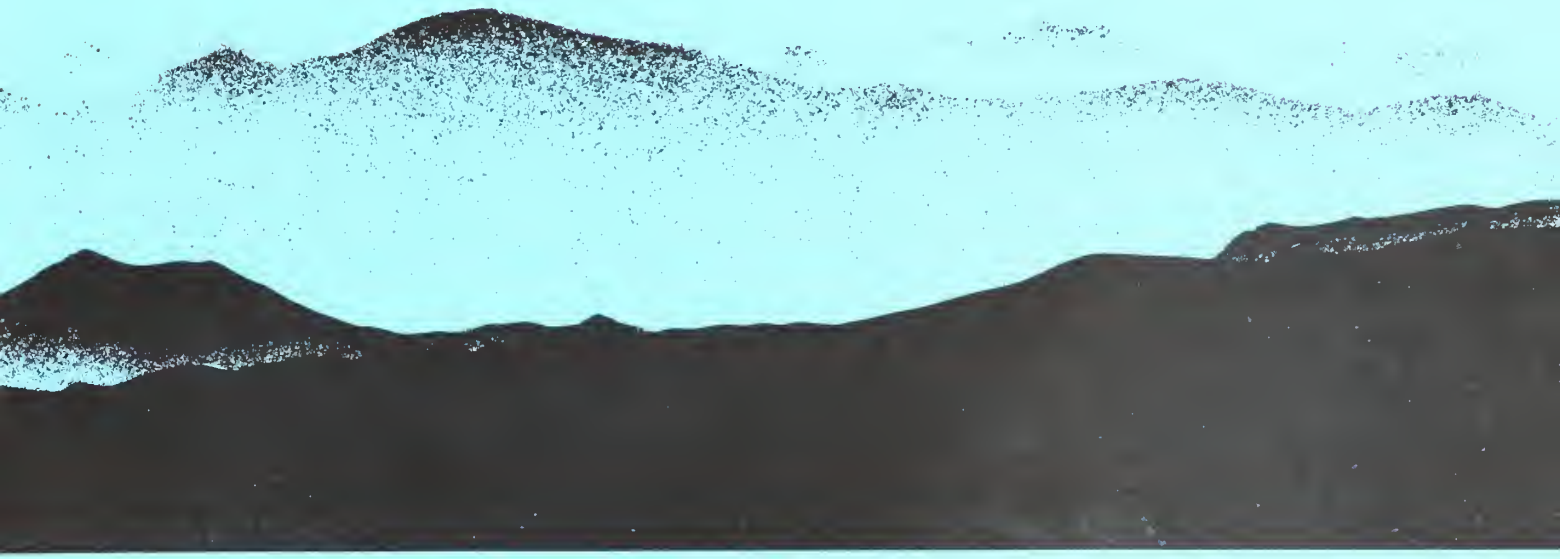
Acid Rain and Air Pollution In Desert Park Areas

Proceedings of a Workshop, May 16-18, 1988
and
Management Recommendations
Tucson, Arizona

Technical Report NPS/NRAQD/NRTR-91/02



United States Department of the Interior • National Park Service

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Introduction

The National Park Service (NPS) sponsored a workshop,"Acid Rain and Air Pollution in Desert Park Areas," in Tucson, Arizona, May 16-18, 1988. Its purpose was to assess what pollutants are now affecting desert ecosystems and what are likely trends for future years. We considered pollutants to include acidic wet and dry deposition, metals, organic compounds and gaseous pollutants (such as ozone, sulfur dioxide, hydrogen fluoride, and nitrogen oxides). The effects of air pollution have been addressed in more mesic environments, but their effects on desert ecosystems have not been scrutinized. The objectives were to: (1) ascertain the state of knowledge regarding current levels and future trends of air pollutants in the arid west, (2) determine what natural and cultural resources are sensitive and how they are likely to be affected, and (3) develop recommendations for future research and monitoring of causes and effects of air pollution in these park areas.

The workshop participants included resource managers and superintendents of 17 desert parks, the Rocky Mountain, Western and Southwest Regional Office Air Quality Coordinators, several representatives from the NPS Washington office, and state and local government, industry, and academic representatives. Formal presentations were made to introduce workshop participants to the state of knowledge regarding sources of pollutants and their sensitive receptors. These included summaries of emissions and types of deposition, presentations on effects of different pollutants to biological and cultural resources, and specific park case studies of how pollutants affect resources. Ways in which scientific information regarding causes and effects could be applied by land managers to mitigate pollution impacts on national park units were also discussed.

The workshop closed with a general discussion summarizing what we know and don't know regarding air pollution and its effects in desert areas. Participants outlined strategies for obtaining and using information to protect NPS biological and cultural resources against pollutant degradation. The workshop was successful in raising awareness of the threats of pollution to desert parks. It emphasized the paucity of information available on the effects of pollutants on desert ecosystems. The need to acquire better understanding of these effects was made apparent. A dialogue developed between managers and scientists which emphasized the need to include air quality issues in resource management plans. Managers became aware that if air quality issues are important in their parks, they need to work with their regional Air Quality Coordinator and staff of the Air Quality Division and Water Resources Division to address issues through resource management planning, research and monitoring programs, and political activity of the State and local levels.

Summary of Workshop

Western United States emissions of sulfur dioxide (SO_2) have historically been dominated by smelters in Arizona; these emissions declined as smelters closed. Future emissions are not likely to increase to the levels seen during the copper era unless a synfuel industry develops or the use of coal increases. While the regional picture is thus encouraging, individual urban areas will continue to grow, contributing nitrogen oxides (NO_x) and SO_2 to more local receptor areas. Blanchard uses a mass balance approach to make the observation that less than one third of the SO_2 and NO_x emitted in the region can be accounted for in precipitation. The remainder is either deposited to surfaces dry, or is transported out of the region.

The National Atmospheric Deposition Program (NADP) monitors precipitation chemistry at a number of sites in the Southwest. The mean annual precipitation pH has generally been less than or equal to 4.8 at two of the 14 sites examined, Mesa Verde, CO, and Oliver Knoll, AZ. At many sites, levels of sulfate and nitrate exceed background levels. Most of the 14 NADP sites examined exhibited relatively high concentrations of calcium (Ca), representing a sizeable neutralizing capacity. Sites closest to urban or industrial sources showed strong influences from these sources. Some national park units, including Saguaro and Joshua Tree National Monuments, are located close enough to major sources of acid precursors that precipitation chemistry monitoring is warranted. It was concluded that acid rain is not a threat to resources of desert park areas by itself, but the effects of cumulative deposition of both wet and dry acidifying materials must be further explored.

Gaseous pollutants of concern in NPS desert parks include: ozone, sulfur oxides, nitrogen oxides, and volatile organic compounds (VOC). The NPS Air Quality Division maintains a network of monitoring sites in desert parks that records information on spatial and temporal trends of pollutant concentrations. Scruggs concluded that even in remote desert parks pollutants often exceed background levels.

Controlled exposures and field studies have shown that some desert plant species are sensitive to levels of gaseous pollutants that occur in park units. Foliar injury has been documented on shrub and tree species. Of particular concern are the effects of ozone on annual riparian and montane plants species. The effects of nitrogen fertilization on the structure of desert plant communities and phenological cycles of cacti need to be investigated.

Researchers have not extensively investigated the possible effects of acidic deposition on desert ecosystems. Ferenbaugh discusses how deposition of dry particulate matter can be of importance to plants (creating an insulating layer on plants, lodging in open stomates, or interfering with stomatal closure). This dry-deposited material can form acidic solutions when dissolved in water.

Gladney presents methods for determining what chemical elements deposited to NPS units are from natural or anthropogenic sources. A comparison of soils from Saguaro National Monument and the nearby San Manuel Smelter shows that most of the elements in both soil samples are from natural crustal sources, while cesium, indium, antimony, zinc, and hafnium show evidence of input from non-crustal sources (smelters). Analyzing the fine-particle fraction collected by the NPS visibility program at Saguaro, Gladney found that zinc, bromine, lead, sulfur, and copper in the fine-particle aerosol have large, non-crustal sources. Titanium, manganese, iron, aluminum, and potassium can be ascribed to local soil materials.

In addition to affecting plants and soils, acid deposition can alter aquatic ecosystems. The major aquatic habitat that could be adversely affected by acid deposition are rock pools. Many are located on metamorphic rocks which do not have any acid-neutralizing capacity. The pools are usually ephemeral - drying up after the rainy season. Organisms which survive in these pools have very rapid life cycles, or specialized adaptations. Acidification of water can result in reproductive failure of resident organisms. Preliminary results presented by Graham on Colorado Plateau potholes indicate that some potholes may be resistent to acid deposition effects due to buffering by sediments. However, other rockpool ecosystems in National Park units, such as Glen Canyon National Recreation Area and Saguaro National Monuments, are in proximity to sources of acidic pollutants. The buffering capacity of these systems may be lower due to different rock types.

Cryptogamic soil crusts (composed of bacteria, green algae, cyanobacteria, microfungi, and lichens) are extremely important in desert ecosystems. They stabilize topsoil and contribute fixed nitrogen to nutrient deficient systems. Rock lichens are also important components of desert ecosystems. Studies are being conducted by Belnap to determine if pollutants are injuring these resources. Rock lichens and cryptogamic crusts exhibit physiological damage in desert areas adjacent to the Navajo Generating Station in Page, Arizona. Increased electrolyte leakage, chlorophyll degradation, and reduced nitrogen fixation in crusts and lichens are possible symptoms of air pollution damage.

Most of us do not consider cultural resources in desert parks to be at risk from air pollution. However, Sherwood discusses some of the resources that may be affected. White mineral pigments may be subject to accelerated deterioration from sulfur oxides and atmospheric acidity; iron pigments change color or mobilize depending on the acidity of the surface environment. Organic materials (textiles, baskets, leather, and feather objects) may be affected by indoor pollutants. Filtration and ventilation systems should be installed if ozone or nitric acid levels are documented to exceed background levels for collections containing pigmented textiles and baskets. Pollution adds to mechanical weathering of rocks by providing soluble salts which crystallize and re-crystallize within rock pore structure, exerting pressure that weakens the stone matrix.

Saguaro National Monument is the site of the most comprehensive air pollution research program being carried out at a desert park. This Monument is in proximity to a growing urban area with pollution problems. Hall outlines the research and monitoring program that includes air quality monitoring, biomonitoring gardens, ozone studies on pines, and studies of saguaro physiology.

It is important for park managers to be aware that air pollution can affect desert parks. Air pollution issues should be addressed in park planning documents. Research programs need to be well-designed to answer questions of interest to land managers and regulatory agencies. Every effort must be made to publish results in peer-reviewed journals so that they can be used in permit review and standard setting. While air pollution impacts in desert parks are not as severe as in some other park areas, the growth of cities and energy-related industry in desert areas requires that we continue to monitor air quality and assess the potential for ecological effects.

Emissions Affecting the Arid West

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Abstract. Current emission rates, historical trends, and projections of future emissions are described to help gauge the extent to which air quality and acidic deposition have changed, or may change, in western parks. In 1985, emissions of SO_2 in the West were 8.5 percent of the national total of 23 million tons, while NO_x emissions comprised 16 percent of the 1985 national total of 21 million tons (Zimmerman et al., 1988).

