



# 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.



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National Center for Environmental Assessment  
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## **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-yr) 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  $\text{PM}_{10}$  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.

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## 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  $\mu\text{m}$  in size). The 1987 revision of the TSP NAAQS to  $\text{PM}_{10}$  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  $\text{PM}_{10}$  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



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

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

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 (Hicks, 1986).

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

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

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

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

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

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

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

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

### **9.2.1.1 Direct Plant Response**

#### ***Introduction***

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

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

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

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

### ***Effects of Coarse Particles***

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

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

## ***Effects of Fine Particles***

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

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

***Acidic Deposition.*** The effects of acidic deposition have been given wide exposure in the media and elsewhere (U. S. Environmental Protection Agency, 1984; Linthurst, 1984; Hogan et al., 1998). Probably the most extensive assessment of acidic deposition processes and, effects is the NAPAP Biennial Report to Congress: An Integrated Assessment (National Science and Technology Council, 1998). Concern regarding the effects on crops and forest trees has resulted in extensive monitoring and research. Exposures to acidic rain or clouds can be divided into ‘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 O<sub>3</sub> and  
6 SO<sub>2</sub>. Chevone et al. (1986) observed increased visible injury on soybean and pinto bean when  
7 acid aerosol exposure preceded O<sub>3</sub> exposure, while linear decreases in dry root weight of yellow  
8 poplar as acidity increased when exposures were to O<sub>3</sub> 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 O<sub>3</sub> 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 SO<sub>2</sub> or O<sub>3</sub>.

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<sup>-1</sup>). These are termed “trace” elements.  
16 Trace elements with a density greater than 6g·cm<sup>-3</sup> 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 SO<sub>2</sub> 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 *Chaetomium 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 ( $\text{C}_{10}\text{H}_8$ ) 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  $\alpha$ -pinene,  $\beta$ -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).

## 25 26 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

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

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

Human existence on this planet depends on nature and the life-support services ecosystems 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).

ecosystems, and the species of which they are comprised, sustain and fulfill human life (Daily, 1997. 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 (Westman,1978; Daily, 1997). The economic benefits and values associated with ecosystem functions and services and the need to preserve them because of their value to human life are discussed by Constanza et al. (1997) and (Pimentel et al., 1997).

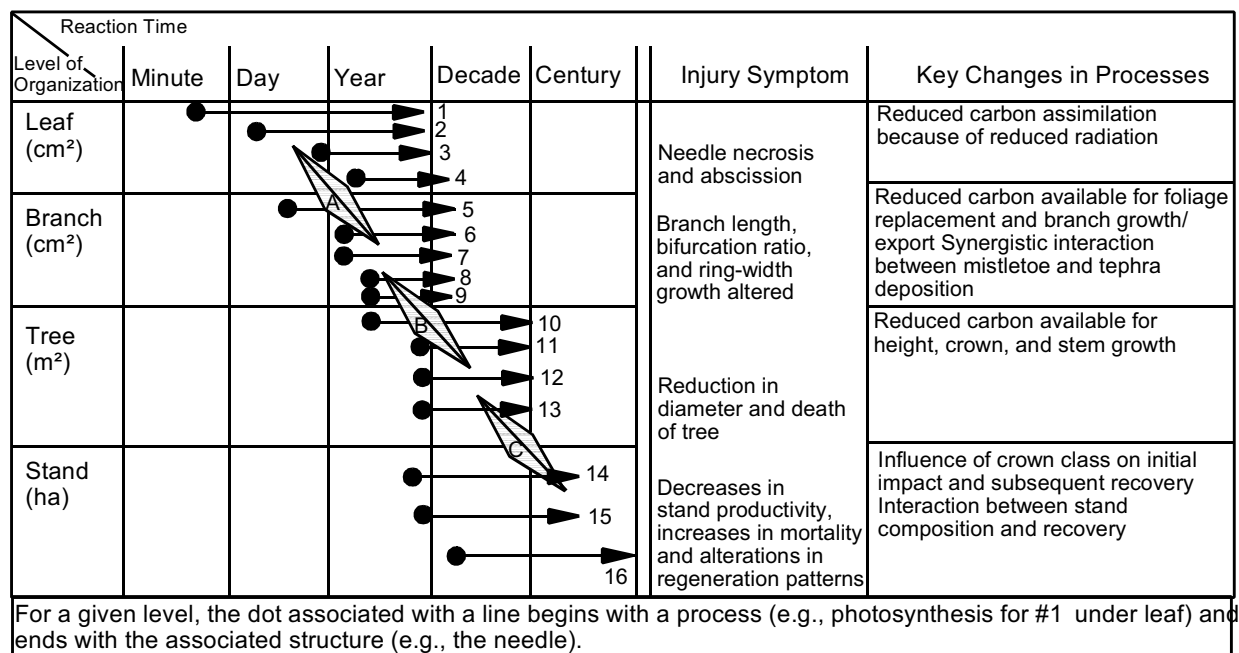
Ecosystem functions are characterized by the way components interact. These are the functions that maintain clean water, pure air, a green earth, and a balance of creatures, the

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 (Table 9-1; Westman, 1978; Daily, 1997).

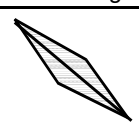
Concern has risen in recent years concerning the integrity of ecosystems (Harwell et al., 1999). There are few ecosystems on planet earth today that are not influenced by humans (Freudenburg and Alario, 1999; Vitousek et. al., 1997; Matson et al. 1997; Noble and Dirzo, 1997). The scientific literature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

### **9.3.2 Ecosystem Response to Stress**

Ecosystem responses to stresses begin at the population level. Population changes begin with the response of individual plants or animals. Plant responses, both structural and functional, must be propagated from the individual to the more complex levels of community interaction to produce observable changes in an ecosystem (Figure 9-1). At least three levels of biological interaction are involved: (1) the individual plant and its environment, (2) the population and its environment, and (3) the biological community composed of many species and its environment (Billings, 1978). The response of individual organisms within a population based on their genetic constitution (genotype), stage of growth at time of exposure, and the microhabitats in which they are growing vary in their ability to withstand the stress of environmental changes (Levin, 1998). The range of variability within which the species of a population can exist and function determines the ability of a population to survive. Individual organisms within a population vary in their ability to withstand the stress of environmental changes. The range within which these organisms can exist and function determines the ability of the population to 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<br>Carbon pools-2<br>Needle number and size-3<br>Needle retention/abscission-4      | Tree Level  | Height and diameter growth-10<br>Crown shape and size-11<br>Tree vigor-12<br>Mortality-13 |
| Branch Level                                      | Carbon allocation-5<br>Branch growth-6<br>Branch morphology-7<br>Branch vigor-8<br>Branch retention-9 | Stand Level | Productivity-14<br>Mortality-15<br>Species composition-16                                 |

| Evaluating Interactions Between Different Levels of Organization                    |  |
|---|--|
|  | <p>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.</p> <p>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.</p> <p>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.</p> <p>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.</p> |

**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).

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

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

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

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



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

### **9.3.3 Direct Effects of Particulate Matter**

#### **9.3.3.1 Introduction**

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

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

Evidence from studies of effects of PM deposition, specifically chemically inert and active dusts indicates that, within a population, plants exhibit a wide range of sensitivity, which is the basis for the natural selection of tolerant individuals (Saunders and Godzik, 1986). Rapid evolution of certain populations of tolerant species at sites with heavy trace element and nitrate deposition has been observed. Tolerant individuals present in low frequencies in populations when growing in unpolluted areas have been selected for tolerance at both the seedling and adult stages when exposed to trace metal or nitrate deposition (Ormrod, 1984; U.S. Environmental Protection Agency, 1993). Chronic pollutant injury to a forest community may result in the loss of sensitive species, loss of tree canopy, and maintenance of a residual cover of pollutant-tolerant herbs or shrubs that are recognized as successional species (Table 9-2; Smith, 1990). Frequently, trace metals that penetrate the above-ground plant parts are less injurious than when taken up 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"> <li>a. Reduced litter decomposition</li> <li>b. Increased plant and soil leaching and soil weathering</li> <li>c. Disturbance of microbial symbioses</li> </ul>                                      | 2. Reduced growth, less biomass  |
| 3. Forest metabolism <ul style="list-style-type: none"> <li>a. Decreased photosynthesis</li> <li>b. Increased respiration</li> <li>c. Altered carbon allocation</li> </ul>   | 3. Reduced growth, less biomass  |
| 4. Forest stress, alteration <ul style="list-style-type: none"> <li>a. Phytophagous insects, increased or decreased activity</li> <li>b. Microbial pathogens, increased or decreased activity</li> <li>c. Foliar damage increased by direct air pollution influence</li> </ul> | 4. Altered ecosystem stress: increased or decreased insect infestations; increased or decreased disease epidemics; reduced growth, less biomass, altered species composition |

Source: Smith (1990).

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

### 9.3.3.2 Direct Effects

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

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

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

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

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

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

### **9.3.4 Indirect Effects of Particulate Matter**

#### **9.3.4.1 Introduction**

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

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

#### 9.3.4.2 Nitrogen

Nitrogen has long been recognized as the nutrient most important for plant growth. Plants usually absorb nitrogen through their roots by absorbing  $\text{NH}_4^+$  or  $\text{NO}_3^-$  or by symbiotic organisms. Plants, however, vary in their ability to absorb ammonium and nitrate (Chapin et al., 1987). Nitrogen is of overriding importance in plant metabolism and, to a large extent, governs the utilization of phosphorus, potassium and other nutrients. Most of the nitrogen in soils is associated with organic matter. Typically, the availability of nitrogen via the nitrogen cycle controls net primary productivity and the possibly decomposition rate. Photosynthesis is influence by nitrogen uptake in that approximately 75% of the nitrogen in a plant leaf is used during the process of photosynthesis. The nitrogen-photosynthesis relationship is, therefore, critical to the growth of trees and other plants (Chapin et al., (1987).

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

The impact of increasing nitrogen deposition on the nitrogen cycle in forests, wetlands, and aquatic ecosystems is discussed in detail in the oxides of nitrogen criteria document (U.S. Environmental Protection Agency, 1993, 1997; Garner, 1994; World Health Organization, 1997). A major concern is “nitrogen saturation”, the result of the deposition of large amounts of nitrates 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  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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 ( $\text{Al}^{3+}$ ) 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

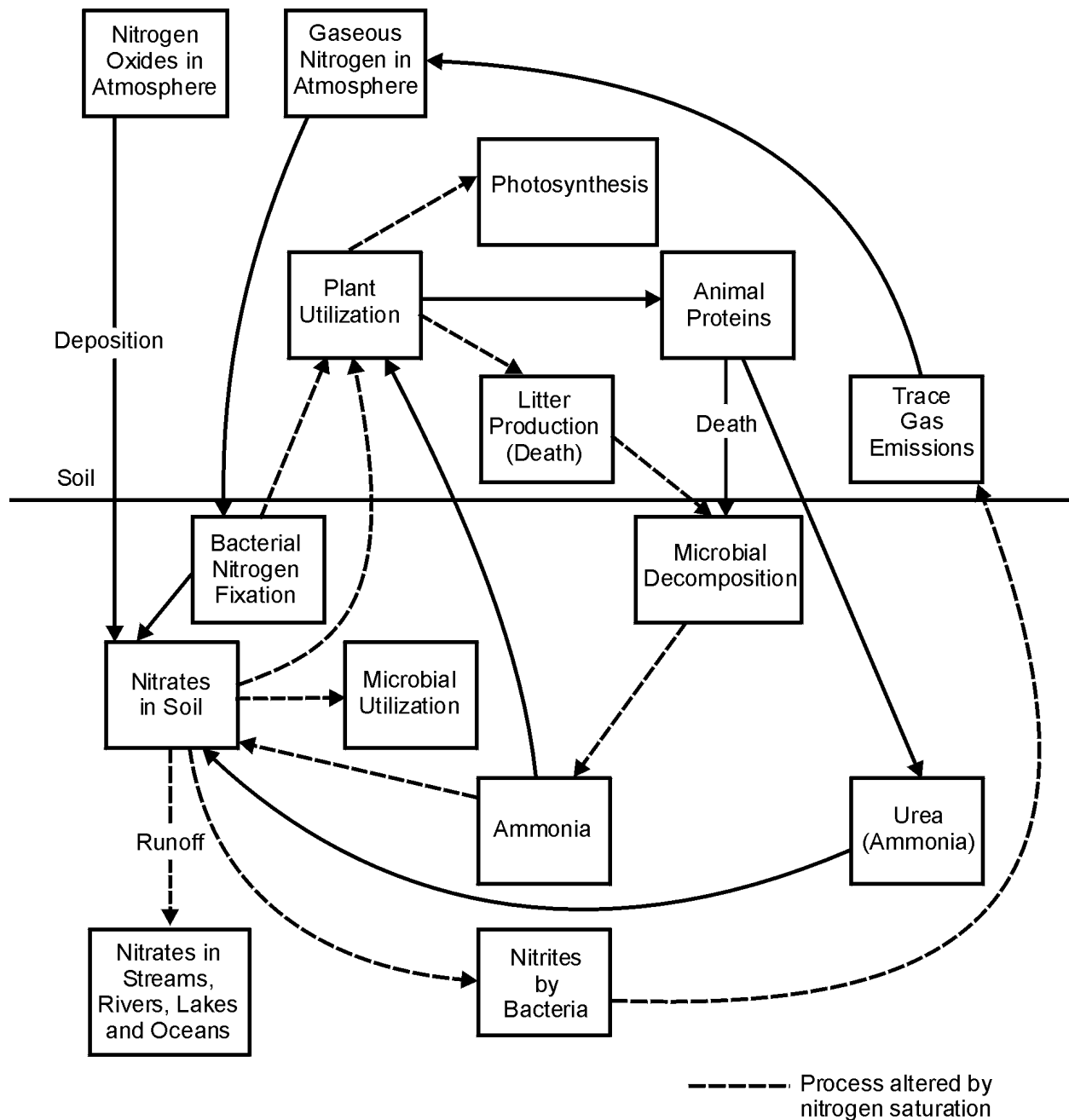
1 and alter many plant and soil processes involved in nitrogen cycling (Aber et al., 1989). Among  
2 the processes affected are (1) plant uptake and allocation, (2) litter production,  
3 (3) immobilization, (includes ammonification [the release of ammonia] and nitrification  
4 [conversion of ammonia to nitrate during decay of little 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 (Pearcy 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).

