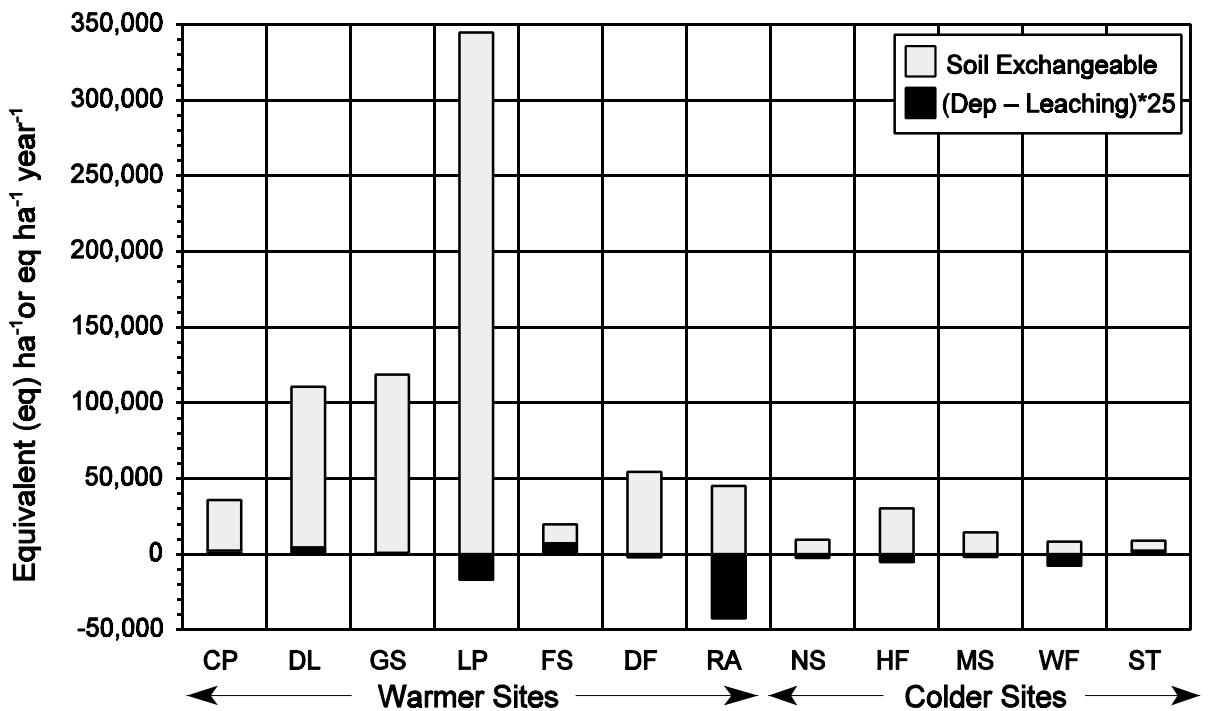


Figure 9-11. Soil exchangeable Ca^{++} pools and net annual export of Ca^{++} (deposition minus leaching times 25 years) in the Integrated Forest Study sites. See Figure 9-6 for legend.

1 made for exchangeable pools and net balances for a 25-year period in Figures 9-11 to 9-13.
 2 It readily is seen that net leaching losses of cations pose no threat in terms of depleting
 3 soil-exchangeable Ca^{2+} , K^+ , or magnesium ion within 25 years at the Coweeta, Duke, Georgia,
 4 Oak Ridge, or Douglas-fir sites. There is a potential for significant depletion at the red alder,
 5 Whiteface Mountain (magnesium), and Smokies red spruce sites, however.

6 The range of values for soil-exchangeable turnover is very large, reflecting variations in
 7 both the size of the exchangeable pool and the net balance of the system. Soils with the highest
 8 turnover rates are those most likely to experience changes in the shortest time interval, other
 9 things being equal. Thus, the Whiteface Mountain, Smokies, and Maine red spruce sites; the
 10 Thompson red alder site; and the Huntington Forest northern hardwood site appear to be most
 11 sensitive to change. The actual rates, directions, and magnitudes of changes that may occur in
 12 these soils (if any) will depend on weathering inputs and vegetation outputs, in addition to

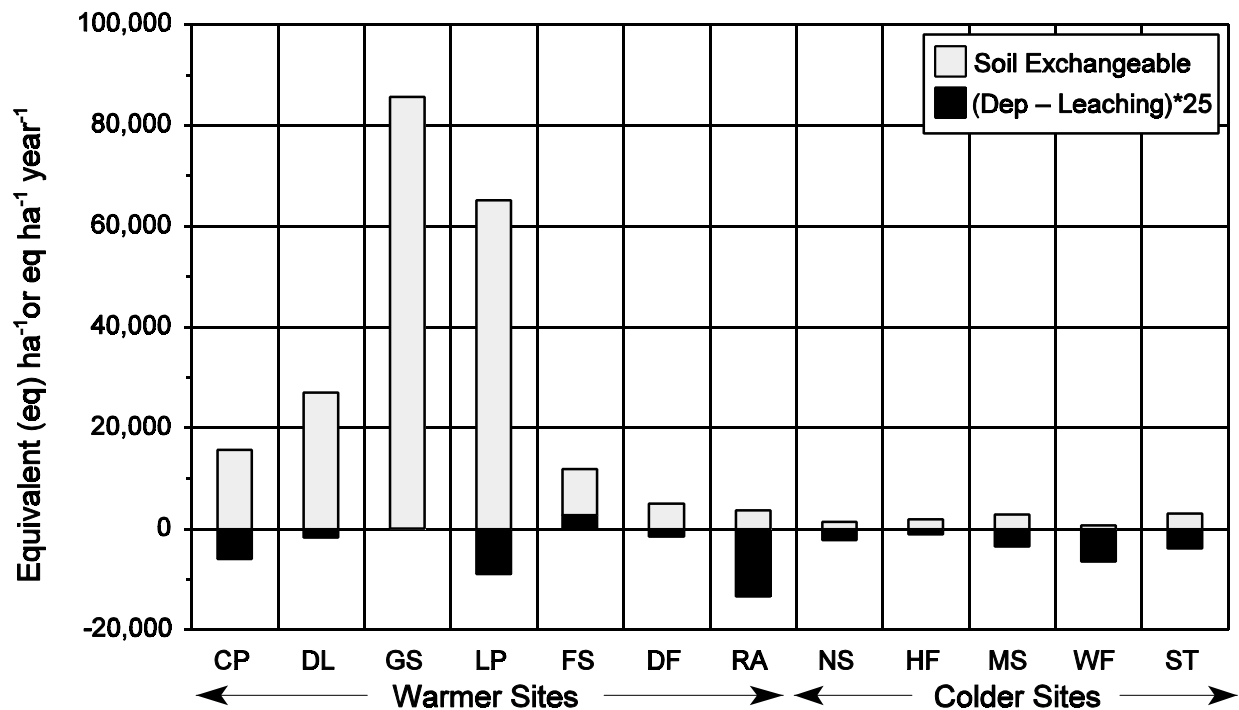


Figure 9-12. Soil exchangeable Mg⁺⁺ pools and net annual export of Mg⁺⁺ (deposition minus leaching times 25 years) in the Integrated Forest Study sites. See Figure 9-6 for legend.

1 deposition and leaching. It is noteworthy that each of the sites listed above as sensitive has a
 2 large store of weatherable minerals, whereas many of the other soils, with larger exchangeable
 3 cation reserves, have a small store of weatherable minerals (e.g., Coweeta white pine, Duke
 4 loblolly pine, Georgia loblolly pine, and Oak Ridge loblolly pine) (Johnson and Lindberg, 1992a;
 5 April and Newton, 1992).

6 Base cation inputs are especially important to the Smokies red spruce site because of
 7 potential aluminum toxicity and calcium and magnesium deficiencies. Johnson et al. (1991a)
 8 found that soil solution aluminum concentrations occasionally reached levels found to inhibit
 9 calcium uptake and cause changes in root morphology in solution culture studies of red spruce
 10 (Raynal et al., 1990). In a follow-up study, Van Miegroet et al. (1993) found a slight but
 11 significant growth response to calcium and magnesium fertilizer in red spruce saplings near the

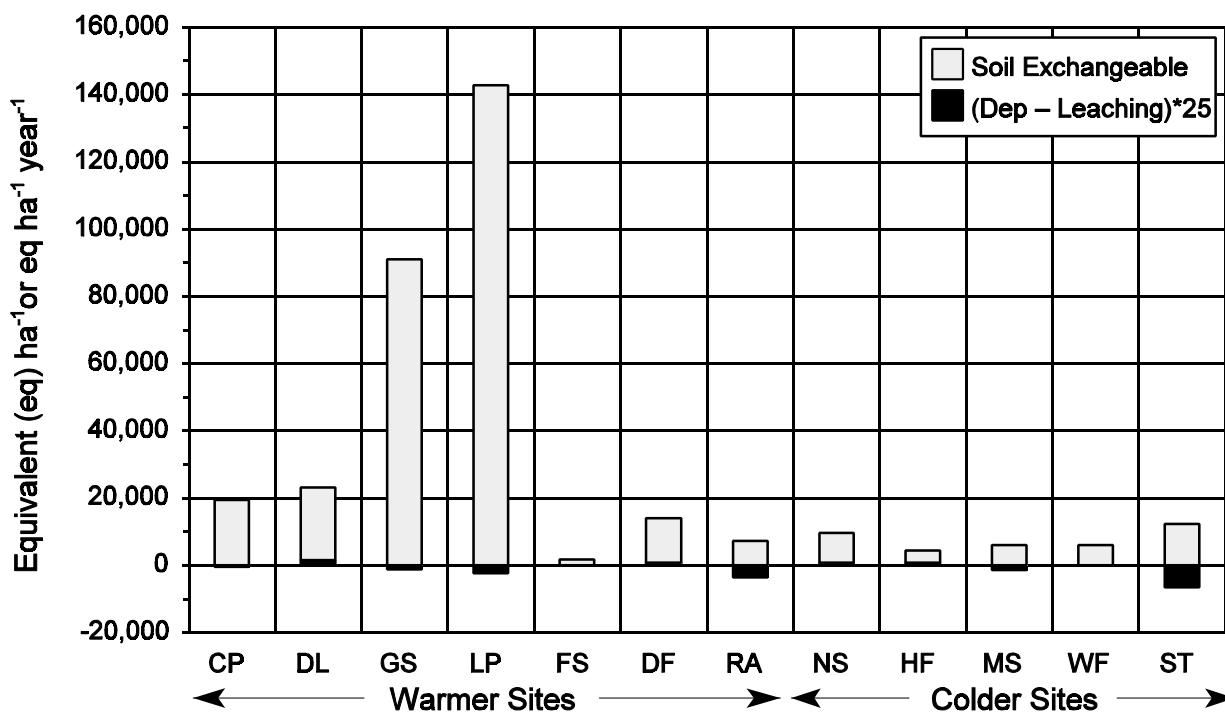


Figure 9-13. Soil exchangeable K⁺ pools and net annual export of K⁺ (deposition minus leaching times 25 years) in the Integrated Forest Study sites. See Figure 9-6 for legend.

1 Smokies red spruce site. Joslin et al. (1992) reviewed soil and solution characteristics of red
 2 spruce in the southern Appalachians, and it would appear that the IFS site is rather typical.

3 The simple calculations shown above give some idea of the importance of particulate
 4 deposition in these forest ecosystems, but they cannot account for the numerous potential
 5 feedbacks between vegetation and soils nor for the dynamics through time that can influence the
 6 ultimate response. One way to examine some of these interactions and dynamics is to use
 7 simulation modeling. The nutrient cycling model (NuCM) has been developed specifically for
 8 this purpose and has been used to explore the effects of atmospheric deposition, fertilization, and
 9 harvesting on some of the IFS sites (Johnson et al., 1993). The NuCM model is a stand-level
 10 model that incorporates all major nutrient cycling processes (uptake, translocation, leaching,
 11 weathering, organic matter decay, and accumulation).

1 For this study, the NuCM model was used to examine the effects of particulate deposition
2 at the Duke loblolly and Smokies red spruce sites. These two sites were chosen as extremes of
3 nitrogen deposition, growth, and soil acidity, all of which should affect responses to deposition.
4 In each case, four scenarios were run: (1) no change, (2) particulate nitrogen, sulfur, and base
5 cations removed (no particles), (3) nitrogen and sulfur particles removed (no nitrogen or sulfur
6 particles), and (4) particulate base cations removed (no base cation particles). Tables 9-3 and 9-4
7 give simulation results for the Duke and Smokies sites, respectively.

8 For the Duke site, simple budget calculations indicated that removing nitrogen and sulfur
9 particulate deposition would lower base cation leaching by only 7% and would have minimal
10 effects on soil base cation pools. The NuCM simulations indicated that removing nitrogen and
11 sulfur particles would reduce leaching by 10, 7, and 3% for potassium, calcium, and magnesium,
12 respectively (Table 9-3). Thus, in this case, estimates of effects from the simple calculations
13 were approximately the same as the much more sophisticated estimates from the NuCM model.
14 Removing nitrogen and sulfur particles caused reduced base cation uptake by trees (because of a
15 growth reduction; the site was nitrogen-limited). This, combined with reduced base cation
16 leaching, caused greater soil exchangeable base cation pools at the end of the 30-year simulation
17 in the no-nitrogen, sulfur particles scenario than in the no-change scenario.

18 The NuCM simulations, like the simple budget calculations, suggest that particulate
19 deposition of base cations has a greater effect on soils and base cation nutrient budgets than
20 would nitrogen and sulfur particulate deposition. The removal of base cation, as well as nitrogen
21 and sulfur particulate deposition (no particles), causes a growth reduction and less base cation
22 uptake as in the no-nitrogen, sulfur particle scenario, but soil exchangeable base cation pools are
23 much reduced compared to the no-nitrogen, sulfur particle scenario (Table 9-3). When base
24 cations are removed and N and S particles are left (NO BC particles) soil-based cations are
25 reduced even more -21, -8, and -5%, compared to the no-change scenario as opposed to +11,
26 +0.3, and +4% in the no nitrogen, sulfur particulate scenario.

27 There were some significant differences in the responses of the Smokies site to simulated
28 changes in particulate deposition. First, the site was slow-growing, nitrogen-saturated, and not
29 yet limited by other nutrients, and, thus, there were no effects of deposition on simulated growth
30 or nutrient uptake (Table 9-3). Secondly, the fluxes were greater and the pool sizes were smaller,
31 thus the effects of changing deposition were somewhat greater than for the Duke site.

**TABLE 9-3. SIMULATED DEPOSITION, LEACHING, AND ECOSYSTEM POOLS
AT THE DUKE SITE WITH AND WITHOUT PARTICULATE DEPOSITION
USING THE NuCM MODEL**

Scenario	No Change	No Particles	No N, S Particles	No Base Particles
	kmol ha ⁻¹			
Nitrogen				
<u>Cumulative Fluxes</u>				
Deposition	34.06	21.36	21.36	34.06
Leaching	1.27	0.52	0.52	1.27
Balance	32.79	20.84	20.84	32.79
<u>Nutrient Pools after 30 Years</u>				
Vegetation	44.42	37.27	37.3	44.12
Litter	42.1	38.48	38.5	42.35
Soil, Exch.	<0.1	<0.1	<0.1	<0.1
Sulfur				
<u>Cumulative Fluxes</u>				
Deposition	17.01	5.53	5.53	17.01
Leaching	14.61	12.64	13.09	14.06
Balance	2.4	-7.11	-7.56	2.95
<u>Nutrient Pools after 30 Years</u>				
Vegetation	1.84	1.73	1.73	1.84
Litter	1.44	1.34	1.34	1.46
Soil, Exch.	56.03	46.71	46.27	56.55
Potassium				
<u>Cumulative Fluxes</u>				
Deposition	3.01	0.72	3.01	0.72
Leaching	4.16	3.76	3.6	4.24
Balance	-1.15	-3.04	-0.59	-3.52
<u>Nutrient Pools after 30 Years</u>				
Vegetation	4.95	4.49	4.49	4.95
Litter	3.85	3.47	3.47	3.89
Soil, Exch.	12.57	11.51	13.97	10.16
Calcium				
<u>Cumulative Fluxes</u>				
Deposition	5.79	3.41	5.79	3.41
Leaching	14	13.14	12.83	14.33
Balance	-8.21	-9.72	-7.04	-10.92

TABLE 9-3 (cont'd). SIMULATED DEPOSITION, LEACHING, AND ECOSYSTEM POOLS AT THE DUKE SITE WITH AND WITHOUT PARTICULATE DEPOSITION USING THE NuCM MODEL

Scenario	No Change	No Particles	No N, S Particles	No Base Particles
	kmol ha ⁻¹			
<u>Nutrient Pools after 30 Years</u>				
Vegetation	5.81	5.48	5.47	5.82
Litter	2.08	1.18	1.8	2.13
Soil, Exch.	34.19	33.29	35.98	31.43
Magnesium				
<u>Cumulative Fluxes</u>				
Deposition	1.18	0.6	1.18	0.6
Leaching	4.91	4.76	4.63	5.04
Balance	-3.73	-4.15	-3.15	-4.43
<u>Nutrient Pools after 30 Years</u>				
Vegetation	2.85	2.68	2.68	2.85
Litter	0.99	0.88	0.87	1.01
Soil, Exch.	15.113	14.98	15.69	14.41

1 Therefore, although removing nitrogen and sulfur particles caused a mere 6% increase in soil
 2 exchangeable potassium, calcium, and magnesium pools, removing base cation particles caused
 3 8, 25, and 13% decreases in exchangeable potassium, calcium, and magnesium, respectively.

4 Thus, the NuCM simulations indicate that simple calculations such as those made
 5 previously give a relatively good first approximation of the effects of changing deposition. The
 6 NuCM simulations add some factors (such as reduced growth with reduced nitrogen deposition)
 7 and some more precise quantitative estimates, but they do not reverse or contradict the simpler
 8 calculations.

9 Wesselink et al. (1995) reported on the complicated interactions among changing
 10 deposition and soils at this site (including repeated sampling of soil exchangeable base cation
 11 pools) from 1969 to 1991 and compared these results with those of a simulation model. They
 12 identified three basic stages of change in this ecosystem. During Stage 1, there was increased
 13 deposition of sulfur and constant deposition of base cations, causing increased base cation

TABLE 9-4. SIMULATED DEPOSITION, LEACHING, AND ECOSYSTEM POOLS AT THE SMOKIES TOWER SITE WITH AND WITHOUT PARTICULATE DEPOSITION USING THE NuCM MODEL

Scenario	No Change	No Particles	No N, S Particles	No Base Particles
	kmol ha ⁻¹			
Nitrogen				
<u>Cumulative Fluxes</u>				
Deposition	61.94	53.88	53.88	61.94
Leaching	54.76	48.28	48.26	54.82
Balance	7.18	5.6	5.63	7.12
<u>Nutrient Pools after 30 Years</u>				
Vegetation	24.48	24.48	24.48	24.48
Litter	35.77	35.77	35.77	335.77
Soil, Exch.	0.13	0.12	0.12	0.13
Sulfur				
<u>Cumulative Fluxes</u>				
Deposition	34.41	29.94	29.94	34.41
Leaching	33.92	29.69	29.93	33.73
Balance	0.49	0.25	0.01	0.69
<u>Nutrient Pools after 30 Years</u>				
Vegetation	4.25	4.25	4.25	4.25
Litter	12.54	12.54	12.54	12.54
Soil, Exch.	4.92	4.68	4.45	5.12
Potassium				
<u>Cumulative Fluxes</u>				
Deposition	5.24	4.87	5.24	4.87
Leaching	6.38	6.2	5.99	6.53
Balance	-1.15	-1.33	-0.76	-1.66

TABLE 9-4 (cont'd). SIMULATED DEPOSITION, LEACHING, AND ECOSYSTEM POOLS AT THE SMOKIES TOWER SITE WITH AND WITHOUT PARTICULATE DEPOSITION USING THE NuCM MODEL

Scenario	No Change	No Particles	No N, S Particles	No Base Particles
	kmol ha ⁻¹			
Potassium (cont'd)				
<u>Nutrient Pools after 30 Years</u>				
Vegetation	3.14	3.14	3.14	3.14
Litter	6.07	6.07	6.07	6.07
Soil, Exch.	6.12	5.93	6.49	5.62
Calcium				
<u>Cumulative Fluxes</u>				
Deposition	12.51	6.75	15.51	6.75
Leaching	12.41	7.17	12.27	7.26
Balance	0.1	-0.42	0.24	-0.51
<u>Nutrient Pools after 30 Years</u>				
Vegetation	10.65	10.62	10.65	10.62
Litter	4.22	4.18	4.22	4.18
Soil, Exch.	2.09	1.65	2.23	1.56
Magnesium				
<u>Cumulative Fluxes</u>				
Deposition	3.07	2.27	3.07	2.27
Leaching	7.24	6.62	6.99	6.83
Balance	-4.17	-4.35	-3.92	-4.56
<u>Nutrient Pools after 30 Years</u>				
Vegetation	1.73	1.73	1.73	1.73
Litter	0.86	0.86	0.86	0.86
Soil, Exch.	2.18	1.99	2.31	1.89

1 leaching and reduced base saturation in the soils. During Stage II, sulfur deposition is reduced,
2 and soil solution sulfate and base cation leaching decline accordingly, but base saturation
3 continues to decrease. During Stage III, two alternative scenarios are introduced: (a) sulfur
4 deposition continues to decline while base cation deposition stays constant, or (b) both sulfur and
5 base cation deposition decline. Under Stage IIIa, sulfate and base cation leaching continue to
6 decline, and base saturation begins to increase as base cations displace exchangeable aluminum
7 and cause it to transfer to the gibbsite pool. Under Stage IIIb, this recovery in base saturation is
8 over-ridden by the reduction in base cation deposition.

9 Given the potential importance of particulate deposition for base cation status of forest
10 ecosystems, the findings of Driscoll et al. (1989) and Hedin et al. (1994) discussed previously are
11 especially relevant. Driscoll et al. (1989) noted a decline in both SO_4^{2-} and base cations in both
12 atmospheric deposition and stream water over the last two decades at Hubbard Brook Watershed,
13 NH. The causes of declining deposition were attributed to declines in emissions, and the decline
14 in stream water SO_4^{2-} was attributed to the decline in sulfur deposition. Two alternative
15 hypotheses were presented for the decline in base cation export via stream water: (1) the decline
16 in base cation deposition or (2) the necessary decline in total cations because of the decline in
17 stream water SO_4^{2-} export. Of the two, the second is most consistent with cation exchange theory
18 and the necessity of charge balance in solution.

19 Hedin et al. (1994) report steep declines in atmospheric base cation concentrations in both
20 Europe and North America over the last 10 to 26 years. The authors assert that these declines in
21 base cations have offset concurrent declines in sulfur deposition, and may be contributing “to the
22 increased sensitivity of poorly buffered ecosystems.” The analysis of the IFS data set supports
23 the contention of Hedin et al. (1994) that atmospheric base cation inputs are important to
24 ecosystems with extremely acidic soils, and reductions in base cation inputs may seriously affect
25 ecosystem processes. Johnson et al. (1994a) analyzed base cation cycles of one of the IFS sites
26 (Whiteface Mountain) in detail and concluded that losses of calcium from the forest floor were
27 much greater than historical losses, based on historical changes in forest floor calcium content in
28 an earlier study (Johnson et al., 1994b). The authors suggest that “the difference between
29 historical and current net loss rates of forest floor calcium may be caused by sharply reduced
30 atmospheric inputs of calcium after about 1970, exacerbated by sulfate leaching.”

1 **9.4 EFFECTS ON MATERIALS**

2 Effects of SO₂ and particles on materials are related to both aesthetic appeal and physical
3 damage. Studies have demonstrated particles, primarily consisting of carbonaceous compounds,
4 cause soiling of commonly used building materials and culturally important items such as
5 statues and works of art. Physical damage from the dry deposition of SO₂, particles, and the
6 absorption or adsorption of corrosive agents on deposited particles can also result in the
7 acceleration of the weathering of manmade building and naturally occurring cultural materials.

8 Limited new studies have been published that better define the role of SO₂ and particles in
9 materials damage. This section will briefly summarize the information on SO₂ and particle
10 exposure-related effects on materials addressed in the previous Air Quality Criteria Document for
11 Particulate Matter (U.S. Environmental Protection Agency, 1996b) and present relevant
12 information published since completion of that document.

13
14 **9.4.1 Corrosive Effects of SO₂ and Particles on Man-Made Surfaces**

15 **9.4.1.1 Metals**

16 The additive effect of pollutants on the natural weathering processes will depend on the
17 nature of the pollutant and the deposition rate (the uptake of a pollutant by the material's
18 surface), and the presence of moisture. The influence of the metal protective corrosion film, the
19 presence of other surface electrolytes, the orientation of the metal surface, the presence of surface
20 moisture, and the variability in the electrochemical reactions will also contribute to the affect of
21 pollutant exposure on metal surfaces.

22 Several studies demonstrate the importance of time of surface wetness caused by dew and
23 fog condensation and rain on metals. Surface moisture facilitates the deposition of pollutants,
24 especially SO₂, and also promotes corrosive electrochemical reactions on the metal (Haynie and
25 Upham, 1974; Sydberger and Ericsson, 1977). Of critical importance is the formation of
26 hygroscopic salts on the metal that will increase the time of surfaces wetness and, thereby,
27 enhance the corrosion process.

28 Pitchford and McMurry (1994) and Zhang et al. (1993) demonstrated particle size-related
29 effects of relative humidity. The effect of temperature on the rate of corrosion is complex.
30 Under normal temperature conditions, temperature would not have an affect on the rate of

1 corrosion. When the temperature decreases the relative humidity increases and the diffusivity
2 decreases. The corrosion rate decreases as the temperature approaches freezing because ice
3 prohibits the diffusion of SO₂ to the metal surface and minimizes electrochemical processes
4 (Haynie, 1980; Biefer, 1981; Sereda, 1974).

5 The metal protective corrosion film (i.e., the rust layer on metal surfaces) provides some
6 protection against further corrosion. The effectiveness of the corrosion film in slowing down the
7 corrosion process is affected by the solubility of the corrosion layer, and the concentration and
8 deposition rate of pollutants. An atmospheric corrosion model that considers the formation and
9 dissolution of the corrosion film on galvanized steel has been proposed (Spence et al., 1992).
10 The model considers the effects of SO₂, rain acidity, and the time of wetness on the rate of
11 corrosion. While the model does not characterize particle effects, the contribution of particulate
12 sulfate was considered in model development.

13 The corrosion of most ferrous metals (iron, steel, and steel alloys) is increased by increasing
14 SO₂ exposure. Steels are susceptible to corrosion when exposed to SO₂ in the absence of
15 protective organic or metallic coatings. Studies on the corrosive effects of SO₂ on steel indicate
16 that the rate of corrosion increases with increasing SO₂ and is dependent on the deposition rate of
17 the SO₂ (Baedecker et al., 1991; Butlin et al., 1992a). The corrosive effects of SO₂ on aluminum
18 is exposure-dependent, but appears to be insignificant (Haynie, 1976; Fink et al., 1971; Butlin
19 et al., 1992a). The rate of formation of the patina on copper (protective covering) can take as
20 long as 5 years and is dependent on the SO₂ concentration, deposition rate, temperature, and
21 relative humidity (Simpson and Horrobin, 1970). Further corrosion is controlled by the
22 availability of copper to react with deposited pollutants (Graedel et al., 1987). Butlin et al.
23 (1992a), Baedecker et al. (1991), and Cramer et al. (1989) reported an average corrosion rate of
24 1 μm/y for copper; however, less than a third of the corrosion was attributed to SO₂ exposure,
25 suggesting that the rate of patina formation was more dependent on factors other than SO₂.
26 A recent report by Strandberg and Johansson (1997) showed relative humidity to be the primary
27 factor in copper corrosion and patina formation. The results of the studies on SO₂ corrosion of
28 metals are summarized in Table 9-5.

29 Whether suspended particles actually impact on the corrosion of metals is not clear.
30 Several studies suggest that suspended particles will promote the corrosion of metals (Goodwin
31 et al., 1969; Barton, 1958; Sanyal and Singhania, 1956; Baedecker et al., 1991); however, other

TABLE 9-5. EFFECTS OF SO₂ AND PARTICULATE MATTER ON METALS

Metal	Exposure Conditions	Comments	Bibliography
Mild Steel Galvanized Steel	Specimens exposed to SO ₂ and O ₃ under natural and artificial conditions, and to NO ₂ under natural conditions. SO ₂ concentrations ranged from 2.1 to 60 µg/m ³ . Annual average concentrations were about 20 µg/m ³ . Meteorological conditions were unaltered. Specimens exposed at 29 sites for 2 y for mild steel and 1 y for galvanized steel.	Steel corrosion was dependent on long-term SO ₂ exposure. The corrosion rate was about 50 µm/y for mild steel specimens for most industrial sites, but ranged from 21 to 71 µm/y. The corrosion rate ranged from 1.45 to 4.25 µm/y for galvanized steel. The authors concluded that rainfall may also have a significant effect on galvanized steel based on a corrosion rate of 3.4 µm/y seen at a very wet site.	Butlin et al. (1992a)
Zinc	Rolled zinc specimens exposed at various sites around the country (rural, industrialized, marine) for up to 20 y. Actual pollutant exposures not reported.	The highest corrosion rates were associated with industrialized environments and marine environments in direct contact with salt spray.	Showak and Dunbar (1982)
Zinc	Specimens exposed at 5 sites for 1 to 5 y. Average SO ₂ concentrations ranged from 2 ± 4 to 15 ± 17 ppb (5.2 ± 10.4 to 39.3 ± 44.5 µg/m ³). PM concentrations ranged from 14 to 60 µg/m ³ . Highest pollutant concentrations recorded at 1 y exposure site.	Average corrosion rate ranged from 0.63 to 1.33 µm/y. The highest corrosion was noted in the most industrialized area. However, the corrosion rates did not differ significantly regardless of the SO ₂ concentration, suggesting that SO ₂ exposure may not be the dominant factor in zinc corrosion.	Baedecker et al. (1991) Cramer et al. (1989)
Carbon Steel Weathering Steel	See Baedecker et al. (1991) above for exposure conditions.	Average corrosion rate for samples exposed for 5 y ranged from 6.6 to 12.8 µm/y for carbon steel and 3.7 to 5.0 µm/y for weathering steel. Highest corrosion rate noted for samples exposed for 1 y.	Baedecker et al. (1991) Cramer et al. (1989)
Aluminum	See Baedecker et al. (1991) above for exposure conditions.	Corrosion rate was very low at all sites and ranged from 0.036 to 0.106 µm/y.	Baedecker et al. (1991)
Aluminum	See Butlin et al. (1992a) above for exposure conditions.	Corrosion greater on the under side of specimens, possibly due to lack of washoff and increased PM in area. Maximum corrosion rate was 0.85 µm/y. Pit depths of up to 72 µm were noted after 2 y of exposure.	Butlin et al. (1992a)

TABLE 9-5 (cont'd). EFFECTS OF SO₂ AND PARTICULATE MATTER ON METALS

Metal	Exposure Conditions	Comments	Bibliography
Copper	See Baedecker et al. (1991) above for exposure conditions.	Average corrosion rate for 3 and 5 y exposures was about 1 $\mu\text{m}/\text{y}$ but the soluble portion was less than a third of that which could be contributed to SO ₂ exposure. Dry deposition of SO ₂ was not as important in patina formation as wet deposition of H ⁺ .	Baedecker et al. (1991)
Copper	See Butlin et al. (1992a) above for exposure conditions.	Majority of test sites showed a corrosion rate of $1 \pm 0.2 \mu\text{m}/\text{y}$. The corrosion rate was 1.48 $\mu\text{m}/\text{y}$ at the site receiving the most rainfall. The lowest corrosion rate, 0.66 $\mu\text{m}/\text{y}$, was associated with low rainfall, low SO ₂ .	Butlin et al. (1992a)
Copper	Specimens exposed to 4 to 69 ppb (10.4 to 180.7 $\mu\text{g}/\text{m}^3$) and 1.0 ppm (2,618.7 $\mu\text{g}/\text{m}^3$) SO ₂ for 20h at various relative humidities.	SO ₂ had no effect on copper when relative humidity was <75%. Increasing relative humidity increases patina formation in presence of trace SO ₂ . No SO ₂ -related effects were noted on copper specimens exposed to high SO ₂ regardless of the percent relative humidity.	Strandberg and Johansson (1998)
Copper	Specimens exposed artificially to 0.49 ± 0.01 ppm ($187 \pm 3.8 \mu\text{g}/\text{m}^3$) SO ₂ for 4 weeks at 70 and 90% relative humidity.	Corrosive effect of SO ₂ on copper increased with increasing relative humidity.	Ericksson et al. (1993)

1 studies have not demonstrated a correlation between particle exposure and metal corrosion
2 (Mansfeld, 1980; Edney et al., 1989). Walton et al. (1982) suggested that catalytic species within
3 several species in fly ash promote the oxidation of SO_x to a corrosive state. Still other
4 researchers indicate that the catalytic effect of particles is not significant, and that the corrosion
5 rate is dependent on the conductance of the thin-film surface electrolytes during periods of
6 wetness. Soluble particles likely increase the solution conductance (Skerry et al., 1988; Askey
7 et al., 1993).