Emissions of SO_2 in the western U.S. increased from 1900 until the mid-1970s (Gschwandtner, 1985). Emissions of SO_2 from nonferrous smelters decreased by about 70 percent between 1975 and 1986 (Knudson, 1985; Knudson, 1986; Kohout et al., 1987). Emissions of NO_x in the western U.S. increased steadily from 1900 to 1980 (Gschwandtner, 1985). There was little trend in NO_x emissions over the period from 1975 to 1986 (Knudson, 1985; Knudson, 1986; Kohout et al., 1987). As of 1986, smelters and electric utilities were the two largest sources of SO_2 emissions in the West, while electric utilities and vehicles were the largest NO_x sources.

Emission projections typically indicate a period of relatively constant emission levels during the late 1980s and early 1990s for both SO_2 and NO_x in the West. Subsequent increases in NO_x are projected (assuming no new emission control requirements are adopted). Smaller increases in SO_2 emissions may occur in parts of the West during the 1990s and later.

Introduction

The purpose of this paper is to summarize available information on emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) in the western United States. I describe current emission rates, historical trends, and projections of future emissions. By understanding trends in SO_2 and NO_x emissions, one can gauge the extent to which air quality and acidic deposition have changed, or may change, in western parks.

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Contrasts Between the Eastern and Western United States

An emissions comparison of the western and eastern U.S., shows that SO_2 and NO_x differ in both magnitude and distribution in these regions. According to the 1985 inventory compiled for the National Acid Precipitation Assessment Program (NAPAP), emissions of SO_2 in the eleven western states[2] were 1.9 million tons, or 8.5 percent of the national total of 23 million tons (Zimmerman et al., 1988). NO_x emissions in the West were 3.3 million tons, or 16 percent of the 1985 national total of 21 million tons (Zimmerman et al., 1988).

Figure 1 shows the density of SO_2 and NO_x emissions in the United States and southern Canada (NAPAP, 1987). In the eastern U.S., large urban areas and industrial emission sources tend to be geographically contiguous; in contrast, urban areas and industrial emission sources in the West are generally geographically isolated, being separated by mountain ranges (Young et al., 1988). Western mountains modify the prevailing winds, thus affecting surface wind directions and the transport of air pollutants (Young et al., 1988).

Historical SO_2 and NO_x Emissions in the West

Emissions of SO_2 in the western U.S. increased from 1900 until the mid-1970s, with a prominent decrease occurring during the 1930s (Figure 2) (Gschwandtner et al., 1985). The decrease from 1970 to 1980 occurred primarily in Arizona. Historically, western SO_2 emissions derived largely from smelters, and recent decreases in SO_2 emissions have occurred as a result of the closure of some smelters and the installation of emission controls at others (Figure 3).[3]

NO_x emissions in the western U.S. increased steadily from 1900 to 1980 (Figure 4) (Gschwandtner et al., 1985). By 1980, electric utilities accounted for approximately one-half the total NO_x emissions in the mountain states[2], with vehicles representing the second-largest source category (Figure 5).

Current SO_2 and NO_x Emissions in the West

Recent (1975 - 1986) emissions of SO_2 are shown on a monthly basis for eight western states in Figure 6 (Knudson, 1985; Knudson, 1986; Kohout et al., 1987). SO_2 emissions decreased in both California and Arizona during this period. Figure 7 shows SO_2 emission trends in the Southwest[4] from 1975 through 1986 for smelters, electric utilities, and all other emission sources combined (Knudson, 1985; Knudson, 1986; Kohout et al., 1987). Smelter emissions decreased by about 70

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[2] Arizona, California, Colorado, Idaho, Montana, Nevada, New Mexico, Oregon, Utah, Washington, and Wyoming.

[3] Figure 3 includes emissions in the states of Arizona, Colorado, Idaho, Montana, Nevada, New Mexico, Utah, and Wyoming.

[4] Arizona, New Mexico, Nevada, Utah, Colorado, and Wyoming.

percent during this period, which largely accounts for the trend in total SO_2 emissions. By 1986, SO_2 emissions from smelters were less than half the total. Also evident in Figure 7 is the occurrence of a strike that idled most of the western smelters during the summer of 1980.

Kohout et al. (1987) assessed the uncertainties in their emission estimates, and concluded that their estimation methods did not adequately account for fluctuations in the operations of nonferrous smelters. Their emission inventory will be refined by collecting data on smelter operations directly from state environmental agencies and individual smelters. For comparison, the smelter emission estimates obtained by Oppenheimer et al. (1985) and Epstein and Oppenheimer (1986) from state agencies and industry are shown in Figure 8. These emission estimates indicate larger fluctuations in SO_2 emissions by western smelters over the time period from 1979 through 1985.

Recent NO_x emissions in eight of the western states are shown in Figure 9 (Knudson, 1985; Knudson, 1986; Kohout et al., 1987). There was little trend in NO_x emissions in these states over the period from 1975 to 1986.

Figure 10 shows NO_x emissions in the Southwest[5] by sector. Vehicles and electric utilities account for the majority of NO_x emissions in the Southwest, with utilities exhibiting a slightly increasing trend.

Comparison of Emissions to Wet Deposition

The preceding figures show that current emissions of SO_2 and NO_x in the Southwest are each about 100,000 metric tons per month, or somewhat more than 1.2 million tons per year. Most of the National Atmospheric Deposition Program's (NADP/NTN) precipitation monitoring sites in the Southwest have generally registered 0.3 to 0.5 g/m^2 wet sulfate deposition; wet nitrate deposition at these sites has also generally been in the range 0.3 to 0.5 g/m^2 (National Atmospheric Deposition Program, 1988). These ranges correspond to 0.5 to 0.8 million metric tons per year when multiplied by the areas of the states of Arizona, Colorado, New Mexico, Nevada, Utah, and Wyoming. The latter range, in turn, corresponds to emissions of 0.3 to 0.5 million tons per year SO_2 and 0.4 to 0.6 million tons per year and NO_x. Therefore, wet deposition only accounts for approximately 25-40 percent of the SO_2 emissions and 30-50 percent of the NO_x emissions in the Southwest.

Projected Emissions of SO_2 and NO_x in the West

All emission projections have high uncertainties. Projections depend upon assumptions concerning the rate at which old facilities (e.g., power plants) are retired, the use of control technologies, and the rate of economic growth, among others. Given the sensitivity of projections to such assumptions, relative trends are thought to be more reliable than the absolute values of the emission projections.

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[5] Arizona, New Mexico, Nevada, Utah, Colorado, and Wyoming.

The projections summarized here are derived from two sources: the United States - Canada Memorandum of Intent on Transboundary Air Pollution (1982), and the NAPAP Interim Assessment (1987). The NAPAP Interim Assessment summarizes changes in regional emissions between 1980 and 2030 from two studies: Argonne National Laboratory's projections for the Department of Energy's Fifth National Energy Policy Plan (ANL/NEPP) (Placet et al., 1986) and projections by E.H. Pechan & Associates for the U.S. Environmental Protection Agency (EHP/EPA/A and EHP/EPA/B).

Figure 11 shows projected SO_2 and NO_x emissions for Federal Region VI.[6] The projected emission increases for this region occur because population and industry are assumed to shift from the northeastern U.S. to the South and Southwest. SO_2 increases are projected to range from 73 to 266 percent between 1980 and 2030, while NO_x increases are projected to range from 66 to 76 percent (NAPAP, 1987).

Figure 12 shows projected SO_2 and NO_x emissions for Federal Region VIII.[7] The expected trends in SO_2 emissions between 1990 and 2000 are small increases, or no changes. NO_x emissions are projected to increase at a more rapid rate.

Figure 13 shows projected SO_2 and NO_x emissions for Federal Region IX.[8] SO_2 emissions are projected to remain approximately constant, while NO_x emissions are projected to increase by about forty percent between 1980 and 2030.

Summary

We have described current emission rates, historical trends, and projections of future emissions in order to help gauge the extent to which air quality and acidic deposition have changed, or may change, in western parks. Emissions of SO_2 in the West were 8.5 percent of the national total of 23 million tons in 1985, while NO_x emissions comprised 16 percent of the 1985 national total of 21 million tons (Zimmerman et al., 1988). In contrast to the eastern U.S., urban areas and industrial emission sources in the West are generally geographically isolated, being separated by mountain ranges (Young et al., 1988).

Emissions of SO_2 in the western U.S. increased from 1900 until the mid-1970s (Gschwandtner, et al., 1985). SO_2 emissions from nonferrous smelters decreased by about 70 percent between 1975 and 1986 (Knudson, 1985; Knudson, 1986; Kohout et al., 1987). NO_x emissions in the western U.S. increased steadily from 1900 to 1980 (Gschwandtner, et al., 1985). There was little

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[6] Louisiana, Arkansas, Oklahoma, Texas, and New Mexico. Note that the Memorandum of Intent projected values from 1980 for 1990 and 2000. The other inventories projected estimates annually. However, the regional estimates tabled in the NAPAP Interim Assessment (1987) list only the projections for 2030 relative to a 1980 base year. The graphs shown here depict only the 1980 and 2030 estimates for the ANL/NEPP, EHP/EPA/A, and EHP/EPA/B projections.

[7] Montana, North Dakota, South Dakota, Wyoming, Colorado, and Utah.

[8] States within the conterminous U.S. that are located in Region IX are Arizona, California, and Nevada.

trend in NO_x emissions over the period from 1975 to 1986 (Knudson, 1985; Knudson, 1986; Kohout et al., 1987). As of 1986, smelters and electric utilities were the two largest sources of SO_2 emissions in the West, while electric utilities and vehicles were the largest NO_x sources.

Emission projections typically indicate a period of relatively constant emission levels during the late 1980s and early 1990s for both SO_2 and NO_x in the West. Subsequent increases in NO_x are projected (assuming no new emission control requirements are adopted). Smaller increases in SO_2 emissions may occur in parts of the West during the 1990s and later.