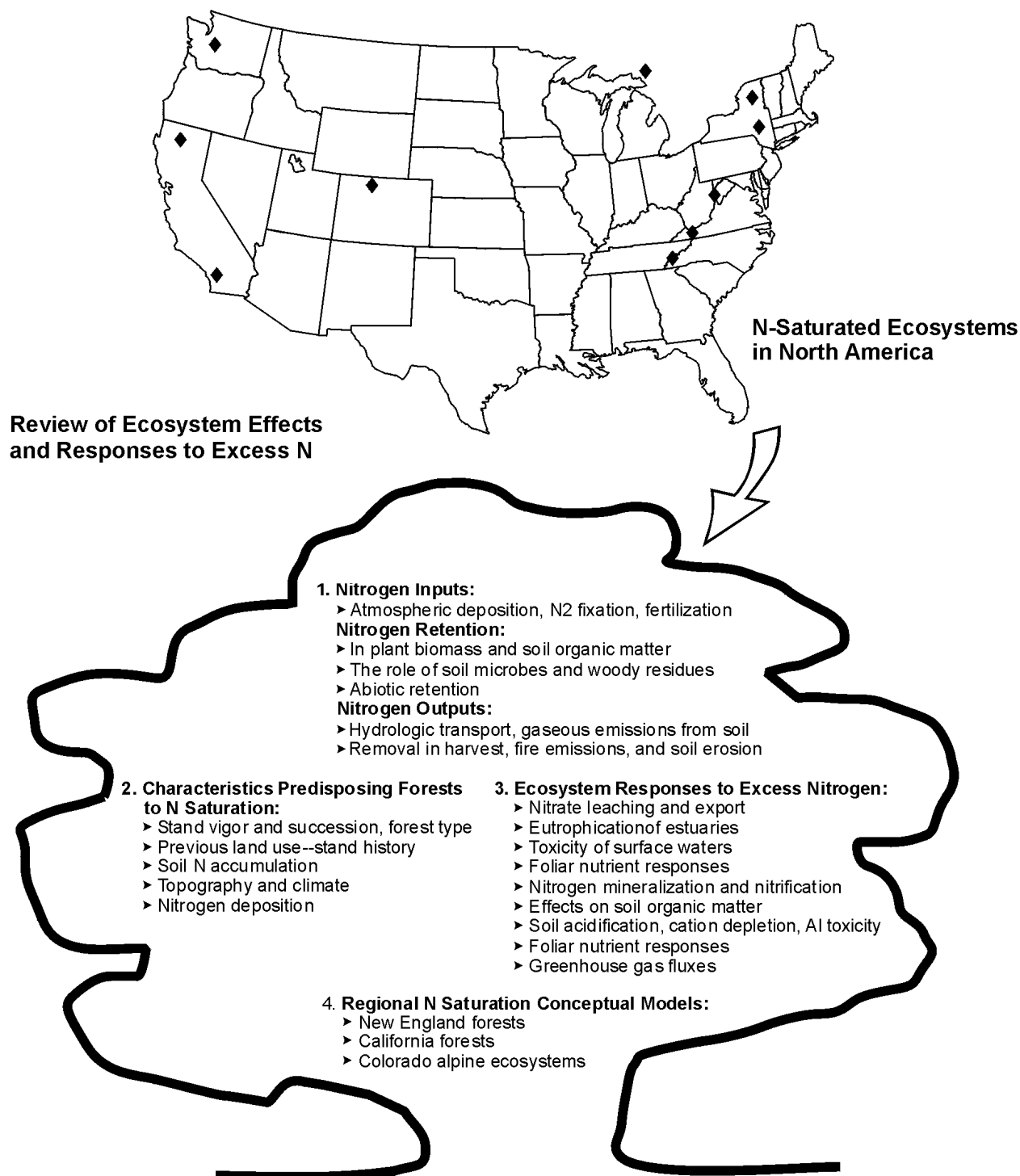
- 1 have been shifting toward species commonly found on nitrogen-rich areas. It also was observed
- 2 that the fruiting bodies of mycorrhizal fungi had decreased in number.

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

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

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

In experimental studies of nitrogen deposition by Wedin and Tilman (1996) on Minnesota grasslands, plots dominated by native warm-season grasses shifted to low-diversity mixtures dominated by cool-season grasses at all but the lowest rates of nitrogen addition. Grasslands 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  $\text{SO}_2$  (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  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  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).

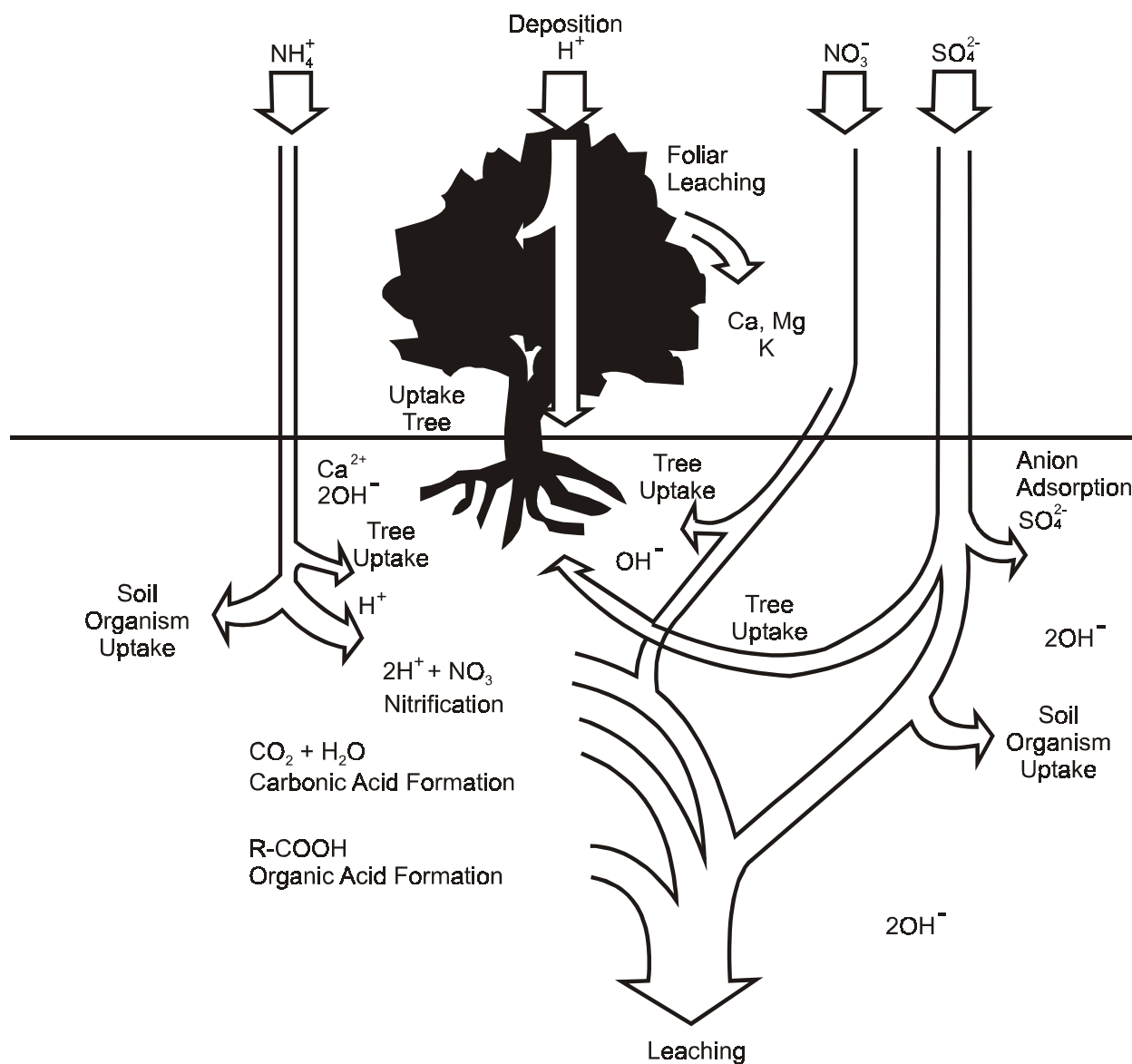
27 These changes are spatially and temporally consistent within emissions of  $\text{SO}_2$  and  $\text{NO}_2$   
28 across the region, suggesting that increased acidification of forest soils has occurred. Increases in  
29 the levels of Al and Fe typically occur as base cations are removed from soils 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 ( $\text{NO}_3^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ) and the associated hydrogen ( $\text{H}^+$ ) 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  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ;  
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  $\text{H}^+$  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  $NH_4^+$  by vegetation or soil microorganisms causes
- 3 the release of  $H^+$  in order to maintain charge balance. Uptake of nutrients in anionic form ( $NO_3^-$ ,
- 4  $SO_4^{2-}$ ,  $PO_4^{3-}$ ) causes the release of  $OH^-$  in order to maintain charge balance. Thus the net

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

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

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

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

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

A major concern has been that soil acidity would lead to nutrient deficiency. Tree species 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  $\text{Ca}^{2+}$  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<sup>-1</sup> as result of  $\text{Ca}^{2+}$  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  $\text{Al}^{3+}$ , 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,

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

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

Air pollution is not the sole cause of soil change. High rates of acidification are occurring in less polluted regions of the western United States and Australia due to internal soil processes such as tree uptake of nitrate and nitrification associated with excessive nitrogen fixation (Johnson et al., 1991a). Many studies have shown that acidic deposition is not a necessary condition for the presence of extremely acid soils, as evidenced by their presence in unpolluted, even pristine forests of the northwestern United States and Alaska (Johnson et al., 1991b). The soil becomes acidic when  $\text{H}^+$  ions attached to  $\text{NH}_4^+$  or  $\text{HNO}_3$  remain in the soil after nitrogen is taken up by plants. For example, Johnson et al. (1982b) found significant reductions in exchangeable  $\text{K}^+$  over a period of only 14 years in a relatively unpolluted Douglas fir Integrated Forest Study (IFS) site in the Washington Cascades. The effects of acid deposition at this site were negligible relative to the effects of natural leaching (primarily carbonic acid) and nitrogen tree uptake (Cole and Johnson, 1977). Even in polluted regions, numerous studies have shown the importance of tree uptake of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in soil acidification. Binkley et al. (1989) attributed the marked acidification (pH decline of 0.3 to 0.8 units and base saturation declines of 30 to 80%) of abandoned agricultural soil in South Carolina over a 20-year period to  $\text{NH}_4^+$  and  $\text{NO}_3^-$  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  $\text{Al}^{3+}$  and decreased soil exchangeable  $\text{Ca}^{2+}$  (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  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  deposition was attributed to a decline in emissions and the decline in stream  
14 water  $\text{SO}_4^{2-}$  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  $\text{SO}_2$  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).