9 **9.4.1.2 Painted Surfaces**

10 Exposure to air pollutants affect the durability of painted surfaces by promoting
11 discoloration, chalking, loss of gloss, and erosion, blistering, and peeling. Studies indicate that
12 exposure to SO₂ can also increase the drying time of some paints by reacting with certain drying
13 oils, and will compete with the auto-oxidative curing mechanism responsible for crosslinking the
14 binder (Holbrow, 1962). The erosion rate of oil-base house paint has been reported to be
15 enhanced by exposure to SO₂ and high humidity. In a study by Spence et al. (1975), an erosion
16 rate of $36.71 \pm 8.03 \mu\text{m}/\text{y}$ was noted for oil-base house paint samples exposed to SO₂
17 ($78.6 \mu\text{g}/\text{m}^3$), O₃ ($156.8 \mu\text{g}/\text{m}^3$), and NO₂ ($94 \mu\text{g}/\text{m}^3$) and low humidity (50%). The erosion rate
18 increased with increased SO₂ and humidity. The authors concluded that SO₂ and humidity
19 accounted for 61% of the erosion. Acrylic coil coating and vinyl coil coating shows less
20 pollutant-related erosion. Erosion rates range from 0.7 to 1.3 $\mu\text{m}/\text{y}$ and 1.4 to 5.3 $\mu\text{m}/\text{y}$,
21 respectively. Similar findings on SO₂-related erosion of oil-base house paints and coil coatings
22 have been reported by other researchers (Davis et al., 1990; Yocom and Grappone, 1976; Yocom
23 and Upham, 1977; Campbell et al., 1974). Several studies suggest that the effect of SO₂ is
24 caused by its reaction with extender pigments such as calcium carbonate and zinc oxide
25 (Campbell et al., 1974; Xu and Balik, 1989; Edney, 1989; Edney et al., 1988, 1989). However,
26 Miller et al. (1992) suggested that calcium carbonate acts to protect paint substrates.

27 Evidence also exists that indicate particles can damage painted finishes by serving as
28 carriers for corrosive pollutants (Cowling and Roberts, 1954) or by staining and pitting of the
29 painted surfaces (Fochtman and Langer, 1957; Wolff et al., 1990).

9.4.1.3 Stone and Concrete

Numerous studies suggest that air pollutants, in particular SO₂, enhance the natural weathering processes on building stone. Details on these studies are discussed in Table 9-6. The stones most susceptible to the deteriorating effects of SO₂ are the calcareous stones (limestone, marble, and carbonated cement). Exposure-related damage to building stones result from the formation of salts in the stone that are subsequently washed away during rain events leaving the stone surface more susceptible to the effects of pollutants. Increased stone damage has also been associated with the presence of sulfur oxidizing bacteria and fungi on stone surfaces (Young, 1996; Saiz-Jimenez, 1993; Diakumaku et al., 1995).

Moisture was found to be the dominant factor in stone deterioration for several sandstones (Petuskey et al., 1995). Dolkse (1995) reported that the deteriorative effects of sulfur-containing rain events, SO₂, and sulfates on marble were largely dependent on the shape of the monument or structure rather than the type of marble. The author attributed the increased fluid turbulence over a non-flat vertical surface versus a flat surface to the increased erosion. Sulfur-containing particles have also been reported to enhance the reactivity of Carrara marble, and Travertine and Trani stone to SO₂ (Sabbioni et al., 1992). Particles with the highest carbon content had the lowest reactivity. The rate of stone deterioration is determined by the pollutant and the pollutant concentration, the stone's permeability and moisture content, and the pollutant deposition velocity. Dry deposition of SO₂ between rain events has been reported to be a major causative factor in pollutant-related erosion of calcareous stones (Baedecker et al., 1991; Dolske, 1995; Cooke and Gibbs, 1994; Schuster et al., 1994; Hamilton et al., 1995; Webb et al., 1992). Sulfur dioxide deposition increases with increasing relative humidity (Spiker et al., 1992), but the pollutant deposition velocity is dependent on the stone type (Wittenburg and Dannecker, 1992), the porosity of the stone, and the presence of hygroscopic contaminants.

Dry deposition of sulfur-containing pollutants promotes the degradation of stone by forming gypsum on the stone's surface. Gypsum is a light colored crusty material comprised mainly of calcium sulfate dihydrate from the reaction of calcium carbonate (calcite) in the stone with atmospheric SO₂ and moisture (relative humidities exceeding 65%). Gypsum is more soluble than calcite and is known to form on limestone, sandstones, and marble when exposed to SO₂. Gypsum has also been reported to form on granite stone by replacing silicate minerals with calcite (Schiavon et al., 1995).

TABLE 9-6. EFFECTS OF SO₂ AND PARTICULATE MATTER ON STONE

Stone	Exposure Conditions	Comments	Bibliography
Vermont marble	Runoff water was analyzed from 7 summer storms. SO ₂ concentration stated to be low.	Between 10 to 50% of calcium in runoff water estimated from gypsum formation from dry deposition of SO ₂ .	Schuster et al. (1994)
Marble sandstone	Analysis of runoff water for 5 slabs test exposed to ambient conditions at a angle of 30° to horizontal.	Pollutant exposure related erosion was primarily due to dry deposition of SO ₂ and nitric acid between rain events and wet deposition of hydrogen ion. Recession estimates ranged from 15 to 30 μm/y for marble and 25 to 45 μm/y for limestone. A large portion of the erosion results from the reaction of CO ₂ with the calcium in the stone.	Baedecker et al. (1992)
Limestone	Ambient air conditions. Exposure ranged from 70 to 1065 d. Averaged pollutant exposure ranged from 1.4 to 20.4 ppb (3.7 to 53.4 μg/m ³) SO ₂ ; 4.1 to 41.1 ppb NO _x ; 2.4 to 17.4 ppb (4.5 to 32.7 μg/m ³) NO ₂ ; 10.1 to 25.6 ppb (19.8 to 50.2 μg/m ³) O ₃ .	Increased stone weight loss with increased SO ₂ . Rainfall did not significantly affect stone degradation. Stone loss associated with SO ₂ exposure estimated to be 24 μm/y. Slight trend in decreasing stone loss with increasing length of exposure.	Webb et al. (1992)
Portland limestone White Mansfield dolomitic sandstone Monk's Park limestone	Experimental tablets exposed under sheltered and unsheltered ambient air conditions. Exposure for 1 and 2 y.	Significant correlations existed between the mean annual SO ₂ concentration, rainfall volume, and hydrogen ion loading and the weight changes.	Butlin et al. (1992b)
Sandstones (calcite and non-calcite stones)	Ambient air; low concentrations of sulfates, SO ₂ , and nitrates; RH sufficient to produce condensation on stones rarely occurred.	Insignificant differences in erosion rate found between calcite and non-calcite sandstone. Moisture affected the rate of pollutant deposition and enhanced susceptibility to pollutant related erosion. Rain events given as primary factor affecting stone erosion. Pollutant related erosion judged to be insignificant.	Petuskey et al. (1995)

TABLE 9-6 (cont'd). EFFECTS OF SO₂ AND PARTICULATE MATTER ON STONE

Stone	Exposure Conditions	Comments	Bibliography
Portland limestone Massangis Jaune Roche limestone White Mansfield dolomitic	Samples exposed to SO ₂ , NO ₂ , and NO at 10 ppmv both with and without O ₃ and under dry (coming to equilibrium with the 84% RH) or wetted with CO ₂ -equilibrated deionized water conditions. Exposure was for 30 d.	In the absence of moisture, little reaction is seen. SO ₂ is oxidized to sulfates in the presence of moisture. The effect is enhanced in the presence of O ₃ . Massangis Jaune Roche limestone was the least affected by the pollutant exposure. Crust lined pores of specimens exposed to SO ₂ .	Haneef et al. (1993)
Monk's Park Portland limestone	Samples exposed for 2 mo under both sheltered and unsheltered conditions. Mean daily atmospheric SO ₂ concentration was 68.7 µg/m ³ and several heavy rainfalls.	Significant amounts of gypsum were noted on the Portland stone. Sheltered stones also showed soiling by carbonaceous particles and other combustion products. Etch holes and deep etching was noted in some of the exposed unsheltered samples.	Viles (1990)
Carrara marble Travertine Tranistone	Sample exposed in laboratory to 3 ppm SO ₂ and 95% RH for 150 d. Samples were also exposed to 3 particle samples from combustion processes, activated carbon and graphite.	Exposure to particles from combustion processes enhanced sulfation of calcareous materials by SO ₂ due to metal content of particles.	Sabbioni et al. (1996)
Carrara marble Georgia marble	Samples exposed in sheltered ambient environment for 6, 12, or 20 mo.	Carrara marble found to be more reactive with SO ₂ than Georgia marble possibly due to the compactness of the Georgia marble. Greater effects noted when samples were also exposed to NO ₂ .	Yerrapragada et al. (1994)
Carrara marble	Samples exposed for 6 mo (cold and hot conditions) in ambient environment. PM concentrations ranged from 57.3 to 116.7 µg/m ³ (site 1) and 88 to 189.8 µg/m ³ (site 2). Some exposures were also associated with high SO ₂ , NO, and NO ₂ .	Pollutant exposed samples showed increased weight gain over that expected from natural weathering processes. There was a blackening of stone samples exposed to carbonaceous rich particulate matter.	Realini et al. (1995)

TABLE 9-6 (cont'd). EFFECTS OF SO₂ AND PARTICULATE MATTER ON STONE

Stone	Exposure Conditions	Comments	Bibliography
Monk's Park limestone Portland limestone	Samples artificially exposed to fly-ash containing 1,309.3 $\mu\text{g}/\text{m}^3$ SO ₂ (0.5 ppm), at 95% RH and 25°C for 81 or 140 d. Fly-ash samples from 5 different sources were used in study.	Exposure to fly-ash did not enhance oxidation of SO ₂ to sulfates. Mineral oxides in fly ash contributed to sulphation of CaCO ₃ .	Hutchinson et al. (1992)
Lime mortar Pozzolan mortar Cement mortar	Samples exposed to 7,856 $\mu\text{g}/\text{m}^3$ (3 ppm) SO ₂ at 100% RH and 25°C for 30, 60, or 90 d; samples sprayed with bidistilled water every 7 d to simulate rainfall.	Exposure to SO ₂ produced significant quantities of calcium sulfite and calcium sulfate on specimens; however, the amount produced was dependent of the porosity, specific surface, and alkalinity of the sample.	Zappia et al. (1994)
Limestone Travertine marble	Samples exposed under actual ambient air conditions at two locations in Rome. Monitoring data obtained for SO ₂ , NO, NO ₂ , and total suspended particulates (TSP) but not reported. Exposure was for four seasons.	TSP exposure increased the cleaning frequency for stone monuments. Monuments are soiled proportionately overtime, based on brightness values. Horizontal surfaces showed higher graying values because of particle sediment.	Lorusso et al. (1997)
Limestone Quartz-cemented sandstone Calcite-cemented sandstone Granite Brick	Samples from structures exposed for varying periods of time under ambient air conditions. Samples selected because of black layer on surface.	Black layers were found to be primarily comprised of iron compounds, quartz, silicate, soot, and dirt.	Nord and Ericsson (1993)
Limestone Sandstone	Samples of ancient grey crust formed between 1180 and 1636 on the Church of Saint Trophime in Arks and formed between 1530 and 1187 on the Palazz d'Accursio in Bologna.	Crust samples contained calcite, soil dust, carbonaceous particles and gypsum crystals.	Ausset et al. (1998)

1 The dark color of gypsum formations sheltered from the rain are caused by surface
2 deposition of carbonaceous particles (non-carbonate carbon) from combustion processes
3 occurring in the area (Sabbioni, 1995; Saiz-Jimenez, 1993; Ausset et al., 1998), trace metals
4 contained in the stone, dust, and numerous other anthropogenic pollutants. After analyzing
5 damaged layers of several stone monuments, Zappia et al. (1993) found that the dark colored
6 damaged surfaces contained 70% gypsum and 20% non-carbonate carbon. The lighter colored
7 damaged layers were exposed to rain and contained 1% gypsum and 4% non-carbonate carbon.
8 It is assumed that rain removes reaction products, permitting further pollutant attack of the stone
9 monument, and likely redeposits some of the reaction products at rain runoffs sites on the stone.

10 While it is clear from the available information that gaseous pollutants, in particular dry
11 deposition of SO₂, will promote the decay of some types of stones under the specific conditions,
12 carbonaceous particles (non-carbonate carbon) may help to promote the decay process by aiding in
13 the transformation of SO₂ to a more acidic species (Del Monte and Vittori, 1985). Several
14 authors have reported enhanced sulfation of calcareous material by SO₂ in the presence of
15 particles containing metal oxides (Sabbioni et al., 1996; Hutchinson et al., 1992).

17 **9.4.2 Soiling and Discoloration of Manmade Surfaces**

18 Ambient particles can cause soiling of manmade surfaces. Soiling has been defined as the
19 deposition of particles of less than 10 μm on surfaces by impingement. Soiling generally is
20 considered an optical effect, that is, soiling changes the reflectance from opaque materials and
21 reduces the transmissions of light through transparent materials. Soiling can represent a
22 significant detrimental effect requiring increased frequency of cleaning of glass windows and
23 concrete structures, washing and repainting of structures, and in some cases, reduction in the
24 useful life of the object. Particles, in particular carbon, may also help catalyze chemical reactions
25 that result in the deterioration of materials during exposure.

26 It is difficult to determine the accumulated particle levels that cause an increase in soiling;
27 however, soiling is dependent on the particle concentration in the ambient environment, particle
28 size distribution, and the deposition rate, and the horizontal or vertical orientation and texture of
29 the surface being exposed (Haynie, 1986). The chemical composition and morphology of the
30 particles and the optical properties of the surface being soiled will determine the time at which
31 soiling is perceived (Nazaroff and Cass, 1991).

1 The rate at which an object is soiled increases linearly with time; however, as the soiling
2 level increases, the rate of soiling decreases. The buildup of particles on a horizontal surface is
3 counterbalanced by an equal and opposite depletion process. The depletion process is based on
4 the scouring and washing effect of wind and rain (Schwar, 1998).

6 **9.4.2.1 Stones and Concrete**

7 Most of the research evaluating the effects of air pollutants on stone structures have
8 concentrated on gaseous pollutants. The deposition of the sulfur-containing pollutants are
9 associated with the conversion of calcium carbonate in the stone to calcium dihydrate (see
10 Section 9.4.1.3). The dark color of gypsum is attributed to soiling by carbonaceous particles
11 from nearby combustion processes. A lighter gray colored crust is attributed to soil dust and
12 metal deposits (Ausset et al., 1998; Camuffo, 1995; Moropoulou et al., 1998). Realini et al.
13 (1995) found the formation of a dark gypsum layer and a loss of luminous reflection in Carrara
14 marble structures exposed for 1 year under ambient air conditions. Dark areas of gypsum were
15 found by McGee and Mossitti (1992) on limestone and marble specimens exposed under ambient
16 air conditions for several years. The black layers of gypsum were located in areas shielded from
17 rainfall. Particles of dirt were concentrated around the edges of the gypsum formations. Lorusso
18 et al. (1997) attributed the need for frequent cleaning and restoration of historic monuments in
19 Rome to exposure to total suspended particulates. They also concluded that, based on a decrease
20 in brightness (graying), surfaces are soiled proportionately over time; however, graying is higher
21 on horizontal surfaces because of sedimented particles. Studies describing the effects of particles
22 on stone surfaces are discussed in Table 9-6.

24 **9.4.2.2 Household and Industrial Paints**

25 Few studies are available that evaluate the soiling effects of particles on painted surfaces.
26 Particles composed of elemental carbon, tarry acids, and various other constituents are
27 responsible for soiling of structural painted surfaces. Coarse mode particles ($>2.5 \mu\text{m}$) initially
28 contribute more soiling of horizontal and vertical painted surfaces than do fine mode particles
29 ($<2.5 \mu\text{m}$), but are more easily removed by rain (Haynie and Lemmons, 1990). The
30 accumulation of fine particles likely promotes remedial action, i.e., cleaning of the painted
31 surfaces. Coarse mode particles are primarily responsible for soiling of horizontal surfaces.

1 Rain interacts with coarse particles, dissolving the particle and leaving stains on the painted
2 surface (Creighton et al., 1990; Haynie and Lemmons, 1990). Haynie and Lemmons (1990)
3 proposed empirical predictive equations for changes in surface reflectance of gloss painted
4 surfaces that were exposed, protected, and unprotected to rain and oriented horizontally and
5 vertically.

6 Early studies by Parker (1955) and Spence and Haynie (1972) demonstrated an association
7 between particle exposure and increased frequency of cleaning of painted surfaces. Particle
8 exposures also caused physical damage to the painted surface (Parker, 1955). Unsheltered
9 painted surfaces are initially more soiled by particles than sheltered surfaces but the effect is
10 reduced by rain washing. Reflectivity is decreased more rapidly on glossy paint than on flat paint
11 (Haynie and Lemmons, 1990). However, surface chalking of the flat paint was reported during
12 the exposure. The chalking interfered with the reflectance measurements for particle soiling.
13 Particle composition measurements that were taken during exposure of the painted surfaces
14 indicated sulfates to be a large fraction of the fine mode and only a small fraction of the coarse
15 mode. Although no direct measurements were taken, fine mode particles likely also contained
16 large amounts of carbon and possibly nitrogen and/or hydrogen (Haynie and Lemmons, 1990).

19 **9.5 EFFECTS ON VISIBILITY**

20 **9.5.1 Introduction**

21 Visibility is defined as the degree to which the atmosphere is transparent to visible light and
22 the clarity (transparency) and color fidelity of the atmosphere (National Research Council, 1993).
23 Visibility impairment is defined as any humanly perceptible change in visibility (light extinction,
24 visual range, contrast, coloration). Visual range is described as the farthest distance at which a
25 large black object can be distinguished against the horizontal sky (U.S. Environmental Protection
26 Agency, 1979). For regulatory purposes, visibility impairment is classified into two principal
27 forms: “reasonably attributable” impairment, attributable to a single source/small group of
28 sources, and regional haze, described as any perceivable change in visibility (light extinction,
29 visual range, contrast, coloration) from which would have existed under natural conditions that is

1 caused predominantly by a combination of many sources over a wide geographical area (U.S.
2 Environmental Protection Agency, 1999).

3 The objective of the visibility discussion in this section is to summarize the linkage
4 between air pollution, in particular particulate matter, and visibility. This section summarizes the
5 information discussed in the previous particulate matter criteria document and includes
6 additional relevant information available since publication of that document. For a more detailed
7 discussion on visibility, the reader is referred to the Air Quality Criteria for Particulate Matter
8 (U.S. Environmental Protection Agency, 1996b), the Recommendations of the Grand Canyon
9 Visibility Transport Commission (Grand Canyon Visibility Transport Commission, 1996), the
10 National Research Council (National Research Council, 1993), the National Acid Precipitation
11 Assessment Program (Trijonis et al., 1991), and the U.S. Environmental Protection Agency
12 (1995e).

14 **9.5.2 Factors Affecting Atmospheric Visibility**

15 **9.5.2.1 Anthropogenic Pollutants**

16 Visibility impairment may be connected to air pollutant properties, including size
17 distribution, aerosol chemical composition, and relative humidity. In the United States visibility
18 impairment is caused by sulfate and nitrate particles in the 0.1 to 1.0 micron (μm) range, and
19 organic aerosols, carbon soot, and crustal dust. Generally, sulfates are responsible for most of
20 the visibility impairment in the United States, as measured by light extinction, accounting for
21 approximately two-thirds of the light extinction in the eastern United States. Sulfate
22 concentrations are higher in summer months than in the wintertime (Malm et al., 1994).
23 Exceptions to the sulfate-related effects on visibility include California where the primary cause
24 of visibility effects is ambient nitrate, and in Alaska where visibility impairment is due to fine
25 soil plus coarse mass (classified as coarse extinction) or organics, thought to be from natural
26 sources (Sisler and Cahill, 1993).

28 **9.5.2.2 Human Vision**

29 Human vision is one of the factors that affects the way an object is viewed. Vision is the
30 response to the electromagnetic radiation that enters the eye between wavelengths of 400 and
31 700 nanometers. The cones, a receptor cell in the retina, govern visibility interpretations.

1 The eye perceives the lightest and brightest object in a scene as white, and determines the
2 color of other objects by comparison. The ability of the eye to perceive contrasts, the degree of
3 color difference between the lightest and darkest object in a scene, changes in response to the
4 illumination and setting. The effects of illumination on visibility are discussed in the following
5 subsection. At increasing distances the brightness of a target or object will approach the
6 brightness of the horizon making the target indistinguishable from the horizon, hence, visual
7 range.

9 **9.5.2.3 Characteristics of the Atmosphere**

10 The appearance of a distant object is determined by illumination of the sight path by the
11 direct rays of the sun, diffused skylight, and light that has been reflected from the surface of the
12 Earth (path radiance or air light) and the light reflected from the object itself. Some of the light
13 in the sight path is absorbed or scattered towards the observer and the remaining light is absorbed
14 or scattered in other directions. The portion of scattered light from the object being viewed that
15 reaches the observer is the transmitted radiance. The radiance seen by the observer looking at a
16 distant object is the sum of the transmitted radiance and the path radiance. Figure 9-14
17 demonstrates light being absorbed and scattered by the atmosphere and a target object.

18 On a clear day when the sun is high in the sky, 80 to 90% of the visible solar radiation
19 reaches the surface of the Earth without being scattered or absorbed. Many of the naturally
20 scattering. Raleigh scattering by gases is the major component of light extinction in relatively
21 unpolluted areas. Mie scattering is the scattering of all visible wavelengths equally (Shodor
22 Education Foundation, Inc., 1996). It is the attenuation of light in the atmosphere by scattering
23 due to particles of a size comparable to the wave length of the incident light (National Acid
24 Precipitation Assessment Program, 1991). The term, multiple scattering, is used when light is
25 scattered more than once in a turbid medium. The great majority of light absorption by particles
26 is caused by black carbonaceous particles, assumed to be elemental carbon, that are products of
27 incomplete combustion (Rosen et al., 1978, Japar et al., 1986; Watson and Chow, 1994). Malm
28 et al. (1996) suggested that organic carbon also acts to scatter and absorb light. The estimated
29 natural visibility for the east and west is 60 to 80 and 110 to 115 miles, respectively.

30 At the surface, a variable fraction of the solar radiation is reflected back upwards, referred
31 to as surface reflectance or the albedo, illuminating the atmosphere from above and below. The

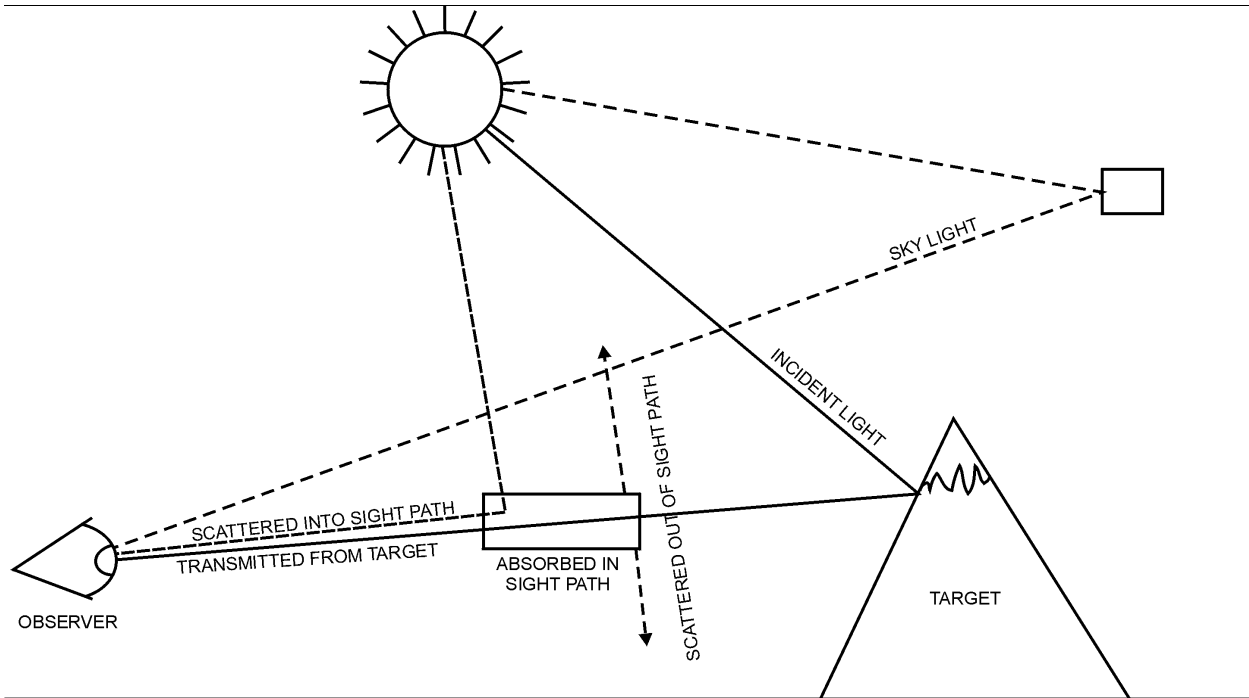


Figure 9-14. Light reflected from a target toward an observer. The intervening atmosphere scatters a portion of this light out of the sight path and scatters light from the sun into the sight path. Some particles and gases also absorb a portion of the light from the target. The light scattered into the sight path increases with distance from the target, while the light transmitted from the target decreases with distance from the target. The visual range is the closest distance between the target and the observer at which the transmitted light can no longer be distinguished from the light scattered into the sight path.

Source: Watson and Chow (1994).

1 amount of solar radiation reflected depends on the color of the terrain. Dark colored terrain
 2 reflects less radiation than light colored terrain.

3 Visibility within a sight path longer than approximately 100 km (60 mi) is affected by
 4 changes in the properties of the atmosphere over the length of the sight path. The atmosphere
 5 will not generally have uniform optical properties over distances greater than a few tens of
 6 kilometers. Air quality within a sight path can affect the illumination of the sight path by
 7 scattering or absorbing solar radiation before it reaches the Earth's surface. The light-extinction
 8 coefficient, σ_{ext} , is a measure of the fraction of light that is lost as it travels through the

1 atmosphere. The light-extinction coefficient is the sum of the light-scattering coefficient, σ_{scat} ,
2 and the light-absorption coefficient, σ_{abs} , expressed in units of inverse lengths of the atmosphere
3 (megameters ; Mm^{-1}). Typical extinction coefficients range from 0.01 km^{-1} (10 Mm^{-1}) in
4 relatively clean air to $\sim 1000 \text{ Mm}^{-1}$ in highly polluted areas (Watson and Chow, 1994).

5 The light-extinction coefficient can be divided into coefficients for the following
6 components:

7 σ_{ag} , light absorption by gases,

8 σ_{sg} , light scattering by gases (Rayleigh scattering),

9 σ_{ap} , light absorption by particles, and

10 σ_{sp} , light scattering by particles.

11 Light scattering by particles, σ_{sp} , can be divided to indicate scattering by coarse and fine particles,

12 σ_{sfp} , light scattering by fine particles and

13 σ_{scp} , light scattering by coarse particles.

15 **9.5.3 Optical Properties of Particles**

16 Visibility impairment is typically caused by fine particles. Fine particles are small enough
17 in comparison with the wavelength of visible light that their optical properties are nearly the
18 same as those of homogeneous spheres of the same volume and average index of refraction.
19 Accordingly, Mie equations (Mie, 1908; Kerker, 1969), for calculating the optical properties of
20 homogeneous spheres may also be used to calculate the optical properties of fine particles with
21 the only uncertainties being in the fine particle size distribution and index of refraction (Richards,
22 1973). However, within the range of indices of refraction that most commonly occur in
23 atmospheric fine particles, the results of Mie calculations can be scaled to account for the effect
24 of the index of refraction. Coarse particles have less of an impact on visibility than do fine
25 particles. However, in most actual cases, the dominant uncertainty in using the optical properties
26 for coarse particles calculated with Mie equations is the uncertainty in the particle size
27 distribution. Uncertainties exist in the use of Mie calculations for calculating light absorption for
28 course particles because the refractive index of the particle is generally not known and the
29 light-absorbing particles are not spherical in shape, making the calculated light absorption
30 efficiency factor less reliable. Also, light absorption by elemental carbon particles can be
31 reduced when the particle is covered by some chemical species (Dobbins et al., 1994).

1 The output of the Mie calculations includes efficiency factors for extinction, Q_{ext} ,
2 scattering, Q_{scat} , and absorption, Q_{abs} . The Q_{ext} , Q_{scat} , and Q_{abs} give the fraction of the incident
3 radiation falling on a circle with the same diameter as the particle that is either scattered or
4 absorbed. The light scattering efficiency factor (in units of m^2/g) is the change in the light
5 scattering efficiencies per unit change in mass of the fine particle constituent. The scattering
6 efficiencies are determined by estimating the size distribution of each particle. Multiplying the
7 values of the light-scattering efficiency factor by the aerosol volume concentration (in units
8 of $\mu\text{m}^3/\text{cm}^3$) gives the value of the light-scattering coefficient, σ_{sp} , (in units of Mm^{-1}) for these
9 particles.

10 Richards et al. (1991) reported a scattering efficiency for fine particles of ammonium
11 sulfate of $1.2 \text{ m}^2/\text{g}$ based on Mie calculations. The value was in agreement with the value
12 determined using the integrating nephelometer readings and the sulfate concentrations. Sulfate
13 scattering efficiencies have been reported to increase by a factor of two when the size distribution
14 went from 0.15 to $0.5 \mu\text{m}$ (McMurry et al., 1996). The calculated scattering efficiencies for
15 sulfates were $4.1 \text{ m}^2/\text{g}$ for 100% mass removal and 3.4 and $5.6 \text{ m}^2/\text{g}$ for 25% mass removal.
16 There was also a relative humidity-related effect on the scattering efficiency. Ammonium sulfate
17 fine particle scattering efficiency varied from 1.5 to $4.5 \text{ m}^2/\text{g}$ with low relative humidity and
18 median particle sizes ranging from 0.07 to $0.66 \mu\text{m}$. Sloane et al. (1991) reported scattering
19 efficiencies of 7.1 to $8.2 \text{ m}^2/\text{g}$ for sulfate at 74% relative humidity and 2.1 to $2.9 \text{ m}^2/\text{g}$ at 38%
20 relative humidity. Average dry scattering efficiencies for sulfate ranged from 2.03 to $2.23 \text{ m}^2/\text{g}$
21 for two western sites and one eastern site (Malm and Pitchford, 1997). The dry scattering
22 efficiency increased with increasing particle size. Dry specific scattering efficiencies of $3 \text{ m}^2/\text{g}$
23 were reported for sulfates and nitrates (Sisler and Malm, 1999). Omar et al. (1999) reported a
24 calculated scattering efficiency range of $1.23 \text{ m}^2/\text{g}$ for sulfate when the relative humidity was
25 $<63\%$ to $5.78 \text{ m}^2/\text{g}$ when the relative humidity was $>75\%$. The calculated scattering efficiencies
26 for organic carbon ranged from $3.81 \text{ m}^2/\text{g}$ when the relative humidity was $<63\%$ to $6.9 \text{ m}^2/\text{g}$ at
27 relative humidities above 75% (Omar et al., 1999). Calculated scattering efficiencies for carbon
28 particles ranged from 0.9 to $8.1 \text{ m}^2/\text{g}$ (Zhang et al., 1994; Sisler and Malm, 1999; Sloane et al.,
29 1991). A scattering efficiency of 1.0 and $0.6 \text{ m}^2/\text{g}$ was reported for soil and coarse mass,
30 respectively (Trigonis and Pitchford, 1987).

1 Scattering efficiencies of 2.4 and 3.1 m²/g for fine particles were reported by White et al.
2 (1994) and Waggoner et al. (1981), using an integrating nephelometer. Coarse particle scatter
3 less light, resulting in lower scattering efficiencies. Scattering efficiencies for coarse particles
4 ranged from 0.4 to 0.6 m²/g, based on integrating nephelometer readings (White et al., 1994;
5 Trijonis and Pitchford, 1987; White and Macias, 1990; Watson et al., 1991).

6 Absorption efficiencies for elemental carbon particles have been reported to range from 9 to
7 10 m²/g (Japar et al., 1984; Adams et al., 1989; Sloane et al., 1991). Based on a review of the
8 available data, Horvath (1993) reported that measured light absorption efficiencies for light
9 absorbing carbon ranges from 3.8 to 17 m²/g and calculated absorption efficiencies ranges from
10 8 to 12 m²/g. Malm et al. (1996) suggested a combined scattering and absorption efficiency of
11 10 m²/g for organic carbon.