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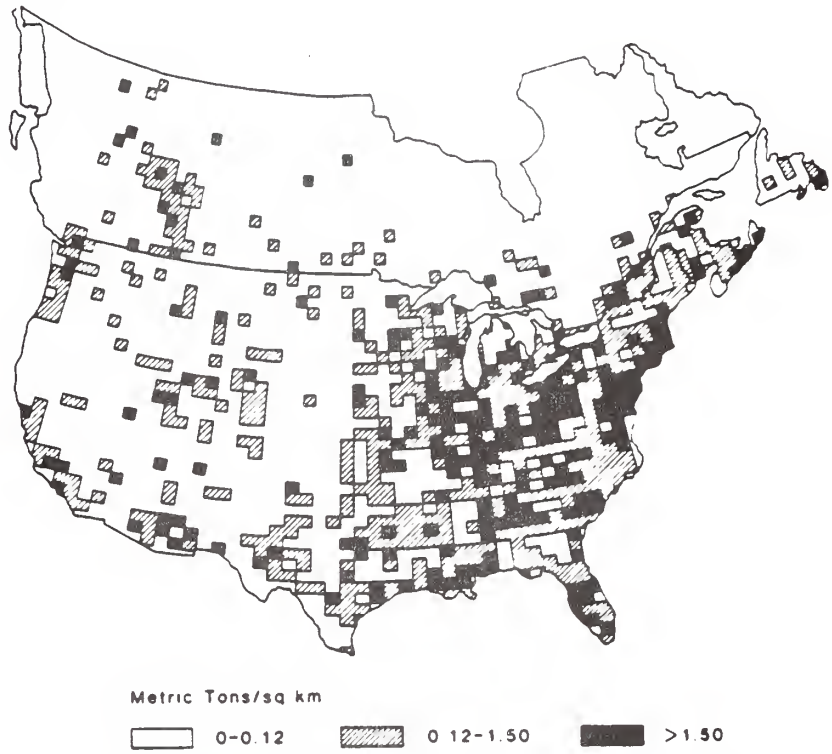
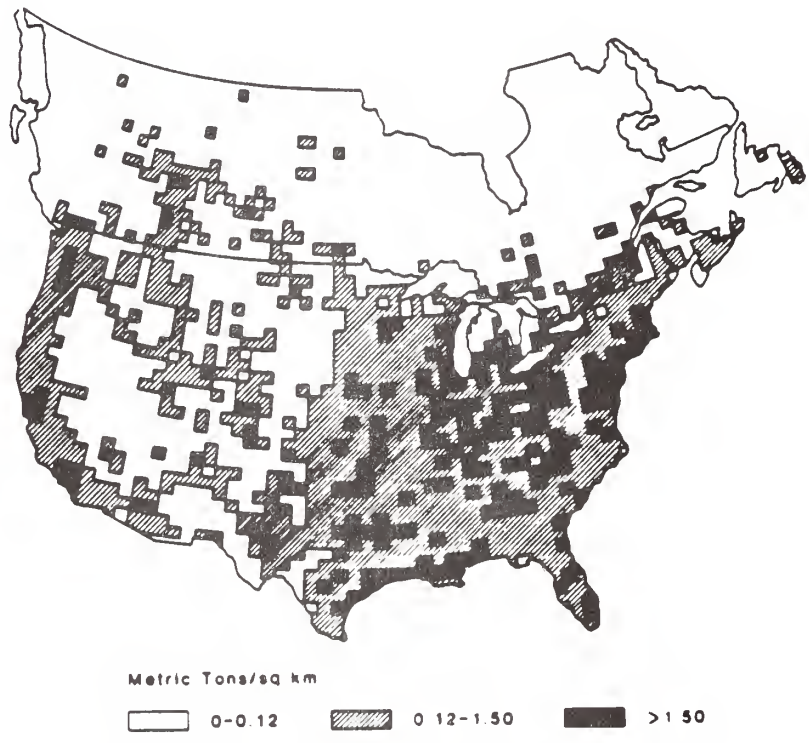
Figure 1

Density of Anthropogenic SO2 Emissions in 1980



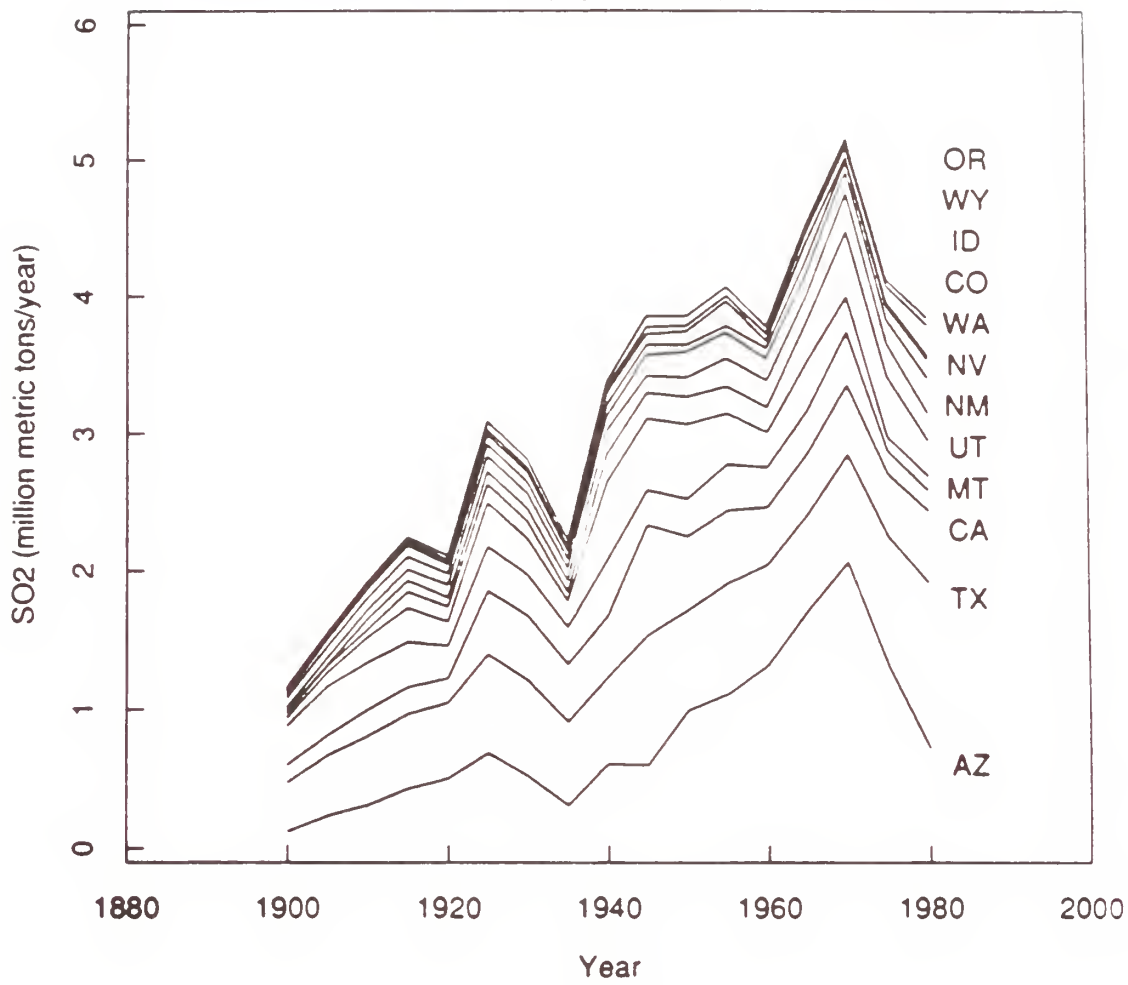
Density of Anthropogenic NOx Emissions in 1980



Source: NAPAP Interim Assessment (1987)

Figure 2

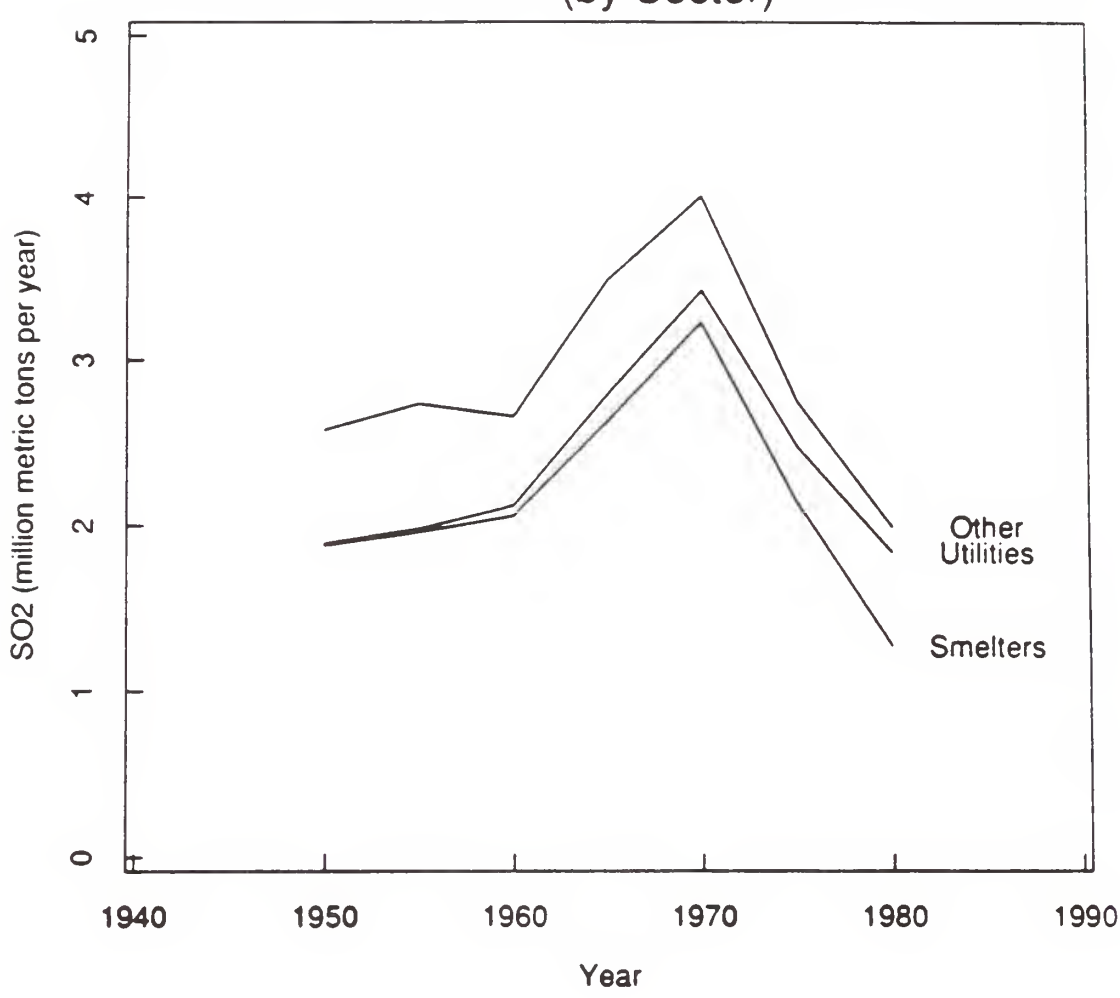
Historical SO2 Emissions in the Western U.S. (by State)



Source: Derived from data in Gschwandtner et al. (1985)