#### 9.3.4.5 Trace Elements

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

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

Accumulation of heavy metals in litter presents the greatest potential for interference with nutrient cycling. Accumulation of metals in the litter occurs chiefly around brass works and lead and zinc smelters. There is some evidence that invertebrates inhabiting soil litter do accumulate metals. Earthworms from roadsides were shown to contain elevated concentrations of cadmium, 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

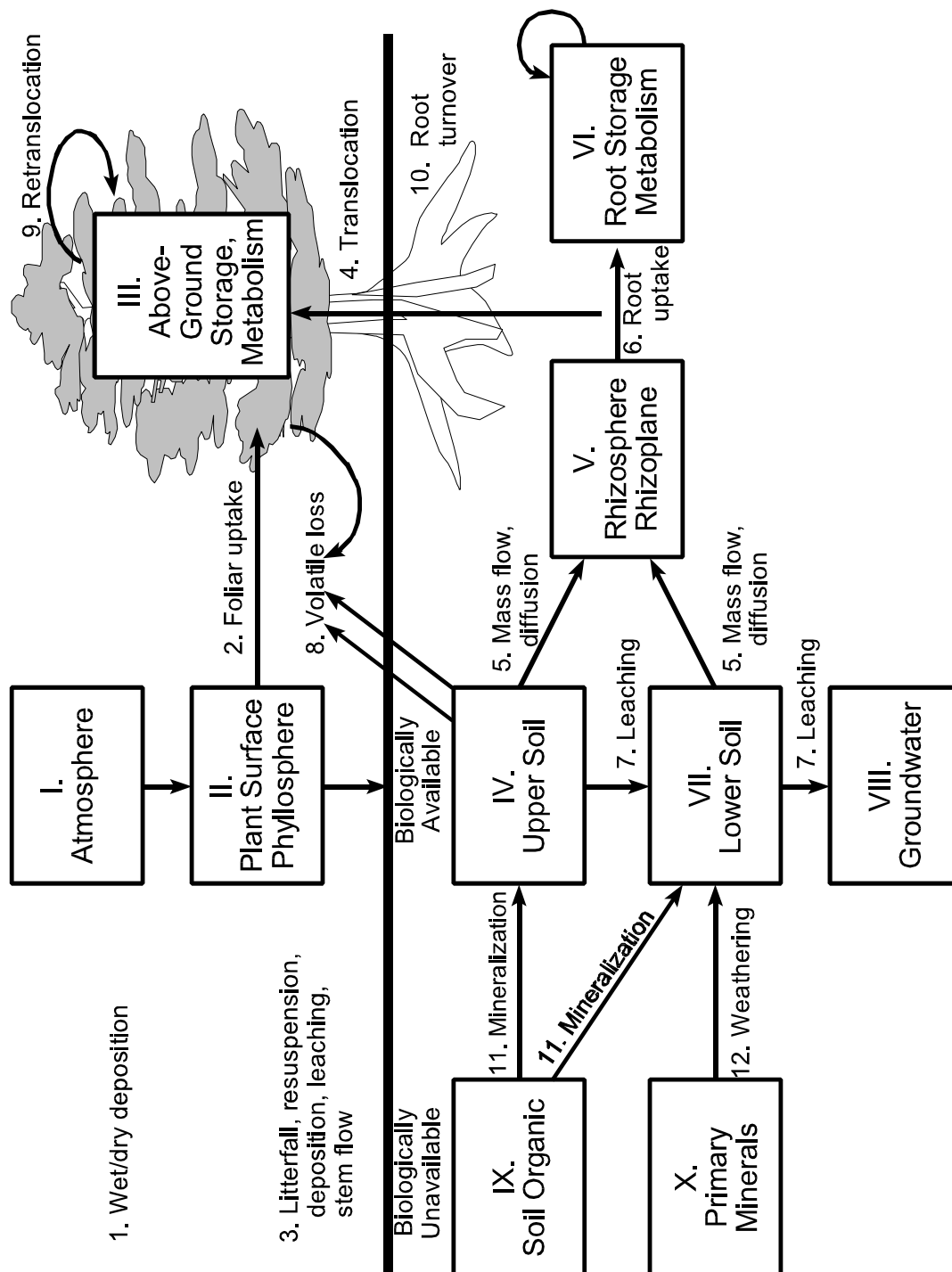


Figure 9-5. Relationship of plant nutrients and trace metals with vegetation. Compartments (Roman numerals) represent potential storage sites, whereas arrows (Arabic numerals) represent potential transfer routes.

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-detritivore 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 virginicus*) 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



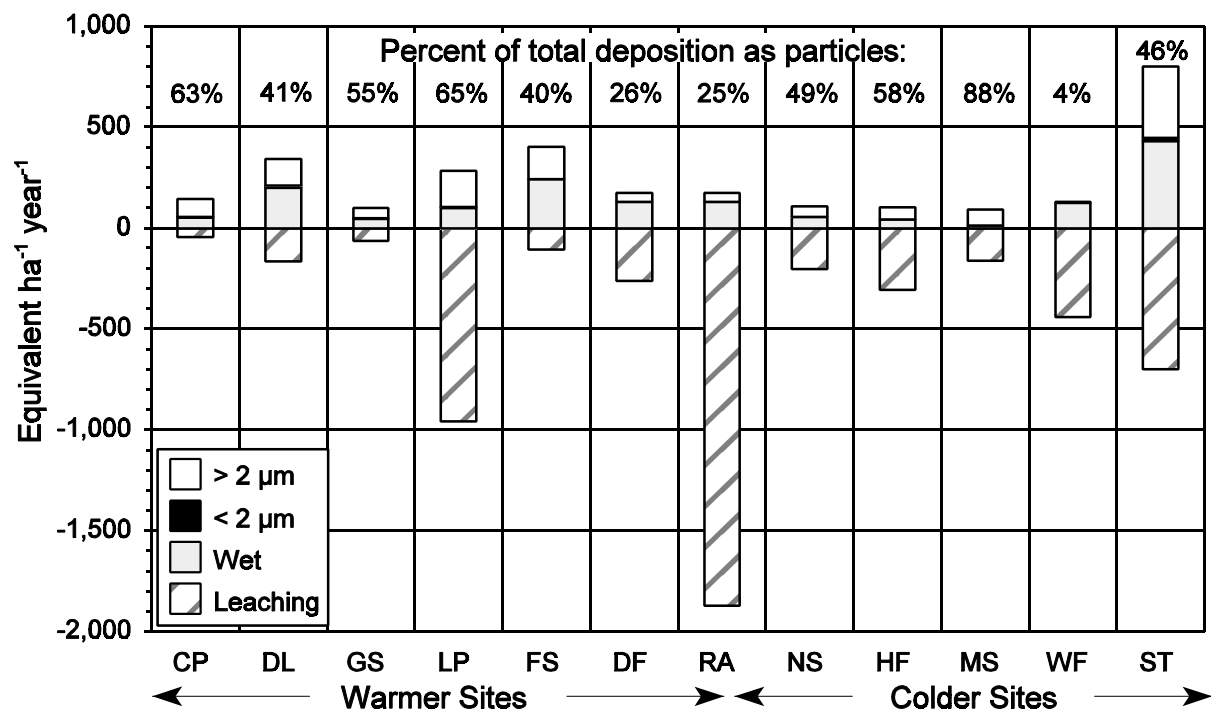
summarized by Johnson and Lindberg (1992a), and the reader is referred to that reference for details. The following is a summary of particulate deposition, total deposition, and leaching in the IFS sites.

Particulate deposition in the IFS was separated at the 2- $\mu\text{m}$  level; a decision was made to include total particulate deposition in this analysis, and may include the deposition of particles larger than 10  $\mu\text{m}$ .

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

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

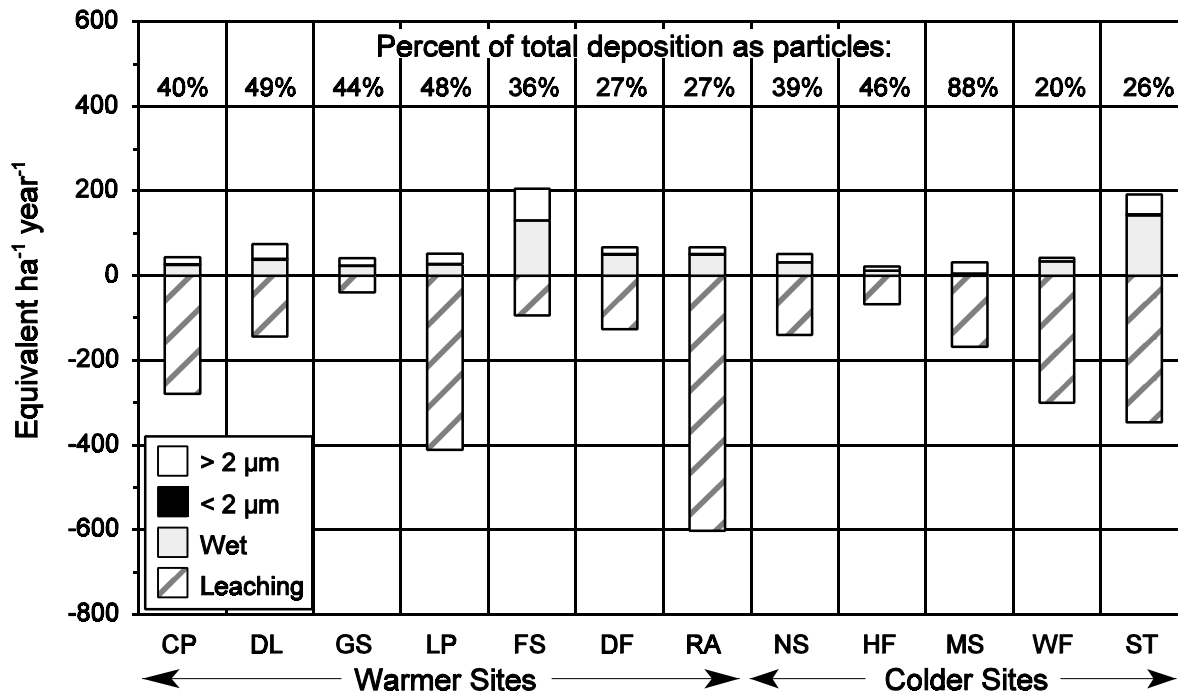
The factors affecting net calcium accumulation or loss include the soil-exchangeable cation composition, as noted previously; base cation deposition rate; the total leaching pressure due to atmospheric sulfur and nitrogen inputs, as well as natural (carbonic and organic) acids; and biological demand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



**Figure 9-6. Calcium deposition in  $>2 \mu\text{m}$  particles,  $<2 \mu\text{m}$  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** = *Psuedotsuga 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.

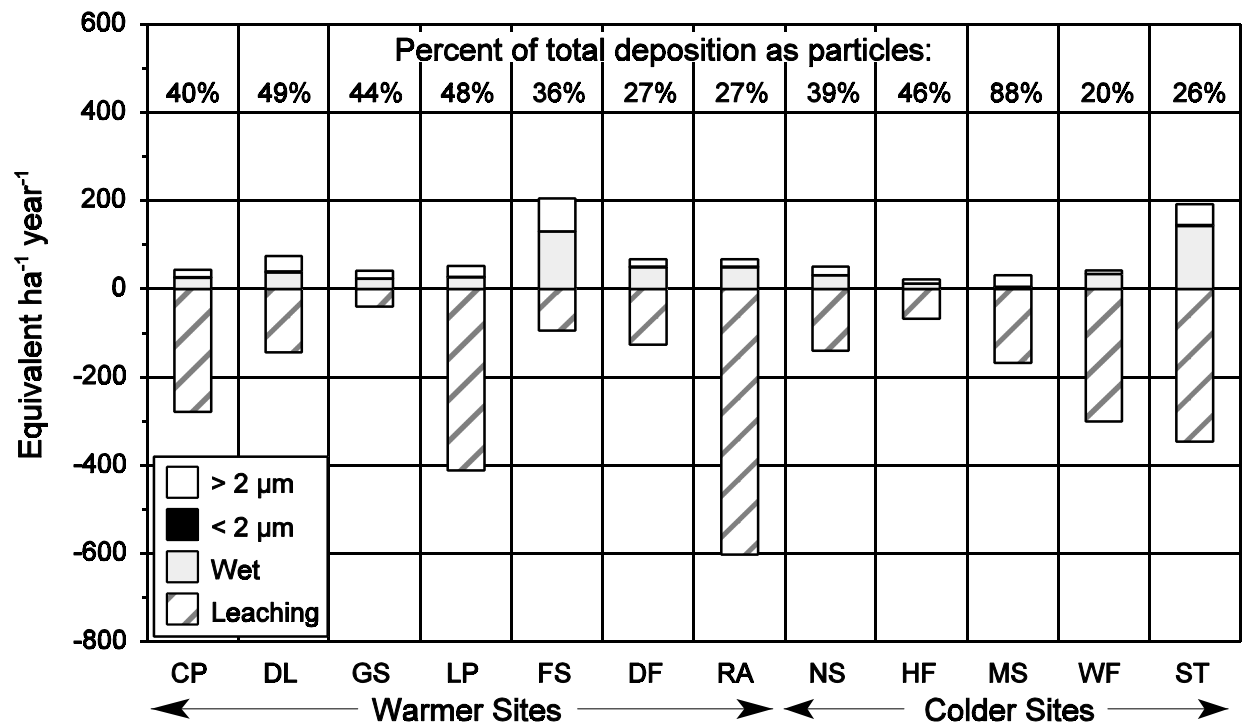
the combined effects of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  leaching are even greater than in the red alder site (Figure 9-10), but a considerable proportion of the cations leached from this extremely acid soil consist of  $\text{H}^+$  and  $\text{Al}^{3+}$  rather than of base cations (Johnson and Lindberg, 1992a). Thus the red spruce site in the Smokies is approximately in balance with respect to calcium and total base cations, despite the very high leaching pressure at this site (Figures 9-10 and 9-12).