12 Light-extinction budgets may be estimated using the light extinction efficiency and the
13 measured species concentrations. Light-extinction budgets estimate the fraction of the total light
14 extinction contributed by each chemical species in the sight path; however, the values obtained
15 will depend on the assumptions used (Malm et al., 1996; Lowenthal et al., 1995; Sisler and
16 Malm, 1994).

18 **9.5.4 Effect of Relative Humidity on Particle Size and Light Scattering** 19 **Properties**

20 Ambient particles contain water, even on relatively dry days. As the relative humidity
21 increases, the particle absorbs more water and increase in size and volume. It is the increase in
22 particle size and volume that acts to increase the light scattering properties of most particles
23 (Malm et al., 1996).

24 Ambient particles are a mixture of chemical compounds. The amount of increase in
25 particle size with increasing relative humidity is dependent on the particle composition (Zhang
26 et al., 1993). Available data indicate that particles containing ammonium salts are in a liquid
27 solution at relative humidities above 80%. Particles containing inorganic salts and acids are
28 more hygroscopic than particles composed primarily of organic species (Day et al., 1996;
29 McMurry and Stolzenburg, 1989; Saxena et al., 1995; Zhang et al., 1993, 1994; Sloane et al.,
30 1991). Particles containing the more hygroscopic salts and acid species deliquesce and undergo
31 changes in particle size in response to changes in relative humidity. For sulfate and nitrate

1 aerosols, light-scattering properties are similar for all mixture types and compositions as long as
2 there is the same particle size distribution (Tang, 1997). Saxena et al. (1995) found that the
3 hygroscopic properties of inorganic particles can be altered positively or negatively in the
4 presence of organics. Based on limited data, nonurban organics were found to add to water
5 absorption by inorganics, while the urban organics diminished the absorption of water by
6 inorganic particles at relative humidities of 80 to 93%. Figure 9-15 demonstrates the humidity
7 effect on the scattering coefficients for several internally mixed (individual particles containing
8 one or more species) and externally mixed (species that co-exist as separate particles) aerosols.
9 Figure 9-16 demonstrates changes in the scattering coefficient ratio, $\sigma_{spw}/\sigma_{spd}$, where σ_{spw} is the
10 scattering coefficient under humid conditions and σ_{spd} is the scattering coefficient under dry
11 conditions. The figure demonstrates that light scattering is a function of relative humidity and
12 chemical composition. The monitoring data were generated as part of the Southeastern Aerosol
13 and Visibility Study (Day et al., 1999). A more detailed discussion of the effects of relative
14 humidity on the size distribution of ambient particles appears in Chapter 3 of this document.

15 16 **9.5.5 Measures of Visibility**

17 **9.5.5.1 Human Observations**

18 The National Weather Service has in recent decades recorded hourly visibility readings at
19 all major airports in the United States based on human observations of the most distant targeted
20 object's perceivability. Human observation of visibility, while providing an historical record of
21 visibility readings in the United States, are dependent on the individual and the availability of a
22 target and are generally poorly related to air quality.

23 24 **9.5.5.2 Light-Extinction Coefficient and Parameters Related to the Light-Extinction** 25 **Coefficient**

26 The most frequently used indicator for visibility characterization for air quality is the
27 light-extinction coefficient because it is closely linked to air quality (U.S. Environmental
28 Protection Agency, 1996). Various meteorological conditions (moisture and cloud cover) can
29 affect the light-extinction coefficient; however, these effects can be minimized (Husar et al.,
30 1994; Blandford, 1994; Mercer, 1994). The light-extinction coefficient can be measured directly
31 using a transmissometer (Molenaar et al., 1990, 1992) or can be estimated by measuring the

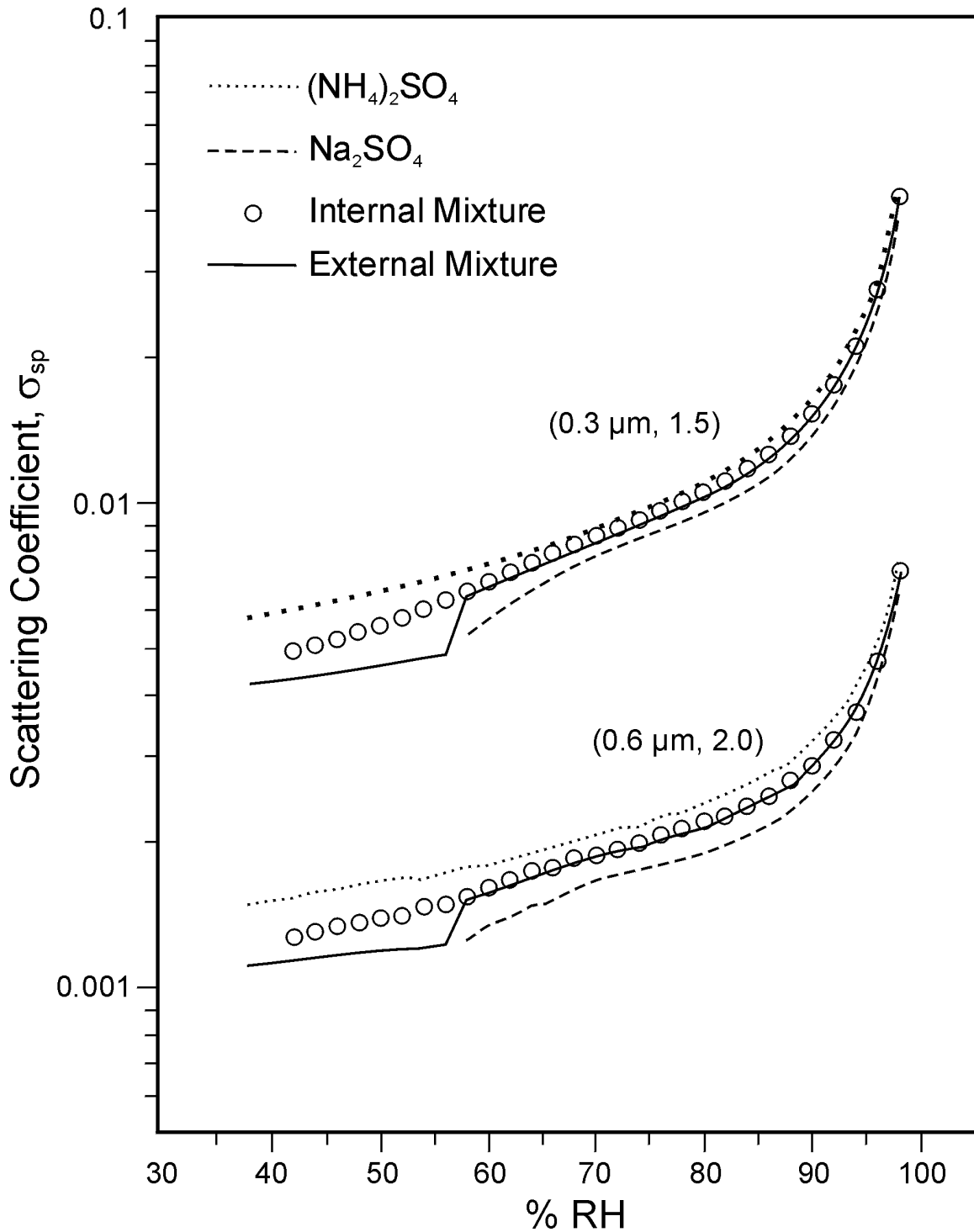


Figure 9-15. Humidity effect on scattering coefficients computed for internal and external mixtures of the mixed-salt aerosol: $\text{Na}_2\text{SO}_4(x_2=0.5)-(\text{NH}_4)_2\text{SO}_4(x_3=0.5)$, for two dry-salt particle size distributions, where x is the mass fraction of the dry solutes. Particle size distributions are stated in the parenthesis.

Source: Tang (1997).

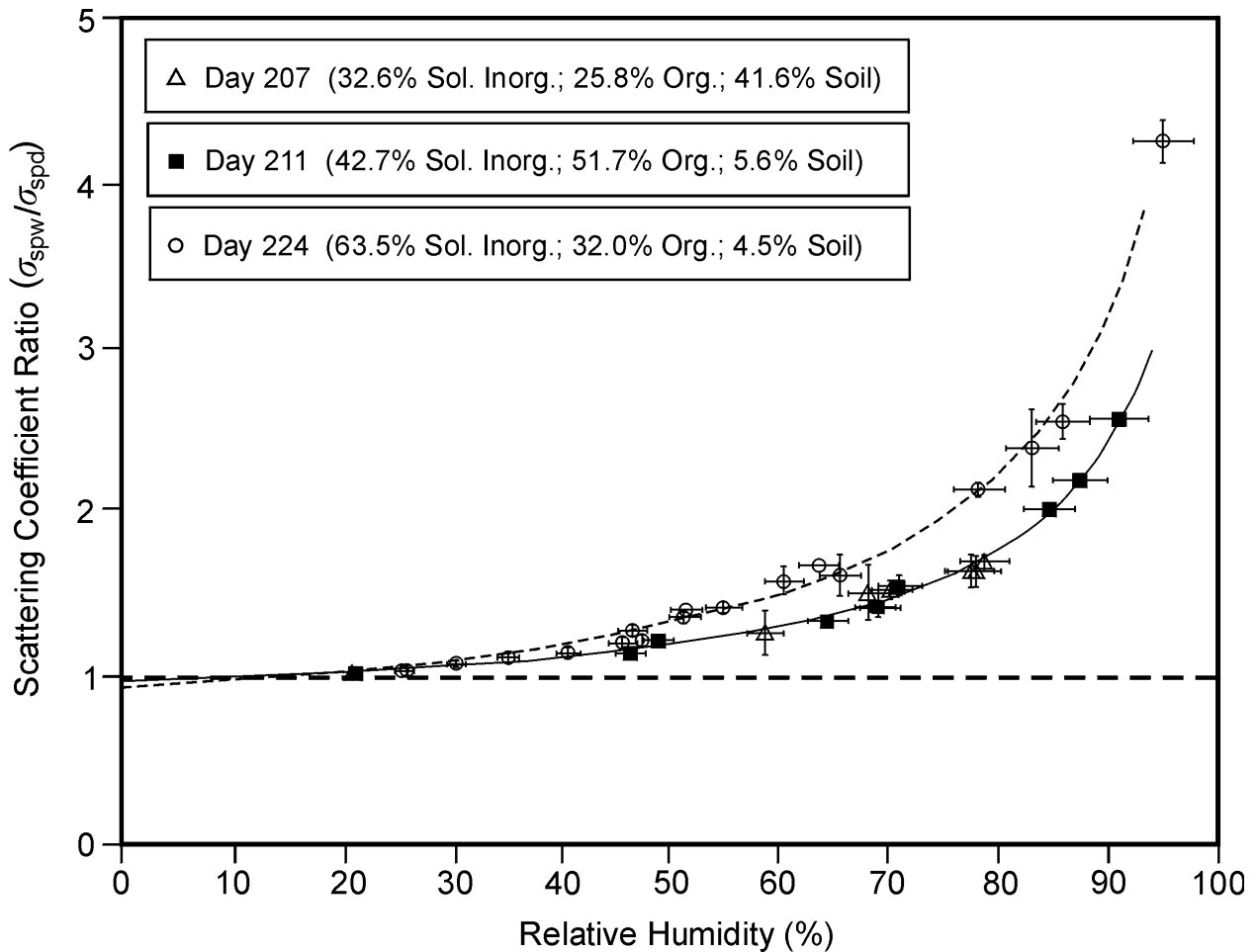


Figure 9-16. Scattering ratios, $\sigma_{spw}/\sigma_{spd}$, for different chemical compositions as a function of relative humidity.

Source: Day et al. (1999).

1 components of light extinction (scattering and absorption) and calculating the sum (Malm et al.,
 2 1994; Richards, 1995).

3 The visual range may be calculated from the light-extinction coefficient using the
 4 Koschmieder equation by assuming the atmosphere and the illumination over a sight path in the
 5 daytime is uniform and that the threshold contrast is 2% (Katsev and Zegre, 1994; Koschmieder,
 6 1924). These assumptions are, however, invalid for visual ranges greater than 100 km (U.S.
 7 Environmental Protection Agency 1996).

8

9

$$Visual\ Range = 3.91/\sigma_{ext}$$

1 The deciview index is an atmospheric haze index that expresses uniform changes in
2 haziness in common increments from pristine conditions to extremely visibility impaired
3 environments. The deciview scale is linear with perceived visual changes, starting near zero for
4 a pristine atmosphere (particle-free) at a 1.8 km elevation, and increases with increasing
5 haziness. The deciview index may be calculated from the light-extinction coefficient for green
6 light. Under ideal conditions, a just noticeable change in the light-extinction coefficient should
7 represent a one or two deciview change in the deciview scale, about a 10 to 20% change in the
8 extinction coefficient. Any change in the deciview scale should have a change of similar
9 magnitude in the visual appearance of the scene in cases where the assumptions used to develop
10 the deciview scale are met (Pitchford and Malm, 1994; Sisler and Malm, 1999). For consistency,
11 a Raleigh scattering value of 10 Mm^{-1} is used.

$$dv = 10 \log_{10} (\sigma_{ext}/10 \text{ Mm}^{-1})$$

12
13
14
15 Figures 9-17a,b illustrate a change in deciview scale based on reconstructed extinction
16 coefficients for the Great Plains Region (Badlands) using data from the Interagency Monitoring
17 of Protected Visual Environments Network (IMPROVE). Details about the IMPROVE network
18 appears in section 9.5.6. The data are sorted by year into three groups based on the cumulative
19 frequency of occurrence of $\text{PM}_{2.5}$: best visibility days (10th percentile), median (50th percentile),
20 and worst visibility days (90th percentile) (Sisler et al., 1999).

21 22 **9.5.5.3 Light-Scattering Coefficient**

23 Light-scattering by particles has been reported to account for 68 to 86% of the total
24 extinction coefficient in several cities in California (Eldering et al., 1994). The light-scattering
25 coefficient is closely linked to fine particle concentrations, making it a good tool for determining
26 small particle-related effects on visibility. When the light-scattering coefficient is increased,
27 visibility is impaired because the transmitted radiance is decreased and the path radiance is
28 increased. (See discussion in the previous sections on transmitted radiance and path radiance.)
29 The light-scattering coefficient can be measured directly with an open and enclosed integrating
30 nephelometer and a forward scatter visibility monitor (Molenar et al., 1992; National Oceanic

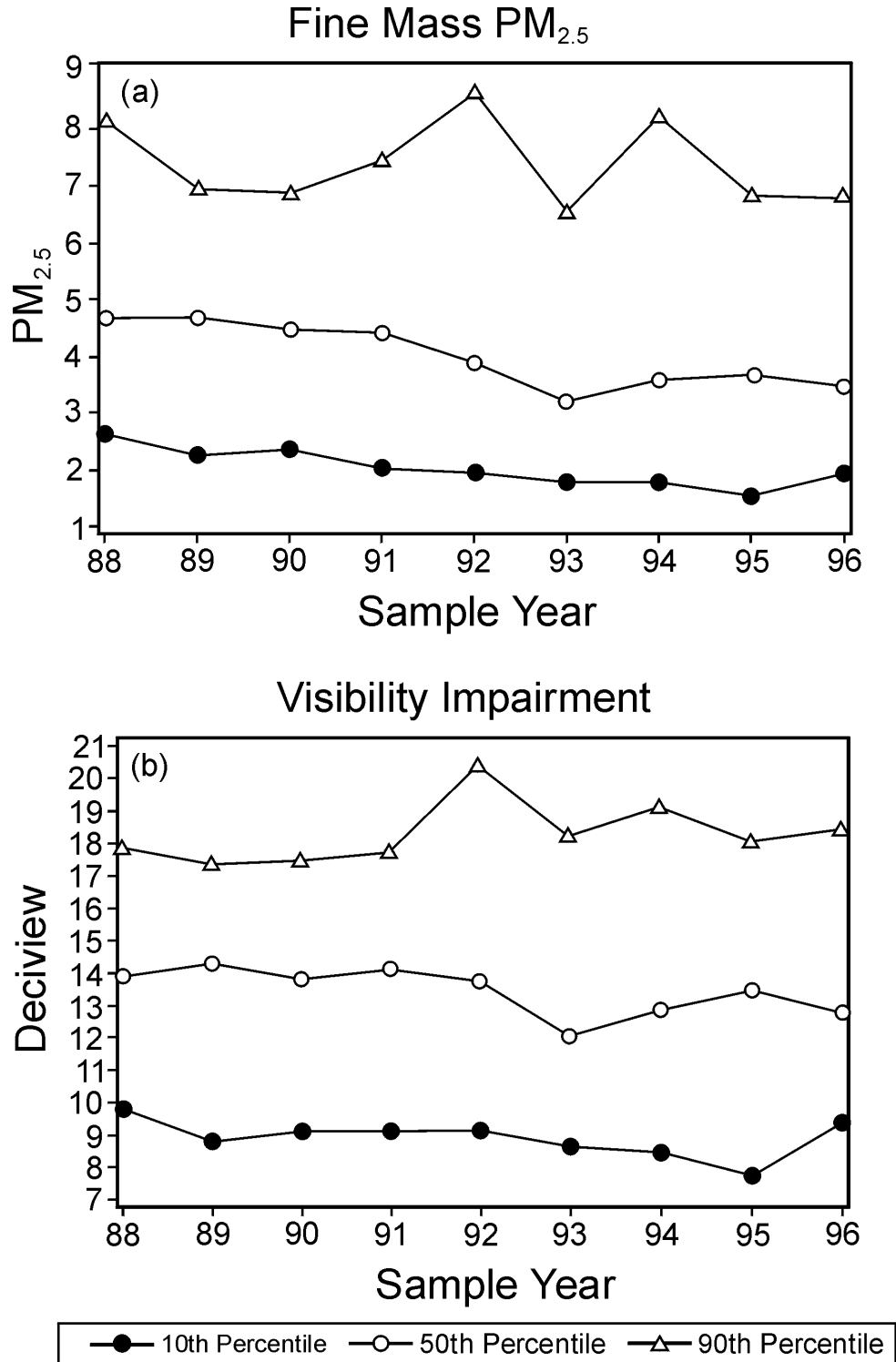


Figure 9-17a,b. Plots of the 10th, 50th, and 90th percentile groups for PM_{2.5} and deciview at the Badlands National Park. The sample year began in March of each year.

Source: Sisler et al. (1999).

1 and Atmospheric Administration, 1992). The light-scattering coefficient may also be calculated
2 using analytical approximations of the particle size distributions, log normal size distributions, or
3 sectional particle size distributions. In the sectional approach, the size composition distribution
4 is represented by a set of particle size sections. The chemical composition of each size section is
5 assumed to be the same (Wu et al., 1996).

7 **9.5.5.4 Fine Particulate Matter Concentrations**

8 The influence of particles on visibility degradation is dependent on the particle
9 composition, solubility, and size (Pryor and Stegn, 1994). Fine particle species have been
10 classified into five major types: sulfates, nitrates, organics, light absorbing carbon, and soil
11 (Malm et al., 1994). The coefficient of light-scattering by fine particles is primarily responsible
12 for visibility impairment making fine particle concentration a suitable indicator of particle related
13 effects on visibility. Several studies have demonstrated a relationship between the coefficient for
14 light-scattering by particles, measured using an integrating nephelometer, and fine particle
15 concentrations (Dattner, 1995; Waggoner and Weiss, 1980; Waggoner et al., 1981; White et al.,
16 1994). Figure 9-18 demonstrates visual range based on particle concentrations and extinction
17 efficiencies for road dust and sulfate.

19 **9.5.5.5 Discoloration**

20 Discoloration may be used as a quantitative measurement of atmospheric color changes in
21 urban hazes. Atmospheric color changes is a component of plume visibility models. The color
22 of haze will primarily depend on the scene used and human vision. For plume visibility, the
23 threshold for perception of color differences depend on the apparent width of the plume and is
24 greater for color patches separated by sharp edges. Methods for specifying the colors of hazes
25 include the CIE XYZ system of color matching, the Hunt94 color-appearance model, and the
26 visual colorimeter, VISUAL colorimeter for Atmospheric Research (Trijonis et al., 1991;
27 Mahadev and Henry, 1999).

29 **9.5.6 Visibility Monitoring Methods and Networks**

30 Visibility monitoring studies measure the properties of the atmosphere either at the sampler
31 inlets (point measurements), as is the case with air quality measurements, or by determining the

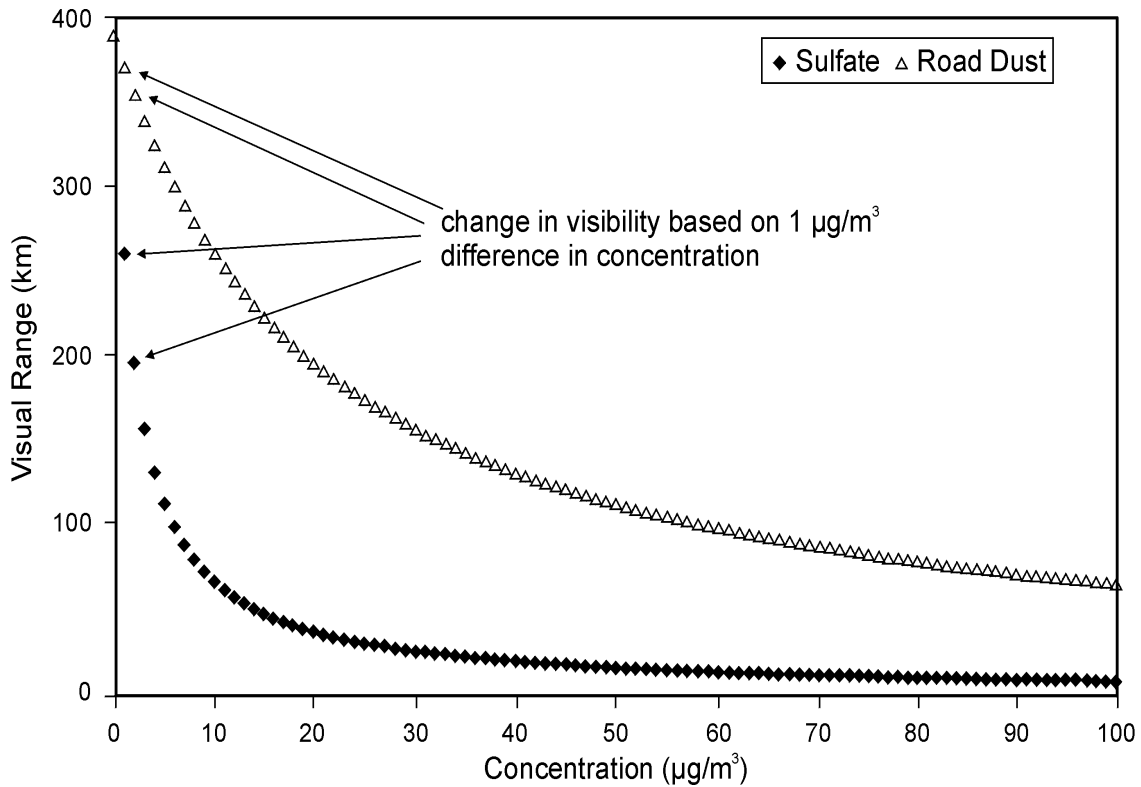


Figure 9-18. Reduction in visual range as a function of increasing fine (sulfate) and coarse (dust) particle concentrations.

Source: Watson and Chow (1994).

1 optical properties of a sight path through the atmosphere (path measurements). Instrumental
 2 methods for measuring visibility are generally of three types: (1) direct measurement of light
 3 extinction of a sight path using a transmissometer; (2) measurement of light scattering at one
 4 location using an integrating nephelometer; and (3) measurement of ambient aerosol mass
 5 concentration and composition (Mathai, 1995).

6 The largest instrumental visibility monitoring network in the United States is designed to
 7 provide real-time data for runway visibility to aid in controlling airport operations. Automated
 8 observing systems, Automated Surface Observing System (ASOS) and Automated Weather
 9 Observing System (AWOS), are being placed at airports around the country. The visibility
 10 sensor, instead of measuring how far one can see, measures the clarity of the air using a forward
 11 scatter visibility meter. The clarity is then converted to what would be perceived by the human

1 eye using a value called Sensor Equivalent Visibility (SEV). Values derived from the sensor are
2 not affected by terrain, location, buildings, trees, lights, or cloud layers near the surface. The
3 sensor transmits an average 1-min value for a 10-min period. The sensor only samples 0.75-foot
4 of the atmosphere. An algorithm processes the air passing through the sensor over the 10-min
5 measurement period to provide a generally accurate visibility measurement for within 2 to
6 3 miles of the site. Moisture, dust, snow, rain, or particles in the light beam affect the amount of
7 light scattered (National Weather Service, 1995). Data for visibility at larger distances from
8 ASOS sites are available at the sensors for only a short period of time. The data can be directly
9 downloaded from the site. The largest monitoring network that includes both visibility and air
10 quality measurements is the Interagency Monitoring of Protected Visual Environments
11 (IMPROVE) network. The IMPROVE network was formed as a collaborative effort between the
12 U.S. Environmental Protection Agency and federal land management agencies (National Park
13 Service, U.S. Forest Service, Bureau of Land Management, and Fish and Wildlife Service)
14 responsible for Class I areas and the land around them (National Park Service, 1998; Malm et al.,
15 1994; Sisler et al., 1993; U.S. Environmental Protection Agency, 1995e; Eldred et al., 1997;
16 Perry et al., 1997). The primary monitoring objectives of the IMPROVE program are to
17 (1) establish visibility levels; (2) identify anthropogenic sources of impairment; (3) document
18 progress towards elimination of visibility impairment in protected areas from anthropogenic
19 sources; and (4) promote the development of visibility monitoring equipment and the collection
20 of comparable visibility data (National Park Service, 1998; Evans and Pitchford, 1991).

21 Table 9-7 contains PM_{2.5} monitoring data from 30 IMPROVE sites for the years 1988 to
22 1996. The data includes averaged PM_{2.5} mass and specific species contributions. The data are
23 divided into eastern and western regions. The eastern regions, in addition to Washington, DC,
24 include Acadia National Park and Appalachia and consist of data from Shenandoah and the Great
25 Smoky Mountains National Parks. The western regions include the Northern Great Plains,
26 West Texas, Sonora, the Colorado Plateau, Central Rockies, Cascade, Sierra Humbolt, West
27 Coast, Sierra Nevada, Southern California, and Alaska (Sisler and Malm, 1999).

28 The U.S. Environmental Protection Agency is currently in the process of establishing a
29 national PM_{2.5} monitoring network of approximately 1,500 sites. The PM_{2.5} monitoring effort
30 will be coordinated with visibility monitoring efforts currently in place, such as IMPROVE, to

TABLE 9-7. AVERAGED REGIONAL PM_{2.5} MASS AND EXTINCTION SUMMARIES FOR THE YEARS 1988 TO 1996^a

REGION	PM _{2.5}	Sulfate	Nitrate Organics	Organics	Fine Soil	Elemental Carbon
Alaska	1.71 (11.9)	0.55 (5.1)	0.06 (0.06)	0.77 (3.1)	0.22 (1.0)	0.10 (2.2)
Appalachia	10.81 (97.6)	6.53 (71.7)	0.60 (6.9)	2.73 (10.9)	0.52 (4.3)	0.43 (3.8)
Cascades	4.67 (50.6)	1.30 (29.1)	0.23 (5.0)	2.51 (10.0)	0.22 (4.1)	0.41 (2.3)
Colorado Plateau	3.15 (17.3)	1.06 (6.7)	0.21 (1.3)	1.08 (4.3)	0.64 (1.7)	0.17 (3.3)
Central Rockies	2.87 (15.8)	0.80 (5.5)	0.18 (1.2)	1.11 (4.4)	0.64 (1.4)	0.14 (3.2)
Coastal	4.40 (43.5)	1.35 (18.4)	0.90 (10.9)	1.65 (6.6)	0.25 (2.5)	0.25 (5.1)
Northeast	6.13 (59.3)	3.32 (40.6)	0.40 (4.8)	1.84 (7.3)	0.23 (3.4)	0.34 (3.0)
Northern Great Plains	4.26 (30.3)	1.61 (14.6)	0.51 (4.7)	1.35 (5.4)	0.63 (1.6)	0.16 (4.0)
Northern Rockies	5.15 (39.5)	0.98 (15.0)	0.31 (4.7)	2.88 (11.5)	0.57 (4.1)	0.41 (4.1)
Southern California	8.64 (51.7)	1.45 (9.3)	3.53 (22.6)	2.29 (9.2)	0.94 (4.2)	0.42 (6.3)
Sonora	4.09 (21.3)	1.52 (8.3)	0.24 (1.3)	1.28 (5.1)	0.84 (2.0)	0.20 (4.6)
Sierra Nevada	4.40 (25.2)	0.96 (7.0)	0.47 (3.5)	2.16 (8.6)	0.55 (2.6)	0.26 (3.5)
Sierra Humbolt	2.67 (16.7)	0.52 (5.2)	0.16 (1.5)	1.36 (5.5)	0.42 (2.0)	0.20 (2.5)
Washington, DC	16.90 (132.8)	7.91 (73.2)	2.16 (19.9)	4.44 (17.8)	0.82 (15.6)	1.56 (6.3)
West Texas	5.11 (27.0)	2.13 (12.9)	0.25 (1.5)	1.29 (5.2)	1.27 (1.7)	0.17 (5.7)

^aMass is in $\mu\text{g}/\text{m}^3$. Extinction summaries in parenthesis are in Mm.

Adapted: Sisler and Malm (1999)

1 maximize benefits of both programs. The monitoring network is expected to be implemented by
2 the end of 1999 (U.S. Environmental Protection Agency, 1997).

3 4 **9.5.7 Visibility Modeling**

5 There are several types of models available for the evaluation of pollution-related effects on
6 visibility. Plume visibility models and regional haze models are source models which simulate
7 the transport, dispersion, and transformation of chemical species in the atmosphere. Plume
8 models use the resulting air quality data to calculate the values of parameters related to human
9 perception, such as contrast and color differences. Regional haze models calculate aerosol
10 species concentrations and the light-extinction coefficient. Models for the photographic
11 representation of haze use air quality data as an input, and perform the optical calculations
12 required to create images that represent the visual effects of the air quality.

13 14 **9.5.7.1 Regional Haze**

15 Regional haze models may be used to assess the impact of pollutant sources on an
16 identified area or region, in most cases identified Class I wilderness areas, or to evaluate the
17 impact of new or existing air quality regulations. Light extinction by fine particles is used to
18 determine the effect of anthropogenic pollutants on regional visibility degradation (regional
19 haze). In the United States, these anthropogenic particles are composed primarily of sulfate
20 compounds, organic compounds, and to a much lesser extent nitrate compounds, with the
21 exception of California where nitrates are the largest single contributor to light extinction. The
22 contribution to light extinction by these compounds will vary based on the particle composition
23 and size distribution. Once the particles are formed, their size can change, resulting in a change
24 in their light extinction efficiency. Model calculations take into consideration the mass of the
25 particulate constituents and the relative humidity.

26 The model requirements for regional-scale multiple-source haze models are nearly identical
27 to the model requirements for simulations of regional-scale multiple-source fine particle impacts.
28 Hence, the Eulerian-based grid models currently under development to support fine particle
29 impact assessments will be relied upon to provide a means for assessing large-scale multiple-
30 source haze impacts.

1 Middleton (1996, 1997) described the findings of a Eulerian-based grid model, the Denver
2 Air Quality Model (DAQM). The DAQM is the principal component of the Brown Cloud II
3 study which is part of earlier work investigating visibility in Denver over the last 20 years. The
4 DAQM is derived from the Regional Acid Deposition Model (RADM) and includes aerosol
5 processes, meteorological modeling analysis, and visibility analysis procedures. The DAQM has
6 been used to determine the relationship between emissions and concentrations of fine and coarse
7 particles and all major gaseous pollutants under various emission scenarios and meteorological
8 conditions. The results of the study demonstrated an association between visibility and air
9 quality issues in the Colorado Front Range area.

10 Neff (1997), in his evaluation of the DAQM model, suggested that the meteorological
11 model does not adequately address mesoscale structures responsible for the initiation and
12 maintenance of the brown cloud episodes or cloud systems and surface moisture fluxes. Given
13 these model uncertainties, it was suggested that there may be errors in the quantification of
14 emissions and in the calculated optical extinction and scattering.

15 The Visibility Assessment Scoping Model (VASM) uses Monte Carlo techniques to
16 generate multiple realizations of daily concentrations of sulfates, nitrates, elemental carbon,
17 organic carbon, fine and coarse dust, and the relative humidity to determine particle effects on
18 regional haze. Species-specific light attenuation is calculated based on particle concentration and
19 relative humidity, producing short-term haze intensity or visual range information (Shannon
20 et al., 1997).