Figure 3

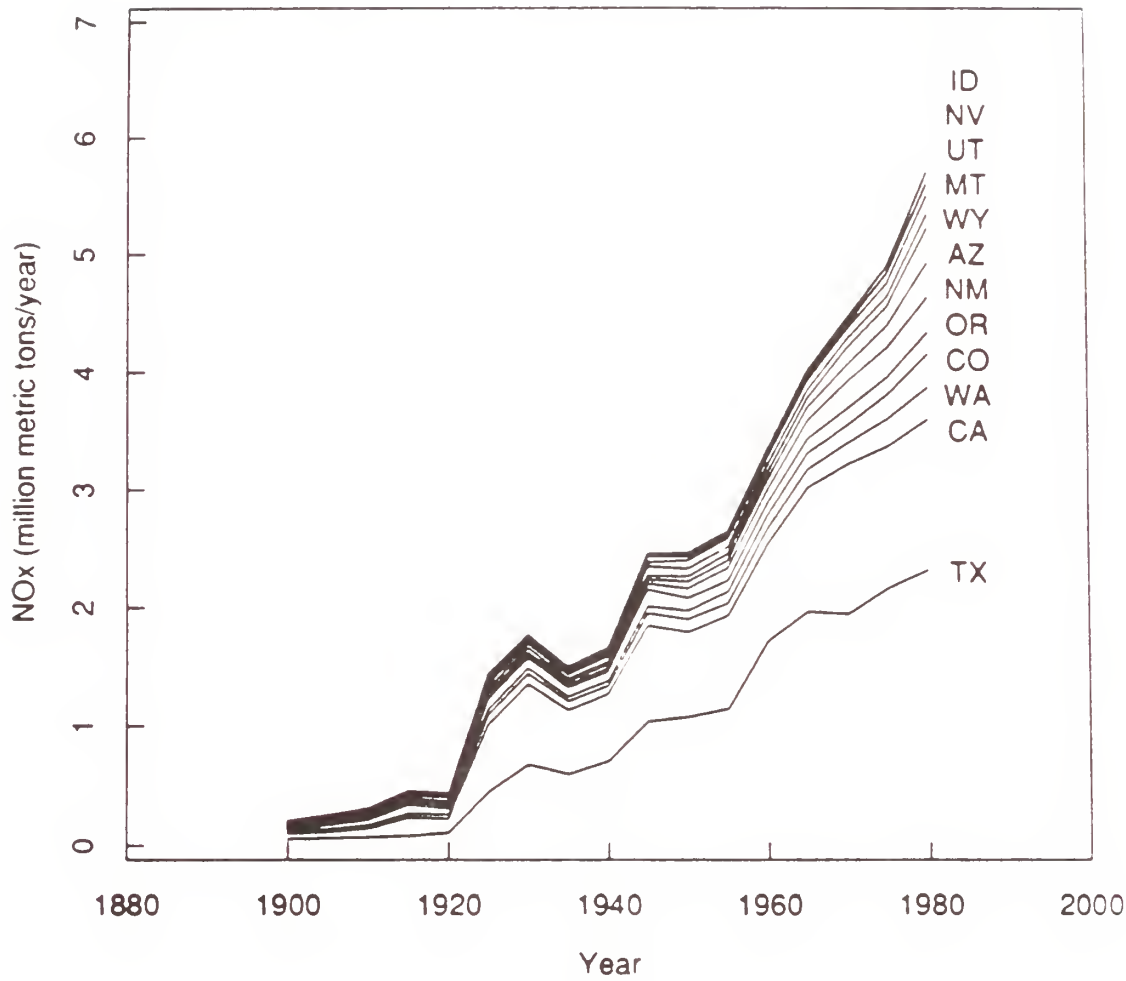
Historical SO2 Emissions in the Mountain States (by Sector)



Source: Derived from data in Gschwandtner et al. (1985)

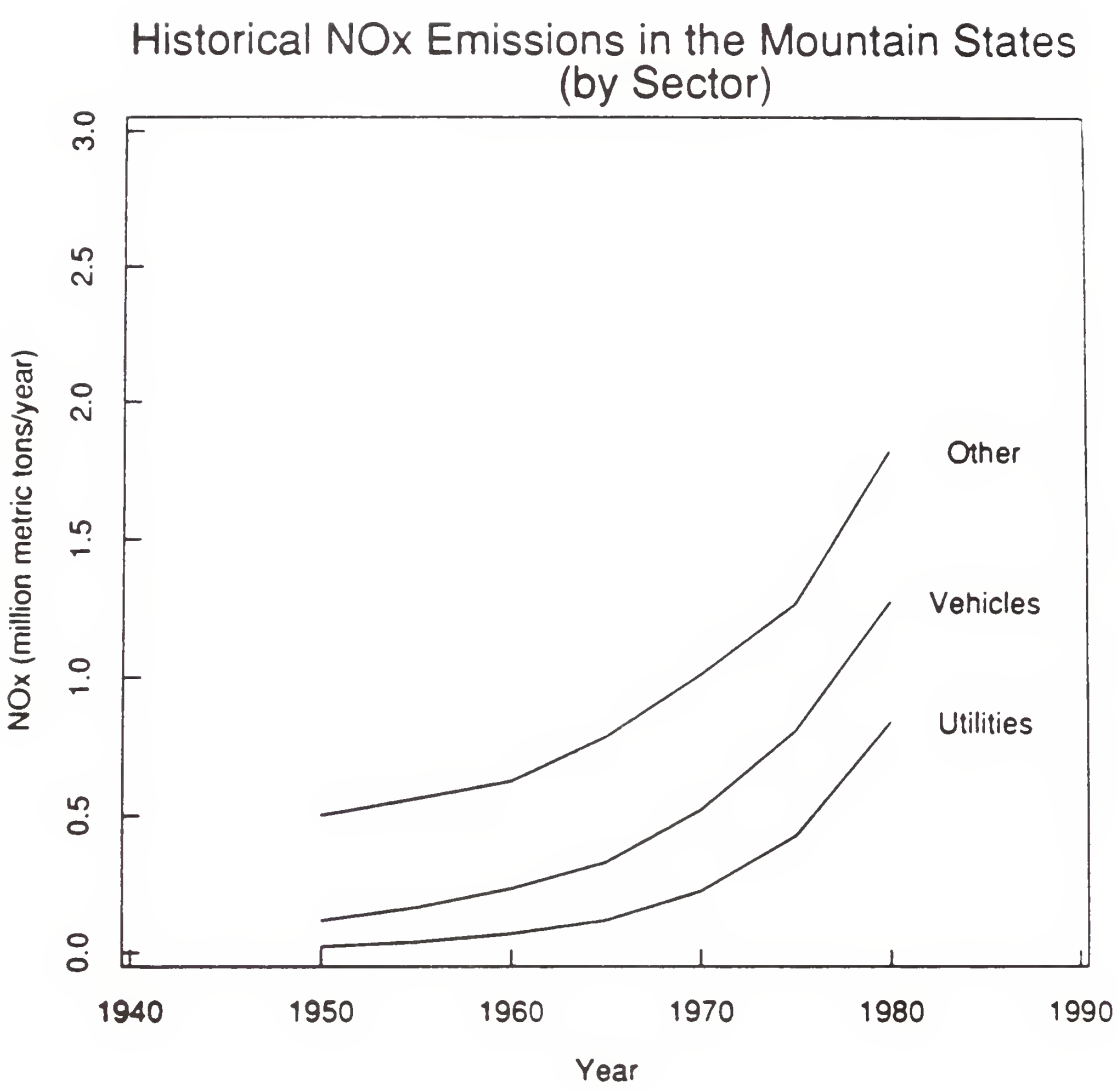
Figure 4

Historical NOx Emissions in the Western U.S. (by State)



Source: Derived from data in Gschwandtner et al. (1985)

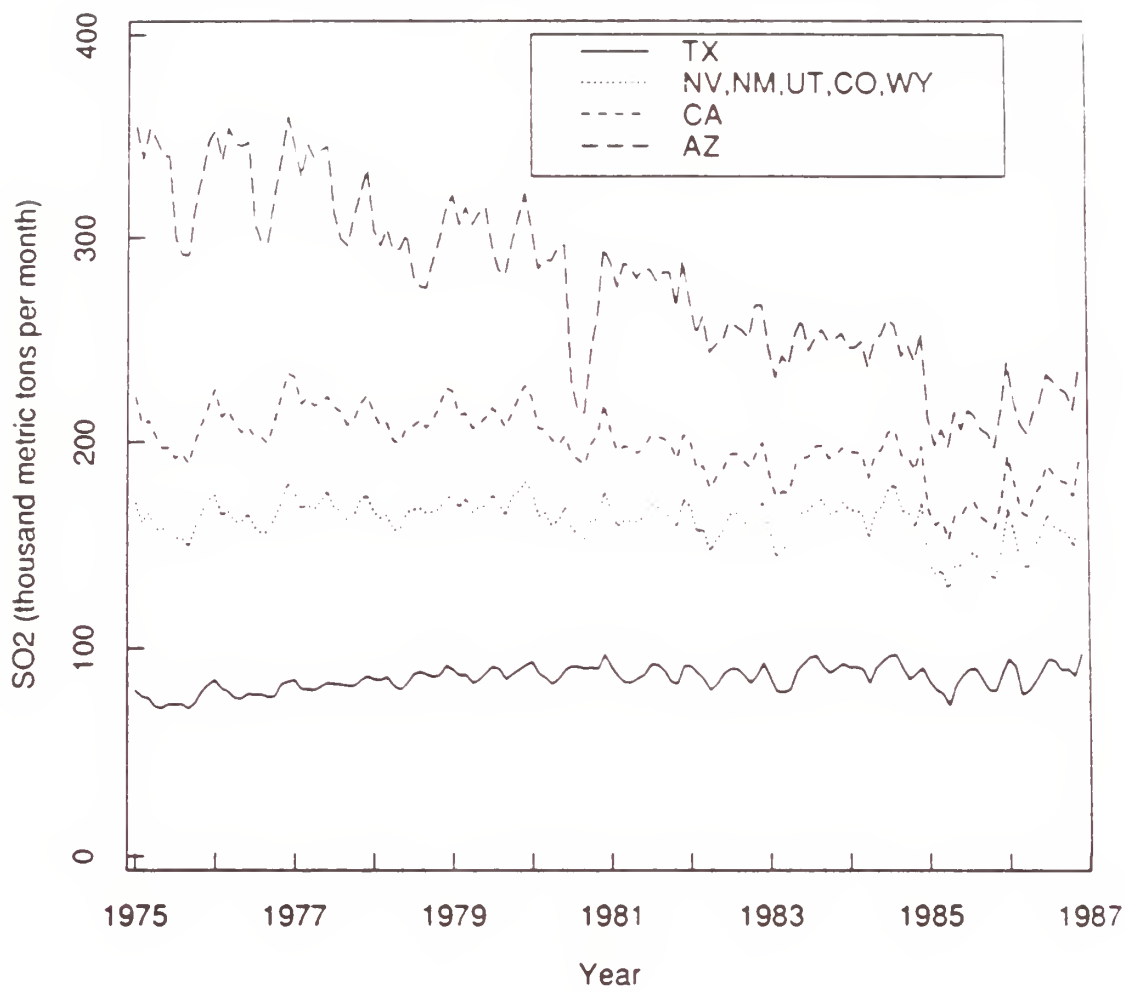
Figure 5



Source: Derived from data in Gschwandtner et al. (1985)