The relative importance of particulate base cation deposition varies widely with site and cation and is not always related to the total deposition rate. The proportion of calcium deposition 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  $\mu\text{m}$  particles, <2  $\mu\text{m}$  particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. See Figure 9-6 for legend.**

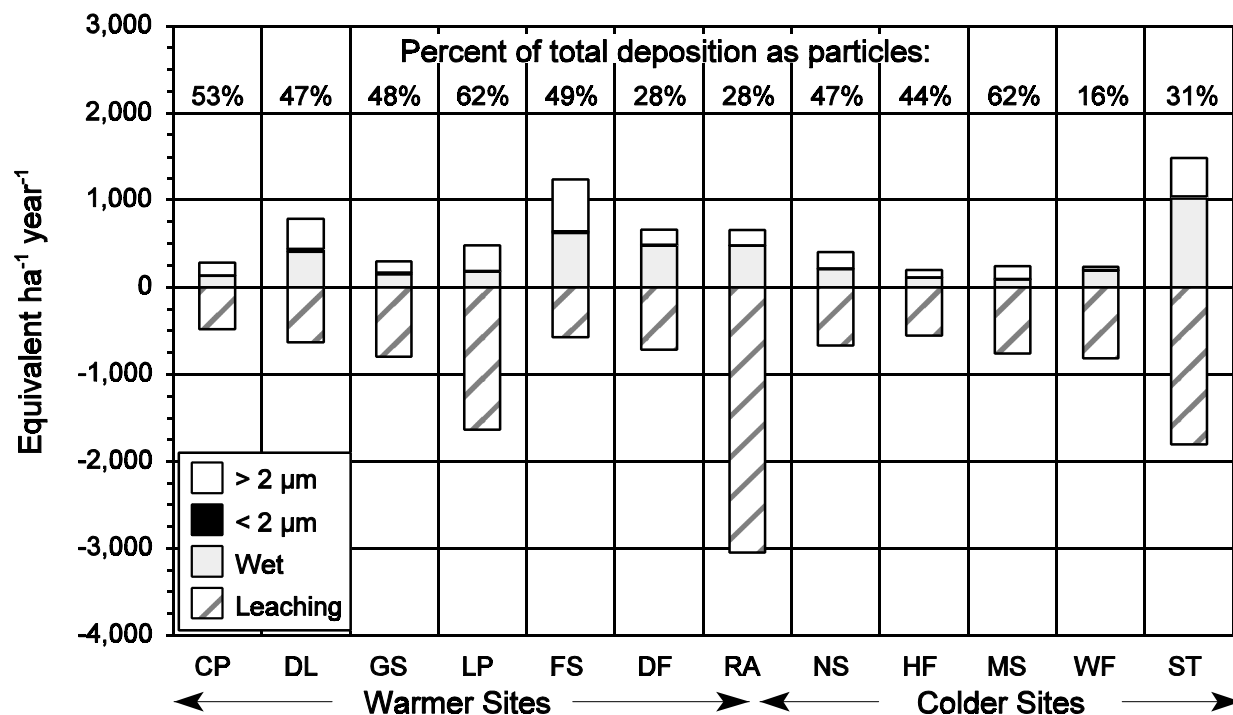
the Maine site (Figure 9-6), and the proportion of magnesium deposition as particles ranges from >20% at the Whiteface Mountain site to 88% at the Maine site. The proportion of magnesium deposition as particles ranges from >20% at the Whiteface Mountain site to 88% at the Maine site, and the proportion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



**Figure 9-8. Potassium deposition in >2  $\mu\text{m}$  particles, <2  $\mu\text{m}$  particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. See Figure 9-6 for legend.**

As noted in the IFS synthesis,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  leaching often are dominated by atmospheric sulfur and nitrogen (Johnson and Lindberg, 1992a). The exceptions to this are in cases where natural nitrogen inputs are high (i.e., the nitrogen-fixing red alder stand), as are  $\text{NO}_3^-$  leaching rates, even though nitrogen deposition is low, and where soils adsorb much of the atmospherically deposited  $\text{SO}_4^{2-}$ , thus reducing  $\text{SO}_4^{2-}$  leaching compared to atmospheric sulfur input.

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

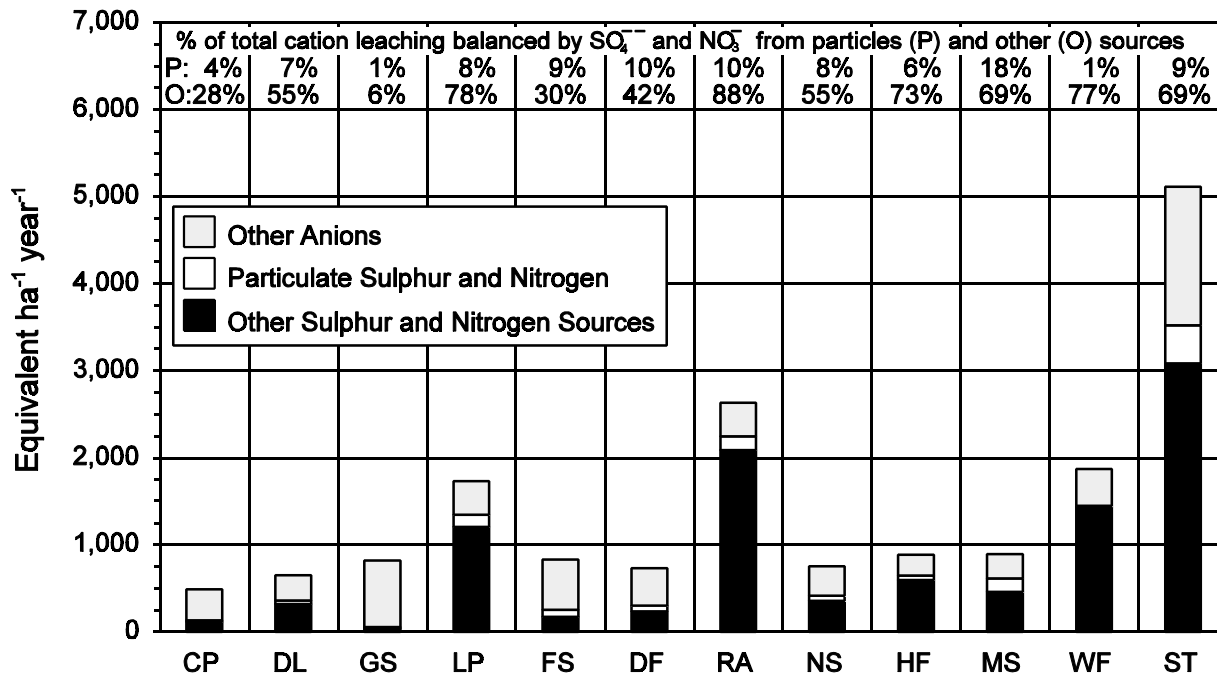


**Figure 9-9. Base cation deposition in  $>2\ \mu\text{m}$  particles,  $<2\ \mu\text{m}$  particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. See Figure 9-6 for legend.**

As noted in the IFS synthesis,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  account for a large proportion (28 to 88%) total cation leaching in most sites. The exception is the Georgia loblolly pine site where there were high rates of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  leaching (Johnson and Lindberg, 1992a). The role of particulate sulfur and nitrogen deposition in this leaching is generally very small ( $<10\%$ ), however, even if it is assumed that there is no ecosystem sulfur or nitrogen retention.

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

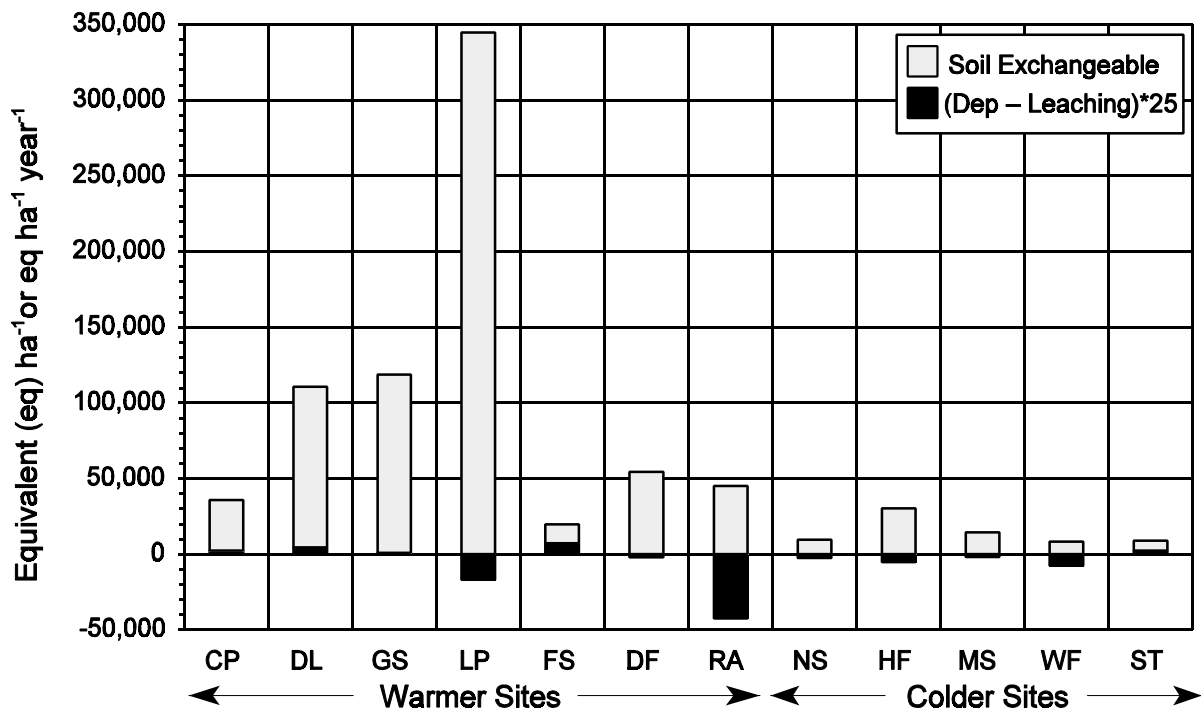
From the IFS data, then, it appears that the particulate deposition has a greater effect on base cation inputs to soils than on base cation losses associated with inputs of sulfur, nitrogen,



**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.**

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

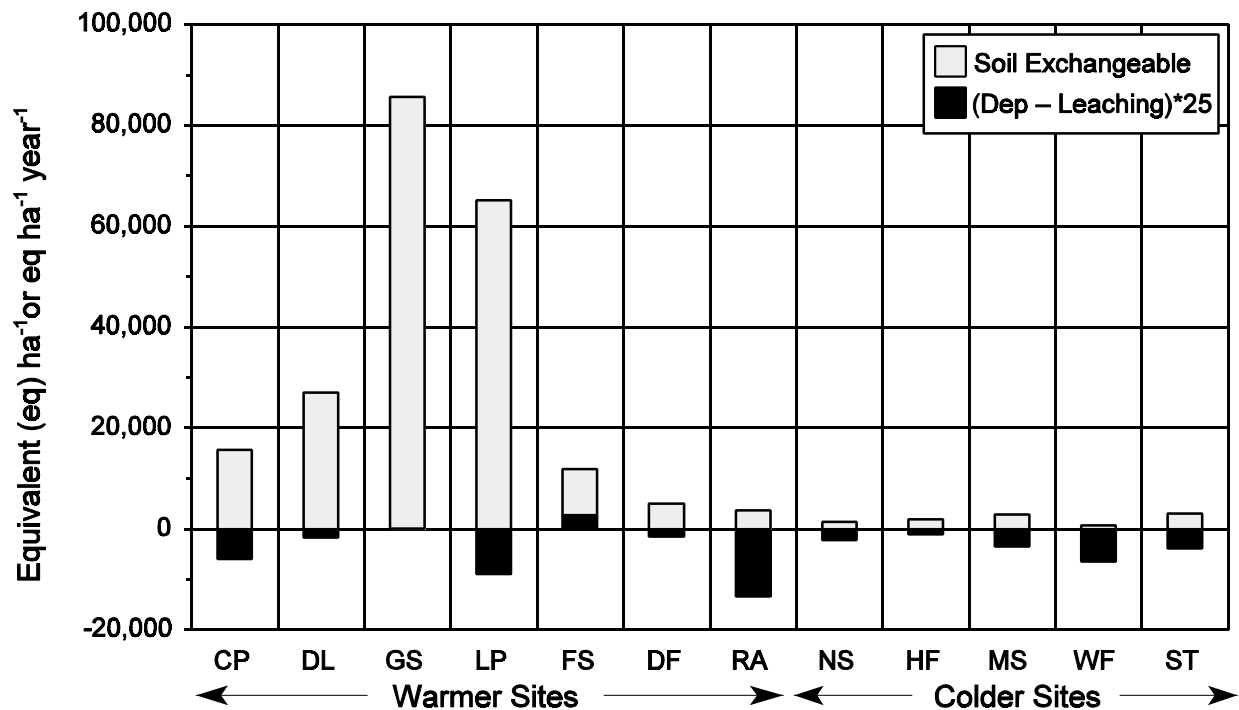
Net balances of base cations tell only part of the story as to potential effects on soils; these net losses or gains must be placed in the perspective of the soil pool size. One way to express this perspective is to simply compare soil pool sizes with the net balances. This comparison is