21 The Elastic Light Scattering and Interactive Efficiency (ELSIE) model was used by Omar
22 et al. (1999) to determine the species concentrations and to relate apportionment to the extinction
23 coefficient in an aerosol mixture. The model assumes the aerosol is an internal inhomogeneous
24 mixture of chemical species and size distributions. Model input parameters included the size
25 distributions, prevailing relative humidity, refractive indices of the constituents, percent
26 solubility of the aerosol components, and the growth function of the aerosol particles. The model
27 assumes that the particles grow with increasing relative humidity according to a predetermined
28 growth function.

29 Several source-oriented models have been developed to evaluate the effects of pollutants on
30 regional haze. The U.S. Environmental Protection Agency, in cooperation with the U.S. Forest
31 Service, the Fish and Wildlife Service, the National Park Service (the Interagency Workgroup for

1 Air Quality Modeling), developed the MESOPUFF II system of assessing regional haze impacts.
2 The MESOPUFF II system uses the light extinction for sulfates and nitrates for an estimated 3- to
3 24-h average concentration (U.S. Environmental Protection Agency, 1994; U.S. Environmental
4 Protection Agency, 1995a). The CALPUFF modeling system can process mesoscale
5 meteorological data and address dispersive processes of a regional nature. Simulated long-range
6 pollutant trajectories have been successfully compared to results from a field study involving
7 transport to 1000 km downwind (U.S. Environmental Protection Agency, 1995b). However,
8 Lagrangian puff dispersion modeling involving transport of 200 km or more tend to
9 underestimate the horizontal extent of the dispersion, causing the surface concentration to be
10 overestimated (Moran and Pielke, 1994). Another source-oriented Lagrangian trajectory model
11 capable of computing light extinction and scattering and estimating visual range from gas phase
12 and primary particle phase air pollutant emissions directly from sources was reported by Eldering
13 and Cass (1996). The model is comprised of several modules that take into consideration particle
14 size distribution and chemical composition, the speciation of organic vapor emissions,
15 atmospheric chemical reactions, transport of condensible material between the gas and particle
16 phase, fog chemistry, dry deposition, and light scattering and absorption. The model is, however,
17 not suitable for predicting visibility over great distances through nonuniform hazes and for
18 visualization of pollutant effects of isolated major point source plumes. Single line Lagrangian
19 trajectory models can not represent horizontal turbulent diffusion, the effects of wind shear, and
20 advection by turbulent wind components. Error in transport calculations have been reported of
21 up to $\pm 50\%$ (Eldering and Cass, 1996).

22 Gray and Cass (1998) developed a lagrangian particle-in-cell model for predicting source
23 class contributions of fine particle total carbon and elemental carbon. The model simulates the
24 motion and deposition of pollutants in an air basin with varying meteorological conditions. The
25 model also takes into consideration the vertical mixing characteristics of pollutants in areas
26 located near the source. The model is useful in determining changes in long-term average
27 pollutant concentrations from implementing specific emission control measures.

28 The Regional Particulate Model (RPM) simulates secondary fine particulate matter ($PM_{2.5}$)
29 formation and long-range transport. The RPM is used with the Regional Acid Deposition Model
30 (RADM), a comprehensive acid rain model. Predictions from the RADM are used to simulate
31 the formation of sulfate and nitrate, ammonium particles, and secondary organic aerosols. The

1 external RADM includes particle physics from the RPM and operates at an 80 and 20 kilometer
2 resolution. Additional work is currently being done that will incorporate the RADM/RPM and
3 external RADM models into a more comprehensive air quality modeling system,
4 Models-3/Community Multi-Scale Air Quality (CMAQ). This modeling system simulates the
5 processes involved in primary and secondary PM_{10} and $PM_{2.5}$ and ozone formation, regional haze,
6 acid deposition, and nutrient deposition. The modeling system includes a mesoscale
7 meteorological model, emission model, and a version of the CMAQ.

8 The Regulatory Modeling System for Aerosols and Deposition (REMSAD) also simulates
9 $PM_{2.5}$ formation. The REMSAD was derived from the Urban Airshed Model Version V
10 (UAM-V) for primary and secondary $PM_{2.5}$ and PM_{10} formation, and acid nutrient and toxic
11 deposition. The REMSAD system consists of a meteorological data preprocessor, the core
12 aerosol and toxic deposition model (ATDM), and postprocessing programs. The ATDM is a
13 three-dimensional Eulerian grid model designed to calculate the concentrations of both inert and
14 chemically reactive pollutants by simulating the physical and chemical processes in the
15 atmosphere that affect pollutant concentrations. The basis for the model is the atmospheric
16 diffusion or species continuity equation. This equation represents a mass balance in which all of
17 the relevant emissions, transport, diffusion, chemical reactions, and removal processes are
18 expressed in mathematical terms (Guthrie et al., 1999).

19 Zannetti et al. (1990, 1993) and Fox et al. (1997) described a semi-empirical model that
20 could be used to estimate the visibility impact on one region resulting from sulfur dioxide
21 emission controls in a different region. The model combined four different input parameters:
22 (1) chemical transport; (2) possible nonlinearity of pollutant chemical transformation; (3) sulfate
23 fraction of fine particulate matter, including the amount of water absorbed by the fine particles;
24 and (4) the fraction of light extinction due to fine particles. The model uses physically realistic
25 concepts of atmospheric transport, chemical transformation, and physical effects. However,
26 actual data sets, mathematical constructs, or expert opinions may also be used. Models have also
27 been developed that predict the downwind concentration of smoke particulate and other
28 combustion products from the burning of crude oil from accidental spills (McGrattan et al., 1995,
29 1996).

30

9.5.7.2 Plume Models

Several plume visibility models are currently available. Plume visibility models estimate the value of optical parameters related to human perception, such as contrast and color differences and compare these values with perception thresholds to determine whether the plume is likely to be perceptible under various simulated conditions (U.S. Environmental Protection Agency, 1988; Latimer, 1988). An empirical algorithm, Probability of Detection Algorithm (PROBDET), allows the prediction of the lower limit of plume contrast that can be detected visually. The PROBDET can be used to estimate the detection level for plumes that fall within the bounds defined by the full length, oval, and circular plume stimuli (Ross et al., 1997).

A simplified dispersion model using a second-order turbulence closure scheme to account for averaging time effects on the dispersion rate was described by Sykes and Gabruk (1997). The lateral and vertical spread is estimated using a Gaussian plume framework. A simplified representation of the turbulence spectrum is used to predict the reduced spread rate for short averaging times.

Earlier plume models included PLUVUE I and II, used during the preparation of a permit application to determine whether or not a proposed new facility would cause visibility impairment in a Class I area (Latimer et al., 1978; Johnson et al., 1980; White et al., 1985; U.S. Environmental Protection Agency, 1992). Seigneur et al. (1997) developed a plume visibility model, the Reactive and Optics Model Emissions (ROME), that improves on the existing plume visibility models. The model simulates the momentum and buoyancy forces of the plume rise, the dispersion and chemistry, and condensation and evaporation of the aqueous phase.

A second-order closure algorithm is used to estimate instantaneous plume concentrations, or the time-averaged plume concentration may be estimated using a first-order closure algorithm.

A comprehensive chemical kinetic mechanism simulates chemical transformation processes in the gas, aqueous, and particle phases. Particle dynamics and chemical composition is based on sectional representation of the particle size distribution. The model includes a radioactive transfer module that provides optical properties using sectional particle size distributions. Deposition velocities based on atmospheric stability, surface type, chemical type, and particle size are derived using a resistance-based dry deposition algorithm. The ROME can be used with other models to estimate a stack plume opacity, the percentage of light intensity attenuated by the plume near the stack after any condensed water has evaporated (Meng et al., 1998).

1 When compared with the PLUVUE II, the ROME, with the second-order dispersion algorithm,
2 was found to present a more accurate estimate of plume height, width, nitrogen oxide
3 concentration, nitrogen dioxide/nitrogen oxide ratio, and visibility. Error, bias, correlation
4 coefficients, and simulations were within a factor of two of that observed (Gabruk et al., 1999).
5

6 **9.5.7.3 Photographs**

7 Computer-generated photographs are sometimes used to illustrate the effects of pollution
8 on visibility. To begin, a photograph is taken on a very clean, cloud-free day to serve as the
9 initial scene image. As previously indicated, the appearance of an object is determined by the
10 path radiance and the transmitted radiance. To determine the transmitted radiance, an estimate of
11 the light-extinction coefficient from the photograph is used to determine the initial radiance for
12 each element in the scene. The transmitted radiance is equal to the initial radiance of the
13 element in the scene multiplied by the transmittance of the atmosphere in the sight path.
14 Since the path radiance changes over the distance of the sight path, the source function, the rate
15 of change over the distance of the sight path, must also be determined.

16 Eldering et al. (1996) proposed the use of a model that uses simulated photographs from
17 satellite and topographic images to evaluate the effect of atmospheric aerosols and gases on
18 visibility. Use of this model requires ground-based photography and size distribution and
19 chemical composition of atmospheric aerosols, NO₂ concentration, temperature, and relative
20 humidity for a clear day, for comparison purposes. Light extinction and sky color are then
21 calculated based on differences in aerosol size distribution, NO₂ concentration, temperature, and
22 relative humidity. The images created represent natural landscape elements.

23 One of the limitations in using photographic models for representation of haze is that haze
24 is assumed to be uniformly distributed throughout the scene and selected conditions are
25 idealized, so the full range of conditions that occur in a scene are not represented. Photographs
26 are also expensive to produce. More detailed information on the use of photographic
27 representation of haze may be found in the U.S. Environmental Protection Agency (1996),
28 Trijonis et al. (1991), Molenaar et al. (1994), and Eldering et al. (1993).
29
30
31

9.5.8 Trends in Visibility Impairment

Trends in visibility impairment or haziness are often associated with fine mass concentrations. Generally, visibility impairment is greatest in the eastern United States and southern California. Haziness in the southeastern United States is greatest in the summer months, followed by the spring and fall, and winter. Summer haziness in the southeastern United States has increased by approximately 80% since the 1950s (Husar and Wilson, 1993) due to increased sulfate from increased sulfur dioxide (SO₂) emissions (Husar et al., 1994). The resulting sulfate, considered to be ammonium sulfate, accounts for 40 to 70% of the fine particle mass (Husar and Wilson, 1993). Sulfate-related effects on visibility in the southeast is a factor of 20 higher than the Great Basin area, and 10 higher than the desert southwest, central Rocky Mountains, and Sierra Mountains (Malm et al., 1994). A statistically significant increase in summer sulfate concentrations was noted in two Class I areas in the eastern United States (Shenandoah and the Great Smoky Mountains) from 1982 to 1992 (Eldred et al., 1993; Cahill et al., 1996). The increase was largest in the summer and decreased in the winter. The majority of the southwest showed decreasing sulfur (Eldred et al., 1993; Eldred and Cahill, 1994). White (1997) suggested that the increase in fine-particle sulfur may be the result of the measurement method and not an upward trend in fine particle concentrations in those Class I areas. However, Iyer et al. (1999), using the Spearman correlation of trend, reported an increased trend in hazy days during the summer months in Shenandoah and the Great Smoky Mountains based on monitoring data for the period 1979 to 1996 showing high sulfur concentrations.

Based on PM_{2.5} concentrations and changes in the deciview scale, calculated from reconstructed extinction coefficients, Sisler and Malm (1999) reported no significant deterioration in air quality and visibility conditions at 30 IMPROVE network sites for the years 1988 to 1996. The sites were divided into eastern and western regions. Averaged PM_{2.5} mass and extinction summaries for the sites appear in Table 9-7. The annual best visibility (10th percentile) and median visibility days (50th percentile) are improving at approximately 70% of the sites. However, several sites are not showing steady improvements in either visibility or PM_{2.5}, particularly in the number of worst visibility days (90th percentile). The sites included the Badlands, Big Bend, Crater Lake, Great Smoky Mountains, Mesa Verde, Shenandoah and Yosemite National Parks, Chiricahua National Monument, and the District of Columbia.

1 Some of the visibility impairment in northern California and Nevada, including Oregon,
2 southern Idaho and western Wyoming, results from coarse mass and soil, primarily considered
3 natural extinction. In some areas of the United States, extinction from coarse mass is almost
4 negligible because the overall extinction is so high. High dust concentrations from southern
5 California have contributed to regional haze in the Grand Canyon and other class I areas in the
6 southwestern United States (Vasconcelos et al., 1996). White et al. (1999) reported that some of
7 the worst haze near the Grand Canyon is associated with pollutant transport from southern
8 California and subtropics.

9 Organics are the second largest contributor to light extinction in most areas in the United
10 States. Extinction caused by organic carbon is greatest in the Pacific Northwest, Oregon, Idaho,
11 and Montana, accounting for 40 to 45% of the total extinction. Organic carbon contributes
12 between 15 to 20% to the total extinction in most of the western United States and 20 to 30% in
13 the remaining areas of the United States. Light absorption by carbon is relatively insignificant
14 but is highest in the Pacific Northwest (up to 15%) and in the eastern United States (3%) (Malm
15 et al., 1994).

16 Visibility impairment in southern California is primarily caused by light extinction by
17 nitrates. Nitrates contribute about 40% to the total light extinction in Southern California.
18 Nitrates account for 10 to 20% of the total extinction in other areas of the United States.

21 **9.6 THE EFFECTS OF PARTICLES ON CLIMATE AND ON THE** 22 **TRANSMISSION OF SOLAR ULTRAVIOLET RADIATION**

23 This section deals with the effects of particulate matter on the transmission of
24 electromagnetic radiation emitted by the sun at ultraviolet and visible wavelengths and by the
25 earth at infrared wavelengths. These effects depend on the radiative properties (extinction
26 efficiency, single scattering albedo, and asymmetry parameter) of the particles, which in turn are
27 dependent on the size and shape of the particles, the composition of the particles and the
28 distribution of components within individual particles. In general, the radiative properties of
29 particles are size and wavelength dependent. In addition, the extinction cross section tends to be
30 at a maximum when the particle radius is similar to the wavelength of the incident radiation.
31 Thus, fine particles (present mainly in the accumulation mode) would be expected to exert a

1 greater influence on the transmission of electromagnetic radiation than would coarse particles.
2 The composition of particles can be crudely summarized in terms of the broad classes introduced
3 in Chapter 6 of PM AQCD 96 and in Chapter 4 of the current document, i.e., nitrate, sulfate,
4 mineral dust, organic carbon and elemental carbon. The major sources of these components are
5 shown in Table 4.1. Knowledge of the factors controlling the transfer of solar radiation in the
6 ultraviolet spectral region is needed for assessing the extent of biological damage associated with
7 exposure to UV-B radiation (290 to 315 nm). Knowledge of the effects of PM on the transfer of
8 radiation in the visible and infrared spectral regions is needed for assessing the relation between
9 particles and climate change.

11 **9.6.1 Effects of Particles on the Transmission of Solar Ultraviolet Radiation**

12 The transmission of solar UV-B radiation through the earth's atmosphere is controlled by
13 ozone, clouds, and particles. The depletion of stratospheric ozone caused by the release of
14 chlorofluorocarbons has resulted in heightened concern over potentially serious increases in the
15 amount of solar UV-B radiation (SUVB) reaching the surface. Issues related to the depletion of
16 stratospheric ozone will not be treated here. Exposure to SUVB is associated with various health
17 outcomes such as sunburn, DNA damage, immune system suppression, cataracts and various
18 forms of skin cancers as well as ecosystem damage (Kodama and Lee, 1993; Longstreth et al.,
19 1998). SUVB is also responsible for initiating the production of OH radicals which oxidize a
20 wide variety of volatile organic compounds which can deplete stratospheric ozone (e.g., CH₃Cl,
21 CH₃Br); absorb terrestrial infrared radiation (e.g., CH₄); and contribute to photochemical smog
22 formation (e.g., C₂H₄, C₃H₈).

23 A given amount of ozone in the lower troposphere has been shown to absorb more solar
24 radiation than an equal amount of ozone in the stratosphere because of the increase in its
25 effective optical path produced by Rayleigh scattering in the lower atmosphere (Bruehl and
26 Crutzen, 1988). The effects of particles are more complex. The impact of particles on the SUVB
27 flux throughout the boundary layer are highly sensitive to the altitude of the particles and to their
28 single scattering albedo. Even the sign of the effect can reverse as the composition of the
29 particles changes from scattering to absorbing (e.g., from sulfate to elemental carbon) (Dickerson
30 et al., 1997). In addition, scattering by particles may also increase the effective optical path of
31 absorbing molecules in the lower atmosphere.

1 The effects of particles present in the lower troposphere on the transmission of SUVB have
2 been examined both by field measurements and by radiative transfer model calculations. The
3 presence of particles in urban areas modifies the spectral distribution of solar irradiance at the
4 surface. Shorter wavelength radiation (i.e., in the ultraviolet) is attenuated more than visible
5 radiation (e.g., Peterson et al., 1978; Jacobson, 1999a). Wenny et al. (1998) also found greater
6 attenuation of SUVB than SUVA (315 to 400 nm). However, this effect will depend on the
7 nature of the particles and is expected to depend strongly on location. Lorente et al. (1994)
8 observed an attenuation of SUVB ranging from 14% to 37%, for solar zenith angles ranging from
9 about 30° to about 60° , in the total (direct and diffuse) SUVB reaching the surface in Barcelona
10 during cloudless conditions on very polluted days (aerosol scattering optical depth at 500 nm,
11 $0.46 \leq \tau_{500 \text{ nm}} \leq 1.15$ compared to days on which the turbidity of urban air was similar to that for
12 rural air ($\tau_{500 \text{ nm}} \leq 0.23$). A rough estimate of the particle concentrations which can account for
13 these observations can be made by combining Koschmeider's relation for expressing visual range
14 in terms of extinction coefficient with one for expressing the mass of PM_{2.5} particles in terms of
15 visual range (Stevens et al., 1984). By assuming a scale height (i.e., the height in which the
16 concentration of a substance falls off to 1/e of its value at the surface) of 1 km for PM_{2.5}, an
17 upper limit of 30 µg/ m³ can be derived for the clear case and between 60 and 150 µg/m³ for the
18 polluted case. Estupinan et al. (1996) found that summertime haze under clear sky conditions
19 attenuates SUVB between 5% and 23% for a solar zenith angle of 34° compared to a clear sky
20 day in autumn. Mims (1996) measured a decrease in SUVB by about 80% downwind of major
21 biomass burning areas in Amazonia in 1995. This decrease in transmission corresponded to
22 optical depths at 340 nm ranging from three to four. Justus et al. (1994) found that SUVB
23 reaching the surface decreased by about 10% due to changes in aerosol loading in Atlanta, GA
24 from 1980 to 1984. In addition, there is evidence that higher particle levels in Germany (48°N)
25 may be responsible for greater attenuation of SUVB than in New Zealand (Seckmeyer and
26 McKenzie, 1992).

27 In a study of the effects of non-urban haze on SUVB transmission, Wenny et al. (1998)
28 derived a very simple regression relation between the measured aerosol optical depth at 312 nm
29

$$\ln(\text{SUVB transmission at solar noon}) = -0.1422 \tau_{312 \text{ nm}} - 0.138, R^2 = 0.90$$

1 In principle, values of $\tau_{312\text{ nm}}$ could be found from knowledge of the aerosol optical properties and
2 values of the visual range. Wenny et al. (1998) also found that absorption by particles accounted
3 for 7% to 25% of the total (scattering + absorption) extinction. Relations such as the one given
4 above are strongly dependent on local conditions and should not be used in other areas without
5 knowledge of the differences in aerosol properties. Although all of the above studies reinforce
6 the idea that particles play a major role in modulating the attenuation of SUVB, none of them
7 included measurements of ambient PM concentrations and so direct relations between PM levels
8 and SUVB transmission could not be determined.

9 Liu et al. (1991) calculated the effects of the increase of anthropogenic particles that has
10 occurred since the beginning of the industrial revolution on the transmission of SUVB. Based on
11 estimates of the reduction in visibility from about 95 km to about 20 km over non-urban areas in
12 the eastern United States and in Europe; calculations of the optical properties of airborne
13 particles found in rural areas to extrapolate the increase in extinction at 550 nm to 310 nm; and
14 radiative transfer model calculations, they concluded that the amount of SUVB reaching the
15 surface has decreased from 5 to 18% since the beginning of the industrial revolution. This
16 decrease was attributed mainly to scattering of SUVB back to space by sulfate containing
17 particles. The radiative transfer model calculations have not been repeated for urban particles.

18 While aerosols are expected to decrease the flux of SUVB reaching the surface, scattering
19 by particles is expected to result in an increase in the actinic flux within and above the aerosol
20 layer. On the other hand, when the particles significantly absorb SUVB, a decrease in the actinic
21 flux is expected. Blackburn et al. (1992) measured the attenuation of the photolysis rate of ozone
22 and found that aerosol optical depths near unity at 50 nm reduced the ozone photolysis rate by as
23 much as a factor of two. The actinic flux is the radiant energy integrated over all directions at a
24 given wavelength incident on a point in the atmosphere. The actinic flux is the quantity needed
25 to calculate the rates of photolytic reactions in the atmosphere. Dickerson et al. (1997) showed
26 that the photolysis rate for NO_2 , a key parameter for calculating the overall intensity of
27 photochemical activity, could be increased within and above a scattering aerosol layer extending
28 from the surface, while it would be decreased at the surface. This effect is qualitatively similar to
29 what is seen in clouds, where photolysis rates are increased in the upper layers of a cloud and
30 above the cloud (Madronich, 1987). For a simulation of an ozone episode which occurred during
31 July 1995 in the mid-Atlantic region, Dickerson et al. (1997) calculated ozone increases of up to

1 20 ppb compared to cases in which the radiative effects of particles were not included in urban
2 airshed model (UAM-IV) simulations. In contrast, Jacobson (1998) found that particles may
3 have caused a 5 to 8% decrease in ozone levels during the Southern California Air Quality Study
4 in 1987. Absorption by organic compounds and nitrated inorganic compounds was hypothesized
5 to account for the reductions in the intensity of UV radiation.

6 In addition, the photolysis of ozone in the Hartley bands leads to the production of
7 electronically excited oxygen atoms, O(¹D), which then react with water vapor to form OH
8 radicals. Thus, enhanced photochemical production of ozone is accompanied by the scavenging
9 of species involved in greenhouse warming and stratospheric depletion. However, these effects
10 may be neutralized or even reversed by the presence of absorbing material in the particles.
11 Any evaluation of the effects of particles on photochemical activity therefore will depend on the
12 composition of the particles and also will be location specific.

14 **9.6.2 Effects of Particles on Climate**

15 Studies of the effects of particles on the transfer of solar and terrestrial radiation through
16 the atmosphere prior to the publication of the 1995 IPCC Report (Intergovernmental Panel on
17 Climate Change, 1995) were reviewed in the previous document “Air Quality Criteria for
18 Particulate Matter” (PM AQCD 1996) (U.S. Environmental Protection Agency, 1996). A brief
19 review of material presented in that volume along with some more recent findings are presented
20 below.

21 Atmospheric particles both scatter and absorb incoming solar radiation at visible
22 wavelengths. The scattering of solar radiation back to space leads to a decrease in the
23 transmission of visible radiation to the surface and hence to a decrease in the heating rate of the
24 surface and the atmosphere. The absorption of either incoming solar radiation or outgoing
25 terrestrial infrared radiation by atmospheric particles results in heating of the lower atmosphere.
26 The interactions of particulate matter with electromagnetic radiation from the visible through the
27 infrared spectral regions are responsible for their direct effects on climate. The direct effects of
28 particles on climate are the result of the same physical processes responsible for visibility
29 degradation. Visibility reduction is caused by particle scattering in all directions while the
30 climate effects result mainly from scattering in the upward direction. The net effect of the above
31 processes can be expressed as a radiative forcing which is the change in the average net radiation

1 at the top of the troposphere because of a change in solar (shortwave, or visible) or terrestrial
2 (longwave, or infrared) radiation (Houghton et al., 1990). The radiative forcing drives the
3 climate to respond, but because of uncertainties in a number of feedback mechanisms involving
4 climate response, radiative forcing is used as a first-order estimate of the potential importance of
5 various substances. Sulfate particles scatter solar radiation effectively and do not absorb at
6 visible wavelengths, while they absorb weakly at infrared wavelengths (IPCC, 1995). Nitrate
7 particles exhibit grossly similar properties. The effects of mineral dust particles are complex,
8 they weakly absorb solar radiation but their overall effect on solar radiation depends on particle
9 size and the reflectivity of the underlying surface. They absorb infrared radiation and thus
10 contribute to greenhouse warming (Tegen et al., 1996). Organic carbon particles mainly reflect
11 solar radiation, while particles containing elemental carbon are strong absorbers of solar radiation
12 (IPCC, 1995). However, the optical properties of black carbon particles are modified if they
13 become coated with water or sulfuric acid. Particles containing elemental carbon can also exert a
14 direct effect after deposition onto surfaces which are more reflective, e.g., snow and ice. In this
15 case, additional solar radiation is absorbed by the surface; conversely, more reflective particles
16 deposited on a dark surface result in additional solar radiation being reflected back to space.

17 In addition to the direct effects by which particles can affect climate, anthropogenic
18 (Twomey, 1974; Twomey, 1977) and biogenic (Charlson et al., 1987) sulfate particles also exert
19 an indirect effect on climate by serving as cloud condensation nuclei which results in changes in
20 the size distribution of cloud droplets by producing more particles with smaller sizes. The same
21 mass of liquid water in smaller particles leads to an increase in amount of solar radiation that
22 clouds reflect back to space because the total surface area of the cloud droplets is increased. This
23 suggestion has been supported by satellite observations which indicate that the effective radius of
24 cloud droplets is smaller in the Northern Hemisphere than in the Southern Hemisphere (Han
25 et al., 1994). Smaller cloud droplets also have a lower probability of precipitating and thus they
26 would have a longer lifetime than larger ones. Although the effects of sulfate have been most
27 widely considered, interactions with other aerosol components may also be important. Novakov
28 and Penner (1993) have provided evidence that carbonaceous particles can modify the nucleation
29 properties of sulfate particles.

30 The amount of solar radiation incident on the earth-atmosphere system, or the solar
31 constant, is 1370 W m^{-2} , or 342.5 W m^{-2} on a globally averaged basis (calculated by dividing the

1 solar constant by 4). The addition of sulfate and organic carbon as airborne particulate matter
2 results in enhanced scattering and net cooling, while the addition of particles containing
3 elemental carbon results in the absorption of solar and terrestrial radiation and net heating. The
4 estimated radiative forcing due to the scattering of solar radiation back to space caused mainly by
5 sulfate particles is -0.4 W m^{-2} (IPCC, 1995) with an uncertainty range of a factor of two. The
6 uncertainty range reflects uncertainties in the emissions of SO_2 , the amount of SO_2 that is
7 oxidized to sulfate, the atmospheric lifetime of sulfate, and the optical properties of the sulfate
8 particles. These values may be compared to the radiative forcing exerted by greenhouse gases of
9 about $+2.4 \text{ W m}^{-2}$ with an uncertainty factor of 1.15 from the pre-industrial era (ca. 1800) to
10 1994. (Since the latter part of the 19th century the mean surface temperature of the earth has
11 increased from 0.3°C to 0.6°C according to the IPCC (1995) assessment). Estimates of the
12 indirect effects of particles range from 0 to -1.5 W m^{-2} (IPCC, 1995). Because of a lack of
13 quantitative knowledge no central value could be given. Therefore, on a globally averaged basis,
14 the direct and indirect effects of anthropogenic sulfate particles have partially offset the warming
15 effects caused by increases in levels of greenhouse gases (Charlson et al., 1992).

16 Much of the work investigating the effects of particles on climate has focused on sulfate
17 particles. However, particles containing elemental carbon from fossil fuel combustion and
18 biomass burning, or mineral dust may exert radiative forcing with a spatial distribution very
19 different from that for sulfate. Tegen et al. (1996) and Tegen and Lacis (1996) used a global
20 scale three-dimensional model to evaluate the radiative forcing due to mineral dust particles.
21 Tegen and Lacis (1996) found that the sign and the magnitude of the radiative forcing depends on
22 the height distribution of the dust and the effective radius of the particles. In particular, for a dust
23 layer extending from 0 km to 3 km, positive radiative forcing at visible wavelengths is found for
24 particle radii greater than $1.8 \mu\text{m}$ whereas negative forcing is found for smaller particles. They
25 calculated a global mean radiative forcing due to mineral dust from all sources of 0.14 W m^{-2} and
26 from mineral dust from lands disturbed by human activity of 0.09 W m^{-2} . This value represents a
27 near cancellation between a much larger solar forcing of -0.25 W m^{-2} and a thermal forcing of
28 0.34 W m^{-2} . Uncertainty factors could not be estimated for these calculations as they were
29 judged to be largely unknown. Haywood and Shine (1995) estimated a global mean radiative
30 forcing of 0.1 W m^{-2} , with an uncertainty factor > 3 , caused by the absorption of solar radiation
31 by elemental carbon released by fossil fuel combustion. The IPCC (1995) estimated a global

1 mean radiative forcing of -0.1 W m^{-2} caused by particles produced by biomass burning with an
 2 uncertainty factor of three. The global mean radiative forcing exerted by particles is then -
 3 0.5 W m^{-2} with an uncertainty of about a factor of 2.4. Global mean radiative forcing exerted by
 4 greenhouse gases and particles are summarized in Figure 9-19.

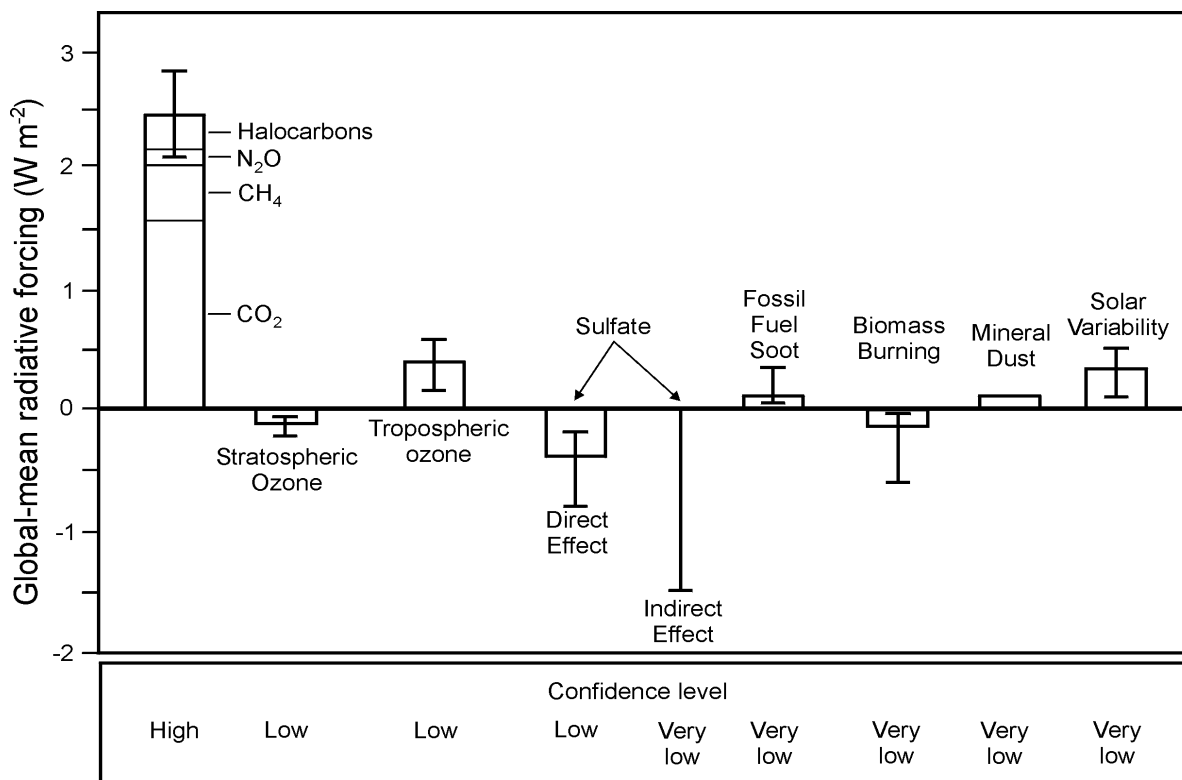


Figure 9-19. Estimated global mean radiative forcing exerted by gas and particle phase species from 1850 to 1950.

Source: Adapted from IPCC (1995) and Tegen and Lacis (1996).

1 Deviations from the global mean values can be very large on the regional scale.
 2 For instance, Tegen et al. (1996) found that the local radiative forcing exerted by dust raised from
 3 disturbed lands ranges from -2.1 W m^{-2} to 5.5 W m^{-2} over desert areas and their adjacent seas.
 4 The largest regional values of radiative forcing due to anthropogenic sulfate are about -3 W m^{-2}
 5 in the eastern United States, south central Europe and eastern China (Kiehl and Briegleb, 1993).