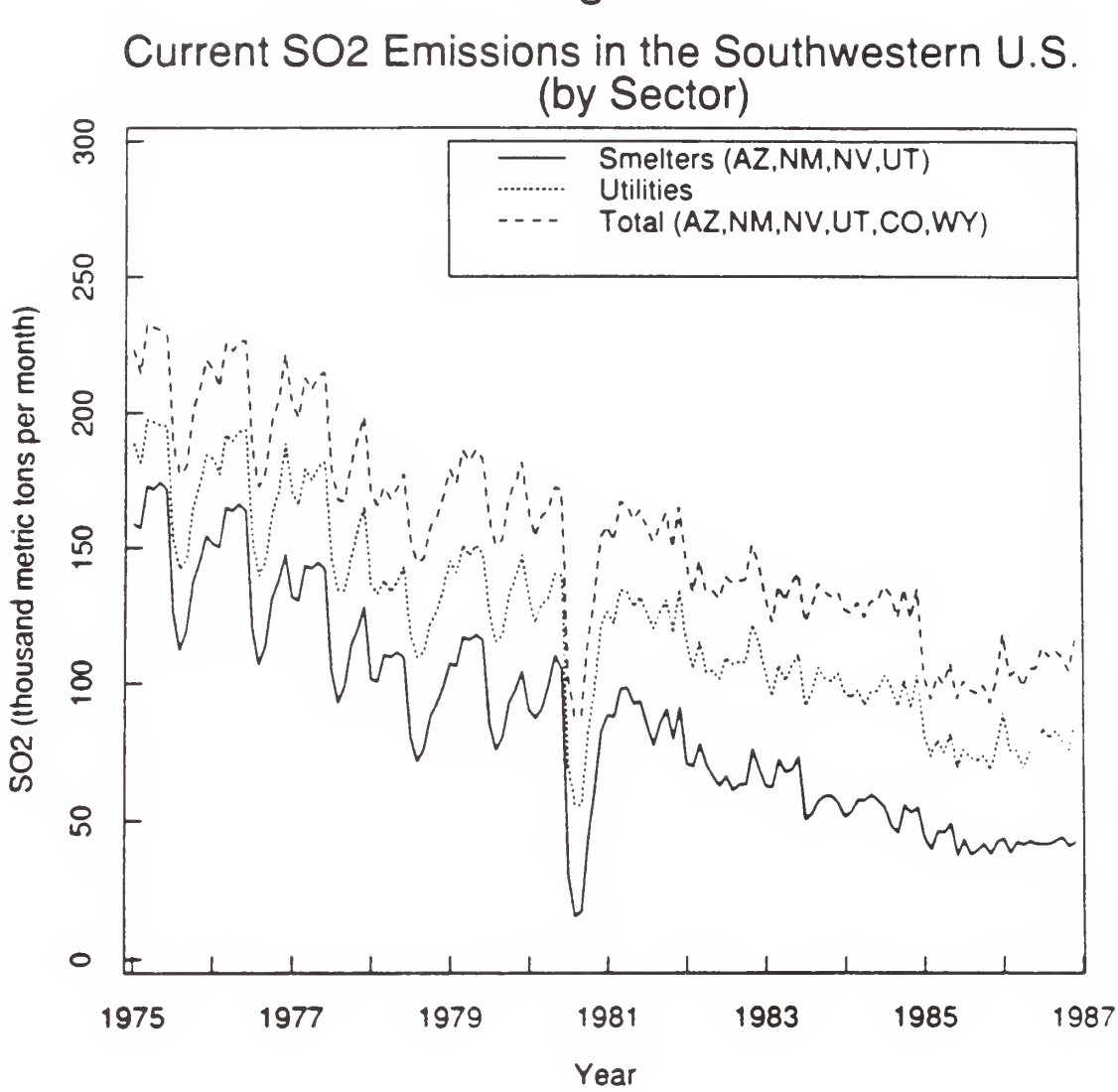
Figure 6

Current SO2 Emissions in the Western U.S.



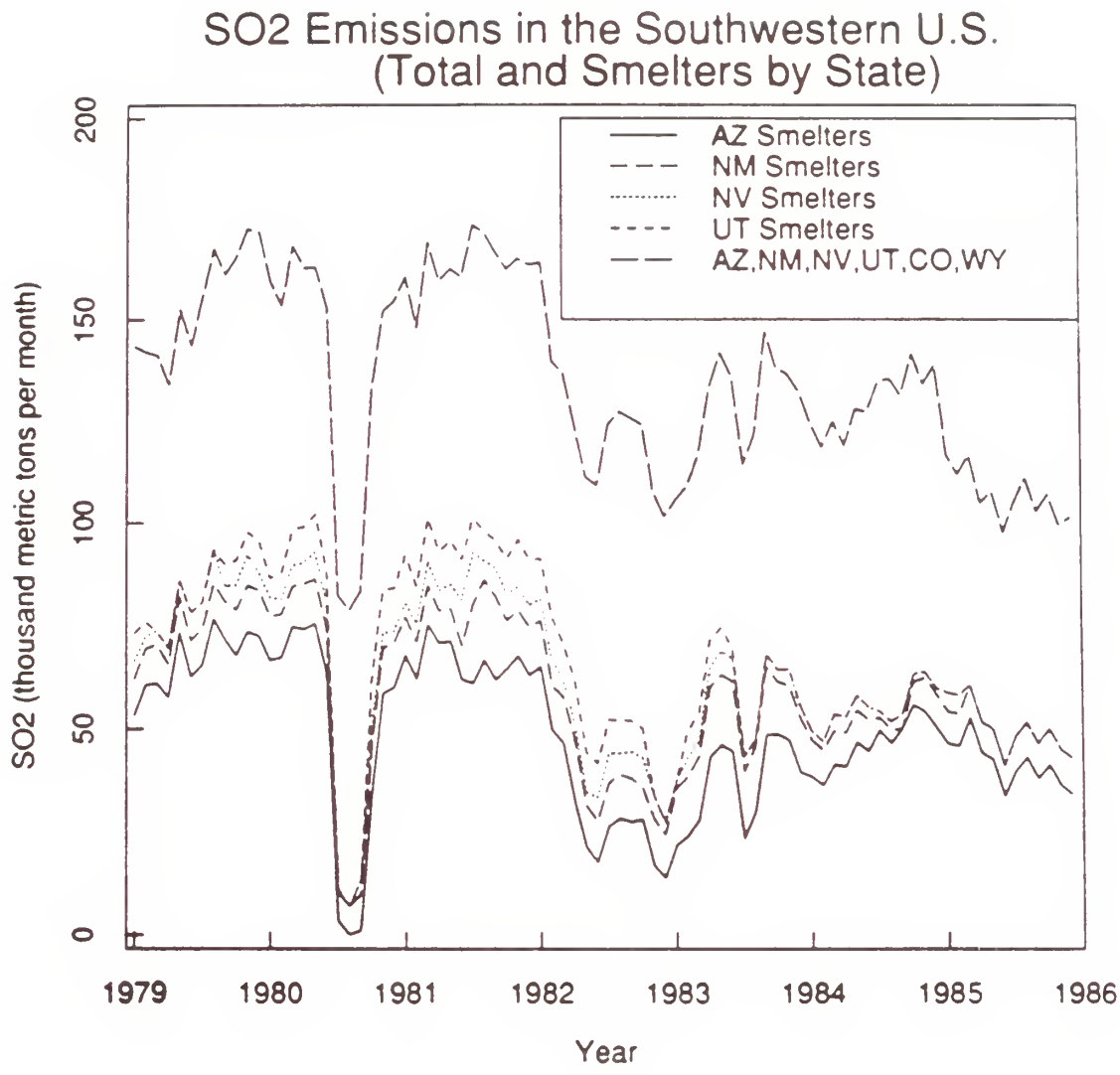
Source: Derived from data in Knudson (1985), Knudson (1986), and Kohout et al. (1987)

Figure 7



Source: Derived from data in Knudson (1985), Knudson (1986), and Kohout et al. (1987)

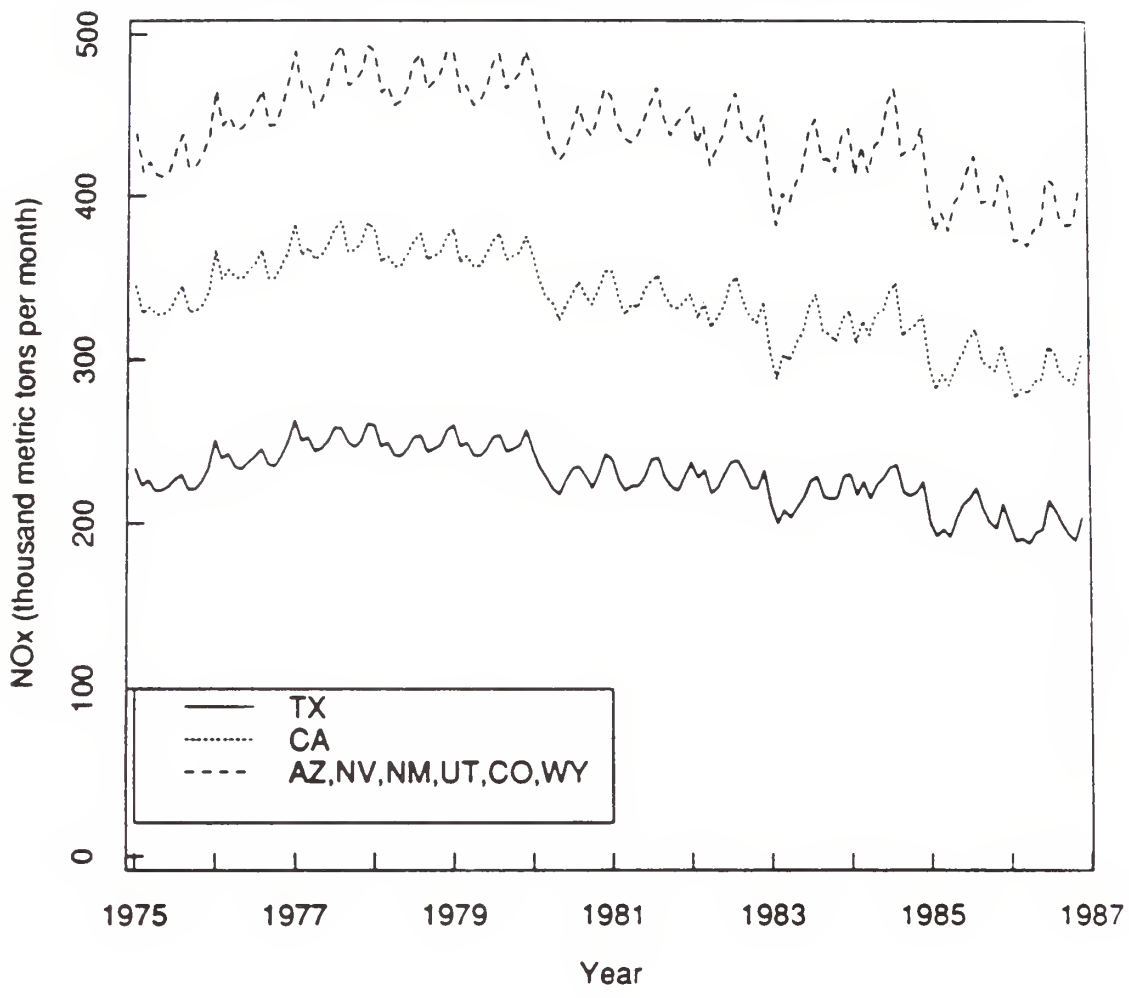
Figure 8



Source: Derived from data in Oppenheimer et al. (1985) and Epstein and Oppenheimer (1986)