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

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

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

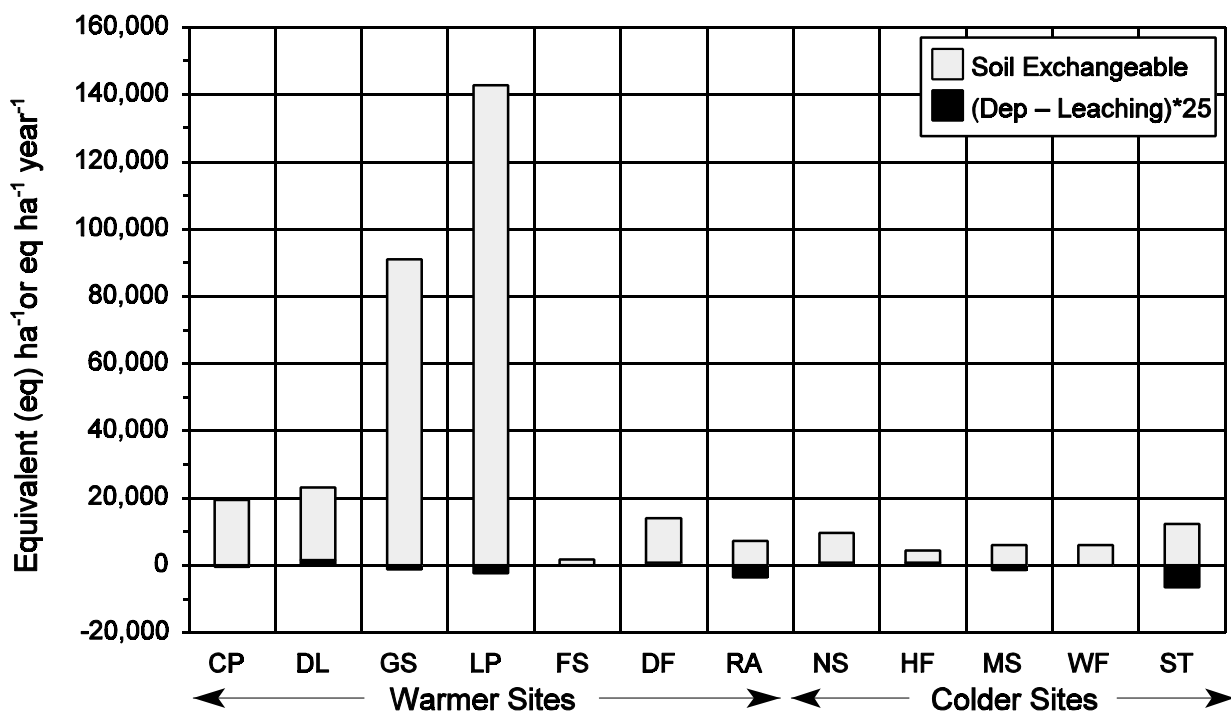


**Figure 9-12. Soil exchangeable Mg<sup>++</sup> pools and net annual export of Mg<sup>++</sup> (deposition minus leaching times 25 years) in the Integrated Forest Study sites. See Figure 9-6 for legend.**

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

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





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

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

The simple calculations shown above give some idea of the importance of particulate deposition in these forest ecosystems, but they cannot account for the numerous potential feedbacks between vegetation and soils nor for the dynamics through time that can influence the ultimate response. One way to examine some of these interactions and dynamics is to use simulation modeling. The nutrient cycling model (NuCM) has been developed specifically for this purpose and has been used to explore the effects of atmospheric deposition, fertilization, and harvesting on some of the IFS sites (Johnson et al., 1993). The NuCM model is a stand-level model that incorporates all major nutrient cycling processes (uptake, translocation, leaching, 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 <sup>-1</sup> |              |                   |                   |
| <b>Nitrogen</b>                      |                       |              |                   |                   |
| <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              |
| <b>Sulfur</b>                        |                       |              |                   |                   |
| <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             |
| <b>Potassium</b>                     |                       |              |                   |                   |
| <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             |
| <b>Calcium</b>                       |                       |              |                   |                   |
| <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**

|                                      | No Change             | No Particles | No N, S Particles | No Base Particles |
|--------------------------------------|-----------------------|--------------|-------------------|-------------------|
| Scenario                             | kmol ha <sup>-1</sup> |              |                   |                   |
| <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             |
| <b>Magnesium</b>                     |                       |              |                   |                   |
| <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             |

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

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

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

|                                      | No Change             | No Particles | No N, S Particles | No Base Particles |
|--------------------------------------|-----------------------|--------------|-------------------|-------------------|
| Scenario                             | kmol ha <sup>-1</sup> |              |                   |                   |
| <b>Nitrogen</b>                      |                       |              |                   |                   |
| <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              |
| <b>Sulfur</b>                        |                       |              |                   |                   |
| <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              |
| <b>Potassium</b>                     |                       |              |                   |                   |
| <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**

|                                      | No Change             | No Particles | No N, S Particles | No Base Particles |
|--------------------------------------|-----------------------|--------------|-------------------|-------------------|
| Scenario                             | kmol ha <sup>-1</sup> |              |                   |                   |
| <b>Potassium (cont'd)</b>            |                       |              |                   |                   |
| <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              |
| <b>Calcium</b>                       |                       |              |                   |                   |
| <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              |
| <b>Magnesium</b>                     |                       |              |                   |                   |
| <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  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  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.”  
31

## **9.4 EFFECTS ON MATERIALS**

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

Limited new studies have been published that better define the role of SO<sub>2</sub> and particles in materials damage. This section will briefly summarize the information on SO<sub>2</sub> and particle exposure-related effects on materials addressed in the previous Air Quality Criteria Document for Particulate Matter (U.S. Environmental Protection Agency, 1996b) and present relevant information published since completion of that document.

### **9.4.1 Corrosive Effects of SO<sub>2</sub> and Particles on Man-Made Surfaces**

#### **9.4.1.1 Metals**

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

Several studies demonstrate the importance of time of surface wetness caused by dew and fog condensation and rain on metals. Surface moisture facilitates the deposition of pollutants, especially SO<sub>2</sub>, and also promotes corrosive electrochemical reactions on the metal (Haynie and Upham, 1974; Sydberger and Ericsson, 1977). Of critical importance is the formation of hygroscopic salts on the metal that will increase the time of surfaces wetness and, thereby, enhance the corrosion process.

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



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

The metal protective corrosion film (i.e., the rust layer on metal surfaces) provides some protection against further corrosion. The effectiveness of the corrosion film in slowing down the corrosion process is affected by the solubility of the corrosion layer, and the concentration and deposition rate of pollutants. An atmospheric corrosion model that considers the formation and dissolution of the corrosion film on galvanized steel has been proposed (Spence et al., 1992). The model considers the effects of SO<sub>2</sub>, rain acidity, and the time of wetness on the rate of corrosion. While the model does not characterize particle effects, the contribution of particulate sulfate was considered in model development.

The corrosion of most ferrous metals (iron, steel, and steel alloys) is increased by increasing SO<sub>2</sub> exposure. Steels are susceptible to corrosion when exposed to SO<sub>2</sub> in the absence of protective organic or metallic coatings. Studies on the corrosive effects of SO<sub>2</sub> on steel indicate that the rate of corrosion increases with increasing SO<sub>2</sub> and is dependent on the deposition rate of the SO<sub>2</sub> (Baedecker et al., 1991; Butlin et al., 1992a). The corrosive effects of SO<sub>2</sub> on aluminum is exposure-dependent, but appears to be insignificant (Haynie, 1976; Fink et al., 1971; Butlin et al., 1992a). The rate of formation of the patina on copper (protective covering) can take as long as 5 years and is dependent on the SO<sub>2</sub> concentration, deposition rate, temperature, and relative humidity (Simpson and Horrobin, 1970). Further corrosion is controlled by the availability of copper to react with deposited pollutants (Graedel et al., 1987). Butlin et al. (1992a), Baedecker et al. (1991), and Cramer et al. (1989) reported an average corrosion rate of 1 μm/y for copper; however, less than a third of the corrosion was attributed to SO<sub>2</sub> exposure, suggesting that the rate of patina formation was more dependent on factors other than SO<sub>2</sub>. A recent report by Strandberg and Johansson (1997) showed relative humidity to be the primary factor in copper corrosion and patina formation. The results of the studies on SO<sub>2</sub> corrosion of metals are summarized in Table 9-5.

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

**TABLE 9-5. EFFECTS OF SO<sub>2</sub> AND PARTICULATE MATTER ON METALS**

| Metal                            | Exposure Conditions   | Comments  | Bibliography                                    |
|----------------------------------|---|---|---|
| Mild Steel<br>Galvanized Steel   | Specimens exposed to SO <sub>2</sub> and O <sub>3</sub> under natural and artificial conditions, and to NO <sub>2</sub> under natural conditions. SO <sub>2</sub> concentrations ranged from 2.1 to 60 µg/m <sup>3</sup> . Annual average concentrations were about 20 µg/m <sup>3</sup> . 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 <sub>2</sub> 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 <sub>2</sub> concentrations ranged from 2 ± 4 to 15 ± 17 ppb (5.2 ± 10.4 to 39.3 ± 44.5 µg/m <sup>3</sup> ). PM concentrations ranged from 14 to 60 µg/m <sup>3</sup> . 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 <sub>2</sub> concentration, suggesting that SO <sub>2</sub> exposure may not be the dominant factor in zinc corrosion.  | Baedecker et al. (1991)<br>Cramer et al. (1989) |
| Carbon Steel<br>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)<br>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 SO<sub>2</sub> 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 $\mu\text{m/y}$ but the soluble portion was less than a third of that which could be contributed to SO <sub>2</sub> exposure. Dry deposition of SO <sub>2</sub> was not as important in patina formation as wet deposition of H <sup>+</sup> .               | Baedecker et al. (1991)         |
| Copper | See Butlin et al. (1992a) above for exposure conditions.   | Majority of test sites showed a corrosion rate of $1 \pm 0.2 \mu\text{m/y}$ . The corrosion rate was 1.48 $\mu\text{m/y}$ at the site receiving the most rainfall. The lowest corrosion rate, 0.66 $\mu\text{m/y}$ , was associated with low rainfall, low SO <sub>2</sub> .  | Butlin et al. (1992a)           |
| Copper | Specimens exposed to 4 to 69 ppb (10.4 to 180.7 $\mu\text{g/m}^3$ ) and 1.0 ppm (2,618.7 $\mu\text{g/m}^3$ ) SO <sub>2</sub> for 20h at various relative humidities. | SO <sub>2</sub> had no effect on copper when relative humidity was <75%. Increasing relative humidity increases patina formation in presence of trace SO <sub>2</sub> . No SO <sub>2</sub> -related effects were noted on copper specimens exposed to high SO <sub>2</sub> regardless of the percent relative humidity. | Strandberg and Johansson (1998) |
| Copper | Specimens exposed artificially to $0.49 \pm 0.01$ ppm ( $187 \pm 3.8 \mu\text{g/m}^3$ ) SO <sub>2</sub> for 4 weeks at 70 and 90% relative humidity.                 | Corrosive effect of SO <sub>2</sub> 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  $\text{SO}_x$  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  $\text{SO}_2$  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  $\text{SO}_2$  and high humidity. In a study by Spence et al. (1975), an erosion  
16 rate of  $36.71 \pm 8.03 \mu\text{m/y}$  was noted for oil-base house paint samples exposed to  $\text{SO}_2$   
17 ( $78.6 \mu\text{g/m}^3$ ),  $\text{O}_3$  ( $156.8 \mu\text{g/m}^3$ ), and  $\text{NO}_2$  ( $94 \mu\text{g/m}^3$ ) and low humidity (50%). The erosion rate  
18 increased with increased  $\text{SO}_2$  and humidity. The authors concluded that  $\text{SO}_2$  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  $1.3 \mu\text{m/y}$  and 1.4 to  $5.3 \mu\text{m/y}$ ,  
21 respectively. Similar findings on  $\text{SO}_2$ -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  $\text{SO}_2$  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 SO<sub>2</sub>, 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 SO<sub>2</sub> 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, SO<sub>2</sub>, 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 SO<sub>2</sub> (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 SO<sub>2</sub> 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 SO<sub>2</sub> 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 SO<sub>2</sub>. 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 SO<sub>2</sub> AND PARTICULATE MATTER ON STONE**