1 These regional maxima in aerosol forcing are at least a factor of ten greater than their global
2 mean values shown in Figure 9-19. By comparison, regional maxima in forcing by the
3 well-mixed greenhouse gases are only about 50% greater than their global mean value (Kiehl and
4 Briegleb, 1993). Thus the estimates of local radiative forcing by particles also are large enough
5 to completely cancel the effects of greenhouse gases in many regions and to cause a number of
6 changes in the dynamical structure of the atmosphere which still need to be evaluated. A number
7 of anthropogenic pollutants whose distributions are highly variable are also effective greenhouse
8 absorbers. These gases include O₃ and possibly also HNO₃, C₂H₄, NH₃ and SO₂ which are not
9 commonly considered in radiative forcing calculations (Wang et al. 1976). High ozone values
10 are found downwind of urban areas and areas where there is biomass burning. However,
11 Van Dorland et al. (1997) found that there is not much cancellation between the radiative effects
12 for ozone and for sulfate because both species have different seasonal cycles and show
13 significant differences in their spatial distribution.

14 Observational evidence for the climatic effects of particles is sparse. Harwood et al. (1999)
15 found that the inclusion of anthropogenic aerosols results in a significant improvement between
16 calculations of reflected sunlight at the top of the atmosphere and satellite observations in
17 oceanic regions close to sources of anthropogenic PM.

18 Uncertainties in calculating the direct effect of airborne particles arise from a lack of
19 knowledge of their vertical and horizontal variability, their size distribution, chemical
20 composition and the distribution of components within individual particles. For instance, gas
21 phase sulfur species may be oxidized to form a layer of sulfate around existing particles in
22 continental environments or they may be incorporated in sea salt particles (e.g., Li-Jones and
23 Prospero, 1998). In either case, the radiative effects of a given mass of the sulfate will be much
24 lower than if pure sulfate particles were formed. It must also be stressed that the overall radiative
25 effect of particles at a given location is not simply given by the sum of effects caused by
26 individual classes of particles because of interactions between particles with different radiative
27 characteristics and with gases.

28 Calculations of the indirect effects of particles on climate are subject to much larger
29 uncertainties than are calculations of their direct effects, reflecting uncertainties in a large
30 number of chemical and microphysical processes in describing the effects of sulfate on the size
31 distribution and number of droplets within a cloud. A complete assessment of the radiative

1 effects of PM will require calculations which incorporate the spatial and temporal behavior of
2 particles of varying composition which have been emitted from different sources. Refining
3 values of input parameters to models (such as improving emissions estimates) may be more
4 important than improving models in calculations of the direct radiative forcing (Pan et al., 1997)
5 and indirect radiative forcing (Pan et al., 1998) due to sulfate. However, uncertainties associated
6 with the calculation of radiative effects of particles will likely remain much larger than those
7 associated with well-mixed greenhouse gases.

10 **9.7 ECONOMICS OF PM ENVIRONMENTAL EFFECTS**

11 **9.7.1 Introduction**

12 This section will discuss four important categories of economic impacts of PM: agriculture
13 and forestry, cleaning and materials damage, visibility, and ecosystem functions. Section 9.7.2
14 discusses the importance of defining effects and baselines, and Section 9.7.3 outlines the basic
15 economic methods that are used. Sections 9.7.4 through 9.7.7 give more details about each of
16 the above categories, including the appropriate application of methods, basic results of existing
17 research, and the strengths and limitations of the resulting analyses.

19 **9.7.2 Need for Defining Exposure-Effect Relations**

20 The initial challenge in measuring economic impacts associated with PM pollution is
21 defining appropriate effects. Any given level of particulate matter will be associated with
22 resulting environmental effects that potentially have economic significance. Examples include
23 the level of crop damage or visibility impairment that result from specified levels of PM.
24 Defining the welfare effects of PM changes requires that baseline levels of effects be defined as
25 well - for example, the point at which PM begins to affect visibility in ways that are important to
26 people. Sections 9.2 through 9.5 have described the scientific evidence relating the temporal and
27 geographical loadings of PM on relevant environmental effects.

9.7.3 Valuation Approaches

Given the evidence of potential economically significant effects, economic analysis proceeds by quantifying in monetary terms the costs associated with different ambient levels of PM. Where possible, direct economic valuation can take place using prices that are determined in the market. For example, the economic value associated with changes in agricultural output resulting from higher pollution can be based on resulting changes in the price and quantity of overall output.

There are a variety of ways to estimate benefits. Avoided cost methods estimate the costs of pollution by using the expenditures that are made necessary by pollution damage. For example, if buildings must be cleaned or painted more frequently as levels of PM increase, then the appropriately calculated increase in these costs is a reasonable estimate of true economic damage. Benefits associated with reductions in PM levels are then represented by the avoided costs of these damages.

Estimating benefits for visibility and for ecosystem services is a more difficult and less precise exercise because the effects are not valued in markets. For example, the loss of a species of insect or plant from a particular habitat does not have a well-defined price. There are several methods that economists have developed to estimate changes in environmental effects that are not valued in markets (Freeman, 1993). These include hedonic price analysis, stated preference models (including contingent valuation, contingent choice, and contingent ranking), and travel cost models. Hedonic price analysis works by analyzing the way that market prices change when an associated environmental effect changes. Part of the economic costs imposed by the reduced visibility caused by PM can be estimated by looking at the differences in sales price between otherwise identical houses that have different degrees of visibility impairment (see Section 9.7.6).

The contingent valuation method (CVM) has been used to value changes in both visibility and ecosystem functions (Hanley and Spash, 1993; Chestnut, 1997). CVM values changes in effects by using carefully structured surveys to ask a sample of people what amount of compensation is equivalent to a given change in environmental quality (or equivalently, how much they would be willing to pay to obtain a given change in environmental quality). There is an extensive scientific literature and body of practice on both the theory and technique of CVM.

1 There are a number of state-of-the-art CVM studies whose results can be utilized to help assess
2 the alternative particulate matter standards; details are provided in Section 9.7.6.

3 Other methods exist to value non-market goods and services. These include other forms of
4 stated preference models, including contingent choice and contingent ranking (also known as
5 conjoint analysis), as well as travel cost models (Johnson and Desvousges, 1997; Hanley and
6 Spash, 1993). However, the primary methods used to date in the literature on the valuation of
7 visibility and ecosystems have been the hedonic price and contingent valuation methods (Hanley
8 and Spash).

9 10 **9.7.4 Effects on Agriculture and Forestry**

11 PM causes the loss of terrestrial resources by increasing the acidity in forests, which
12 destroys their plant life. It can destroy crops in farming areas and reduce yields. Once effects
13 have been defined in terms of changes in agricultural yields that result from different ambient
14 PM levels, there are several agricultural sector models that can be used to obtain changes in
15 economic benefits. Two of these models, the Regional Model Farm (RMF) (Mathtech, 1998)
16 and AGSIM[®] (Taylor, et al., 1993; Abt Associates, 1998) have been used in analyzing
17 agricultural impacts from air pollution (Ozone and PM NAAQS, NO_x SIP Call RIA, and
18 Section 812 Report to Congress). RMF uses a microeconomic model of agricultural supply and
19 demand to determine the welfare changes associated with yield changes from pollution.
20 AGSIM[®] is an econometric-simulation model that is based on a large set of statistically estimated
21 demand and supply equations for agricultural commodities produced in the United States. The
22 welfare effects of changes in silvicultural output require a similar model for forest products. The
23 most state of the art forest sector model is the Timber Assessment Market Model (TAMM),
24 developed by the U.S. Forest Service (Adams and Haynes, 1996). TAMM is a spatial model of
25 the solidwood and timber inventory elements of the U.S. forest products sector. The model
26 provides projections of solidwood and timber inventory elements of the U.S. forest products
27 sector through the year 2040.

28 Increases in nitrogen deposition associated with PM may also have positive effects on
29 agricultural output. Nutrients deposited on crops from atmospheric sources are often referred to
30 as passive fertilization. Nitrogen is a fundamental nutrient for primary production in both
31 managed and un-managed ecosystems. Most productive agricultural systems require external

1 sources of nitrogen in order to satisfy nutrient requirements. Nitrogen uptake by crops varies, but
2 typical requirements for wheat and corn are approximately 150 kg/ha/yr and 300 kg/ha/yr,
3 respectively (NAPAP, 1990). These rates compare to estimated rates of passive nitrogen
4 fertilization in the range of 0 to 5.5 kg/ha/yr (NAPAP, 1991). So, for these crops, deposited
5 nitrogen could account for as much as two to four percent of nitrogen needs. Holding all other
6 factors constant, farmers' use of purchased fertilizers or manure may increase as deposited
7 nitrogen is reduced. Estimates of the potential value of this possible increase in the use of
8 purchased fertilizers are not available, but it is likely that the overall value is very small relative
9 to other PM effects. The share of nitrogen requirements provided by this deposition is small, and
10 the marginal cost of providing this nitrogen from alternative sources is quite low. In some areas,
11 agricultural lands suffer from nitrogen over-saturation due to an abundance of on-farm nitrogen
12 production, primarily from animal manure. In these areas, atmospheric deposition of nitrogen
13 from PM may represent an additional agricultural cost.

15 **9.7.5 Materials Damage Effects and Valuation**

16 Addressing the effects of materials damages related to reductions in criteria pollutants was
17 first included in the benefits analysis supporting the secondary NAAQS for SO₂ and Total
18 Suspended Particles (Manuel, et al., 1982). More recently, the 1990 NAPAP State of Science
19 and Technology Report includes three of its twenty-seven chapters on materials damage and
20 economic valuation methods. (Lipfert, 1996). Materials that are susceptible to exposure to
21 particulate matter include, but are not limited to, painted and coated surfaces, metals, mortar and
22 concrete, stone masonry, fabrics, and glass. The two primary categories of effects on these
23 materials include the following:

- 24 (1) Household soiling, or the accumulation of dirt, ash, and dust on exposed surfaces.
- 25 (2) Corrosive effects, or the material damage to industrial/commercial buildings and structures
26 and to cultural/historical resources (e.g., historic monuments and structures, and outdoor
27 works of art).

28 The focus of studies on materials damage is to estimate the economic benefits associated with
29 reductions in exposure of buildings, structures, and other materials to pollutants of concern.

9.7.5.1 Valuation Methods

There are two basic approaches to valuing reductions in material damages. These include willingness-to-pay measures and the damage function approach as described below.

Willingness to Pay/Averting Behavior This approach accounts for behavioral responses to damages and employs the household production model that combines air quality with cleaning goods and services and other products to produce “cleanliness.” Examples in the literature of this approach include Courant and Porter (1981), Watson and Jaksch (1982), and Harford (1984). In this context, the willingness to pay (WTP) for air quality involves the cost of averting behavior and increased cleaning costs used to maintain material service flows, as well as the disutility from any decline in these flows remaining after these adjustments (Desvousges, Johnson, and Banzhaf, 1998). Therefore, the costs of averting and mitigating behavior will be a lower bound of the total benefits of reducing materials damages.

Methods available to estimate WTP values include stated preference methods such as contingent valuation and conjoint analysis (contingent choice), and revealed preference methods included hedonic price analysis and expenditure function approaches. Revealed preference methods are used to estimate averting and mitigating costs and, thus, provide only the lower bound estimate of WTP. Stated preference methods are used to estimate the full WTP value, but suffer from various estimation and data issues (Freeman, 1993).

Damage Function Approach This approach, also known as the replacement or restoration cost approach, values damaged materials as if they were replaced or restored at their full cost (Desvousges, Johnson, and Banzhaf, 1998). This approach is often referred to as an “engineering cost” method since it does not account for behavioral responses to damages. This approach will generate greater values than the lower-bound WTP estimate for averting and mitigating behavior, which accounts for people being willing to accept lower service flows as opposed to the replacement price. However, the damage function approach will be less than the full WTP estimate because it neglects disutility from lower service flows.

The basic steps to the damage function approach are the following:

- 1 (1) Identify and inventory material stocks at risk such as paints and coatings, mortar and
2 concrete, stone masonry, metals, and other materials (roofing, asphalt, plastics, misc.
3 materials).
- 4 (2) Develop damage functions, or dose-response functions, that quantify relationships
5 between physical damage and changes in pollutant levels.
- 6 (3) Estimate the physical damage by linking the damage functions to the material
7 inventory, as well as to repair, replacement, and maintenance decisions.
- 8 (4) Combine these damage estimates with information on repair, replacement, and
9 maintenance costs to estimate economic cost of damage (NAPAP, 1990).

10 Several key issues associated with this approach include the extrapolation methods for
11 applying damage functions developed under controlled test conditions to real-world situations,
12 the ability to conduct regional assessments of materials damages from limited material
13 inventories across the United States, separating the damages associated with the pollutant of
14 concern from other environmental effects (e.g., sunlight, extreme temperature, and precipitation),
15 and the ability to determine functions relating damage levels to repair, replacement, and
16 maintenance decisions (Gregory et al, 1996 and NAPAP, 1990).

17 The following sections focus on each category of material effects with the appropriate
18 valuation method and summary of literature estimates of economic value.

20 **9.7.5.2 Household Soiling**

21 Studies addressing the costs of household soiling focus on estimating WTP measures of
22 averting and mitigating behaviors. Manuel et al (1982) employ a theoretically consistent
23 approach based on the household production model to assess the soiling and materials damage
24 from decreasing SO₂ and TSP concentrations. Conceptually, an improvement in air quality
25 generates benefits because fewer resources are required to produce a given level of cleanliness.
26 Based on price and expenditure data for household products from the early 1970s, this study
27 estimates the household demand for cleanliness and the change in consumer surplus associated
28 with air quality induced changes in the price of cleanliness. This study estimates benefits related
29 to household soiling of a unit reduction in ambient concentrations of TSP at \$0.35 per household
30 in 1993 dollars. However, the date of this study reduces the applicability of its results since
31 relative prices and consumer preferences have changed significantly since the early 1970s.

1 Using a damage function approach, Mathtech (1990) estimated materials damage of
2 \$0.32 to \$0.82 per household (in 1988 dollars) for acid deposition effects on painted wood
3 surfaces in the south coast air basin. Similarly, Acres International Limited (1991) evaluated
4 household soiling damages from particulate matter related to the generation of electricity by
5 Ontario Hydro. Based on surveys of cleaning companies in Ontario and cleaning frequency from
6 Salmon (1970), this study assumed that the economic value of soiling is equal to the cost of
7 cleaning incurred if consumers always chose to clean soiled materials.

9 **9.7.5.3 Materials Damage to Industrial/Commercial Structures**

10 The household production model is not applicable for estimating materials damages to
11 industrial and commercial buildings and structures because of theoretical and data limitations.
12 Therefore, studies focusing on the cost of damage to these buildings and structures employ the
13 damage function approach based on repair, replacement, or maintenance costs. Specific
14 examples of this type of approach are summarized in NAPAP (1990), Lipfert (1996), and
15 Desvousges, Johnson, and Banzhaf (1998). Based on previous studies employing the damage
16 function approach, Tasdemiroglu (1991) developed cost estimates of materials and soiling
17 damage (paint, textiles and fibers, and household soiling) that range from \$0.62 to \$0.98 per kg
18 of PM (in 1990 dollars), or \$45 to \$57 per household. This estimate may be an overstatement as
19 it includes materials damages to motor vehicles and other materials not included in this damage
20 category.

22 **9.7.5.4 Materials Damage to Cultural/Historical Structures**

23 For buildings and structures of cultural or historical significance, the cost of damage
24 extends beyond repair, replacement, or maintenance costs. Individuals not only lose utility
25 associated with admiring these buildings (i.e., use value), but also because they and others may
26 not be able to admire them in the future (i.e., existence value). Contingent valuation is the
27 typical method employed to estimate the total WTP for damage to these types of buildings and
28 structures. This method involves surveying individuals with hypothetical market scenarios for
29 environmental goods or services to elicit their valuation, or WTP, for them (See Mitchell and
30 Carson, 1989 or Cummings et al, 1986 for summary of this approach). This approach has been
31 used extensively in externality costing studies by electric utilities to account for environmental

1 damage of electricity generation in their pricing decisions (i.e., social versus private marginal
2 costs). Grosclaude and Soguel (1994) utilize a contingent valuation approach to predict WTP for
3 damage caused to cultural and historical buildings in Switzerland by traffic-related air pollution.
4 Based on a survey asking individuals to contribute towards a fund to finance the maintenance of
5 these buildings, the authors estimate full WTP at \$71.95 to \$80.61 per household reflecting the
6 median and mean estimates.

8 **9.7.6 Effects on Visibility**

9 PM has well-documented and significant effects on visibility (see chapter X). Visibility
10 can be defined in several ways. The deciview is a unitless measure that is useful for comparing
11 the effects of air quality on visibility (Sisler, 1996). This measure is directly related to two other
12 common visibility measures: visual range (measured in km) and light extinction (measured in
13 km^{-1}). Modeled changes in visibility are measured in terms of changes in light extinction, which
14 are then transformed into deciviews. A change of one deciview represents a change of
15 approximately 10 percent in the light extinction budget, “Awhich is a small but perceptible
16 scenic change under many circumstances.” (Sisler, 1996) A change of less than 10 percent in
17 the light extinction budget represents a measurable improvement in visibility, but may not be
18 perceptible to the eye in many cases.

19 The welfare effects of visibility effect changes may differ widely between urban residential
20 areas and recreational (e.g., federally designated Class I areas such as national parks) areas.
21 One of the most recent estimates of the economic value of changes in urban and residential
22 visibility can be derived from a peer-reviewed visibility study (McClelland et al., 1991; NAPAP,
23 1996; Chestnut and Dennis, 1997). Households’ willingness to pay (WTP) for visibility
24 improvements can be calculated from this study by dividing the value reported in McClelland
25 et al. by the corresponding hypothesized change in deciview, yielding an estimate of \$17 per unit
26 change in deciview.

27 Separate estimates are needed to account for the welfare changes associated with
28 improvements in visibility in national parks and other public lands (collectively known as “Class
29 I areas”). Chestnut and Dennis (1997) developed a method for estimating the value to the U.S.
30 public of visibility improvements in Class I visibility areas. The approach was based on the
31 results of a 1990 Cooperative Agreement project jointly funded by the EPA and the National

1 Park Service, “Preservation Values For Visibility Protection at the National Parks.” Based on
2 that contingent valuation study of visibility improvements, Chestnut calculates a household WTP
3 for visibility improvements in Class I-area National Parks, capturing both use and non-use
4 recreational values. This analysis also accounts for geographic variations in the willingness to
5 pay. The results indicate a WTP per deciview improvement of between \$5 and \$17 per
6 household.

8 **9.7.7 Effects on Ecosystems**

9 Excess nutrient loads, especially that of nitrogen, cause a variety of adverse consequences
10 to the health of estuarine and coastal waters. These effects include toxic and/or noxious algal
11 blooms such as brown and red tides, low (hypoxic) or zero (anoxic) concentrations of dissolved
12 oxygen in bottom waters, the loss of submerged aquatic vegetation due to the light-filtering effect
13 of thick algal mats, and fundamental shifts in phytoplankton community structure (Haire et al.,
14 1992). Direct Concentration-Response (C-R) functions relating deposited nitrogen and
15 reductions in estuarine benefits are not available. The preferred willingness-to-pay based
16 measure of benefits depends on the availability of these C-R functions and on estimates of the
17 value of environmental responses. Because neither appropriate C-R functions nor sufficient
18 information to estimate the marginal value of changes in water quality exist at present, a possible
19 alternative is to use an avoided cost approach instead of willingness-to-pay to estimate the
20 welfare effects of PM on estuarine ecosystems. The use of the avoided cost approach to establish
21 the value of a reduction in nitrogen deposition is problematic if there is not a direct link between
22 reductions in air deposited nitrogen and the abandonment of a costly regulatory program.
23 However, there are currently no readily available alternatives to this approach.¹

24 Avoided costs to surrounding communities of reduced nitrogen loadings have been
25 calculated for three case study estuaries (EPA, 1998).² The three case study estuaries are chosen
26 because they have agreed upon nitrogen reduction goals and the necessary nitrogen control cost
27 data. The values of atmospheric nitrogen reductions are determined on the basis of avoided costs

¹ Avoided cost is only a proxy for benefits, and should be viewed as inferior to willingness-to-pay based measures. Current research is underway to develop other approaches for valuing estuarine benefits, including contingent valuation and hedonic property studies. However, this research is still sparse, and does not contain sufficient information on the marginal willingness-to-pay for changes in concentrations of nitrogen (or changes in water quality or water resources as a result of changes in nitrogen concentrations).

² The case study estuaries are Albemarle-Pamlico Sounds, Chesapeake Bay, and Tampa Bay.

1 associated with agreed upon controls of nonpoint water pollution sources. Benefits are estimated
2 using a weighted-average, locally-based cost for nitrogen removal from water pollution (U.S.
3 EPA, 1998a). Valuation reflects water pollution control cost avoidance based on the weighted
4 average cost/pound of current non-point source water pollution controls for nitrogen in the three
5 case study estuaries. Taking the weighted cost/pound of these available controls assumes States
6 will combine low cost and high cost controls, which could inflate avoided cost estimates.

7 The fixed capital costs for non-point controls in the case study estuaries ranged from
8 \$0.75 to \$55.59 per pound for agricultural and other rural best management practices and from
9 \$42.98 to \$175.16 per pound for urban nonpoint source controls (stormwater controls, reservoir
10 management, onsite disposal system changes, onsite BMPs).³ Using these as a base, the total
11 fixed capital cost per pound (weighted on the basis of fractional relationship of nitrogen load
12 controlled for the estuary goal) for each of the case-study estuaries is calculated and applied in
13 the valuation of their avoided nitrogen load controlled. The weighted capital costs per pound for
14 the case-study estuaries are \$40.95 for Albemarle-Pamlico Sounds, \$26.79 for Chesapeake Bay,
15 and \$108.36 for Tampa Bay⁴.

16 If better ecological effects can be defined, EPA believes that progress can be made in
17 estimating WTP measures for ecosystem functions. These estimates would be superior to
18 avoided cost estimates in placing economic values on the welfare changes associated with PM
19 damage to ecosystem health. For example, if PM loadings can be linked to measurable and
20 definable changes in fish populations or definable indexes of biodiversity, then CVM studies can
21 be designed to elicit individuals' willingness to pay for changes in these effects. This is an
22 important area for further research and analysis, and will require close collaboration among air
23 quality modelers, natural scientists, and economists.

³ The figures in the original work have been updated to 1997 \$ using an all-good CPI index.

⁴ The value for Tampa Bay is not a true weighted cost per pound, but a midpoint of a range of \$71.89 to \$144.47 developed by Apogee Research for the control possibilities (mostly urban BMPs) in the Tampa Bay estuary.

9.8 SUMMARY

9.8.1 Particulate Matter Effects on Vegetation and Ecosystems

Human existence on this planet depends on nature and the life-support services ecosystems provide. Both ecosystem structure and function play an essential role in providing societal benefits. Society derives two types of benefits from the structural aspects of an ecosystem: (1) products with market value such as fish, minerals, forage, forest products, biomass fuels, natural fiber, and many pharmaceuticals, and the genetic resources of valuable species (e.g., plants for crops and timber and animals for domestication); and (2) the use and appreciation of ecosystem for recreation, aesthetic enjoyment, and study.

Ecosystem functions that maintain clean water, pure air, a green earth, and a balance of creatures, are functions that enable humans to survive. They are the dynamics of ecosystems. The benefits they impart include absorption and breakdown of pollutants, cycling of nutrients, binding of soil, degradation of organic waste, maintenance of a balance of gases in the air, regulation of radiation balance, climate, and the fixation of solar energy.

Concern has risen in recent years concerning the integrity of ecosystems because there are few ecosystems on the Earth today that are not influenced by humans. For this reason, the deposition of PM and its impact on vegetation and ecosystems is of great importance.

The PM whose effects on vegetation and ecosystems are considered in this chapter is not a single pollutant, but a heterogeneous mixture of particles of differing in size, origin, and chemical constituents. The effects of exposure to a given mass concentration of PM of particular size (measured as PM_{10} ; $PM_{2.5}$, etc.) may, depending on the particular mix of deposited particles, lead to widely differing phytotoxic responses. This variable has not been adequately characterized.

Atmospheric deposition of particles to ecosystems takes place via both wet and dry processes through the three major routes indicated below:

- (1) Precipitation scavenging in which particles are deposited in rain and snow
- (2) Fog, cloud-water, and mist interception
- (3) Dry deposition, a much slower, yet more continuous removal to surfaces.

Deposition of heavy metal particles to ecosystems occurs by wet and dry processes. Dry deposition is considered more effective for coarse particles of natural origin and elements such as

1 iron and manganese, whereas wet deposition generally is more effective for fine particles of
2 atmospheric origin and elements such as cadmium, chromium, lead, nickel, and vanadium. The
3 actual importance of wet versus dry deposition, however, is highly variable, depending on the
4 type of ecosystem, location and elevation.

5 Deposition of PM on above-ground plant parts can have either a physical and or chemical
6 impact, or both. Particles transferred from the atmosphere to plant surfaces may cause direct
7 effects if they: (1) reside on the leaf, twig or bark surface for an extended period; (2) be taken up
8 through the leaf surface: or (3) are removed from the plant via suspension to the atmosphere,
9 washing by rainfall, or litter-fall with subsequent transfer to the soil.

10 Chemical effects include excessive alkalinity or acidity. The effects of “inert” PM are
11 mainly physical, while the effects of toxic particles are both chemical and physical. The effects
12 of dust deposited on plant surfaces or on soil are more likely to be associated with their chemistry
13 than with the mass deposited particles and are usually of more importance than any physical
14 effects. The majority of the easily identifiable direct and indirect effects, other than climate,
15 occur in severely polluted areas around heavily industrialized point sources such as limestone
16 quarries, cement kilns, iron, lead, and various smelting factories. Studies of the direct effects of
17 chemical additions to foliage in particulate deposition have found little or no effects of PM on
18 foliar processes unless exposure levels were significantly higher than would typically be
19 experienced in the ambient environment.

20 Indirect effects of PM are usually the most significant because they can alter nutrient
21 cycling and inhibit plant uptake of nutrients. Indirect effects occur through the soil and result
22 from the deposition of heavy metals, nitrates, sulfates or acidic deposition and their impact on the
23 soil environment. The soil environment is, one of the most dynamic sites of biological
24 interaction in nature. Bacteria in the soil are essential components of the nitrogen and sulfur
25 cycles that make these elements available for plant uptake. Fungi form mycorrhizae,
26 a mutualistic, symbiotic relationship, that is integral in the uptake of mineral nutrients. Changes
27 in the soil environment that influence the role of the bacteria and fungi in nutrient cycling
28 determine plant and ecosystem response.

29 The major impact of PM on the soil environment occurs through the deposition of nitrates
30 and sulfates and the acidifying of the H⁺ ion associated with these compounds in wet and dry
31 deposition. Although the soils of most of the North American forest ecosystems are nitrogen

1 limited, there are forests that exhibit severe symptoms of nitrogen saturation. They include the
2 high-elevation spruce-fir ecosystems in the Appalachian Mountains, the eastern hardwood
3 watersheds at the Fernow Experimental Forest near Parsons, West Virginia, the mixed conifer
4 forest and chaparral watershed with high smog exposure in the Los Angeles Air Basin, the
5 high-elevation alpine watersheds in the Colorado Front Range and a deciduous forest in Ontario,
6 Canada.

7 Nitrogen saturation results when additions to soil background nitrogen (nitrogen loading)
8 exceed the capacity of plants and soil microorganisms to utilize and retain nitrogen.

9 An ecosystem no longer functions as a sink under these circumstances. Possible ecosystem
10 responses to nitrate saturation, as postulated by Aber and his coworkers, include (1) a permanent
11 increase in foliar nitrogen and reduced foliar phosphorus, and lignin due to the lower availability
12 of carbon, phosphorus, and water; (2) reduced productivity in conifer stands due to disruptions of
13 physiological function; (3) decreased root biomass and increased nitrification and nitrate
14 leaching; (4) reduced soil fertility, the results of increased cation leaching, increased nitrate and
15 aluminum concentrations in streams, and decreased water quality. Saturation implies that some
16 resource other than nitrogen is limiting biotic function. Water and phosphorus for plants and
17 carbon for microorganisms are the resources most likely to be the secondary limiting factors.
18 The appearance of nitrogen in soil solution is an early symptom of excess nitrogen. In the final
19 stage, disruption of forest structure becomes visible.

20 Changes in nitrogen supply can have a considerable impact on an ecosystem's nutrient
21 balance. Increases in nitrogen soil nitrogen play a selective role. Plant succession patterns and
22 biodiversity are significantly affected by chronic nitrogen additions in some ecosystems.
23 Long-term nitrogen fertilization studies in both New England and Europe suggest that some
24 forests receiving chronic inputs of nitrogen may decline in productivity and experience greater
25 mortality. Long-term fertilization experiments at Mount Ascutney, Vermont, suggest that
26 declining coniferous forest stands with slow nitrogen cycling may be replaced by deciduous
27 fast-growing forests that cycle nitrogen rapidly. Excess nitrogen inputs to unmanaged heathlands
28 in the Netherlands has resulted in nitrophilous grass species replacing slower growing heath
29 species. Over the past several decades the composition of plants in the forest herb layers had
30 been shifting toward species commonly found on nitrogen-rich areas. It also was observed that
31 the fruiting bodies of mycorrhizal fungi had decreased in number.

1 Acidic deposition has played a major role in recent soil acidification in some areas of
2 Europe, Sweden and eastern North America. Soil acidification and its effects result from the
3 deposition of nitrates, sulfates and the associated H^+ . A major concern is that soil acidity will
4 lead to nutrient deficiency. Growth of tree species can be affected when high aluminum to
5 nutrient ratios limit uptake of calcium and magnesium and create a nutrient deficiency. Calcium
6 is essential in the formation of wood and the maintenance of cells, the primary plant tissues
7 necessary for tree growth. Calcium must be dissolved in the soil water to be taken up by plants.
8 Acid deposition can increase the aluminum concentrations in soil water by lowering the pH in
9 aluminum-rich soils through dissolution and ion-exchange processes. Aluminum in soil can be
10 taken up by roots more readily than calcium because of its greater affinity for negatively charged
11 surfaces. Tree species can be adversely affected if high Ca/Al ratios impair Ca and Mg uptake.

13 **9.8.2 Particulate Matter-Related Effects on Materials**

14 Building materials (metals, stones and cements, and paints) undergo a natural weathering
15 process from exposure to environmental elements (wind, moisture, sun, temperature fluctuations,
16 etc.). Metals form a protective film that protects against environmentally induced corrosion. The
17 natural process of metal corrosion from exposure to natural environmental elements is enhanced
18 by exposure to anthropogenic pollutants, in particular SO_2 , rendering the protective film less
19 effective.

20 Dry deposition of SO_2 enhances the effects of environmental elements on calcereous stones
21 (limestone, marble, and carbonated cemented) by converting calcium carbonate (calcite) to
22 calcium sulphate dihydrate (gypsum). The rate of deterioration is determined by the SO_2
23 concentration, the stone's permeability and moisture content, and the deposition rate; however,
24 the extent of the damage to stones produced by the pollutant species apart from the natural
25 weathering processes is uncertain. Sulfur dioxide has also been found to limit the life expectancy
26 of paints by causing discoloration, loss of gloss, and loss of thickness of the paint film layer.

27 A significant detrimental effect of particle pollution is the soiling of painted surfaces and
28 other building materials. Soiling changes the reflectance of a material from opaque and reduces
29 the transmission of light through transparent materials. Soiling is a degradation process that
30 requires remediation by cleaning or washing, and depending on the soiled surface, repainting.
31 Available data on pollution exposure indicates that particles can result in increased cleaning

1 frequency of the exposed surface, and may reduce the life usefulness of the material soiled.
2 Attempts have been made to quantify the pollutants exposure levels at which materials damage
3 and soiling have been perceived. However, to date, insufficient data are available to advance our
4 knowledge regarding perception thresholds with respect to pollutant concentration, particle size,
5 and chemical composition.

7 **9.8.3 Particulate Matter-Related Effects on Visibility**

8 Visibility is defined as the degree to which the atmosphere is transparent to visible light and
9 the clarity and color fidelity of the atmosphere. Visual range is the farthest distance a black
10 object can be distinguished against the horizontal sky. Visibility impairment is any humanly
11 perceptible change in visibility. For regulatory purposes, visibility impairment, characterized by
12 light extinction, visual range, contrast, coloration, is classified into two principal forms:
13 “reasonably attributable” impairment, attributable to a single source/small group of sources, and
14 regional haze, any perceivable change in visibility caused by a combination of many sources over
15 a wide geographical area.