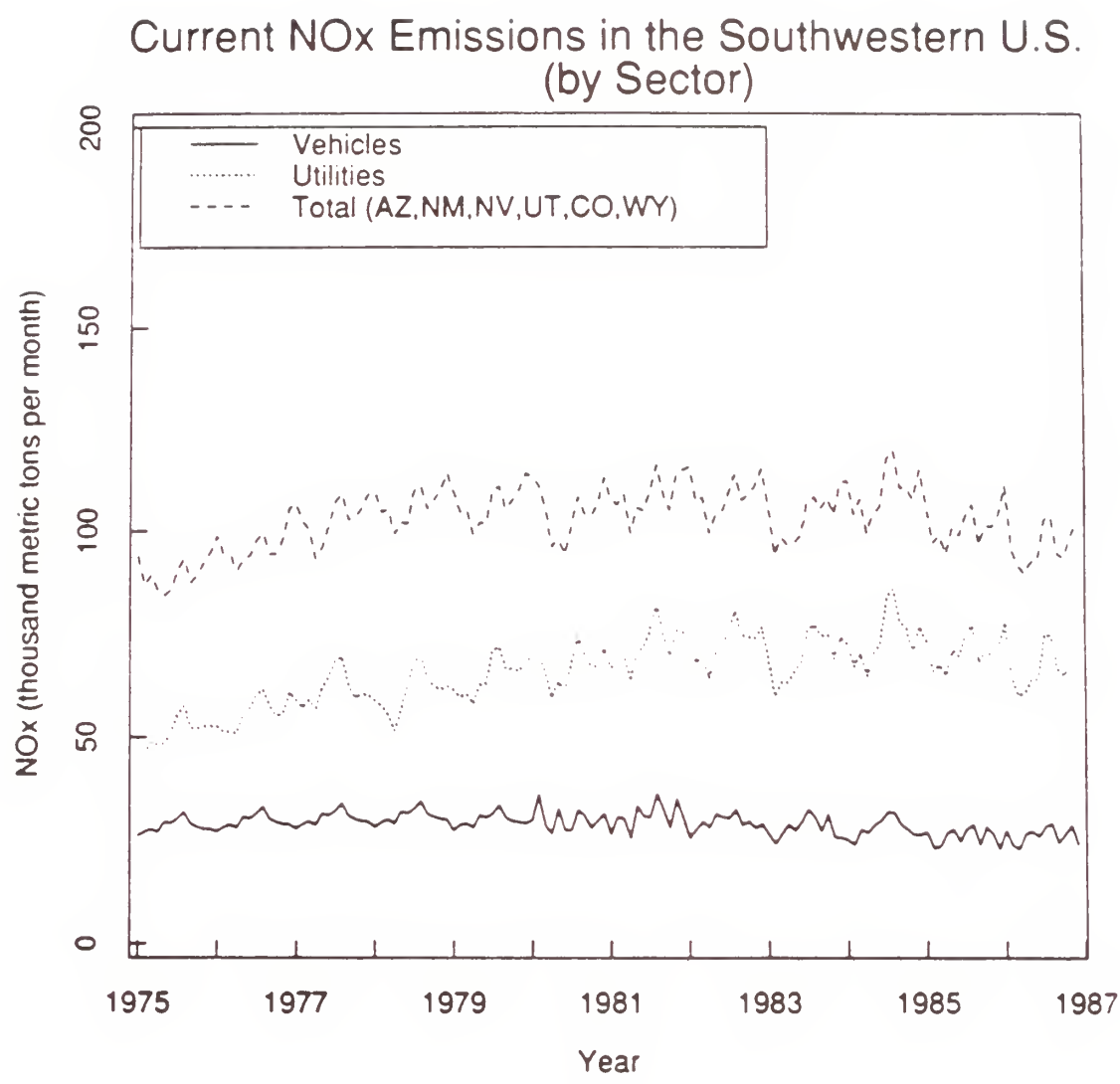
Figure 9

Current NOx Emissions in the Western U.S.



Source: Derived from data in Knudson (1985), Knudson (1986), and Kohout et al. (1987)

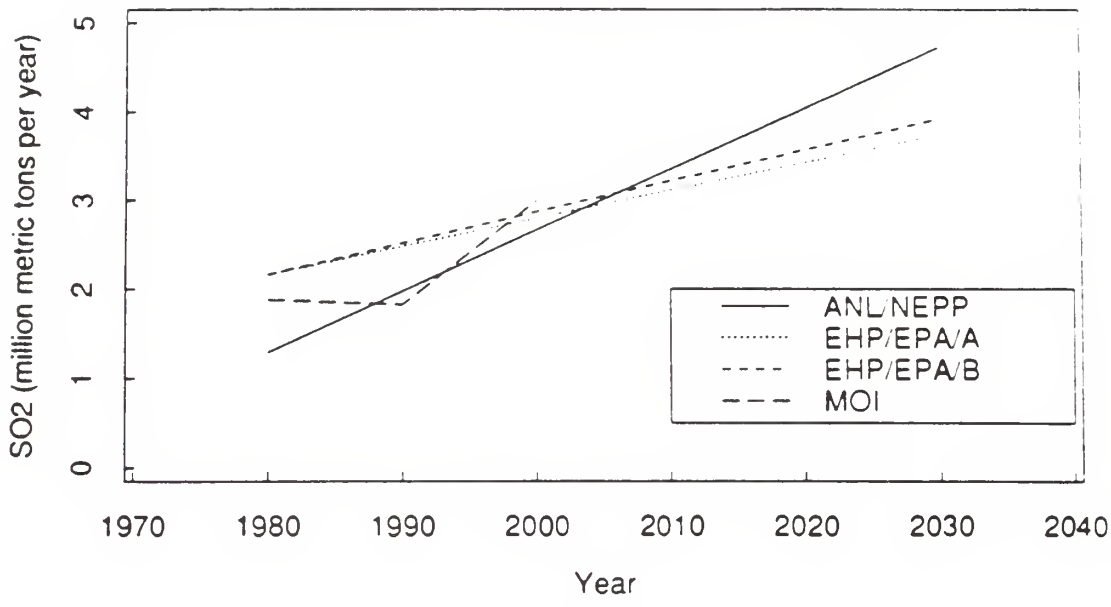
Figure 10



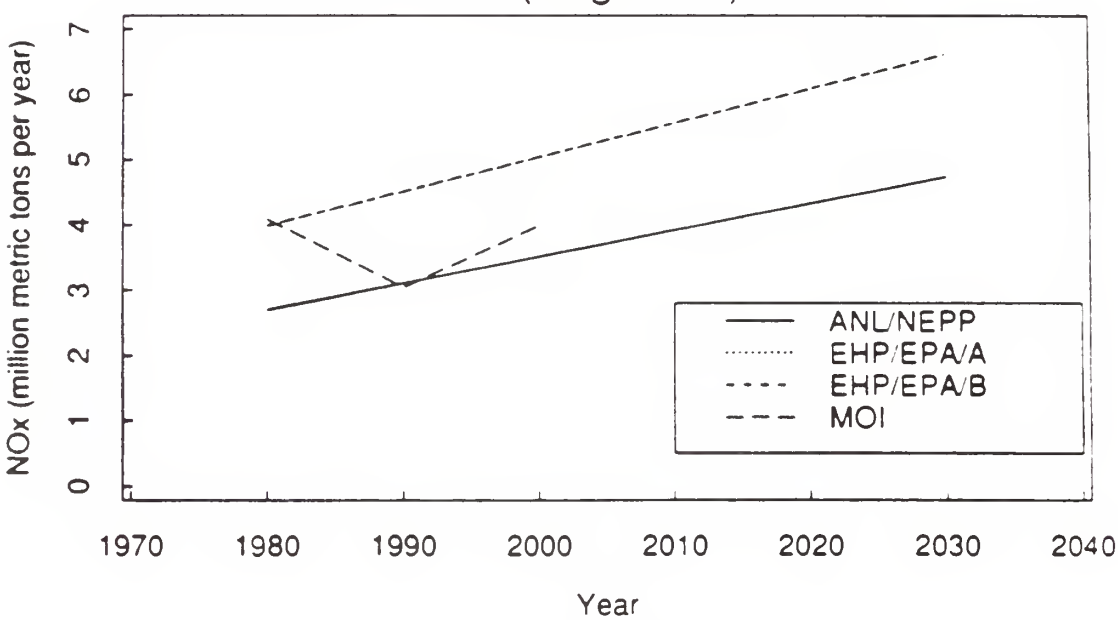
Source: Derived from data in Knudson (1985), Knudson (1986), and Kohout et al. (1987)

Figure 11

Projected SO2 Emissions (Region VI)



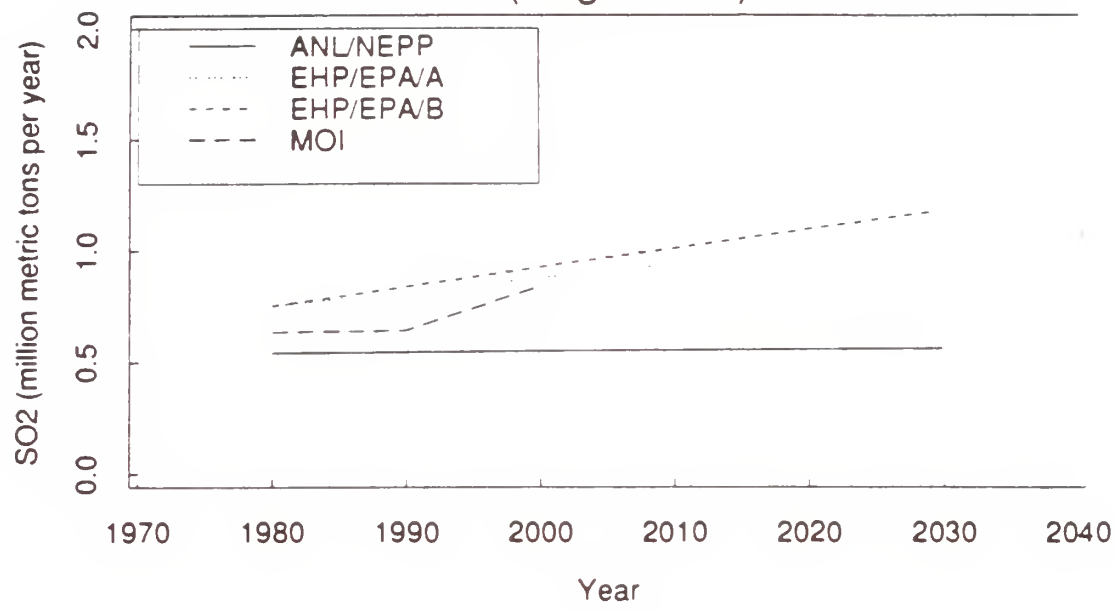
Projected NOx Emissions (Region VI)