| Stone  | Exposure Conditions  | Comments   | Bibliography            |
|--|--|--|-------------------------|
| Vermont marble   | Runoff water was analyzed from 7 summer storms. SO <sub>2</sub> concentration stated to be low.  | Between 10 to 50% of calcium in runoff water estimated from gypsum formation from dry deposition of SO <sub>2</sub> .  | 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 <sub>2</sub> and nitric acid between rain events and wet deposition of hydrogen ion. Recession estimates ranged from 15 to 30 $\mu\text{m/y}$ for marble and 25 to 45 $\mu\text{m/y}$ for limestone. A large portion of the erosion results from the reaction of CO <sub>2</sub> 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 $\mu\text{g/m}^3$ ) SO <sub>2</sub> ; 4.1 to 41.1 ppb NO <sub>x</sub> ; 2.4 to 17.4 ppb (4.5 to 32.7 $\mu\text{g/m}^3$ ) NO <sub>2</sub> ; 10.1 to 25.6 ppb (19.8 to 50.2 $\mu\text{g/m}^3$ ) O <sub>3</sub> . | Increased stone weight loss with increased SO <sub>2</sub> . Rainfall did not significantly affect stone degradation. Stone loss associated with SO <sub>2</sub> exposure estimated to be 24 $\mu\text{m/y}$ . Slight trend in decreasing stone loss with increasing length of exposure.   | Webb et al. (1992)      |
| Portland limestone<br>White Mansfield<br>dolomitic sandstone<br>Monk's Park<br>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 <sub>2</sub> 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 <sub>2</sub> , 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 SO<sub>2</sub> AND PARTICULATE MATTER ON STONE**

| Stone  | Exposure Conditions   | Comments   | Bibliography               |
|--|---|--|----------------------------|
| Portland limestone<br>Massangis Jaune<br>Roche limestone<br>White Mansfield<br>dolomitic | Samples exposed to SO <sub>2</sub> , NO <sub>2</sub> , and NO at 10 ppmv both with and without O <sub>3</sub> and under dry (coming to equilibrium with the 84% RH) or wetted with CO <sub>2</sub> -equilibrated deionized water conditions. Exposure was for 30 d.                     | In the absence of moisture, little reaction is seen. SO <sub>2</sub> is oxidized to sulfates in the presence of moisture. The effect is enhanced in the presence of O <sub>3</sub> . Massangis Jaune Roche limestone was the least affected by the pollutant exposure. Crust lined pores of specimens exposed to SO <sub>2</sub> . | Haneef et al. (1993)       |
| Monk's Park<br>Portland limestone  | Samples exposed for 2 mo under both sheltered and unsheltered conditions. Mean daily atmospheric SO <sub>2</sub> concentration was 68.7 µg/m <sup>3</sup> 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<br>Travertine<br>Tranistone   | Sample exposed in laboratory to 3 ppm SO <sub>2</sub> 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 <sub>2</sub> due to metal content of particles.   | Sabbioni et al. (1996)     |
| Carrara marble<br>Georgia marble   | Samples exposed in sheltered ambient environment for 6, 12, or 20 mo.   | Carrara marble found to be more reactive with SO <sub>2</sub> than Georgia marble possibly due to the compactness of the Georgia marble. Greater effects noted when samples were also exposed to NO <sub>2</sub> .   | 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 <sup>3</sup> (site 1) and 88 to 189.8 µg/m <sup>3</sup> (site 2). Some exposures were also associated with high SO <sub>2</sub> , NO, and NO <sub>2</sub> . | 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 SO<sub>2</sub> AND PARTICULATE MATTER ON STONE**

| Stone  | Exposure Conditions  | Comments   | Bibliography             |
|--|--|--|--------------------------|
| Monk's Park limestone<br>Portland limestone  | Samples artificially exposed to fly-ash containing 1,309.3 $\mu\text{g}/\text{m}^3$ SO <sub>2</sub> (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 <sub>2</sub> to sulfates. Mineral oxides in fly ash contributed to sulphation of CaCO <sub>3</sub> .   | Hutchinson et al. (1992) |
| Lime mortar<br>Pozzolan mortar<br>Cement mortar  | Samples exposed to 7,856 $\mu\text{g}/\text{m}^3$ (3 ppm) SO <sub>2</sub> 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 <sub>2</sub> 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<br>Travertine marble   | Samples exposed under actual ambient air conditions at two locations in Rome. Monitoring data obtained for SO <sub>2</sub> , NO, NO <sub>2</sub> , 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<br>Quartz-cemented sandstone<br>Calcite-cemented sandstone<br>Granite<br>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<br>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 SO<sub>2</sub>, 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 SO<sub>2</sub> to a more acidic species (Del Monte and Vittori, 1985). Several  
14 authors have reported enhanced sulfation of calcareous material by SO<sub>2</sub> 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

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

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

## **9.5.2 Factors Affecting Atmospheric Visibility**

### **9.5.2.1 Anthropogenic Pollutants**

Visibility impairment may be connected to air pollutant properties, including size distribution, aerosol chemical composition, and relative humidity. In the United States visibility impairment is caused by sulfate and nitrate particles in the 0.1 to 1.0 micron ( $\mu\text{m}$ ) range, and organic aerosols, carbon soot, and crustal dust. Generally, sulfates are responsible for most of the visibility impairment in the United States, as measured by light extinction, accounting for approximately two-thirds of the light extinction in the eastern United States. Sulfate concentrations are higher in summer months than in the wintertime (Malm et al., 1994).

Exceptions to the sulfate-related effects on visibility include California where the primary cause of visibility effects is ambient nitrate, and in Alaska where visibility impairment is due to fine soil plus coarse mass (classified as coarse extinction) or organics, thought to be from natural sources (Sisler and Cahill, 1993).

### **9.5.2.2 Human Vision**

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

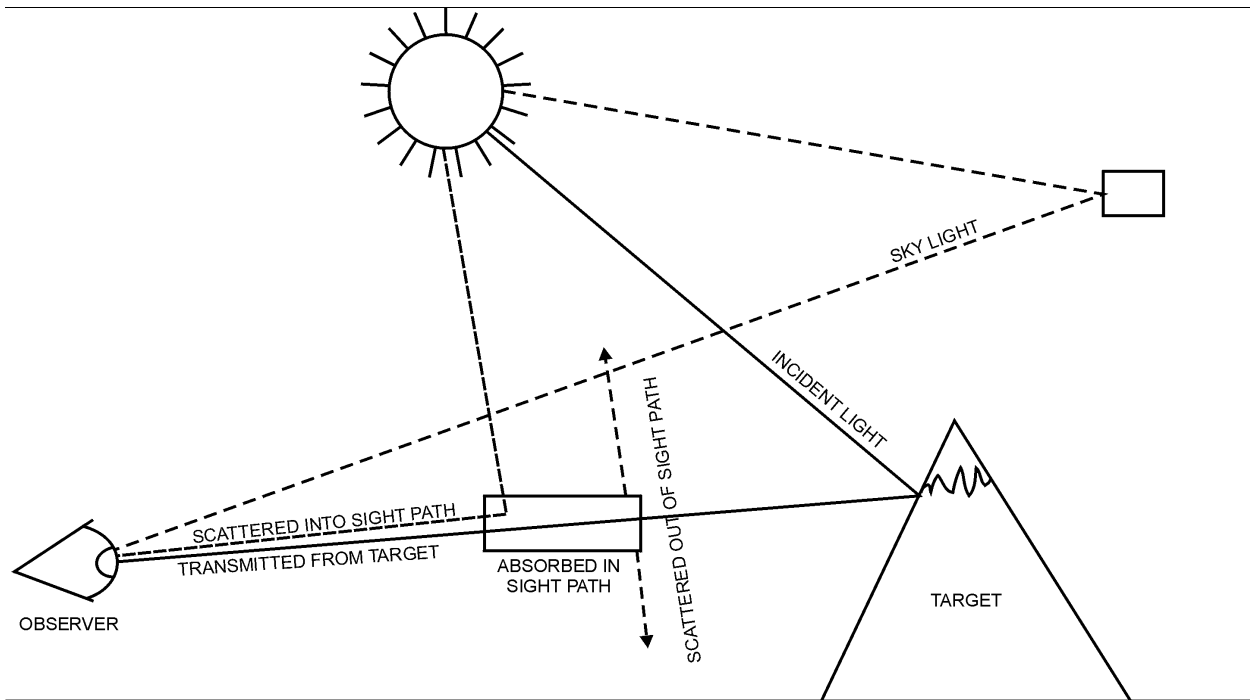
1       The eye perceives the lightest and brightest object in a scene as white, and determines the  
2 color of other objects by comparison. The ability of the eye to perceive contrasts, the degree of  
3 color difference between the lightest and darkest object in a scene, changes in response to the  
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).

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

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

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

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

- $\sigma_{\text{ag}}$ , light absorption by gases,
- $\sigma_{\text{sg}}$ , light scattering by gases (Rayleigh scattering),
- $\sigma_{\text{ap}}$ , light absorption by particles, and
- $\sigma_{\text{sp}}$ , light scattering by particles.

Light scattering by particles,  $\sigma_{\text{sp}}$ , can be divided to indicate scattering by coarse and fine particles,  $\sigma_{\text{sfp}}$ , light scattering by fine particles and  $\sigma_{\text{scp}}$ , light scattering by coarse particles.

### 9.5.3 Optical Properties of Particles

Visibility impairment is typically caused by fine particles. Fine particles are small enough in comparison with the wavelength of visible light that their optical properties are nearly the same as those of homogeneous spheres of the same volume and average index of refraction. Accordingly, Mie equations (Mie, 1908; Kerker, 1969), for calculating the optical properties of homogeneous spheres may also be used to calculate the optical properties of fine particles with the only uncertainties being in the fine particle size distribution and index of refraction (Richards, 1973). However, within the range of indices of refraction that most commonly occur in atmospheric fine particles, the results of Mie calculations can be scaled to account for the effect of the index of refraction. Coarse particles have less of an impact on visibility than do fine particles. However, in most actual cases, the dominant uncertainty in using the optical properties for coarse particles calculated with Mie equations is the uncertainty in the particle size distribution. Uncertainties exist in the use of Mie calculations for calculating light absorption for coarse particles because the refractive index of the particle is generally not known and the light-absorbing particles are not spherical in shape, making the calculated light absorption efficiency factor less reliable. Also, light absorption by elemental carbon particles can be 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,  $Q_{\text{ext}}$ ,  
2       scattering,  $Q_{\text{scat}}$ , and absorption,  $Q_{\text{abs}}$ . The  $Q_{\text{ext}}$ ,  $Q_{\text{scat}}$ , and  $Q_{\text{abs}}$  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  $\text{m}^2/\text{g}$ ) 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,  $\sigma_{\text{sp}}$ , (in units of  $\text{Mm}^{-1}$ ) 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).



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

Absorption efficiencies for elemental carbon particles have been reported to range from 9 to 10 m<sup>2</sup>/g (Japar et al., 1984; Adams et al., 1989; Sloane et al., 1991). Based on a review of the available data, Horvath (1993) reported that measured light absorption efficiencies for light absorbing carbon ranges from 3.8 to 17 m<sup>2</sup>/g and calculated absorption efficiencies ranges from 8 to 12 m<sup>2</sup>/g. Malm et al. (1996) suggested a combined scattering and absorption efficiency of 10 m<sup>2</sup>/g for organic carbon.