16 Visibility is measured by human observation, light scattering by particles, the light
17 extinction-coefficient and parameters related to the light-extinction coefficient (visual range and
18 deciview scale), the light scattering coefficient, and fine particulate matter concentrations. The
19 air quality within a sight path will affect the illumination of the sight path by scattering or
20 absorbing solar radiation before it reaches the Earth’s surface. The rate of energy loss with
21 distance from a beam of light is the light extinction coefficient. The light extinction coefficient
22 is the sum of the coefficients for light absorption by gases (σ_{ag}), light scattering by gases (σ_{sg}),
23 light absorption by particles (σ_{ap}), and light scattering by particles (σ_{sp}). Atmospheric particles
24 are frequently divided into coarse and fine particles. The corresponding coefficients for light
25 scattering and absorption by fine and coarse particles are σ_{sfp} and σ_{afp} and σ_{scp} and σ_{acp} ,
26 respectively. Visibility within a sight path longer than approximately 100 km (60 mi) is affected
27 by change in the optical properties of the atmosphere over the length of the sight path.

28 Visibility impairment is associated with the air pollutant properties, including size
29 distributions (i.e., fine particles in the 0.1 to 1.0 μm size range), aerosol chemical composition,
30 and relative humidity. With increasing relative humidity, the amount of moisture available for
31 absorption by particles increases causing the particles to increase in both size and volume.

1 As the particles increase in size and volume, the light scattering potential of the particles also
2 increases. Visibility impairment is greatest in the eastern United States and southern California.
3 In the eastern United States, visibility impairment is primarily caused by light scattering by
4 sulfate aerosols, and to a lesser extent by nitrate particles and organic aerosols, carbon soot, and
5 crustal dust. Haziness in the southeastern United States, caused by increased atmospheric
6 sulfate, has increased by approximately 80% since the 1950s and is greatest in the summer
7 months, followed by the spring and fall, and winter. Light scattering by nitrate aerosols in the
8 major cause of visibility impairment in southern California. Nitrates contribute about 40% to the
9 total light extinction in southern California and accounts for 10 to 20% of the total extinction in
10 other areas of the United States.

11 Organics are the second largest contributors to light extinction in most areas in the United
12 States. Organic carbon is the greatest cause of light extinction in the Pacific Northwest, Oregon,
13 Idaho, and Montana, accounting for 40 to 45% of the total extinction. Organic carbon
14 contributes between 15 to 20% to the total extinction in most of the western United States and
15 20 to 30% in the remaining areas of the United States.

16 Coarse mass and soil, primarily considered natural extinction, is responsible for some of
17 the visibility impairment in northern California and Nevada, including Oregon, southern Idaho
18 and western Wyoming. Dust transported from southern California and the subtropics has been
19 associated with regional haze in the Grand Canyon and other class I areas in the southwestern
20 United States.

21 22 **9.8.4 Effects of Particulate Matter on Global Climate and the Transmission** 23 **of Solar Ultraviolet Radiation**

24 The physical processes (i.e., scattering and absorption) responsible for the effects of
25 particles on the transmission of solar ultraviolet and visible radiation are the same as those
26 responsible for visibility degradation. The scattering of solar radiation back to space and the
27 absorption of solar radiation determine the effects of an aerosol layer on solar radiation. The
28 transmission of solar UV-B radiation is strongly affected by atmospheric particles. Measured
29 attenuations of UV-B under hazy conditions range up to 37% of the incoming solar radiation.
30 Measurements relating variations in PM mass directly to UV-B transmission are lacking.
31 Particles can also affect the rates of photochemical reactions occurring in the atmosphere.

1 Depending on the amount of absorbing substances in the particles, photolysis rates can either be
2 increased or decreased.

3 In addition to direct climate effects through the scattering and absorption of solar radiation,
4 particles also exert indirect effects on climate by serving as cloud condensation nuclei, thus
5 affecting the abundance and vertical distribution of clouds. The direct and indirect effects of
6 particles have significantly offset the warming effects due to the buildup of greenhouse gases
7 since the onset of the Industrial Revolution on a globally averaged basis. However, since the
8 lifetime of particles is much shorter than that required for complete mixing within the Northern
9 Hemisphere, the climate effects of particles are felt much less homogeneously than are the effects
10 of long-lived greenhouse gases.

11 **9.8.5 Economic Impact of Particulate Matter**

12 The chapter outlined the major categories of non-health related economic costs associated
13 PM pollution. Once endpoints reflecting physical and biological outcomes have been defined,
14 several economic methods may be used to estimate economic damages. Some of the results of
15 existing research were summarized for the major categories of endpoints. The measured
16 economic costs of PM are particularly significant for reduced visibility, both in residential areas
17 and in recreational areas with special value (e.g. the National Parks). It is possible that the costs
18 imposed on ecosystems are significant as well. Making progress on measuring these ecosystem
19 costs depends on improvements in linking environmental endpoints to PM levels, and then on
20 using these endpoints as a basis for improved techniques to elicit willingness to pay for changes
21 in ecosystem quality.
22
23
24
25

REFERENCES

- 1
2
3 Abdullah, U. M.; Iqbal, M. Z. (1991) Response of automobile, stone and cement particulate matters on stomatal
4 clogging of plants. *Geobios (Jodhpur, India)* 18: 196-202.
- 5 Aber, J. D.; Nadelhoffer, K. J.; Steudler, P.; Melillo, J. M. (1989) Nitrogen saturation in northern forest ecosystems:
6 excess nitrogen from fossil fuel combustion may stress the biosphere. *Bioscience* 39: 378-386.
- 7 Aber, J.; McDowell, W.; Nadelhoffer, K.; Magill, A.; Berntson, G.; Kamakea, M.; McNulty, S.; Currie, W.; Rustad,
8 L.; Fernandez, I. (1998) Nitrogen saturation in temperate forest ecosystems. *BioScience* 48: 921-934.
- 9 Abt Associates, Inc. (1998) Air quality estimation for the NO_x SIP call RIA. Research Triangle Park, NC: U.S.
10 Environmental Protection Agency, Office of Air Quality Planning and Standards; contract no. 68-D-98-001;
11 EPA air docket A-96-56, document no. VI-B-09-(gggg).
- 12 Acres International Limited. (1991) The effects and social costs of fossil-fired generating station emissions on
13 structural materials (update). Niagara Falls, Ontario, Canada: Ontario Hydro.
- 14 Adams, D. M.; Haynes, R. W. (1996) The 1993 timber assessment market model: structure, projections and policy
15 simulations. Washington, DC: U.S. Department of Agriculture, Forest Service; technical report no.
16 PNW-GTR-368; November.
- 17 Adams, K. M.; Kavis, L. I., Jr.; Japar, S. M.; Pierson, W. R. (1989) Real-time, *in situ* measurements of atmospheric
18 optical absorption in the visible via photoacoustic spectroscopy - II. validation for atmospheric elemental
19 carbon aerosol. *Atmos. Environ.* 23: 693-700.
- 20 Alexander (1977).
- 21 Allen, M. F. (1991) The ecology of mycorrhizae. New York, NY: Cambridge University Press.
- 22 Altshuller, A. P.; Linthurst, R. A., eds. (1984) Acidic deposition phenomenon and its effects: critical assessment
23 review papers; volume I, atmospheric sciences; volume II, effects sciences. Washington, DC: U.S.
24 Environmental Protection Agency, Office of Research and Development; EPA report nos.
25 EPA/600/8-83/016aF-bF. Available from: NTIS, Springfield, VA; PB85-100030 and PB85-100048.
- 26 Antonovics, J.; Bradshaw, A. D.; Turner, R. G. (1971) Heavy metal tolerance in plants. In: Cragg, J. B., ed.
27 Advances in ecological research. Volume 7. London, United Kingdom: Academic Press; pp. 1-85.
- 28 April, R.; Newton, R. (1992) Mineralogy and mineral weathering. In: Johnson, D. W.; Lindberg, S. E., eds.
29 Atmospheric deposition and forest nutrient cycling: a synthesis of the integrated forest study. New York, NY:
30 Springer-Verlag; pp. 378-425. (Billings, W. D.; Golley, F.; Lange, O. L.; Olson, J. S.; Remmert, H., eds.
31 Ecological studies: analysis and synthesis: v. 91).
- 32 Askey, A.; Lyon, S. B.; Thompson, G. E.; Johnson, J. B.; Wood, G. C.; Sage, P. W.; Cooke, M. J. (1993) The effect
33 of fly-ash particulates on the atmospheric corrosion of zinc and mild steel. *Corros. Sci.* 34: 1055-1081.
- 34 Ausset, P.; Bannery, F.; Del Monte, M.; Lefevre, R. A. (1998) Recording of pre-industrial atmospheric environment
35 by ancient crusts on stone monuments. *Atmos. Environ.* 32: 2859-2863.
- 36 Babich, H.; Stotzky, G. (1978) Effects of cadmium on the biota: influence of environmental factors. In: Perlman, D.,
37 ed. *Advances in applied microbiology*, volume 23. New York, NY: Academic Press; pp. 55-117.
- 38 Baedecker, P. A.; Edney, E. O.; Moran, P. J.; Simpson, T. C.; Williams, R. S. (1991) Effects of acidic deposition on
39 materials. In: Irving, P. M., ed. *Acidic deposition: state of science and technology*, volume III: terrestrial,
40 materials, health and visibility effects. Washington, DC: The U.S. National Acid Precipitation Assessment
41 Program. (State of science and technology report no. 19).
- 42 Baedecker, P. A.; Reddy, M. M.; Reimann, K. J.; Sciammarella, C. A. (1992) Effects of acidic deposition on the
43 erosion of carbonate stone—experimental results from the U.S. National Acid Precipitation Assessment
44 Program (NAPAP). *Atmos. Environ. Part B* 26: 147-158.
- 45 Banzhaf (1998).
- 46 Barton, K. (1958) The influence of dust on atmospheric corrosion of metals. *Werkst. Korros.* 8/9: 547-549.
- 47 Bieffer, G. J. (1981) Atmospheric corrosion of steel in the Canadian Arctic. *Mater. Perform.* 20: 16-19.
- 48 Billings, W. D. (1978) *Plants and the ecosystem*. 3rd ed. Belmont, CA: Wadsworth Publishing Company, Inc.; pp.
49 1-62, 83-108.
- 50 Binkley, D.; Valentine, D.; Wells, C.; Valentine, U. (1989) An empirical analysis of the factors contributing to
51 20-year decrease in soil pH in an old-field plantation of loblolly pine. *Biogeochemistry* 8: 39-54.
- 52 Blackburn et al. (1972).
- 53

- 1 Blandford, J. C. (1994) Transmissometer data reduction and validation (IMPROVE protocol). Fort Collins, CO: Air
2 Resource Specialists, Inc.; technical instruction no. 4400-5000.
- 3 Blaschke, H. (1990) Mycorrhizal populations and fine root development on Norway spruce exposed to controlled
4 doses of gaseous pollutants and simulated acidic rain treatments. *Environ. Pollut.* 68: 409-418.
- 5 Bondietti, E. A.; McLaughlin, S. B. (1992) Evidence of historical influences of acidic deposition on wood and soil
6 chemistry. In: Johnson, D. W.; Lindberg, S. E., eds. *Atmospheric deposition and forest nutrient cycling: a
7 synthesis of the integrated forest study.* New York, NY: Springer-Verlag: pp. 358-377. (Billings, W. D.;
8 Golley, F.; Lange, O. L.; Olson, J. S.; Remmert, H., eds. *Ecological studies analysis and synthesis: v. 91*).
- 9 Bradley, R.; Burt, A. J.; Read, D. J. (1981) Mycorrhizal infection and resistance to heavy metal toxicity in *Calluna
10 vulgaris*. *Nature (London)* 292: 335-337.
- 11 Brandt, C. J.; Rhoades, R. W. (1972) Effects of limestone dust accumulation on composition of a forest community.
12 *Environ. Pollut.* 3: 217-225.
- 13 Brandt, C. J.; Rhoades, R. W. (1973) Effects of limestone dust accumulation on lateral growth of forest trees.
14 *Environ. Pollut.* 4: 207-213.
- 15 Bruel and Crutzen (1988).
- 16 Bruhn, J. N. (1980) Effects of oxidant air pollution on Ponderosa and Jeffrey pine foliage decomposition
17 [dissertation]. Berkeley, CA: University of California. DAI v. 42-07B, p. 2626, 287pp.
- 18 Brunet et al. (1998).
- 19 Butlin, R. N.; Coote, A. T.; Devenish, M.; Hughes, I. S. C.; Hutchens, C. M.; Irwin, J. G.; Lloyd, G. O.; Massey, S.
20 W.; Webb, A. H.; Yates, T. J. S. (1992a) Preliminary results from the analysis of metal samples from the
21 National Materials Exposure Programme (NMEP). *Atmos. Environ. Part B* 26: 199-206.
- 22 Butlin, R. N.; Coote, A. T.; Devenish, M.; Hughes, I. S. C.; Hutchens, C. M.; Irwin, J. G.; Lloyd, G. O.; Massey, S.
23 W.; Webb, A. H.; Yates, T. J. S. (1992b) Preliminary results from the analysis of stone tablets from the
24 National Materials Exposure Programme (NMEP). *Atmos. Environ. Part B* 26: 189-198.
- 25 Cahill, T. A.; Eldred, R. A.; Wakabayashi, P. H. (1996) Trends in fine particle concentrations at Great Smoky
26 Mountains National Park. For presentation at: Annual meeting of the Air & Waste Management Association;
27 June; Nashville, TN. Pittsburgh, PA: Air & Waste Management Association; submitted paper no.
28 96-MP1A.05.
- 29 Campbell, G. G.; Schurr, G. G.; Slawikowski, D. E.; Spence, J. W. (1974) Assessing air pollution damage to
30 coatings. *J. Paint Technol.* 46: 59-71.
- 31 Camuffo, D. (1995) Physical weathering of stones. In: Saiz-Jimenez, C., ed. *The deterioration of monuments:
32 proceedings of the 2nd international symposium on biodeterioration and biodegradation; January 1994;
33 Sevilla, Spain.* *Sci. Total Environ.* 167: 1-14.
- 34 Cape, J. N. (1993) Direct damage to vegetation caused by acid rain and polluted cloud: definition of critical levels
35 for forest trees. *Environ. Pollut.* 82: 167-180.
- 36 Ceccotti, S. P.; Messick, D. L. (1997) A global review of crop requirements, supply, and environmental impact on
37 nutrient sulphur balance. In: Cram, W. J.; De Kok, L. J.; Stulen, I.; Brunold, C.; Rennenberg, H., eds.
38 *Sulphur metabolism in higher plants.* Leiden, The Netherlands: Backhuys Publishers; pp. 155-163.
- 39 Chapin, F. S., III. (1991) Integrated responses of plants to stress: a centralized system of physiological responses.
40 *Bioscience* 41: 29-36.
- 41 Chapin et al. (1987).
- 42 Chapin, F. S., III; Sala, O. E.; Burke, I. C.; Grime, J. P.; Hooper, D. U.; Lauenroth, W. K.; Lombard, A.; Mooney,
43 H. A.; Mosier, A. R.; Naeem, S.; Pacala, S. W.; Roy, J.; Steffen, W. L.; Tilman, D. (1998) Ecosystem
44 consequences of changing biodiversity. *BioScience* 48: 45-52.
- 45 Charlson et al. (1987).
- 46 Charlson et al. (1992).
- 47 Chestnut, L. G. (1997) Draft memorandum: methodology for estimating values for changes in visibility at national
48 parks. EPA air docket A-96-56, document no. VI-B-09-(ooo).
- 49 Chestnut and Dennis (1997)
- 50 Chevone, B. I.; Herzfeld, D. E.; Krupa, S. V.; Chappelka, A. H. (1986) Direct effects of atmospheric sulfate
51 deposition on vegetation. *J. Air Pollut. Control Assoc.* 36: 813-815.
- 52 Clarkson, D. T.; Sanderson, J. (1971) Inhibition of the uptake and long-distance transport of calcium by aluminium
53 and other polyvalent cations. *J. Exp. Bot.* 22: 837-851.
- 54 Clevenger et al. (1991).
- 55

- 1 Cole, D. W.; Johnson, D. W. (1977) Atmospheric sulfate additions and cation leaching in a Douglas fir ecosystem.
2 Water Resour. Res. 13: 313-317.
- 3 Cooke, R. U.; Gibbs, G. B. (1994) Crumbling heritage? Studies of stone weathering in polluted atmospheres.
4 Atmos. Environ. 28: 1355-1356.
- 5 Costanza, R.; d'Arge, R.; De Groot, R.; Farber, S.; Grasso, M.; Hannon, B.; Limburg, K.; Naeem, S.; O'Neill, R. V.;
6 Paruelo, J.; Raskin, R. G.; Sutton, P.; Van Den Belt, M. (1997) The value of the world's ecosystem services
7 and natural capital. Nature (London) 387: 253-259.
- 8 Courant and Porter (1981).
- 9 Cowling, J. E.; Roberts, M. E. (1954) Paints, varnishes, enamels, and lacquers. In: Greathouse, G. A.; Wessel, C. J.,
10 eds. Deterioration of materials: causes and preventive techniques. New York, NY: Reinhold Publishing
11 Corporation; pp. 596-645.
- 12 Cramer, S. D.; McDonald, L. G.; Bhagia, G.; Flinn, D. R.; Linstrom, P. J.; Carter, J. P. (1989) Effects of acid
13 deposition on the atmospheric corrosion of structural metals. Research Triangle Park, NC: U.S.
14 Environmental Protection Agency; internal report.
- 15 Creighton, P. J.; Lioy, P. J.; Haynie, F. H.; Lemmons, T. J.; Miller, J. L.; Gerhart, J. (1990) Soiling by atmospheric
16 aerosols in an urban industrial area. J. Air Waste Manage. Assoc. 40: 1285-1289.
- 17 Cronan and Grigal (1995).
- 18 Cummings, R. G.; Brookshire, D. S.; Schulze, W. D., eds. (1986) Valuing environmental goods: an assessment of
19 the contingent valuation method. Totowa, NJ: Rowman and Allanheld.
- 20 Daily, G. C. (1997) Introduction: what are ecosystem services? In: Daily, G. C., ed. Nature's services: societal
21 dependence on natural ecosystems. Washington, DC: Island Press; pp. 1-10.
- 22 Daily, G. C.; Ehrlich, P. R. (1999) Managing Earth's ecosystems: an interdisciplinary challenge. Ecosystems 2:
23 277-280.
- 24 Darley, E. F. (1966) Studies on the effect of cement-kiln dust on vegetation. J. Air Pollut. Control Assoc. 16:
25 145-150.
- 26 Dattner, S. L. (1995) Urban visibility in the El Paso del Norte airshed. Presented at: 88th annual meeting &
27 exhibition of the Air & Waste Management Association, volume 3B. Basic sciences: air quality and noise;
28 June; San Antonio, TX. Pittsburgh, PA: Air & Waste Management Association; paper no. 95-WA76.02.
- 29 Davis, G. D.; Shaw, B. A.; Arah, C. O.; Fritz, T. L.; Moshier, W. C.; Simpson, T. C.; Moran, P. J.; Zankel, K. L.
30 (1990) Effects of SO₂ deposition on painted steel surfaces. Surf. Interface Anal. 15: 107-112.
- 31 Day, D.; Malm, W. C.; Kreidenweis, S. M. (1996) Aerosol light scattering measurements as a function of relative
32 humidity at Great Smoky Mountains National Park. Presented at: 89th annual meeting & exhibition of the Air
33 & Waste Management Association; June; Nashville, TN. Pittsburgh, PA: Air & Waste Management
34 Association; paper no. 96-TA1B.06.
- 35 Day et al. (1999).
- 36 Del Monte, M.; Vittori, O. (1985) Air pollution and stone decay: the case of Venice. Endeavour 9: 117-122.
- 37 Desvousges, W. H.; Johnson, F. R.; Banzha, H. S. (1998) Environmental policy analysis with limited information:
38 principles and applications of the transfer method. Northampton, MA: Edward Elgar Publishing.
- 39 Diakumaku, E.; Gorbushina, A. A.; Krumbein, W. E.; Panina, L.; Soukharjevski, S. (1995) Black fungi in marble
40 and limestones—an aesthetical, chemical and physical problem for the conservation of monuments. In:
41 Saiz-Jimenez, C., ed. The deterioration of monuments: proceedings of the 2nd international symposium on
42 biodeterioration and biodegradation; January 1994; Sevilla, Spain. Sci. Total Environ. 167: 295-304.
- 43 Dickerson, R. R.; Kondragunta, S.; Stenchikov, G.; Civerolo, K. L.; Doddridge, B. G.; Holben, B. N. (1997) The
44 impact of aerosols on solar ultraviolet radiation and photochemical smog. Science (Washington, DC) 278:
45 827-830.
- 46 Dolske, D. A. (1995) Deposition of atmospheric pollutants to monuments, statues, and buildings. Sci. Total
47 Environ. 167: 15-31.
- 48 Dreisinger, B. R.; McGovern, P. C. (1970) Monitoring atmospheric sulphur dioxide and correlating its effects on
49 crops and forests in the Sudbury area. In: Linzon, S. N., ed. Impact of air pollution on vegetation conference;
50 April; Toronto, ON, Canada. Pittsburgh, PA: Air Pollution Control Association.
- 51 Driscoll, C. T.; Wyskowski, B. J.; DeStaffan, P.; Newton, R. M. (1989) Chemistry and transfer of aluminum in a
52 forested watershed in the Adirondack region of New York, USA. In: Lewis, T. E., ed. Environmental
53 chemistry and toxicology of aluminum. Chelsea, MI: Lewis Publishers, Inc.; pp. 83-105.
- 54

- 1 Edney, E. O. (1989) Paint coatings: controlled field and chamber experiments. Research Triangle Park, NC: U.S.
2 Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory; report no.
3 EPA/600/3-89/032. Available from: NTIS, Springfield, VA; PB89-189849.
- 4 Edney, E. O.; Cheek, S. F.; Stiles, D. C.; Corse, E. W.; Wheeler, M. L.; Spence, J. W.; Haynie, F. H.; Wilson, W.
5 E., Jr. (1988) Effects of acid deposition on paints and metals: results of a controlled field study. *Atmos.*
6 *Environ.* 22: 2263-2274.
- 7 Edney, E. O.; Cheek, S. F.; Corse, E. W.; Spence, J. W.; Haynie, F. H. (1989) Atmospheric weathering caused by
8 dry deposition of acidic compounds. *J. Environ. Sci. Health Part A* 24: 439-457.
- 9 Eldering, A.; Cass, G. R. (1996) Source-oriented model for air pollutant effects on visibility. *J. Geophys. Res.*
10 [*Atmos.*]: 101: 19,343-19,369.
- 11 Eldering, A.; Larson, S. M.; Hall, J. R.; Hussey, K. J.; Cass, G. R. (1993) Development of an improved image
12 processing based visibility model. *Environ. Sci. Technol.* 27: 626-635.
- 13 Eldering, A.; Cass, G. R.; Moon, K. C. (1994) An air monitoring network using continuous particle size distribution
14 monitors: connecting pollutant properties to visibility via Mie scattering calculations. *Atmos. Environ.* 28:
15 2733-2749.
- 16 Eldering, A.; Hall, J. R.; Hussey, K. J.; Cass, G. R. (1996) Visibility model based on satellite-generated landscape
17 data. *Environ. Sci. Tech.* 30: 361-370.
- 18 Eldred et al. (1993).
- 19 Eldred, R. A.; Cahill, T. A. (1994) Trends in elemental concentrations of fine particles at remote sites in the United
20 States of America. *Atmos. Environ.* 28: 1009-1019.
- 21 Eldred, R. A.; Cahill, T. A.; Flocchini, R. G. (1997) Composition of PM_{2.5} and PM₁₀ aerosols in the IMPROVE
22 network. In: Special issue on aerosols and atmospheric optics—part I, [published papers from the
23 international specialty conference; September 1994; Snowbird, UT]. *J. Air Waste Manage. Assoc.* 47:
24 194-203.
- 25 Ellenberg (1987).
- 26 Eller, B. M. (1977) Road dust induced increase of leaf temperature. *Environ. Pollut.* 13: 99-107.
- 27 Eriksson, P.; Johansson, L.-G.; Strandberg, H. (1993) Initial stages of copper corrosion in humid air containing SO₂
28 and NO₂. *J. Electrochem. Soc.* 140: 53-59.
- 29 Estupinan et al. (1996).
- 30 Evans and Pitchford (1991).
- 31 Falkengren-Grerup, U. (1987) Long-term changes in pH of forest soils in southern Sweden. *Environ. Pollut.* 43:
32 79-90.
- 33 Falkengren-Grerup (1998).
- 34 Farmer, A. M. (1993) The effects of dust on vegetation—a review. *Environ. Pollut.* 79: 63-75.
- 35 Fenn, M. E.; Poth, M. A.; Aber, J. D.; Baron, J. S.; Bormann, B. T.; Johnson, D. W.; Lemly, A. D.; McNulty, S. G.;
36 Ryan, D. F.; Stottleyer, R. (1998) Nitrogen excess in North American ecosystems: predisposing factors,
37 ecosystem responses, and management strategies. *Ecol. Appl.* 8: 706-733.
- 38 Fink, F. W.; Buttner, F. H.; Boyd, W. K. (1971) Final report on technical-economic evaluation of air-pollution
39 corrosion costs on metals in the U.S. Columbus, OH: Battelle Memorial Institute, Columbus Laboratories;
40 EPA contract no. CPA 70-86; EPA report no. APTD-0654. Available from: NTIS, Springfield, VA;
41 PB-198-453.
- 42 Fochtman, E. G.; Langer, G. (1957) Automobile paint damaged by airborne iron particles. *J. Air Pollut. Control*
43 *Assoc.* 6: 243-247.
- 44 Foster, J. R. (1991) Effects of organic chemicals in the atmosphere on terrestrial plants. In: Moser, T. J.; Barker, J.
45 R.; Tingey, D. T., eds. *Ecological exposure and effects of airborne toxic chemicals: an overview*. Corvallis,
46 OR: U.S. Environmental Protection Agency, Environmental Research Laboratory; pp. 60-89; EPA report no.
47 EPA-600/3-91-001. Available from: NTIS, Springfield, VA; PB91-148460.
- 48 Fox, D.; McDonald, K.; Zannetti, P.; Nejedley, Z. (1997) Impact of north-western emission changes on visibility in
49 the Rocky Mountain parks. Presented at: Air & Waste Management Association's 90th annual meeting &
50 exhibition; June; Toronto, Ontario, Canada. Pittsburgh, PA: Air & Waste Management Association.
- 51 Freedman, B.; Hutchinson, T. C. (1981) Sources of metal and elemental contamination of terrestrial environments.
52 In: Lepp, N. W., ed. *Effect of heavy metal pollution on plants*. Volume 2: metals in the environment. London,
53 United Kingdom: Applied Science Publishers; pp. 35-94.
- 54

- 1 Freeman, A. M., III. (1993) The measurement of environmental and resource values. Washington, DC: Resources
2 for the future.
- 3 Freudenburg, W. R.; Alario, M. (1999) What ecologists can learn from nuclear scientists. *Ecosystems* 2: 286-291.
- 4 Gabruk, R. S.; Sykes, R. I.; Seigneur, C.; Pai, P.; Gillespie, P.; Bergstrom, R. W.; Saxena, P. (1999) Evaluation of
5 the reactive and optics model of emissions (ROME). *Atmos. Environ.* 33: 383-399.
- 6 Gaggi et al. (1985).
- 7 Garner, J. H. B. (1991) Ozone exposure and nitrogen loading in the forests of eastern North America. In: Berglund,
8 R. L.; Lawson, D. R.; McKee, D. J., eds. *Tropospheric ozone and the environment: papers from an
9 international conference; March 1990; Los Angeles, CA. Pittsburgh, PA: Air & Waste Management
10 Association; pp. 289-310. (A&WMA transactions series no. TR-19).*
- 11 Garner, J. H. B. (1994) Nitrogen oxides, plant metabolism, and forest ecosystem response. In: Alscher, R. G.;
12 Wellburn, A. R., eds. *Plant responses to the gaseous environment: molecular, metabolic and physiological
13 aspects, [3rd international symposium on air pollutants and plant metabolism]; June 1992; Blacksburg, VA.
14 London, United Kingdom: Chapman & Hall; pp. 301-314.*
- 15 Gildon, A.; Tinker, P. B. (1983) Interactions of vesicular-arbuscular mycorrhizal infection and heavy metals in
16 plants: I. the effects of heavy metals on the development of vesicular-arbuscular mycorrhizas. *New Phytol.*
17 95: 247-261.
- 18 Goodwin, J. E.; Sage, W.; Tilly, G. P. (1969) Study of erosion by solid particles. *Proc. Inst. Mech. Eng.* 184:
19 279-292.
- 20 Graedel, T. E.; Nassau, K.; Franey, J. P. (1987) Copper patinas formed in the atmosphere—I. introduction. *Corros.*
21 *Sci.* 27: 639-657.
- 22 Grand Canyon Visibility Transport Commission (1996).
- 23 Gray, H. A.; Cass, G. R. (1998) Source contributions to atmospheric fine carbon particle concentrations. *Atmos.*
24 *Environ.* 32: 3805-3825.
- 25 Gregory, K.; Dirk, S.; Gamble, J. (1996) A critique of estimates of the cost of damage to building materials due to
26 atmospheric attack. *Energy Policy* 24: 641-649.
- 27 Grosclaude, P.; Sogue, N. C. (1994) Valuing damage to historic buildings using a contingent market: a case study of
28 road traffic externalities. *J. Environ. Planning Manage.* 37: 279-287.
- 29 Guderian, R. (1977) Accumulation of pollutants in plant organs. In: Guderian, R., ed. *Air pollution: phytotoxicity of
30 acidic gases and its significance in air pollution control. New York, NY: Springer-Verlag; pp. 66-74.*
31 (Ecological studies: v. 22).
- 32 Guderian, R. (1986) Terrestrial ecosystems: particulate deposition. In: Legge, A. H.; Krupa, S. V., eds. *Air
33 pollutants and their effects on the terrestrial ecosystem. New York, NY: John Wiley & Sons; pp. 339-363.*
34 (Advances in environmental science and technology: v. 18).
- 35 Guderian, R.; Tingey, D. T.; Rabe, R. (1985) Effects of photochemical oxidants on plants. In: Guderian, R., ed. *Air
36 pollution by photochemical oxidants: formation, transport, control, and effects on plants. Berlin, Federal
37 Republic of Germany: Springer-Verlag; pp. 127-333. (Billings, W. D.; Golley, F.; Lange, O. L.; Olson, J. S.;
38 Remmert, H., eds. Ecological studies: analysis and synthesis, v. 52).*
- 39 Guthrie et al. (1999).
- 40 Haire, M. S.; Panday, N. N.; Domotor, D. K.; Flora, D. G. (1992) Chesapeake Bay water quality indices. In:
41 McKenzie, D. H.; Hyatt, D. E.; McDonald, V. J., eds. *Ecological indicators, volume II. New York, NY:
42 Elsevier Applied Science.*
- 43 Hamilton, R. S.; Revitt, D. M.; Vincent, K. J.; Butlin, R. N. (1995) Sulphur and nitrogen particulate pollutant
44 deposition on to building surfaces. In: Saiz-Jimenez, C., ed. *The deterioration of monuments: proceedings of
45 the 2nd international symposium on biodeterioration and biodegradation; January 1994; Sevilla, Spain. Sci.
46 Total Environ.* 167: 57-66.
- 47 Han et al. (1994).
- 48 Haneef, S. J.; Johnson, J. B.; Thompson, G. E.; Wood, G. C. (1993) Simulation of the degradation of limestones
49 and dolomitic sandstone under dry deposition conditions. In: *Corrosion control for low-cost reliability:
50 proceedings [of the] 12th international corrosion congress. Volume 2: process industries plant operation.
51 Houston, TX: National Association of Corrosion Engineers; pp. 700-710.*
- 52 Hanley, N.; Spash, C. L. (1993) Cost-benefit analysis and the environment. Hants, England, United Kingdom:
53 Edward Elgar.
- 54