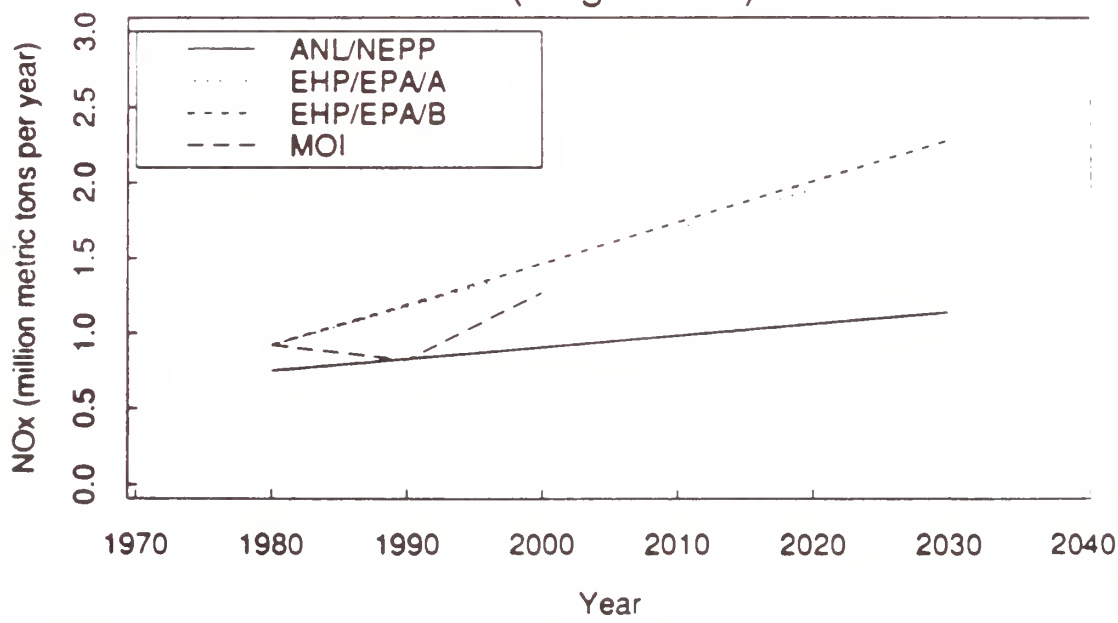
Source: Derived from data in NAPAP Interim Assessment (1987)

Figure 12

Projected SO2 Emissions (Region VIII)

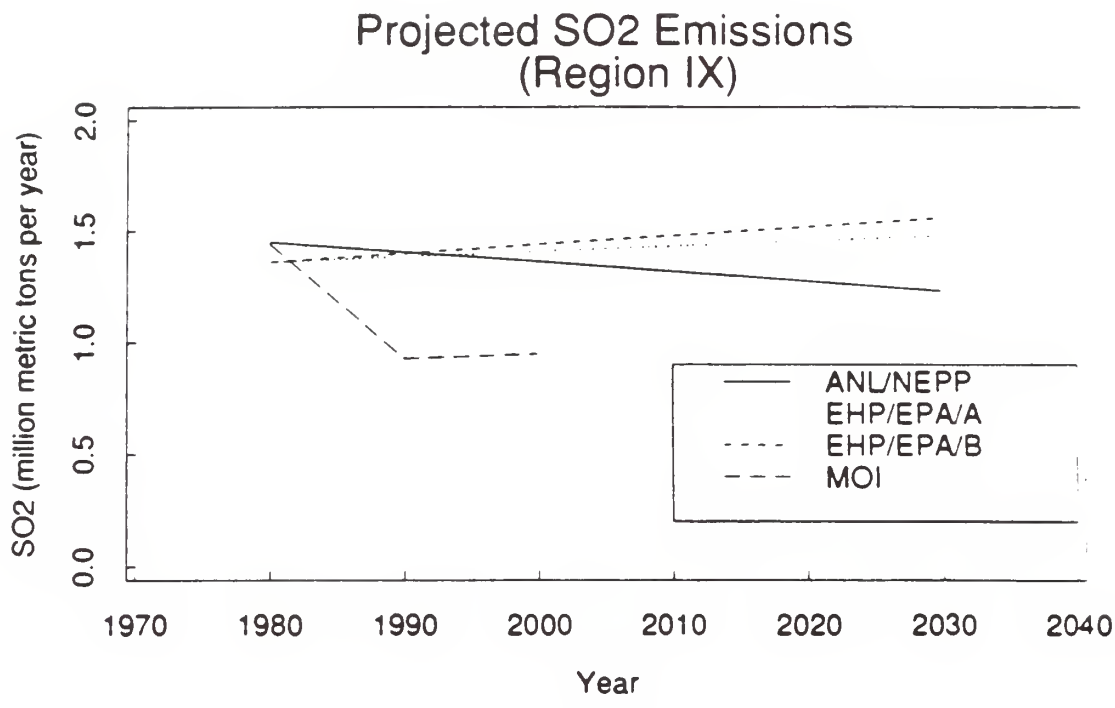


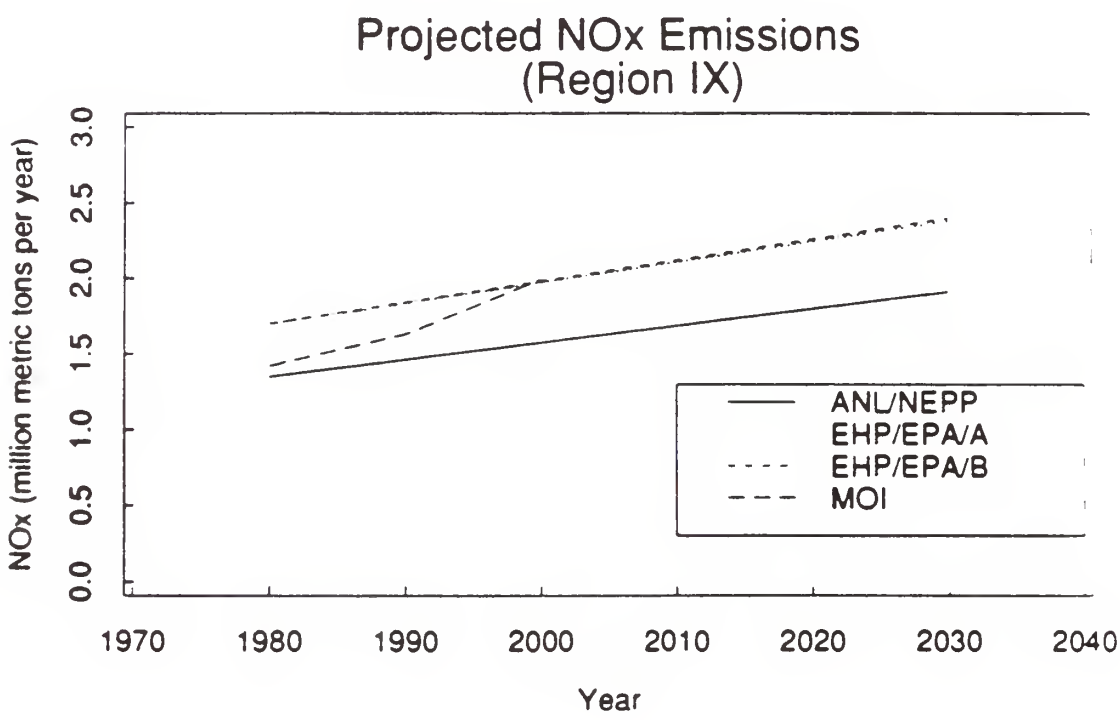
Projected NOx Emissions (Region VIII)



Source: Derived from data in NAPAP Interim Assessment (1987)

Figure 13





Source: Derived from data in NAPAP Interim Assessment (1987)

Factors Influencing Precipitation Chemistry in the Arid West

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Acid rain in the desert seems an unlikely non sequitur, and for that reason the possibility has been almost overlooked as the ten-year national program into the effects of acidic deposition has come and gone. Fortunately, the National Atmospheric Deposition Program (NADP) monitoring network obtained truly national coverage, and the nature of precipitation chemistry from 13 desert collecting sites (Figure 1) is examined. Many of these monitoring stations are located in national park areas, and some of them, such as Organ Pipe Cactus National Monument and Big Bend National Park, have data from 1980.

By standard definitions, acidic atmospheric deposition rarely occurs in the southwestern desert of the United States. Only two sites (Oliver Knoll AZ, pH of 4.68; and Mesa Verde CO, pH of 4.82) maintain an annual volume-weighted mean pH below the natural range of 4.8-6.0 suggested by Charlson and Rodhe (1982). A statistical approach employed by Verry and Harris (1988) suggests that precipitation of less than pH 4.9 is affected by excess sulfate (SO_4^{2-}) or nitrate (NO_3) over background levels. Again, desert sites, with the two exceptions noted before, do not qualify as receiving acidic deposition. Another approach, initially developed by Henriksen (1979), defines a threshold deposition of 30-40 kg SO_4^{2-} per hectare per year, above which adverse effects to sensitive aquatic ecosystems occur. Sensitivity of ecosystems is primarily determined by bedrock type, and slow weathering materials can have their capability to buffer acidity exhausted. The maximum SO_4^{2-} deposition (the product of concentration and precipitation) recorded at an NADP desert site (Oliver Knoll AZ) is still only 13.8 kg per hectare per year. However, an examination of the composition of precipitation in desert locations reveals that there is indeed a sizeable influence from industrial and urban emissions, and these are masked by natural desert processes. These processes do not necessarily obviate atmospheric deposition as an environmental problem.

Summary data shown in Table 1 can be used to interpret wet deposition in parts of Nevada, Utah, Arizona, New Mexico, Texas, and Colorado. The NADP monitoring network was established to provide a regional representation of wet deposition, so an attempt was made to place sites away from the direct influence of nearby point sources. This can be both good and bad for interpretation with respect to specific national park areas. Data can be extrapolated over a broader geographical distance if the collection sites are truly exempt from local pollutant

sources, and that is good, because it means every park need not conduct its own monitoring to know its precipitation composition. On the other hand, some park areas have specific pollutant problems due to their location, such as Saguaro National Monument, located within the Tucson city limits. Because the regional data are not suitable for interpreting the problem, Saguaro lacks needed precipitation composition information. Joshua Tree National Monument is located downwind from the Los Angeles metropolitan area. This is another park area where precipitation data are lacking, and yet might be important to interpreting ecological degradation.

Wind blows generally from the west over the western United States, although air masses travelling from south to north in a clockwise direction can spread throughout the intermountain region. Precipitation is seasonal. Summer monsoons bring rain from both the Gulf of California and the Gulf of Mexico. Polluted air masses can therefore originate in the southern California region, from the industrialized Gulf coasts of Mexico and Texas, and from the smelter regions of southern Arizona and northern Mexico. Local sources of sulfur and nitrogen oxides can also be important precursors to SO_4^{2-} and NO_3^- in precipitation, and include metropolitan areas, power plants, and smelters.

Some of the extent to which SO_4^{2-} and NO_3^- are elevated above natural background levels can be seen (Table 1) by comparing concentrations of the desert locations with a site that receives acidic deposition (Milford, PA), with western locations receiving fairly clean precipitation (two sites in Rocky Mountain National Park), and two truly remote sites, one in Australia and one in Alaska which receive little, if any, industrial emissions. Comparisons will be made among these sites throughout the rest of this paper.