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

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

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

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

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

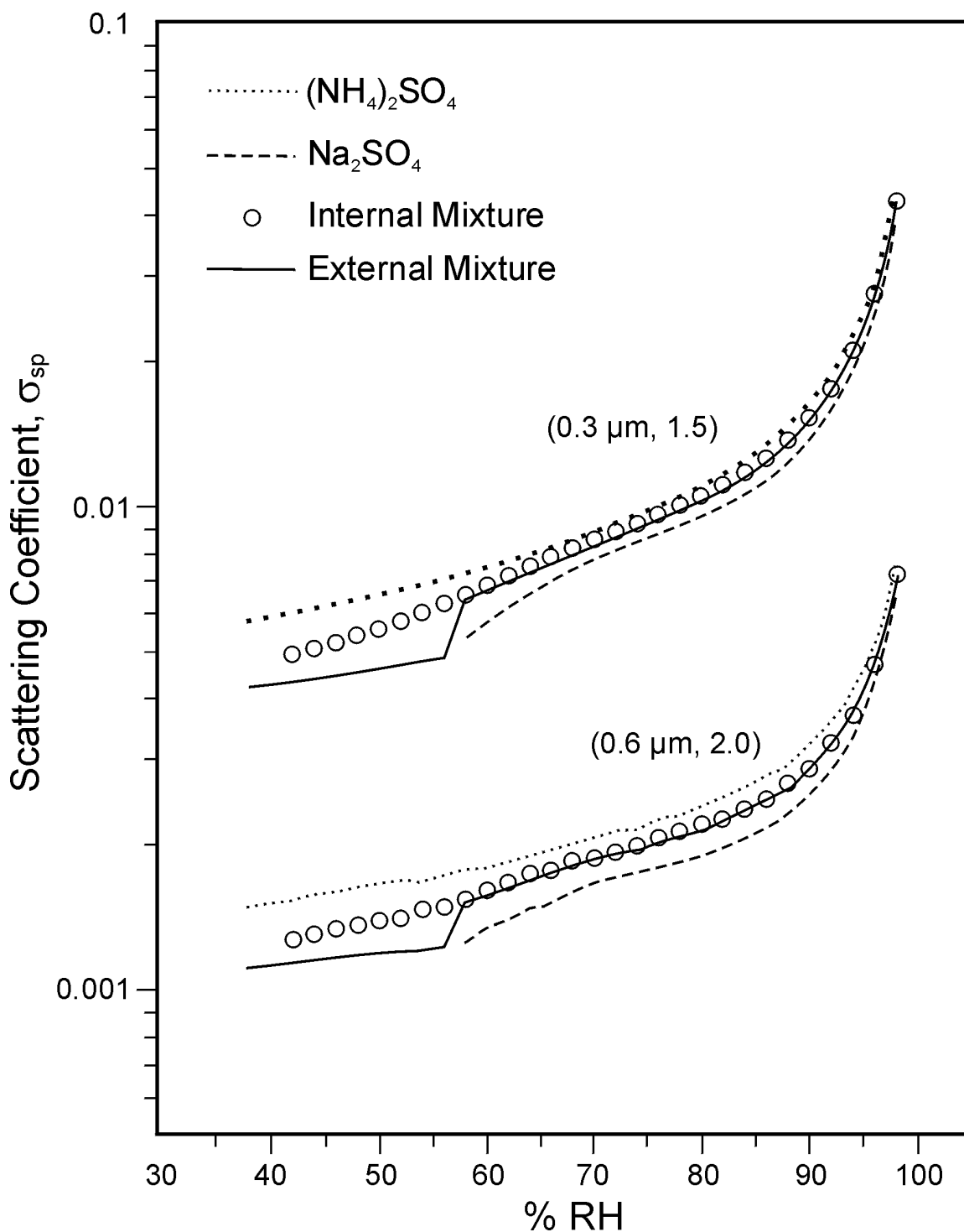
## **9.5.5 Measures of Visibility**

### **9.5.5.1 Human Observations**

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

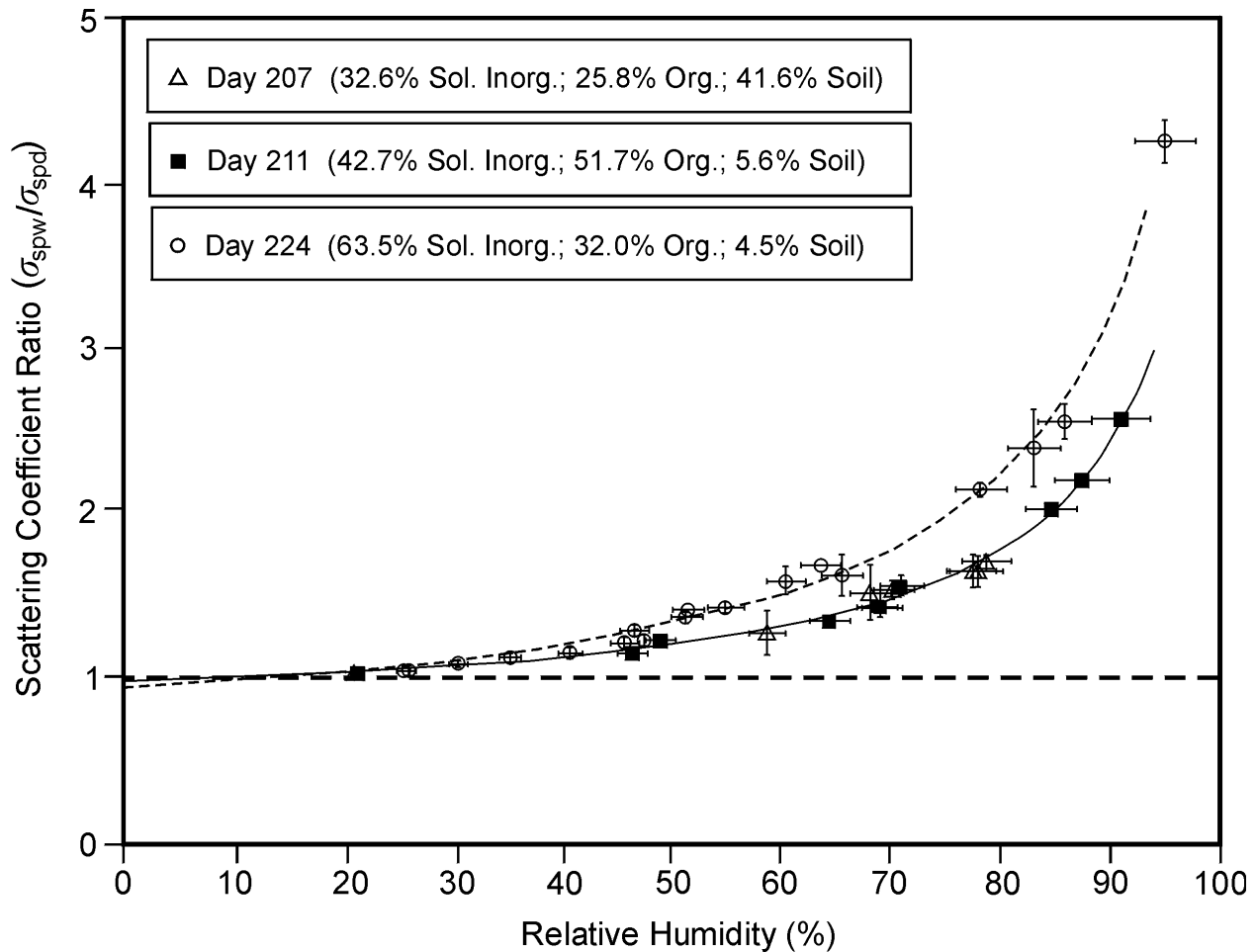
### **9.5.5.2 Light-Extinction Coefficient and Parameters Related to the Light-Extinction Coefficient**

The most frequently used indicator for visibility characterization for air quality is the light-extinction coefficient because it is closely linked to air quality (U.S. Environmental Protection Agency, 1996). Various meteorological conditions (moisture and cloud cover) can affect the light-extinction coefficient; however, these effects can be minimized (Husar et al., 1994; Blandford, 1994; Mercer, 1994). The light-extinction coefficient can be measured directly 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).

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

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

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

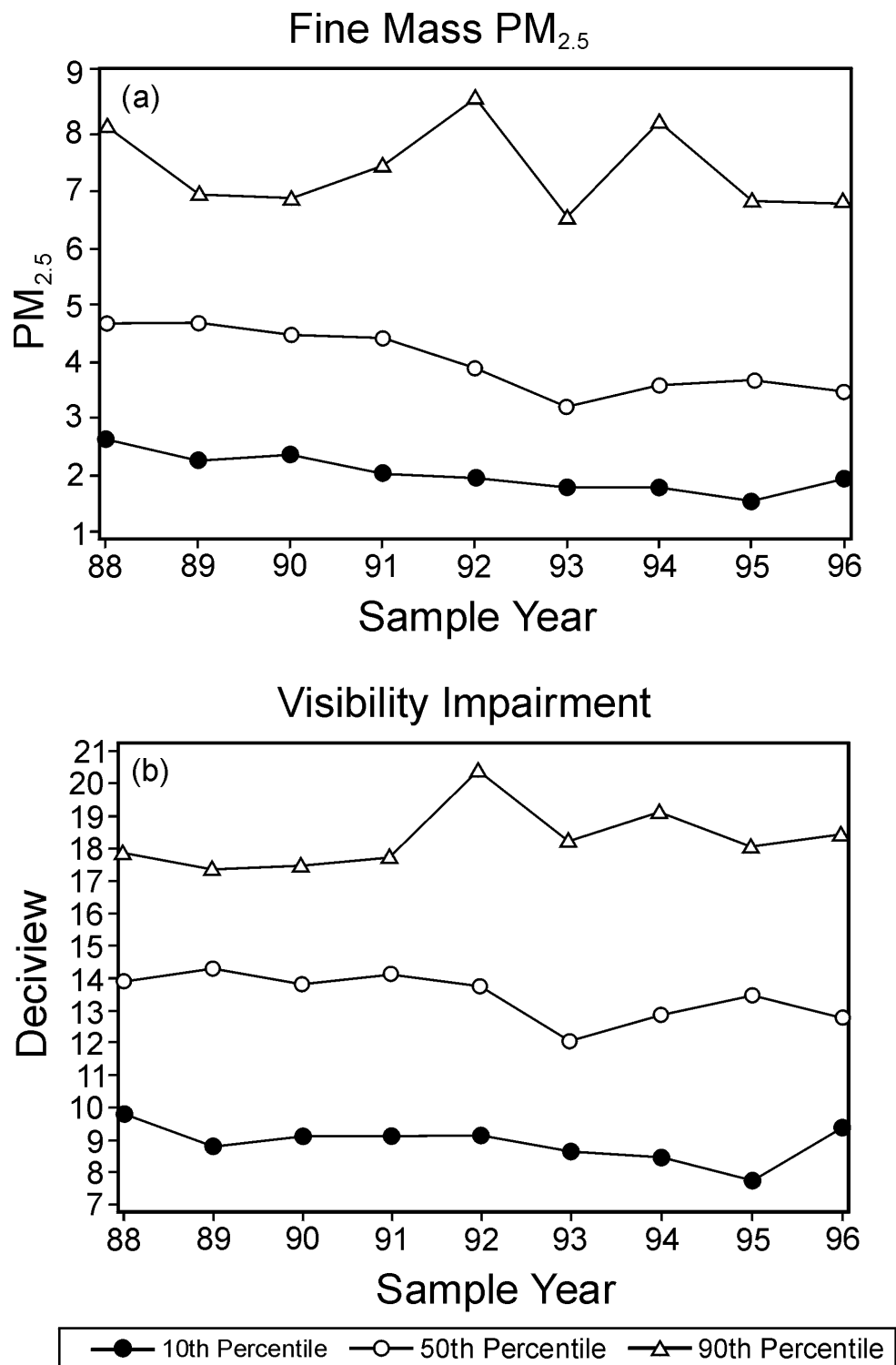
The deciview index is an atmospheric haze index that expresses uniform changes in haziness in common increments from pristine conditions to extremely visibility impaired environments. The deciview scale is linear with perceived visual changes, starting near zero for a pristine atmosphere (particle-free)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

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

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

### 9.5.5.3 Light-Scattering Coefficient

Light-scattering by particles has been reported to account for 68 to 86% of the total extinction coefficient in several cities in California (Eldering et al., 1994). The light-scattering coefficient is closely linked to fine particle concentrations, making it a good tool for determining small particle-related effects on visibility. When the light-scattering coefficient is increased, visibility is impaired because the transmitted radiance is decreased and the path radiance is increased. (See discussion in the previous sections on transmitted radiance and path radiance.) The light-scattering coefficient can be measured directly with an open and enclosed integrating 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<sub>2.5</sub> and deciview at the Badlands National Park. The sample year began in March of each year.**

Source: Sisler et al. (1999).

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

#### **9.5.5.4 Fine Particulate Matter Concentrations**

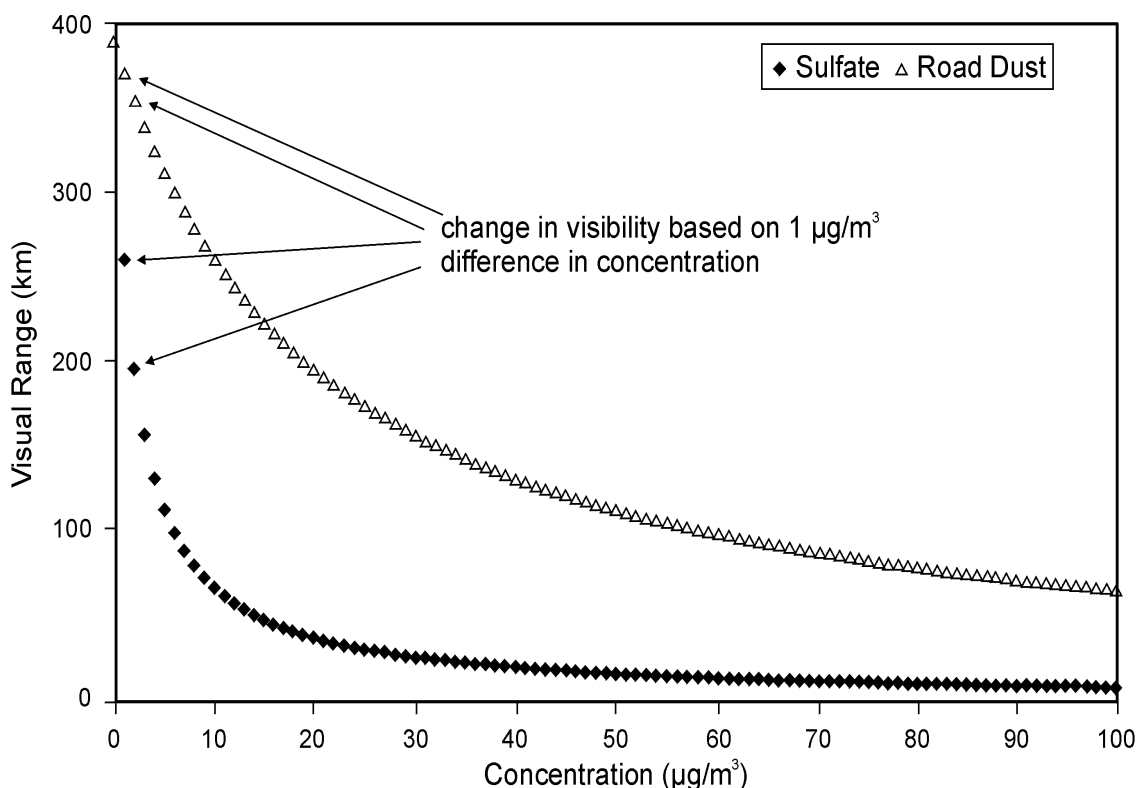
The influence of particles on visibility degradation is dependent on the particle composition, solubility, and size (Pryor and Stegn, 1994). Fine particle species have been classified into five major types: sulfates, nitrates, organics, light absorbing carbon, and soil (Malm et al., 1994). The coefficient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

#### **9.5.5.5 Discoloration**

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

#### **9.5.6 Visibility Monitoring Methods and Networks**

Visibility monitoring studies measure the properties of the atmosphere either at the sampler 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).