- 1 Harford, J. D. (1984) Averting behavior and the benefits of reduced soiling. *J. Environ. Econ. Manage.* 11:
2 296-302.
- 3 Harwell, M. A.; Myers, V.; Young, T.; Bartuska, A.; Gassman, N.; Gentile, J. H.; Harwell, C. C.; Appelbaum, S.;
4 Barko, J.; Causey, B.; Johnson, C.; McLean, A.; Smola, R.; Templet, P.; Tosini, S. (1999) A framework for
5 and ecosystem integrity report card. *BioScience* 49: 543-556.
- 6 Hauhs, M. (1989) Lange Bramke: an ecosystem study of a forested catchment. In: Adriano, D. C.; Havas, M., eds.
7 Acidic precipitation: volume 1, case studies. New York, NY: Springer-Verlag; pp. 275-305. (Adriano, D. C.;
8 Salomons, W., eds. *Advances in environmental science*).
- 9 Haynie, F. H. (1976) Air pollution effects on stress induced intergranular corrosion of 7005-T53 aluminum alloy.
10 In: *Stress corrosion—new approaches*. Philadelphia, PA: American Society for Testing and Materials; pp.
11 32-43. (ASTM special technical publication 610).
- 12 Haynie, F. H. (1980) Theoretical air pollution and climate effects on materials confirmed by zinc corrosion data. In:
13 Sereda, P. J.; Litvan, G. G., eds. *Durability of building materials and components: proceedings of the 1st*
14 *international conference; August 1978; Ottawa, ON, Canada*. Philadelphia, PA: American Society for Testing
15 and Materials; pp. 157-175. (ASTM special technical publication 691).
- 16 Haynie, F. H. (1986) Theoretical model of soiling of surfaces by airborne particles. In: Lee, S. D.; Schneider, T.;
17 Grant, L. D.; Verkerk, P. J., eds. *Aerosols: research, risk assessment and control strategies, proceedings of*
18 *the second U.S.-Dutch international symposium; May 1985; Williamsburg, VA*. Chelsea, MI: Lewis
19 Publishers, Inc.; pp. 951-959.
- 20 Haynie, F. H.; Lemmons, T. J. (1990) Particulate matter soiling of exterior paints at a rural site. *Aerosol Sci.*
21 *Technol.* 13: 356-367.
- 22 Haynie, F. H.; Upham, J. B. (1974) Correlation between corrosion behavior of steel and atmospheric pollution data.
23 In: Coburn, S. K., ed. *Corrosion in natural environments: presented at the 76th annual meeting American*
24 *Society for Testing and Materials; June 1973; Philadelphia, PA*. Philadelphia, PA: American Society for
25 Testing and Materials; pp. 33-51. (ASTM special technical publication 558).
- 26 Hedin, L. O.; Granat, L.; Likens, G. E.; Buishand, T. A.; Galloway, J. N.; Butler, T. J.; Rodhe, H. (1994) Steep
27 declines in atmospheric base cations in regions of Europe and North America. *Nature (London)* 367:
28 351-354.
- 29 Heinsdorf, D. (1993) The role of nitrogen in declining Scots pine forests (*Pinus sylvestris*) in the lowland of East
30 Germany. *Water Air Soil Pollut.* 69: 21-35.
- 31 Herbert, D. A.; Rastetter, E. B.; Shaver, G. R.; Ågren, G. I. (1999) Effects of plant growth characteristics on
32 biogeochemistry and community composition in a changing climate. *Ecosystems* 2: 367-382.
- 33 Hicks (1986).
- 34 Hinkley et al. (1992).
- 35 Hogan, G. D.; Rennenberg, H.; Fink, S. (1998) Role and effect of sulfur in tree biology. In: Maynard, D. G., ed.
36 *Sulfur in the environment*. New York, NY: Marcel Dekker, Inc.; pp. 173-217. (Books in soils, plants, and the
37 environment: v. 67).
- 38 Holbrow, G. L. (1962) Atmospheric pollution: its measurement and some effects on paint. *J. Oil Colour Chem.*
39 *Assoc.* 45: 701-718.
- 40 Houghton et al. (1990).
- 41 Hughes, M. K. (1981) Cycling of trace metals in ecosystems. In: Lepp, N. W., ed. *Effect of heavy metal pollution*
42 *on plants. Volume 2: metals in the environment*. London, United Kingdom: Applied Science Publishers; pp.
43 95-118.
- 44 Humphreys, F. R.; Lambert, M. J.; Kelly, J. (1975) The occurrence of sulphur deficiency in forests. In: McLachlan,
45 K. D., ed. *Sulphur in Australasian agriculture*. Sydney, Australia: Sydney University Press; pp. 154-162.
- 46 Husar, R. B.; Wilson, W. E. (1993) Haze and sulfur emission trends in the eastern United States. *Environ. Sci.*
47 *Technol.* 27: 12-16.
- 48 Husar, R. B.; Elkins, J. B.; Wilson, W. E. (1994) U.S. visibility trends, 1960-1992, regional and national. Presented
49 at: 87th annual meeting of the Air & Waste Management Association; June; Cincinnati, OH. Pittsburgh, PA:
50 Air & Waste Management Association; paper no. 94-MP3.05.
- 51 Hutchinson, A. J.; Johnson, J. B.; Thompson, G. E.; Wood, G. C.; Sage, P. W.; Cooke, M. J. (1992) The role of
52 fly-ash particulate material and oxide catalysts in stone degradation. *Atmos. Environ.* 26A: 2795-2803.
- 53 Intergovernmental Panel on Climate Change (1995).
- 54

- 1 Irving, P. M., ed. (1991) Acidic deposition: state of science and technology: volumes I-IV. Washington, DC: The
2 U.S. National Acid Precipitation Assessment Program.
- 3 Iyer et al. (1999).
- 4 Jacobson et al. (1998)
- 5 Japar, S. M.; Szkarlat, A. C.; Pierson, W. R. (1984) The determination of the optical properties of airborne particle
6 emissions from diesel vehicles. *Sci. Total Environ.* 36: 121-130.
- 7 Japar, S. M.; Brachaczek, W. W.; Gorse, R. A., Jr.; Norbeck, J. M.; Pierson, W. R. (1986) The contribution of
8 elemental carbon to the optical properties of rural atmospheric aerosols. *Atmos. Environ.* 20: 1281-1289.
- 9 Jensen, V. (1974) Decomposition of angiosperm tree leaf litter. In: Dickinson, C. H.; Pugh, G. J. F., eds. *Biology of*
10 *plant litter decomposition: v. I.* London, United Kingdom: Academic Press; pp. 69-104.
- 11 Johnson, D. W. (1984) Sulfur cycling in forests. *Biogeochemistry* 1: 29-43.
- 12 Johnson, F. R.; Desvousges, W. H. (1997) Estimating stated preference with rated-pair data: environmental, health,
13 and employment effects of energy programs. *J. Environ. Econ. Manage.* 34(1) (September).
- 14 Johnson, D. W.; Lindberg, S. E., eds. (1992a) Atmospheric deposition and forest nutrient cycling: a synthesis of the
15 integrated forest study. New York, NY: Springer-Verlag, Inc. (Billings, W. D.; Golley, F.; Lange, O. L.;
16 Olson, J. S.; Rimmert, H., eds. *Ecological studies: analysis and synthesis: v. 91*).
- 17 Johnson, D. W.; Lindberg, S. E., eds. (1992b) Nitrogen chemistry, deposition, and cycling in forests. In: Johnson,
18 D. W.; Lindberg, S. E., eds. *Atmospheric deposition and forest nutrient cycling: a synthesis of the integrated*
19 *forest study.* New York, NY: Springer-Verlag, Inc.; pp. 150-213. (Billings, W. D.; Golley, F.; Lange, O. L.;
20 Olson, J. S.; Rimmert, H., eds. *Ecological studies: analysis and synthesis: v. 91*).
- 21 Johnson, D. W.; Mitchell, M. J. (1998) Responses of forest ecosystems to changing sulfur inputs. In: Maynard, D.
22 G., ed. *Sulfur in the environment.* New York, NY: Marcel Dekker, Inc; pp. 219-262. (Books in soils, plants,
23 and the environment v. 67).
- 24 Johnson, D. W.; Taylor, G. E. (1989) Role of air pollution in forest decline in eastern North America. *Water Air*
25 *Soil Pollut.* 48: 21-43.
- 26 Johnson et al. (1980).
- 27 Johnson, D. W.; Henderson, G. S.; Huff, D. D.; Lindberg, S. E.; Richter, D. D.; Shriner, D. S.; Todd, D. E.; Turner,
28 J. (1982a) Cycling of organic and inorganic sulphur in a chestnut oak forest. *Oecologia* 54: 141-148.
- 29 Johnson, D. W.; Cole, D. W.; Bledsoe, C. S.; Cromack, K.; Edmonds, R. L.; Gessel, S. P.; Grier, C. C.; Richards, B.
30 N.; Vogt, K. A. (1982b) Nutrient cycling in forests of the Pacific Northwest. In: Edmonds, R. L., ed.
31 *Analysis of coniferous forest ecosystems in the Western United States.* Stroudsburg, PA: Hutchinson Ross
32 Publishing Company; pp. 186-232. (US/IBP synthesis series: v. 14).
- 33 Johnson, D. W.; Van Miegroet, H.; Lindberg, S. E.; Todd, D. E.; Harrison, R. B. (1991a) Nutrient cycling in red
34 spruce forests of the Great Smoky Mountains. *Can. J. For. Res.* 21: 769-787.
- 35 Johnson, D. W.; Cresser, M. S.; Nilsson, S. I.; Turner, J.; Ulrich, B.; Binkley, D.; Cole, D. W. (1991b) Soil changes
36 in forest ecosystems: evidence for and probable causes. *Proc. R. Soc. Edinburgh Sect. B: Biol. Sci.* 97B:
37 81-116.
- 38 Johnson, D. W.; Swank, W. T.; Vose, J. M. (1993) Simulated effects of atmospheric sulfur deposition on nutrient
39 cycling in a mixed deciduous forest. *Biogeochemistry* 23: 169-196.
- 40 Johnson, A. H.; Friedland, A. J.; Miller, E. K.; Siccama, T. G. (1994a) Acid rain and soils of the Adirondacks. III.
41 Rates of soil acidification in a montane spruce-fir forest at Whiteface Mountain, New York. *Can. J. For. Res.*
42 24: 663-669.
- 43 Johnson, A. H.; Andersen, S. B.; Siccama, T. G. (1994b) Acid rain and soils of the Adirondacks. I. Changes in pH
44 and available calcium, 1930-1984. *Can. J. For. Res.* 24: 39-45.
- 45 Joslin, J. D.; Kelly, J. M.; Van Miegroet, H. (1992) Soil chemistry and nutrition of North American spruce-fir
46 stands: evidence for recent change. *J. Environ. Qual.* 21: 12-30.
- 47 Justus et al. (1994).
- 48 Katayama and Matsumura (1993).
- 49 Katsev, I. L.; Zege, E. P. (1994) The modern theory of black object visibility and meteorological visibility range.
50 *Atmos. Environ.* 28: 763-767.
- 51 Kelly, J.; Lambert, M. J. (1972) The relationship between sulphur and nitrogen in the foliage of *Pinus radiata*. *Plant*
52 *Soil* 37: 395-407.
- 53 Kenk and Fischer (1988).
- 54

1 Kerker, M. (1969) The scattering of light and other electromagnetic radiation. New York, NY: Academic Press, Inc.
2 (Loebl, E. M., ed. Physical chemistry: a series of monographs, no. 16).

3 Kiehl, J. T.; Briegleb, B. P. (1993) The relative roles of sulfate aerosols and greenhouse gases in climate forcing.
4 Science (Washington, DC) 260: 311-314.

5 Kodama and Lee (1993).

6 Koschmieder (1924).

7 Koslow et al. (1977).

8 Krajičková, A.; Mejstřík, V. (1984) The effect of fly-ash particles on the plugging of stomata. Environ. Pollut. 36:
9 83-93.

10 Krupa, S. V.; Legge, A. H. (1986) Single or joint effects of coarse and fine particulate sulfur aerosols and ozone on
11 vegetation. In: Lee, S. D.; Schneider, T.; Grant, L. D.; Verkerk, P. J., eds. Aerosols: research, risk assessment
12 and control strategies, proceedings of the second U.S.-Dutch international symposium; May 1985;
13 Williamsburg, VA. Chelsea, MI: Lewis Publishers, Inc.; pp. 879-887.

14 Krupa, S. V.; Legge, A. H. (1998) Sulphur dioxide, particulate sulphur and its impacts on a boreal forest ecosystem.
15 In: Ambasht, R. S., ed. Modern trends in ecology and environment. Leiden, The Netherlands: Backhuys
16 Publishers; pp 285-306.

17 Kylin et al. (1994).

18 Lamar et al. (1992).

19 Lamersdorf, N. P.; Meyer, M. (1993) Nutrient cycling and acidification of a northwest German forest site with high
20 atmospheric nitrogen deposition. For. Ecol. Manage. 62: 323-354.

21 Latimer, D. A. (1988) Plume perceptibility thresholds. Presented at: 81st annual meeting of the Air Pollution
22 Control Association; June; Dallas, TX. Pittsburgh, PA: Air Pollution Control Association; paper no. 88-56.6.

23 Latimer, D. A.; Bergstrom, R. W.; Hayes, S. R.; Liu, M.-K.; Seinfeld, J. H.; Whitten, G. Z.; Wojcik, M. A.; Hillyer,
24 M. J. (1978) The development of mathematical models for the prediction of anthropogenic visibility
25 impairment: volumes I-III. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of
26 Air Quality Planning and Standards; EPA report no. EPA-450/3-78-110a-c. Available from: NTIS,
27 Springfield, VA; PB-293118-SET.

28 Lauenroth, W. K.; Milchunas, D. G. (1985) SO₂ effects on plant community function. In: Winner, W. E.; Mooney,
29 H. A.; Goldstein, R. A., eds. Sulfur dioxide and vegetation: physiology, ecology, and policy issues. Stanford,
30 CA: Stanford University Press; pp. 454-477.

31 Lawrence, G. B.; Huntington, T. G. (1999) Soil-Calcium depletion linked to acid rain and forest growth in the
32 eastern United States. Reston, VA: U.S. Geological Survey. Available: <http://btdqs.usgs.gov/acidrain>.

33 Lawrence et al. (1995).

34 Legge, A. H. (1980) Primary productivity, sulfur dioxide, and the forest ecosystem: an overview of a case study. In:
35 Miller, P. R., ed. Proceedings of symposium on effects of air pollutants on Mediterranean and temperate
36 forest ecosystems; June; Riverside, CA. Berkeley, CA: U.S. Department of Agriculture, Pacific Southwest
37 Forest and Range Experiment Station; pp. 51-62; Forest Service general technical report no. PSW-43.
38 Available from: NTIS, Springfield, VA; PB81-133720.

39 Lerman, S. L.; Darley, E. F. (1975) Particulates. In: Mudd, J. B.; Kozlowski, T. T., eds. Responses of plants to air
40 pollution. New York, NY: Academic Press; pp. 141-158.

41 Levin, S. A. (1998) Ecosystems and the biosphere as complex adaptive systems. Ecosystems 1: 431-436.

42 Li-Jones and Prospero (1998).

43 Likens, G. E.; Driscoll, C. T.; Buso, D. C. (1996) Long-term effects of acid rain: response and recovery of a forest
44 ecosystem. Science (Washington, DC) 272: 244-246.

45 Linthurst (1984).

46 Lipfert, F. W. (1996) Estimating the effects of air pollution on building and structures: the U.S. experience since
47 1985 and some lessons for the future (final report prepared for U.S. Department of Energy). Upton, NY:
48 Brookhaven National Laboratory; January.

49 Liu, S. C.; McKeen, S. A.; Madronich, S. (1991) Effect of anthropogenic aerosols on biologically active ultraviolet
50 radiation. Geophys. Res. Lett. 18: 2265-2268.

51 Longstreth, J.; De Gruijl, F. R.; Kripke, M. L.; Abseck, S.; Arnold, F.; Slaper, H. I.; Velders, G.; Takizawa, Y.; Van
52 Der Leun, J. C. (1998) Health risks. J. Photochem. Photobiol. B 46: 20-39.

53 Lorente, J.; Redaño, A.; de Cabo, X. (1994) Influence of urban aerosol on spectral solar irradiance. J. Appl.
54 Meteorol. 33: 406-415.

55

1 Lorusso, S.; Marabelli, M.; Troili, M. (1997) Air pollution and the deterioration of historic monuments. *J. Environ.*
2 *Pathol. Toxicol. Oncol.* 16: 171-173.

3 Lowenthal, D. H.; Rogers, C. F.; Saxena, P.; Watson, J. G.; Chow, J. C. (1995) Sensitivity of estimated light
4 extinction coefficients to model assumptions and measurement errors. *Atmos. Environ.* 29: 751-766.

5 Madronich (1987).

6 Mahadev, S.; Henry, R. C. (1999) Application of a color-appearance model to vision through atmospheric haze.
7 *Color Res. Appl.* 24: 112-120.

8 Majernik, O.; Mansfield, T. A. (1972) Stomatal responses to raised atmospheric CO₂ concentrations during
9 exposure of plants to SO₂ pollution. *Environ. Pollut.* 3: 1-7.

10 Malm, W. C.; Pitchford, M. L. (1997) Comparison of calculated sulfate scattering efficiencies as estimated from
11 size-resolved particle measurements at three national locations. *Atmos. Environ.* 31: 1315-1325.

12 Malm, W. C.; Sisler, J. F.; Huffman, D.; Eldred, R. A.; Cahill, T. A. (1994) Spatial and seasonal trends in particle
13 concentration and optical extinction in the United States. *J. Geophys. Res. [Atmos.]* 99: 1347-1370.

14 Malm, W. C.; Trijonis, J.; Sisler, J.; Pitchford, M.; Dennis, R. L. (1994) Assessing the effect of SO₂ emission
15 changes on visibility. *Atmos. Environ.* 28: 1023-1034.

16 Malm, W. C.; Molenaar, J. V.; Eldred, R. A.; Sisler, J. F. (1996) Examining the relationship among atmospheric
17 aerosols and light scattering and extinction in the Grand Canyon area. *J. Geophys. Res. [Atmos.]* 101:
18 19,251-19,265.

19 Mansfeld, F. (1980) Regional air pollution study: effects of airborne sulfur pollutants on materials. Research
20 Triangle Park, NC: U.S. Environmental Protection Agency, Environmental Sciences Research Laboratory;
21 EPA report no. EPA-600/4-80-007. Available from: NTIS, Springfield, VA; PB81-126351.

22 Manuel, E. H., Jr.; Lanen, W. N.; Horst, R. L., Jr.; Duff, M. C.; Brennan, K. M.; Tapiero, J. K. (1982) Benefits
23 analysis of alternative secondary national ambient air quality standards for sulfur dioxide and total suspended
24 particulates: volume II. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Air
25 Quality Planning and Standards; contract no. 68-02-3392.

26 Marchwińska, E.; Kucharski, R. (1987) The combined influence of SO₂ and heavy metal-containing particulates on
27 beans, carrots and parsley. *Environ. Monit. Assess.* 8: 11-25.

28 Marschner, H. (1995) Sulfur. In: Marschner, H., ed. *Mineral nutrition of higher plants*. 2nd ed. New York, NY:
29 Academic Press; pp. 255-265.

30 Martin, M. H.; Coughtrey, P. J. (1981) Impact of metals on ecosystem function and productivity. In: Lepp, N. W.,
31 ed. *Effect of heavy metal pollution on plants: volume 2, metals in the environment*. Barking, United
32 Kingdom: Applied Science Publishers; pp. 119-158. (Mellanby, K., ed. *Pollution monitoring series*).

33 Martin, C. E.; Gravatt, D. A.; Loesch, V. S. (1992) Photosynthetic responses of three species to acute exposures
34 of nitrate- and sulphate-containing aerosols. *Atmos. Environ. Part A* 26: 381-391.

35 Materna, J. (1984) Impact of atmospheric pollution on natural ecosystems. In: Treshow, M., ed. *Air pollution and
36 plant life*. New York, NY: John Wiley & Sons; pp. 397-416.

37 MathTech, Inc. (1990) Economic assessment of materials damage in the south coast air basin: a case study of acid
38 deposition effects on painted wood surfaces using individual maintenance behavior data. Sacramento CA:
39 California Air Resources Board; May.

40 MathTech, Inc. (1998) Regional model farm benefit estimation of alternative emission controls for the NO_x SIP
41 call. Science Applications International Corporation; August.

42 Mathai, C. V. (1995) The Grand Canyon visibility. *EM (December)*: 20-31.

43 Matson, P. A.; Parton, W. J.; Power, A. G.; Swift, M. J. (1997) Agricultural intensification and ecosystem
44 properties. *Science (Washington, DC)* 277: 504-509.

45 May, P. F.; Till, A. R.; Cumming, M. J. (1972) Systems analysis of sulphur kinetics in pastures grazed by sheep. *J.*
46 *Appl. Ecol.* 9: 25-49.

47 McClelland, G.; Schulze, W.; Waldman, D.; Schenk, D.; Irwin, J.; Stewart, T.; Deck, L.; Thayer, M. (1991) Valuing
48 eastern visibility: a field test of the contingent valuation method. Washington, DC: U.S. Environmental
49 Protection Agency, Office of Policy, Planning and Evaluation; cooperative agreement no. CR-815183.

50 McGee, E. S.; Mossotti, V. G. (1992) Gypsum accumulation on carbonate stone. *Atmos. Environ. Part B* 26:
51 249-253.

52 McGowan et al. (1993).

53 McGrattan et al. (1995).

54 McGrattan et al. (1996).

55

- 1 McMurry, P. H.; Stolzenburg, M. R. (1989) On the sensitivity of particle size to relative humidity for Los Angeles
2 aerosols. *Atmos. Environ.* 23: 497-507.
- 3 McMurry, P. H.; Zhang, X.; Lee, C.-T. (1996) Issues in aerosol measurement for optics assessments. *J. Geophys.*
4 *Res. [Atmos.]* 101: 19,189-19,197.
- 5 Meiwes, K. J.; Khanna, P. K. (1981) Distribution and cycling of sulphur in the vegetation of two forest ecosystems
6 in an acid rain environment. *Plant Soil* 60: 369-375.
- 7 Meng et al. (1998).
- 8 Mercer, G. S. (1994) Transmissometer data reporting (IMPROVE protocol). Fort Collins, CO: Air Resource
9 Specialists, Inc.; technical instruction no. 4500-5100.
- 10 Middleton, P. (1997) DAQM-simulated spatial and temporal differences among visibility, PM, and other air quality
11 concerns under realistic emission change scenarios. In: Special issue on aerosols and atmospheric
12 optics—part II, [published papers from the international specialty conference; September 1994; Snowbird,
13 UT]. *J. Air Waste Manage. Assoc.* 47: 302-316.
- 14 Mie, G. (1908) Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen [Optics of cloudy media,
15 especially colloidal metal solutions]. *Ann. Phys. (Leipzig)* 25: 377-445.
- 16 Millar, C. S. (1974) Decomposition of coniferous leaf litter. In: Dickinson, C. H.; Pugh, G. J. F., eds. *Biology of*
17 *plant litter decomposition: volume I.* New York, NY: Academic Press; pp. 105-128.
- 18 Miller and McBride (1998).
- 19 Mitchell, R. C.; Carson, R. T. (1989) Using surveys to value public goods: the contingent valuation method.
20 Washington, DC: Resources for the Future.
- 21 Mitchell, M. J.; Harrison, R. B.; Fitzgerald, J. W.; Johnson, D. W.; Lindberg, S. E.; Zhang, Y.; Autry, A. (1992a)
22 Sulfur distribution and cycling in forest ecosystems. In: Johnson, D. W.; Lindberg, S. E., eds. *Atmospheric*
23 *deposition and forest nutrient cycling: a synthesis of the integrated forest study.* New York, NY:
24 Springer-Verlag; pp. 90-129. (Billings, W. D.; Golley, F.; Lange, O. L.; Olson, J. S.; R Emmert, H., eds.
25 *Ecological studies: analysis and synthesis: v. 91.*
- 26 Mitchell, M. J.; Foster, N. W.; Shepard, J. P.; Morrison, I. K. (1992b) Nutrient cycling in Huntington Forest and
27 Turkey Lakes deciduous stands: nitrogen and sulfur. *Can. J. For. Res.* 22: 457-464.
- 28 Molenaar, J. V.; Persha, G.; Malm, W. C. (1990) Long path transmissometer for measuring ambient atmospheric
29 extinction. In: Mathai, C. V., ed. *Visibility and fine particles: an A&WMA/EPA international specialty*
30 *conference; October 1989; Estes Park, CO.* Pittsburgh PA: Air & Waste Management Association; pp.
31 293-304. (AWMA transactions series no. TR-17).
- 32 Molenaar, J. V.; Cismoski, D. S.; Tree, R. M. (1992) Intercomparison of ambient optical monitoring techniques.
33 Presented at: 85th annual meeting of the Air & Waste Management Association; June; Kansas City, MO.
34 Pittsburgh, PA: Air & Waste Management Association; paper no. 92-60.09.
- 35 Molenaar et al. (1994).
- 36 Moropoulou, A.; Bisbikou, K.; Torfs, K.; Van Grieken, R.; Zezza, F.; Macri, F. (1998) Origin and growth of
37 weathering crusts on ancient marbles in industrial atmosphere. *Atmos. Environ.* 32: 967-982.
- 38 Naeem et al. (1994).
- 39 Nash, T. H., III. (1975) Influence of effluents from a zinc factory on lichens. *Ecol. Monogr.* 45: 183-198.
- 40 National Acid Precipitation Assessment Program. (1990) Mechanisms for damage. Washington, DC: Office of the
41 Director; report no. 19.
- 42 National Acid Precipitation Assessment Program. (1990) Deposition to structures. Washington, DC: Office of the
43 Director; report no. 20.
- 44 National Acid Precipitation Assessment Program. (1990) Stocks at risk. Washington, DC: Office of the Director;
45 report no. 21.
- 46 National Acid Precipitation Assessment Program. (1990) Economic valuation methods. Washington, DC: Office of
47 the Director; report no. 27.
- 48 National Acid Precipitation Assessment Program. (1991) National acid precipitation assessment program: 1990
49 integrated assessment report. Washington, DC: Office of the Director.
- 50 National Oceanic and Atmospheric Administration (1992).
- 51 National Park Service. (1998) IMPROVE program goals and objectives. Washington, DC: National Park Service.
52 Available: <http://165.83.32.34/ard/impr/goals.html>.
- 53 National Research Council. (1993) Protecting visibility in national parks and wilderness areas. Washington, DC:
54 National Academy Press. 3v.
55

- 1 National Science and Technology Council. (1998) National acid precipitation assessment program biennial report to
2 Congress: an integrated assessment; executive summary. Silver Spring, MD: U.S. Department of Commerce,
3 National Oceanic and Atmospheric Administration. Available:
4 www.nnic.noaa.gov/CENR/NAPAP/NAPAP_96.htm.
- 5 National Weather Service (1995).
- 6 Nazaroff, W. W.; Cass, G. R. (1991) Protecting museum collections from soiling due to the deposition of airborne
7 particles. *Atmos. Environ. Part A* 25: 841-852.
- 8 Neff, W. D. (1997) The Denver brown cloud studies from the perspective of model assessment needs and the role of
9 meteorology. *J. Air Waste Manage. Assoc.*
- 10 Nihlgård, B. (1985) The ammonium hypothesis—an additional explanation to the forest dieback in Europe. *Ambio*
11 14: 2-8.
- 12 Noble, I. R.; Dirzo, R. (1997) Forests as human-dominated ecosystems. *Science (Washington, DC)* 277: 522-525.
- 13 Nord, A. G.; Ericsson, T. (1993) Chemical analysis of thin black layers on building stone. *Stud. Conserv.* 38: 25-35.
- 14 Novakov and Penner (1993).
- 15 Odum, E. P. (1969) The strategy of ecosystem development: an understanding of ecological succession provides a
16 basis for resolving man's conflict with nature. *Science (Washington, DC)* 164: 262-270.
- 17 Odum, E. P. (1993) The ecosystem. In: *Ecology and our endangered life-support systems*. 2nd ed. Sunderland, MA:
18 Sinauer Associates, Inc.; pp. 38-67.
- 19 Olszyk, D. M.; Bytnerowicz, A.; Takemoto, B. K. (1989) Photochemical oxidant pollution and vegetation: effects of
20 gases, fog, and particles. *Environ. Pollut.* 61: 11-29.
- 21 Omar, A. H.; Biegalski, S.; Larson, S. M.; Landsberger, S. (1999) Particulate contributions to light extinction and
22 local forcing at a rural Illinois site. *Atmos. Environ.* 33: 2637-2646.
- 23 Ormrod, D. P. (1984) Impact of trace element pollution on plants. In: Treshow, M., ed. *Air pollution and plant life*.
24 Chichester, United Kingdom: John Wiley & Sons; pp. 291-319.
- 25 Pan et al. (1997).
- 26 Pan et al. (1998).
- 27 Parker, A. (1955) The destructive effects of air pollution on materials. *Colliery Guardian* 191: 447-450.
- 28 Percy, R. W.; Björkman, O.; Caldwell, M. M.; Keeley, J. E.; Monson, R. K.; Strain, B. R. (1987) Carbon gain by
29 plants in natural environments. *BioScience* 37: 21-29.
- 30 Perry, K. D.; Cahill, T. A.; Eldred, R. A.; Dutcher, D. D.; Gill, T. E. (1997) Long-range transport of North African
31 dust to the eastern United States. *J. Geophys. Res. [Atmos]* 102: 11,225-11,238.
- 32 Peterson et al. (1978).
- 33 Peterson, G.; Allen, C. R.; Holling, C. S. (1998) Ecological resilience, biodiversity, and scale. *Ecosystems* 1: 6-18.
- 34 Petuskey, W. T.; Richardson, D. A.; Dolske, D. A. (1995) Aspects of the deterioration of sandstone masonry in
35 Anasazi dwelling ruins at Mesa Verde National Park, Colorado, USA. *Sci. Total Environ.* 167: 145-159.
- 36 Pimentel, D.; Wilson, C.; McCullum, C.; Huang, R.; Dwen, P.; Flack, J.; Tran, Q.; Saltman, T.; Cliff, B. (1997)
37 Economic and environmental benefits of biodiversity. *BioScience* 47: 747-757.
- 38 Pimm, S. L. (1984) The complexity and stability of ecosystems. *Nature (London)* 307: 321-326.
- 39 Pitchford, M. L.; McMurry, P. H. (1994) Relationship between measured water vapor growth and chemistry of
40 atmospheric aerosol for Grand Canyon, Arizona, in winter 1990. *Atmos. Environ.* 28: 827-839.
- 41 Pryor, S.; Steyn, D. (1994) Visibility and ambient aerosols in southwestern British Columbia during REVEAL
42 (REgional Visibility Experimental Assessment in the Lower Fraser Valley): application of analytical
43 techniques for source apportionment and related visibility impacts of the REVEAL fine particulate optical
44 and scene data. Victoria, BC, Canada: British Columbia Ministry of Environment, Lands and Parks.
45 Available from: NTIS, Springfield, VA; MIC-96-00314/INS.
- 46 Rapport, D. J.; Whitford, W. G. (1999) How ecosystems respond to stress. *BioScience* 49: 193-203.
- 47 Raynal, D. J.; Joslin, J. D.; Thornton, F. C.; Schaedle, M.; Henderson, G. S. (1990) Sensitivity of tree seedlings to
48 aluminum: III. Red spruce and loblolly pine. *J. Environ. Qual.* 19: 180-187.
- 49 Realini, M.; Negrotti, R.; Appollonia, L.; Vaudan, D. (1995) Deposition of particulate matter on stone surfaces: an
50 experimental verification of its effects on Carrara marble. In: Saiz-Jimenez, C., ed. *The deterioration of*
51 *monuments: proceedings of the 2nd international symposium on biodeterioration and biodegradation; January*
52 *1994; Sevilla, Spain. Sci. Total Environ.* 167: 67-72.
- 53 Refort and Whitford (1999).
- 54 Rennie, P. J. (1955) The uptake of nutrients by mature forest growth. *Plant Soil* 7: 49-95.
- 55

- 1 Reuss, J. O. (1983) Implications of the calcium-aluminum exchange system for the effect of acid precipitation on
2 soils. *J. Environ. Qual.* 12: 591-595.
- 3 Richards, L. W. (1973) Size distribution of pigment particles: measurement and characterization by light-scattering
4 techniques. In: Patton, T. C., ed. *Pigment handbook*. V. III. Characterization and physical relationships. New
5 York, NY: John Wiley & Sons; pp. 89-100.
- 6 Richards (1995).
- 7 Richards, L. W.; Blanchard, C. L.; Blumenthal, D. L., eds. (1991) Navajo generating station visibility study. Final
8 Report. Petaluma, CA: Sonoma Technology, Inc.; report no. STI-90200-1124-FR.
- 9 Roelofs, J. G. M.; Kempers, A. J.; Houdijk, A. L. F. M.; Jansen, J. (1985) The effect of air-borne ammonium
10 sulphate on *Pinus nigra* var. *maritima* in the Netherlands. *Plant Soil* 84: 45-56.
- 11 Roelofs, J. G. M.; Boxman, A. W.; Van Dijk, H. F. G. (1987) Effects of airborne ammonium on natural vegetation
12 and forests. In: Asman, W. A. H.; Diederer, H. S. M. A., eds. *Ammonia and acidification: proceedings [of a]*
13 *symposium of the European Association for the Science of Air Pollution (EURASAP)*; April; Bilthoven, The
14 Netherlands. European Association for the Science of Air Pollution; pp. 266-276.
- 15 Rogge et al. (1993b).
- 16 Rosen, H.; Hansen, A. D. A.; Gundel, L.; Novakov, T. (1978) Identification of the optically absorbing component in
17 urban aerosols. *Appl. Opt.* 17: 3859-3861.
- 18 Ross, D. M.; Malm, W. C.; Iyer, H. K. (1997) Human visual sensitivity to plumes with a Gaussian luminance
19 distribution: experiments to develop an empirical probability of detection model. *J. Air Waste Manage.*
20 *Assoc.* 47: 370-382.
- 21 Rovira, A. D.; Davey, C. B. (1974) Biology of the rhizosphere. In: Carson, E. W., ed. *The plant root and its*
22 *environment: proceedings of an institute*; July, 1971; Blacksburg, VA. Charlottesville, VA: University Press
23 of Virginia; pp. 153-204.
- 24 Sabbioni, C. (1995) Contribution of atmospheric deposition to the formation of damage layers. In: Jimenez-Saiz, C.,
25 ed. *The deterioration of monuments: proceedings of the 2nd international symposium on biodeterioration and*
26 *biodegradation*; January 1994; Sevilla, Spain. *Sci. Total Environ.* 167: 49-56.
- 27 Sabbioni, C.; Zappia, G.; Gobbi, G. (1992) Carbonaceous particles on carbonate building stones in a simulated
28 system. In: *Proceedings of the 1992 European aerosol conference*; September; Oxford, United Kingdom. *J.*
29 *Aerosol Sci.* 23(suppl. 1): S921-S924.
- 30 Sabbioni, C.; Zappia, G.; Gobbi, G. (1996) Carbonaceous particles and stone damage in a laboratory exposure
31 system. *J. Geophys. Res. [Atmos.]* 101: 19,621-19,627.
- 32 Saiz-Jimenez, C. (1993) Deposition of airborne organic pollutants on historic buildings. *Atmos. Environ. Part B* 27:
33 77-85.
- 34 Salmon, R. L. (1970) *Systems analysis of the effects of air pollution on materials*. Raleigh, NC: National Air
35 Pollution Control Administration, Economic Effects Research Division; report no. APTD-0943. Available
36 from: NTIS, Springfield, VA; PB-209192.
- 37 Samecka-Cymerman, A.; Kempers, A. J. (1999) Bioindication of heavy metals in the town Wrocław (Poland) with
38 evergreen plants. *Atmos. Environ.* 33: 419-430.
- 39 Sanyal, B.; Singhanian, G. K. (1956) Atmospheric corrosion of metals: part I. *J. Sci. Ind. Res. Sect. B* 15: 448-455.
- 40 Saunders, P. J. W.; Godzik, S. (1986) Terrestrial vegetation—air pollutant interactions: nongaseous air pollutants.
41 In: Legge, A. H.; Krupa, S. V., eds. *Air pollutants and their effects on the terrestrial ecosystem*. New York,
42 NY: John Wiley & Sons; pp. 389-394. (*Advances in environmental science and technology*: v. 18).
- 43 Saxena, P.; Hildemann, L. M.; McMurry, P. H.; Seinfeld, J. H. (1995) Organics alter hygroscopic behavior of
44 atmospheric particles. *J. Geophys. Res. [Atmos.]* 100: 18,755-18,770.
- 45 Schiavon, N.; Chiavari, G.; Schiavon, G.; Fabbri, D. (1995) Nature and decay effects of urban soiling on granitic
46 building stones. In: Jimenez-Saiz, C., ed. *The deterioration of monuments: proceedings of the 2nd*
47 *international symposium on biodeterioration and biodegradation*; January 1994; Sevilla, Spain. *Sci. Total*
48 *Environ.* 167: 87-101.
- 49 Schnug, E. (1997) Significance of sulphur for the quality of domesticated plants. In: Cram, W. J.; De Kok, L. J.;
50 Stulen, I.; Brunold, C.; Rennenberg, H., eds. *Sulphur metabolism in higher plants: molecular,*
51 *ecophysiological and nutritional aspects*. Leiden, The Netherlands: Backhuys Publishers; pp. 109-130.
- 52 Schulze, E.-D. (1989) Air pollution and forest decline in a spruce (*Picea abies*) forest. *Science (Washington, DC)*
53 244: 776-783.
- 54

1 Schuster, P. F.; Reddy, M. M.; Sherwood, S. I. (1994) Effects of acid rain and sulfur dioxide on marble dissolution.
2 Mater. Perform. 33: 76-80.