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

The largest instrumental visibility monitoring network in the United States is designed to provide real-time data for runway visibility to aid in controlling airport operations. Automated observing systems, Automated Surface Observing System (ASOS) and Automated Weather Observing System (AWOS), are being placed at airports around the country. The visibility sensor, instead of measuring how far one can see, measures the clarity of the air using a forward 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-feet  
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<sub>2.5</sub> monitoring data from 30 IMPROVE sites for the years 1988 to  
22 1996. The data includes averaged PM<sub>2.5</sub> 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<sub>2.5</sub> monitoring network of approximately 1,500 sites. The PM<sub>2.5</sub> monitoring effort  
30 will be coordinated with visibility monitoring efforts currently in place, such as IMPROVE, to

**TABLE 9-7. AVERAGED REGIONAL PM<sub>2.5</sub> MASS AND EXTINCTION  
SUMMARIES FOR THE YEARS 1988 TO 1996<sup>a</sup>**

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

<sup>a</sup>Mass 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

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

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

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

### 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).

### 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, NO<sub>2</sub> 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, NO<sub>2</sub> 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).



## 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 (SO<sub>2</sub>) 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<sub>2.5</sub> 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<sub>2.5</sub> 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<sub>2.5</sub>, 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 subtrophics.

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

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

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

The transmission of solar UV-B radiation through the earth's atmosphere is controlled by ozone, clouds, and particles. The depletion of stratospheric ozone caused by the release of chlorofluorocarbons has resulted in heightened concern over potentially serious increases in the amount of solar UV-B radiation (SUVB) reaching the surface. Issues related to the depletion of stratospheric ozone will not be treated here. Exposure to SUVB is associated with various health outcomes such as sunburn, DNA damage, immune system suppression, cataracts and various forms of skin cancers as well as ecosystem damage (Kodama and Lee, 1993; Longstreth et al., 1998). SUVB is also responsible for initiating the production of OH radicals which oxidize a wide variety of volatile organic compounds which can deplete stratospheric ozone (e.g., CH<sub>3</sub>Cl, CH<sub>3</sub>Br); absorb terrestrial infrared radiation (e.g., CH<sub>4</sub>) ; and contribute to photochemical smog formation (e.g., C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>).

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

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

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

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

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  $\text{NO}_2$ , 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

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

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

## **9.6.2 Effects of Particles on Climate**

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

Atmospheric particles both scatter and absorb incoming solar radiation at visible wavelengths. The scattering of solar radiation back to space leads to a decrease in the transmission of visible radiation to the surface and hence to a decrease in the heating rate of the surface and the atmosphere. The absorption of either incoming solar radiation or outgoing terrestrial infrared radiation by atmospheric particles results in heating of the lower atmosphere. The interactions of particulate matter with electromagnetic radiation from the visible through the infrared spectral regions are responsible for their direct effects on climate. The direct effects of particles on climate are the result of the same physical processes responsible for visibility degradation. Visibility reduction is caused by particle scattering in all directions while the climate effects result mainly from scattering in the upward direction. The net effect of the above 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.

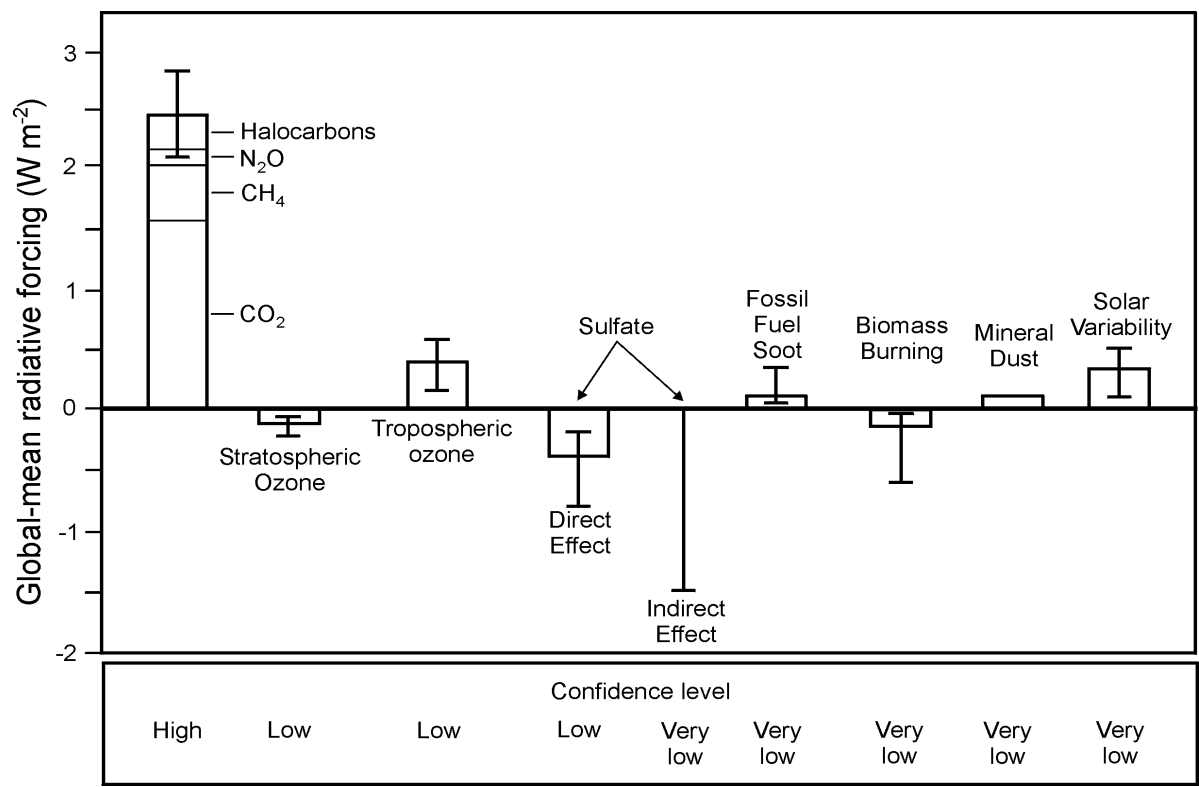
30 The amount of solar radiation incident on the earth-atmosphere system, or the solar  
31 constant, is  $1370 \text{ W m}^{-2}$ , or  $342.5 \text{ W m}^{-2}$  on a globally averaged basis (calculated by dividing the

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  $-0.4 \text{ W m}^{-2}$  (IPCC, 1995) with an uncertainty range of a factor of two. The  
6 uncertainty range reflects uncertainties in the emissions of  $\text{SO}_2$ , the amount of  $\text{SO}_2$  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 19<sup>th</sup> century the mean surface temperature of the earth has  
11 increased from  $0.3^\circ \text{C}$  to  $0.6^\circ \text{C}$  according to the IPCC (1995) assessment). Estimates of the  
12 indirect effects of particles range from 0 to  $-1.5 \text{ W m}^{-2}$  (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  $0.14 \text{ W m}^{-2}$  and  
26 from mineral dust from lands disturbed by human activity of  $0.09 \text{ W m}^{-2}$ . This value represents a  
27 near cancellation between a much larger solar forcing of  $-0.25 \text{ W m}^{-2}$  and a thermal forcing of  
28  $0.34 \text{ W m}^{-2}$ . 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  $0.1 \text{ W m}^{-2}$ , 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



mean radiative forcing of  $-0.1 \text{ W m}^{-2}$  caused by particles produced by biomass burning with an uncertainty factor of three. The global mean radiative forcing exerted by particles is then  $-0.5 \text{ W m}^{-2}$  with an uncertainty of about a factor of 2.4. Global mean radiative forcing exerted by 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).

Deviations from the global mean values can be very large on the regional scale. For instance, Tegen et al. (1996) found that the local radiative forcing exerted by dust raised from disturbed lands ranges from  $-2.1 \text{ W m}^{-2}$  to  $5.5 \text{ W m}^{-2}$  over desert areas and their adjacent seas. The largest regional values of radiative forcing due to anthropogenic sulfate are about  $-3 \text{ W m}^{-2}$  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 O<sub>3</sub> and possibly also HNO<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>, NH<sub>3</sub> and SO<sub>2</sub> 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

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

## **9.7 ECONOMICS OF PM ENVIRONMENTAL EFFECTS**

### **9.7.1 Introduction**

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

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

The initial challenge in measuring economic impacts associated with PM pollution is defining appropriate effects. Any given level of particulate matter will be associated with resulting environmental effects that potentially have economic significance. Examples include the level of crop damage or visibility impairment that result from specified levels of PM. Defining the welfare effects of PM changes requires that baseline levels of effects be defined as well - for example, the point at which PM begins to affect visibility in ways that are important to people. Sections 9.2 through 9.5 have described the scientific evidence relating the temporal and 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<sup>®</sup> (Taylor, et al., 1993; Abt Associates, 1998) have been used in analyzing  
17 agricultural impacts from air pollution (Ozone and PM NAAQS, NO<sub>x</sub> 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<sup>®</sup> 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

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

#### **9.7.5 Materials Damage Effects and Valuation**

Addressing the effects of materials damages related to reductions in criteria pollutants was first included in the benefits analysis supporting the secondary NAAQS for SO<sub>2</sub> and Total Suspended Particles (Manuel, et al., 1982). More recently, the 1990 NAPAP State of Science and Technology Report includes three of its twenty-seven chapters on materials damage and economic valuation methods. (Lipfert, 1996). Materials that are susceptible to exposure to particulate matter include, but are not limited to, painted and coated surfaces, metals, mortar and concrete, stone masonry, fabrics, and glass. The two primary categories of effects on these materials include the following:

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

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

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

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

#### **9.7.5.2 Household Soiling**

Studies addressing the costs of household soiling focus on estimating WTP measures of averting and mitigating behaviors. Manuel et al (1982) employ a theoretically consistent approach based on the household production model to assess the soiling and materials damage from decreasing SO<sub>2</sub> and TSP concentrations. Conceptually, an improvement in air quality generates benefits because fewer resources are required to produce a given level of cleanliness. Based on price and expenditure data for household products from the early 1970s, this study estimates the household demand for cleanliness and the change in consumer surplus associated with air quality induced changes in the price of cleanliness. This study estimates benefits related to household soiling of a unit reduction in ambient concentrations of TSP at \$0.35 per household in 1993 dollars. However, the date of this study reduces the applicability of its results since relative prices and consumer preferences have changed significantly since the early 1970s.



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

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

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

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

For buildings and structures of cultural or historical significance, the cost of damage extends beyond repair, replacement, or maintenance costs. Individuals not only lose utility associated with admiring these buildings (i.e., use value), but also because they and others may not be able to admire them in the future (i.e., existence value). Contingent valuation is the typical method employed to estimate the total WTP for damage to these types of buildings and structures. This method involves surveying individuals with hypothetical market scenarios for environmental goods or services to elicit their valuation, or WTP, for them (See Mitchell and Carson, 1989 or Cummings et al, 1986 for summary of this approach). This approach has been 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  $\text{km}^{-1}$ ). 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.<sup>1</sup>

24 Avoided costs to surrounding communities of reduced nitrogen loadings have been  
25 calculated for three case study estuaries (EPA, 1998).<sup>2</sup> 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

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<sup>1</sup> 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).

<sup>2</sup> 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).<sup>3</sup> 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 Bay<sup>4</sup>.

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.

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

<sup>4</sup> 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 has  
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



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

### 9.8.3 Particulate Matter-Related Effects on Visibility

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

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

Visibility impairment is associated with the air pollutant properties, including size distributions (i.e., fine particles in the 0.1 to 1.0  $\mu\text{m}$  size range), aerosol chemical composition, and relative humidity. With increasing relative humidity, the amount of moisture available for 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

### 12 **9.8.5 Economic Impact of Particulate Matter**

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

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