3 Schwar, M. J. R. (1998) Nuisance dust deposition and soiling rate measurements. Environ. Technol. 19: 223-229.
4 Seckmeyer and McKenzie (1992).

5 Seigneur, C.; Wu, X. A.; Constantinou, E.; Gillespie, P.; Bergstrom, R. W.; Sykes, I.; Venkatram, A.;
6 Karamchandani, P. (1997) Formulation of a second-generation reactive plume and visibility model. J. Air
7 Waste Manage. Assoc. 47: 176-184.

8 Seinfeld (1989).

9 Sereda, P. J. (1974) Weather factors affecting corrosion of metals. In: Corrosion in natural environments: three
10 symposia presented at the seventy-sixth annual meeting [of the] American Society for Testing and Materials;
11 June 1973; Philadelphia, PA. Philadelphia, PA: American Society for Testing and Materials; pp. 7-22.
12 (ASTM special technical publication 558).

13 Shannon, J. D.; Trexler, E. C., Jr.; Sonnenblick, R. (1997) Modeling visibility for assessment. Atmos. Environ. 31:
14 3719-3727.

15 Shodor Education Foundation, Inc.; Industrial Extension Service of North Carolina State University; North Carolina
16 Supercomputing Center. (1996) Air quality meteorology. Session 8: physical meteorology and visibility. Part
17 3: visibility. Research Triangle Park, NC: U.S. Environmental Protection Agency, National Exposure
18 Research Laboratory and U.S. National Oceanic and Atmospheric Administration. Available:
19 www.shodor.org/metweb/index.html.

20 Shortle, W. C.; Smith, K. T. (1988) Aluminum-induced calcium deficiency syndrome in declining red spruce.
21 Science (Washington, DC) 240: 1017-1018.

22 Showak, W.; Dunbar, S. R. (1982) Effect of 1 percent copper addition on atmospheric corrosion of rolled zinc after
23 20 years' exposure. In: Dean, S. W.; Rhea, E. C., eds. Atmospheric corrosion of metals: a symposium; May
24 1980; Denver, CO. Philadelphia, PA: American Society for Testing and Materials; pp. 135-162. (ASTM
25 special technical publication 767).

26 Shriner, D. S.; Henderson, G. S. (1978) Sulfur distribution and cycling in a deciduous forest watershed. J. Environ.
27 Qual. 7: 392-397.

28 Simpson, J. W.; Horrobin, P. J., eds. (1970) The weathering and performance of building materials. New York, NY:
29 Wiley-Interscience.

30 Sisler, J. F. (1996) Spatial and seasonal patterns and long term variability of the composition of the haze in the
31 United States: an analysis of data from the IMPROVE network. Fort Collins, CO: Colorado State University,
32 Cooperative Institute for Research in the Atmosphere; EPA air docket A096-56, document no. VI-B-09-(ee).

33 Sisler, J. F.; Cahill, T. A. (1993) Spacial and temporal patterns and the chemical composition of the haze and its
34 impact on visibility in Alaska. In: Proceedings [of the] 86th annual meeting & exhibition of the Air & Waste
35 Management Association. Volume 8: general environmental topics; June; Denver, CO. Pittsburgh, PA: Air &
36 Waste Management Association; 93-MP-4.03.

37 Sisler, J. F.; Malm, W. C. (1994) The relative importance of soluble aerosols to spatial and seasonal trends of
38 impaired visibility in the United States. Atmos. Environ. 28: 851-862.

39 Sisler, J. F.; Malm, W. C. (1998) Interpretation of trends of PM_{2.5} and reconstructed visibility from the IMPROVE
40 network. J. Air Waste Manage. Assoc.: submitted.

41 Sisler and Malm (1999).

42 Sisler, J. F.; Huffman, D.; Lattimer, D. A.; Malm, W. C.; Pitchford, M. L. (1993) Spatial and temporal patterns and
43 the chemical composition of the haze in the United States: an anlysis of data from the IMPROVE network,
44 1988-1991. Fort Collins, CO: Colorado State University, Cooperative Institute for Research in the
45 Atmosphere (CIRA).

46 Sisler et al. (1999).

47 Skeffington, R. A.; Wilson, E. J. (1988) Excess nitrogen deposition: issues for consideration. Environ. Pollut. 54:
48 159-184.

49 Skerry, B. S.; Alavi, A.; Lindgren, K. I. (1988) Environmental and electrochemical test methods for the evaluation
50 of protective organic coatings. J. Coat. Technol. 60: 97-106.

51 Sloane, C. S.; Watson, J.; Chow, J.; Pritchett, L.; Richards, L. W. (1991) Size-segregated fine particle
52 measurements by chemical species and their impact on visibility impairment in Denver. Atmos. Environ. Part
53 A 25: 1013-1024.

- 1 Smith, W. H. (1987) The atmosphere and the rhizosphere: linkages with potential significance for forest tree health.
2 In: Acidic deposition and forest soil biology. New York, NY: National Council of the Paper Industry for Air
3 and Stream Improvement, Inc.; pp. 30-94; technical bulletin no. 527.
- 4 Smith, W. H. (1990a) Forest nutrient cycling: toxic ions. In: Air pollution and forests: interactions between air
5 contaminants and forest ecosystems. 2nd ed. New York, NY: Springer-Verlag; pp. 225-268. (Springer series
6 on environmental management).
- 7 Smith, W. H. (1990b) Forests as sinks for air contaminants: soil compartment. In: Air pollution and forests:
8 interactions between air contaminants and forest ecosystems. 2nd ed. New York, NY: Springer-Verlag; pp.
9 113-146. (Springer series on environmental management).
- 10 Smith, W. H. (1991) Air pollution and forest damage. *Chem. Eng. News* 69(45): 30-43.
- 11 Smith (1995).
- 12 Smith and Staskawicz (1973).
- 13 Spence, J. W.; Haynie, F. H. (1972) Paint technology and air pollution: a survey and economic assessment.
14 Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Air Programs; publication no.
15 AP-103. Available from: NTIS, Springfield, VA; PB-210736.
- 16 Spence, J. W.; Haynie, F.; Upham, J. B. (1975) Effects of gaseous pollutants on paints: a chamber study. *J. Paint
17 Technol.* 47: 57-63.
- 18 Spence et al. (1992).
- 19 Spiker, E. C.; Comer, V. J.; Hosker, R. P.; Sherwood, S. I. (1992) Dry deposition of SO₂ on limestone and marble:
20 the role of humidity. In: Rodrigues, J. D.; Henriques, F.; Jeremias, F. T., eds. Proceedings of the 7th
21 international congress on deterioration and conservation of stone; June; Lisbon, Portugal. Lisbon, Portugal:
22 Laboratório Nacional de Engenharia Civil; pp. 397-406.
- 23 Storm, G. L.; Fosmire, G. J.; Bellis, E. D. (1994) Persistence of metals in soil and selected vertebrates in the vicinity
24 of the Palmerton zinc smelters. *J. Environ. Qual.* 23: 508-514.
- 25 Strandberg, H.; Johansson, L. G. (1997) The effect of air pollutants on cultural objects: laboratory investigations.
26 In: MacLeod, I. D., Pennec, S. L.; Robbiola, L., eds. Metal 95: actes de la conférence internationale sur la
27 conservation des métaux [Proceedings of the international conference on metals conservation]; September
28 1995; Auxois, France. London, UK: James & James (Science Publishers), Ltd.; pp. 83-85.
- 29 Strandberg, H.; Johansson, L.-G. (1997) The formation of black patina on copper in humid air containing traces of
30 SO₂. *J. Electrochem. Soc.* 144: 81-89.
- 31 Sydberger, T.; Ericsson, R. (1977) Laboratory testing of the atmospheric corrosion of steel. *Werkst. Korros.* 28:
32 154-158.
- 33 Sykes, R. I.; Gabruk, R. S. (1997) A second-order closure model for the effect of averaging time on turbulent plume
34 dispersion. *J. Appl. Meteorol.* 36: 1038-1045.
- 35 Tang, I. N. (1997) Thermodynamic and optical properties of mixed-salt aerosols of atmospheric importance. *J.
36 Geophys. Res. [Atmos.]* 102: 1883-1893.
- 37 Tasdemiroglu, E. (1991) Costs of materials damage due to air pollution in the United States. *Renewable Energy* 1:
38 639-648.
- 39 Taylor, C. R.; Reichelderfer, K. H.; Johnson, S. R. (1993) Agricultural sector models for the United States:
40 descriptions and selected policy applications. Ames, IA: Iowa State University Press.
- 41 Taylor, G. E., Jr.; Johnson, D. W.; Andersen, C. P. (1994) Air pollution and forest ecosystems: a regional to global
42 perspective. *Ecol. Appl.* 4: 662-689.
- 43 Tegen, I.; Lacis, A. A.; Fung, I. (1996) The influence on climate forcing of mineral aerosols from disturbed soils.
44 *Nature (London)* 380: 419-422.
- 45 Thornton, F. C.; Schaedle, M.; Raynal, D. J. (1987) Effects of aluminum on red spruce seedlings in solution culture.
46 *Environ. Exp. Bot.* 27: 489-498.
- 47 Tilman, D. (1996) Biodiversity: population versus ecosystem stability. *Ecology* 77: 350-363.
- 48 Tilman, D.; Downing, J. A. (1994) Biodiversity and stability in grasslands. *Nature (London)* 367: 363-365.
- 49 Tong (1991).
- 50 Trijonios and Pitchford (1987).
- 51 Turner, J.; Kelly, J. (1981) Relationships between soil nutrients and vegetation in a north coast forest, New South
52 Wales. *Aust. For. Res.* 11: 201-208.
- 53

- 1 Turner, J.; Lambert, M. J. (1980) Sulfur nutrition of forests. In: Shriner, D. S.; Richmond, C. R.; Lingberg, S. E.,
2 eds. Atmospheric sulfur deposition: environmental impact and health effects, proceedings of the second life
3 sciences symposium; October 1979; Gatlinburg, TN. Ann Arbor, MI: Ann Arbor Science Publishers, Inc.;
4 pp. 321-333.
- 5 Turner, J.; Lambert, M. J.; Gessel, S. P. (1977) Use of foliage sulphate concentrations to predict response to urea
6 application by Douglas-fir. *Can. J. For. Res.* 7: 476-480.
- 7 Twomey (1974).
- 8 Tyler, G. (1972) Heavy metals pollute nature, may reduce productivity. *Ambio* 1: 52-59.
- 9 U.S. Environmental Protection Agency. (1979) Protecting visibility: an EPA report to Congress. Research Triangle
10 Park, NC: Office of Air Quality Planning and Standards; EPA report no. EPA-450/5-79-008. Available from:
11 NTIS, Springfield, VA; PB80-220320.
- 12 U.S. Environmental Protection Agency. (1982) Air quality criteria for particulate matter and sulfur oxides. Research
13 Triangle Park, NC: Office of Health and Environmental Assessment, Environmental Criteria and Assessment
14 Office; EPA report no. EPA-600/8-82-029aF-cF. 3v. Available from: NTIS, Springfield, VA; PB84-156777.
- 15 U.S. Environmental Protection Agency. (1984).
- 16 U.S. Environmental Protection Agency. (1986a) Air quality criteria for ozone and other photochemical oxidants.
17 Research Triangle Park, NC: Office of Health and Environmental Assessment, Environmental Criteria and
18 Assessment Office; report nos. EPA-600/8-84-020aF-eF. 5v. Available from: NTIS, Springfield, VA;
19 PB87-142949.
- 20 U.S. Environmental Protection Agency. (1986b) Air quality criteria for lead. Research Triangle Park, NC: Office of
21 Health and Environmental Assessment, Environmental Criteria and Assessment Office; EPA report no.
22 EPA-600/8-83/028aF-dF. 4v. Available from: NTIS, Springfield, VA; PB87-142378.
- 23 U.S. Environmental Protection Agency. (1988) Workbook for plume visual impact screening and analysis. Research
24 Triangle Park, NC: Office of Air Quality Planning and Standards; report no. EPA-450/4-88-015. Available
25 from: NTIS, Springfield, VA; PB89-151286.
- 26 U.S. Environmental Protection Agency. (1992) Interagency workgroup on air quality modeling (IWAQM) work
27 plan rationale. Research Triangle Park, NC: Office of Air Quality Planning and Standards; report no.
28 EPA-454/R-92-001.
- 29 U.S. Environmental Protection Agency. (1993) Air quality criteria for oxides of nitrogen. Research Triangle Park,
30 NC: Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office; report
31 nos. EPA/600/8-91/049aF-cF. 3v. Available from: NTIS, Springfield, VA; PB95-124533, PB95-124525, and
32 PB95-124517.
- 33 U.S. Environmental Protection Agency. (1994).
- 34 U.S. Environmental Protection Agency. (1995a) Inter-agency workgroup on air quality modeling (IWAQM):
35 assessment of phase I recommendations regarding the use of MESOPUFF II. Research Triangle Park, NC:
36 U.S. Environmental Protection Agency, Emissions, Monitoring and Analysis Division; report no.
37 EPA-454/R-95-006. Available from: NTIS, Springfield, VA; PB95-241931.
- 38 U.S. Environmental Protection Agency. (1995b) Testing of meteorological and dispersion models for use in
39 regional air quality modeling. Research Triangle Park, NC: Office of Air Quality Planning and Standards;
40 report no. EPA-454/R-95-005. Available from: NTIS, Springfield, VA; PB95-215638.
- 41 U.S. Environmental Protection Agency. (1995c) A user's guide for the CALMET meteorological model. Research
42 Triangle Park, NC: Office of Air Quality Planning and Standards; report no. EPA-454/B-95-002. Available
43 from: NTIS, Springfield, VA; PB95-266383.
- 44 U.S. Environmental Protection Agency. (1995d) A user's guide for the CALPUFF dispersion model. Research
45 Triangle Park, NC: Emissions, Monitoring and Analysis Division; report no. EPA-454/B-95-006. Available
46 from: NTIS, Springfield, VA; PB96-144258.
- 47 U.S. Environmental Protection Agency. (1995e) Interim findings on the status of visibility research. Research
48 Triangle Park, NC: Office of Research and Development; report no. EPA/600/R-95/021.
- 49 U.S. Environmental Protection Agency. (1996a) Air quality criteria for ozone and related photochemical oxidants.
50 Research Triangle Park, NC: Office of Research and Development; report nos. EPA/600/AP-93/004aF-cF.
51 3v. Available from: NTIS, Springfield, VA; PB96-185582, PB96-185590, and PB96-185608. Available
52 online at: www.epa.gov/ncea/ozone.htm.
- 53 U.S. Environmental Protection Agency. (1996b) Air quality criteria for particulate matter. Research Triangle Park,
54 NC: National Center for Environmental Assessment-RTP Office; report nos. EPA/600/P-95/001aF-cF. 3v.
55 Available from: NTIS, Springfield, VA; PB96-168224.

- 1 U.S. Environmental Protection Agency. (1996) The benefits and costs of the Clean Air Act, 1970 to 1990 [draft
2 report to Congress]. Washington, DC: Office of Air and Radiation, Office of Policy Analysis and Review,
3 and Office of Policy Planning and Evaluation; October.
- 4 U.S. Environmental Protection Agency. (1997) Summary of the particulate monitoring program. Washington, DC:
5 Office of Air and Radiation. Available: <http://ttnwww.rtpnc.epa.gov/implement>.
- 6 U.S. Environmental Protection Agency. (1997) Nitrogen oxides: impacts on public health and the environment.
7 Washington, DC: Office of Air and Radiation; August. Available online at:
8 www.epa.gov/ttncaaa1/t1ria.html.
- 9 U.S. Environmental Protection Agency. (1997) Regulatory Impact analyses for the particulate matter and ozone
10 national ambient air quality standards and proposed regional haze rule. Research Triangle Park, NC: Office
11 of Air Quality Planning and Standards; EPA air docket A-96-56, document no. VI-B-09-(r).
- 12 U.S. Environmental Protection Agency. (1998) The regional NOx SIP call & reduced atmospheric deposition of
13 nitrogen: benefits to selected estuaries. September.
- 14 U.S. Environmental Protection Agency. (1998) National air pollutant emission trends, proceedings document,
15 1900-1996. Section 4.0 national criteria pollutant estimates 1985-1996 methodology. Research Triangle Park,
16 NC: Office of Air Quality Planning and Standards; report no. EPA/454/R-98/008. Available:
17 www.epa.gov/ttn/chief/ei/index.html#Guidance.
- 18 U.S. Environmental Protection Agency. (1999) Regulatory impact analysis for the final regional haze rule. April.
- 19 U.S. Environmental Protection Agency. (1999) Effects of particulate matter on vegetation and ecosystems (draft).
20 Research Triangle Park, NC: National Center for Environmental Assessment; Office of Research and
21 Development; July.
- 22 U.S. Environmental Protection Agency. (1999) Integrated air quality modeling for regulatory applications: 1.
23 Description of REMSAD. 2. Evaluation of REMSAD 1990 base case. Washington, DC: Office of Air
24 Quality Planning and Standards.
- 25 Van Breemen, N.; Burrough, P. A.; Velthorst, E. J.; Van Dobben, H. F.; De Wit, T.; Ridder, T. B.; Reijnders, H. F.
26 R. (1982) Soil acidification from atmospheric ammonium sulphate in forest canopy throughfall. *Nature*
27 (London) 299: 548-550.
- 28 Van Breemen, N.; Mulder, J.; Driscoll, C. T. (1983) Acidification and alkalization of soils. *Plant Soil* 75:
29 283-308.
- 30 Van Breemen, N.; Van Dijk, H. F. G. (1988) Ecosystem effects of atmospheric deposition of nitrogen in The
31 Netherlands. In: Dempster, J. P.; Manning, W. J., eds. Excess nitrogen deposition. *Environ. Pollut.* 54:
32 249-274.
- 33 Van Dijk, H. F. G.; Roelofs, J. G. M. (1988) Effects of excessive ammonium deposition on the nutritional status
34 and condition of pine needles. *Physiol. Plant.* 73: 494-501.
- 35 Van Dorland, R.; Dentener, F. J.; Lelieveld, J. (1997) Radiative forcing due to tropospheric ozone and sulfate
36 aerosols. *J. Geophys. Res. [Atmos.]* 102: 28,079-28,100.
- 37 Van Miegroet, H.; Cole, D. W. (1984) The impact of nitrification on soil acidification and cation leaching in red
38 alder ecosystem. *J. Environ. Qual.* 13: 586-590.
- 39 Van Miegroet, H.; Johnson, D. W.; Todd, D. E. (1993) Foliar response of red spruce saplings to fertilization with
40 Ca and Mg in the Great Smoky Mountains National Park. *Can. J. For. Res.* 23: 89-95.
- 41 Vasconcelos, L. A. de P.; Kahl, J. D. W.; Liu, D.; Macias, E. S.; White, W. H. (1996) Patterns of dust transport to
42 the Grand Canyon. *Geophys. Res. Lett.* 23: 3187-3190.
- 43 Viles, H. A. (1990) The early stages of building stone decay in an urban environment. *Atmos. Environ.* 24A:
44 229-232.
- 45 Vitousek, P. M.; Mooney, H. A.; Lubchenco, J.; Melillo, J. M. (1997) Human domination of Earth's ecosystems.
46 *Science (Washington, DC)* 277: 494-499.
- 47 Vogt, K. A.; Dahlgren, R.; Ugolini, F.; Zabowski, D.; Moore, E. E.; Zasoski, R. (1987a) Aluminum, Fe, Ca, Mg, K,
48 Mn, Cu, Zn and P in above- and belowground biomass. I. *Abies amabilis* and *Tsuga mertensiana*.
49 *Biogeochemistry* 4: 277-294.
- 50 Vogt, K. A.; Dahlgren, R.; Ugolini, F.; Zabowski, D.; Moore, E. E.; Zasoski, R. (1987b) Aluminum, Fe, Ca, Mg, K,
51 Mn, Cu, Zn and P in above- and belowground biomass. II. Pools, and circulation in a subalpine *Abies*
52 *amabilis* stand. *Biogeochemistry* 4: 295-311.
- 53 Waggoner, A. P.; Weiss, R. E. (1980) Comparison of fine particle mass concentration and light scattering extinction
54 in ambient aerosol. *Atmos. Environ.* 14: 623-626.

- 1 Waggoner, A. P.; Weiss, R. E.; Ahlquist, N. C.; Covert, D. S.; Will, S.; Charlson, R. J. (1981) Optical
2 characteristics of atmospheric aerosols. In: White, W. H.; Moore, D. J.; Lodge, J. P., Jr., eds. Plumes and
3 visibility: measurements and model components: proceedings of the symposium; November 1980; Grand
4 Canyon National Park, AZ. *Atmos. Environ.* 15: 1891-1909.
- 5 Wall, D. H. (1999) Biodiversity and ecosystem functioning. *BioScience* 49: 107-108.
- 6 Walton, J. R.; Johnson, J. B.; Wood, G. C. (1982) Atmospheric corrosion initiation by sulphur dioxide and
7 particulate matter: I. test-cell apparatus for simulated atmospheric corrosion studies. *Br. Corros. J.* 17: 59-64.
- 8 Walton, J. R.; Johnson, J. B.; Wood, G. C. (1982) Atmospheric corrosion initiation by sulphur dioxide and
9 particulate matter: II. characterisation and corrosivity of individual particulate atmospheric pollutants. *Br.*
10 *Corros. J.* 17: 65-70.
- 11 Waring (1987).
- 12 Waring, R. H.; Schlesinger, W. H. (1985) The carbon balance of trees. In: *Forest ecosystems: concepts and*
13 *management.* Orlando, FL: Academic Press, Inc.; pp. 7-37.
- 14 Watson, J. G.; Chow, J. C. (1994) Clear sky visibility as a challenge for society. *Annu. Rev. Energy Environ.* 19:
15 241-266.
- 16 Watson, W. D.; Jaksch, J. A. (1982) Air pollution: household soiling and consumer welfare losses. *J. Environ.*
17 *Econ. Manage.* 9: 248-262.
- 18 Watson, J. G.; Chow, J. C.; Richards, L. W.; Haase, D. L.; McDade, C.; Dietrich, D. L.; Moon, D.; Sloane, C.
19 (1991) The 1989-90 Phoenix urban haze study, volume II: the apportionment of light extinction to sources
20 [final report]. Reno, NV: University and Community College System of Nevada, Desert Research Institute;
21 DRI document no. 8931.5F1.
- 22 Watson, J. G.; Chow, J. C.; Fujita, E. M.; Frazier, C. A.; Lu, Z.; Heisler, S. L.; Moore, C. T. (1994) Aerosol data
23 validation for the 1992-93 Tuscon urban haze study. In: *Proceedings [of the] 87th annual meeting &*
24 *exhibition of the Air & Waste Management Association. Volume 1A: atmospheric Sciences & ozone; June;*
25 *Cincinnati, OH. Pittsburgh, PA: Air & Waste Management Association; 94-TA24.02.*
- 26 Webb, A. H.; Bawden, R. J.; Busby, A. K.; Hopkins, J. N. (1992) Studies on the effects of air pollution on
27 limestone degradation in Great Britain. *Atmos. Environ. Part B* 26: 165-181.
- 28 Wedin and Tilman (1996).
- 29 Wenny, B. N.; Schafer, J. S.; DeLuisi, J. J.; Saxena, V. K.; Barnard, W. F.; Petropavlovskikh, I. V.; Vergamini, A.
30 J. (1998) A study of regional aerosol radiative properties and effects on ultraviolet-B radiation. *J. Geophys.*
31 *Res. [Atmos.]* 103: 17,083-17,097.
- 32 Wesselink, L. G.; Meiwes, K.-J.; Matzner, E.; Stein, A. (1995) Long-term changes in water and soil chemistry in
33 spruce and beech forests, Solling, Germany. *Environ. Sci. Technol.* 29: 51-58.
- 34 Whitby (1978).
- 35 White, W. H.; Macias, E. S. (1990) Light scattering by haze and dust at Spirit Mountain, Nevada. In: Mathai, C. V.,
36 ed. *Visibility and fine particles: an A&WMA/EPA international specialty conference; October 1989; Estes*
37 *Park, CO. Pittsburgh, PA; Air & Waste Management Association; pp. 914-922. (A&WMA transactions*
38 *series no. TR-17).*
- 39 White, W. H.; Seigneur, C.; Heinold, D. W.; Eltgroth, M. W.; Richards, L. W.; Roberts, P. T.; Bhardwaja, P. S.;
40 Conner, W. D.; Wilson, W. E., Jr. (1985) Predicting the visibility of chimney plumes: an intercomparison of
41 four models with observations at a well-controlled power plant. *Atmos. Environ.* 19: 515-528.
- 42 White, W. H.; Macias, E. S.; Niningger, R. C.; Schorran, D. (1994) Size-resolved measurements of light scattering by
43 ambient particles in the southwestern U.S.A. *Atmos. Environ.* 28: 909-921.
- 44 White, W. H.; Macias, E. S.; Vasconcelos, L. A. de P.; Farber, R. J.; Mirabella, V. A.; Green, M. C.; Pitchford, M.
45 L. (1999) Tracking regional background in a haze attribution experiment. *J. Air Waste Manage. Assoc.* 49:
46 599-602.
- 47 Wilson and Suh (1997).
- 48 Winner, W. E.; Bewley, J. D. (1978a) Terrestrial mosses as bioindicators of SO₂ pollution stress: synecological
49 analysis and the index of atmospheric purity. *Oecologia* 35: 221-230.
- 50 Winner, W. E.; Bewley, J. D. (1978b) Contrasts between bryophyte and vascular plant synecological responses in
51 an SO₂-stressed white spruce association in central Alberta. *Oecologia* 33: 311-325.
- 52 Wittenburg, C.; Dannecker, W. (1992) Dry deposition and deposition velocity of airborne acidic species upon
53 different sandstones. In: *Proceedings of the 1992 European aerosol conference; September; Oxford, United*
54 *Kingdom. J. Aerosol Sci.* 23(suppl. 1): S869-S872.
- 55

1 Wolff, G. T.; Collins, D. C.; Rodgers, W. R.; Verma, M. H.; Wong, C. A. (1990) Spotting of automotive finishes
2 from the interactions between dry deposition of crustal material and wet deposition of sulfate. *J. Air Waste*
3 *Manage. Assoc.* 40: 1638-1648.

4 World Health Organization. (1997) Nitrogen oxides. 2nd ed. Geneva, Switzerland: World Health Organization.
5 (Environmental health criteria 188).

6 Wu, P.-M.; Okada, K. (1994) Nature of coarse nitrate particles in the atmosphere—a single particle approach.
7 *Atmos. Environ.* 28: 2053-2060.

8 Wu, X. A.; Seigneur, C.; Bergstrom, R. W. (1996) Evaluation of a sectional representation of size distributions for
9 calculating aerosol optical properties. *J. Geophys. Res. [Atmos.]* 101: 19,277-19,283.

10 Xu and Balik (1989).

11 Yerrapragada, S. S.; Jaynes, J. H.; Chirra, S. R.; Gauri, K. L. (1994) Rate of weathering of marble due to dry
12 deposition of ambient sulfur and nitrogen dioxides. *Anal. Chem.* 66: 655-659.

13 Yocom, J. E.; Grappone, N. (1976) Effects of power plant emissions on materials. Palo Alto, CA: Electric Power
14 Research Institute; report no. EPRI/EC-139. Available from: NTIS, Springfield, VA; PB-257 539.

15 Yocom, J. E.; Upham, J. B. (1977) Effects of economic materials and structures. In: Stern, A. C., ed. *Air pollution.*
16 3rd ed. Volume II. New York, NY: Academic Press; pp. 93-94.

17 Young, P. (1996) Pollution-fueled "biodeterioration" threatens historic stone: researchers are probing the role
18 microorganisms play in the decay of buildings and artwork. *Environ. Sci. Technol.* 30: 206A-208A.

19 Youngs et al. (1993).

20 Zannetti, P.; Tombach, I.; Balson, W. (1990) Calculation of visual range improvements from SO₂ emission
21 controls—I. semi-empirical methodology. *Atmos. Environ. Part A* 24: 2361-2368.

22 Zannetti, P.; Tombach, I.; Cvencek, S.; Balson, W. (1993) Calculation of visual range improvements from SO₂
23 emission controls—II. an application to the eastern United States. *Atmos. Environ. Part A* 27: 1479-1490.

24 Zappia, G.; Sabbioni, C.; Gobbi, G. (1993) Non-carbonate carbon content on black and white areas of damaged
25 stone monuments. *Atmos. Environ.* 27A: 1117-1121.

26 Zappia, G.; Sabbioni, C.; Pauri, M. G.; Gobbi, G. (1994) Mortar damage due to airborne sulfur compounds in a
27 simulation chamber. *Mater. Struct.* 27: 469-473.

28 Zhang, X. Q.; McMurry, P. H.; Hering, S. V.; Casuccio, G. S. (1993) Mixing characteristics and water content of
29 submicron aerosols measured in Los Angeles and at the Grand Canyon. *Atmos. Environ. Part A* 27:
30 1593-1607.

31 Zhang, X.; Turpin, B. J.; McMurry, P. H.; Hering, S. V.; Stolzenburg, M. R. (1994) Mie theory evaluation of
32 species contributions to 1990 wintertime visibility reduction in the Grand Canyon. *Air Waste* 44: 153-162.

33
34