The major natural sources of sulfur compounds in the atmosphere listed in the NAPAP Interim Assessment document (1987) are terrestrial biogenic (from marshes, crops, soils, and natural vegetation), marine (in the form of dimethyl sulfide), and volcanic. Natural salts, such as gypsum (Ca_2SO_4), are not discussed, and it is unknown how important they are in the overall sulfate component in precipitation of desert areas. Gypsum is chemically neutral, and will not contribute to acidity in precipitation. The proportion of natural sulfate salts will certainly vary geographically, and one could suggest that gypsum accounts for up to one third of the observed SO_4^{2-} concentration at Oliver Knoll, for example. At Oliver Knoll, then, at least two thirds of the sulfate probably came from an industrial source, since marine, biogenic, or volcanic sources are minimal at this site. Situated downwind of the Douglas copper smelter (which closed in January 1987), it is not surprising that precipitation was acidic between 1981 and 1986, and an investigation by Blanchard and Stromberg (1987) correlated high sulfur events at this site with winds blowing up from Douglas. Chiricahua and Coronado National Monuments are two park areas that have comparable precipitation compositions. Sulfate concentrations at Oliver Knoll are still not as great as at Milford PA, where annual pH is 4.26.

Sulfate concentrations in wet deposition at the other desert sites range from 14.3 ueq/l to 26.6 ueq/l, and their sources are not as obvious as that suggested for Oliver Knoll. All the sites appear to have concentrations greater than background values, and none of them, except Mesa Verde National Park, receive acidic wet deposition. Mesa Verde lies in the Four Corners area, where there are two large coal-fired power plants. While these appear to be the obvious sources of acid precursors, precipitation composition did not change when controls were placed on one of the plants in 1985.

A regional redistribution of sulfur oxide emissions from Arizona, Mexico, and New Mexico copper smelters throughout the intermountain region has been strongly supported by

Oppenheimer et al. (1985) and by Epstein and Oppenheimer (1986). Trajectory analyses by Bresch et al. (1987) have also implicated southern California as an important source of sulfur gases and aerosols.

Natural sources of nitrogen oxides are primarily lightening and biogenic processes in soils. Neither are very important contributors to desert wet deposition. The NO_3^- in precipitation comes mainly from automobile exhaust and combustion processes in power plants. Monitoring sites that are located close to urban areas or power plants should therefore show higher concentrations of NO_3^- in precipitation, and, in one instance, they do. Red Rock Canyon NV is located near Las Vegas, and exhibits high NO_3^- concentrations comparable to those from Milford PA. The next highest value, 17.5 ueq/l, is found at Green River, UT, and all the other desert sites have very similar values for NO_3- ranging between 10.3 and 14.2 ueq/l.

The influence of the strong acid anions, SO_4^{2-} and NO_3^-, on precipitation acidity is determined to a large extent by levels of base cations, such as Ca^{2+}, in precipitation. These cations, of which Ca^{2+} is the most abundant, represent the natural carbonate buffering or neutral salts provided to the atmosphere by soil materials. Where contributions of these cations are naturally low, as illustrated for the eastern U.S. at Milford, strong acid anions will have a greater acidifying effect on precipitation. In the arid West these cations are abundant, and serve to neutralize much of the acidity. If all the 36.1 ueq SO_4^{2-} per liter in precipitation originated from man-made sources at Oliver Knoll, for example, and was not neutralized by 11.2 ueq $CaCO_3$ per liter, pH would be even more acidic, averaging 4.44, rather than 4.68. Where calcium is abundant in precipitation, as at Green River, UT, pH values are high, reflecting the presence of carbonates in precipitation. All of the Southwestern sites had greater Ca^{2+} values than the eastern comparison site.

If concentrations of sulfate and nitrate are typically low when compared to a site which receives acidic deposition, and if levels of cations are typically high serving to buffer precipitation and prevent its acidification, is there still reason for concern over a potential acidic deposition problem? The answer is believed to be yes, and this requires an examination of sensitive resources in the region, and better understanding of all depositional processes which could bring pollutants in contact with sensitive receptors.

Precipitation amount in the Southwest is naturally low, and this has an influence on both precipitation concentrations and total deposition. Total emissions of strong acid anions in this region are roughly twice the amount recovered in precipitation (Blanchard, this volume), partly because rain or snow are too infrequent to capture and remove these pollutants from the atmosphere. This leads to the conclusion that acid rain by itself will not be an important source of environmental or cultural damage in park areas of the Southwest. But the effects of a combination of both wet and dry atmospheric deposition must be further explored.

If half of the anthropogenic emissions affecting this region are unaccounted for in precipitation they are either transported out of the Southwest, or are deposited in gaseous, particulate, or aerosol form. Films of dry-deposited material can accumulate on plant leaf surfaces or artifacts. Ensuing precipitation events might wet the depositional surface and create a concentrated solution which washes the surface, possibly with damaging effects. Many Southwestern sites are located in deserts, where vegetation growth is directly keyed to precipitation events. Few, if any, desert plants have been studied as to the sensitivity of their flowering parts, seeds, or vegetative tissues to acidity. The possible effects of a coincidence of acidic wet deposition or wet deposition combined with accumulated dry materials on desert plant tissues must be further explored before acidic deposition is ruled out as a problem.

Other possible sensitive natural receptors include organisms in desert potholes. Little information is available regarding the chemical characteristics of these potholes, but it is known they undergo dramatic changes in concentration as evaporation reduces the volume of water in each pothole between rain or snow events. Organisms in those potholes located on granitic bedrock, such as occur in Joshua Tree National Monument, or sandstone, such as in Capital Reef National Park, may well be vulnerable to increases in SO_4^{2-} deposition.

Elevated concentrations of sulfur oxides, acidity, and, particularly, nitrogen oxides may also affect cultural resources such as petroglyphs, pictographs, and ruins.

To conclude, wet acidic deposition has been recorded for two sites in the Southwestern U.S., Mesa Verde National Park, CO, and Oliver Knoll, AZ. While precipitation is not acidified at other locations, levels of SO_4^{2-} and NO_3^-, the anions associated with acidic deposition, are elevated above background levels of truly remote areas such as Katherine, Australia. Some national park units, including Saguaro and Joshua Tree National Monuments, are located close enough to major sources of acid precursors that precipitation chemistry monitoring is warranted. The possible effects of the cumulative deposition of both wet and dry acidifying materials must be further explored. Possible sensitive resources, including desert plant species, aquatic organisms in desert potholes, and cultural artifacts might well exist. Surveys and studies of these resources are encouraged.

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Table 1. Precipitation characteristics from NADP desert sites and comparison sites. Concentrations are volume-weighted means reported in ueq/l of all acceptable weekly values since the start date of each site (NADP 1987). Values for Katherine, Australia and Poker Flat, Alaska are from NAPAP, 1987.

NADP

SOUTHWESTERN NADP SITES

STATION NAME	START DATE	ANNUAL PPT(cm)	CONCENTRATION (UEQ/L) CA	SO_4	NO_3	H	pH
Oliver Knoll, AZ	8/81	38.3	11.2	36.1	12.3	20.9	4.68
Grand Canyon, AZ	8/81	45.2	15.4	17.2	11.5	6.3	5.20
Organ Pipe Cactus, AZ	4/80	28.3	12.7	22.5	12.0	8.7	5.06
Mayhill, NM	1/84	67.5	14.6	21.0	10.0	7.4	5.13
Cuba, NM	2/82	36.5	13.9	22.8	14.1	11.9	4.92
Capulin Mountain, NM	11/84	35.8	12.8	16.7	12.5	6.9	5.16
Big Bend, TX	4/80	37.6	30.3	22.8	10.6	3.0	5.52
Guadalupe Mountains, TX	6/84	69.3	13.7	23.3	10.3	8.3	5.08
Red Rock Canyon, NV	1/85	14.0	24.4	16.4	22.9	5.7	5.24
Lehman Caves, NV	1/85	29.6	22.8	14.3	13.4	2.5	5.60
Green River, UT	4/85	17.7	49.3	26.6	17.5	1.2	5.93
Bryce Canyon, UT	1/85	34.0	10.8	14.4	11.2	7.7	5.11
Mesa Verde, CO	4/81	56.1	17.5	24.9	13.3	15.0	4.82

COMPARISON SITES

STATION NAME	START DATE	ANNUAL PPT(cm)	CONCENTRATION (UEQ/L) Ca	SO_4	NO_3	H	pH
Milford, PA	12/83	116.0	4.4	50.8	28.0	54.9	4.26
RMNP-Beaver Meadows, CO	5/80	40.7	29.1	20.0	16.6	9.3	5.03
RMNP-Loch Vale, CO	8/83	109.1	8.7	14.6	11.2	7.6	5.12
Katherine, Australia	11/80	-	2.1	4.2	4.5	19.1	4.72
Poker Flat, Alaska	11/79	-	1.4	9.1	2.4	11.3	4.95

Figure 1. National Acid Deposition Program Desert Monitoring Sites

Gaseous Pollutants in the West

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Abstract. The principal gaseous pollutants of concern to the NPS desert parks are sulfur dioxide, nitrogen oxides, volatile organic compounds (VOC), and ozone. The primary source of sulfur dioxide is fossil fuel combustion. Nitrogen oxides emissions are divided about evenly between industrial and transportation sources. VOC are predominantly attributable to transportation sources and, to a lesser extent, attributable to industrial sources. Industrial and transportation sources do not produce ozone in significant quantities directly. Rather, ozone is formed by photochemical reactions of other chemical species emitted into the atmosphere by these source types.

The Environmental Protection Agency (EPA) and State and local governments have the responsibility to protect human health and cultural and biological resources from the effects of air pollution. They meet this responsibility by developing and enforcing plans that limit the amount of pollution that sources are allowed to emit. They ensure the attainment and maintenance of ambient air quality standards for regulated pollutants.

The EPA, States, and the NPS have deployed extensive monitoring networks to measure the concentrations of many pollutants through out the United States. Data collected have shown that even NPS units located in remote areas are subject to high concentrations of pollutants.

Introduction

Elsewhere in these proceedings, authors have provided information on the amount and projected changes in the amount of pollutants emitted into the air. Also presented by the other authors is an overview of precipitation chemistry and the results of several years of monitoring for precipitation events, amounts, and acidic levels. In what follows we turn to a consideration of what researchers know about the emission, transport, source, regulatory mechanism of control, chemical transformation, deposition, and ambient concentration of several pollutants of concern, with a special focus on gaseous pollutants. Gaseous pollutants, as emitted, may directly affect natural resources. Compounds formed (either gases or particulates) by reactions with other gases in the atmosphere may also produce undesirable effects on terrestrial and aquatic ecosystems.

Therefore, the discussion that follows will include some references to pollutants which occur in the particulate form.

Emission and Formation of Principal Pollutants of Concern

Sulfur Dioxide

Sulfur dioxide emissions result primarily from fossil fuel combustion (approximately 84 percent of all manmade sulfur dioxide emissions result from this source category). Of these emissions, nearly 72 percent are emitted from coal-fired utility boilers. Hence, the emphasis on this source type when agencies consider strategies for the reduction of sulfur dioxide emitted into the air. The remaining sulfur dioxide emissions come from industrial processes and transportation sources. Sulfur dioxide can transform in the atmosphere to sulfuric acid and sulfate particulates. The sulfate particulates can then contribute to acidic deposition to terrestrial and aquatic ecosystems through dry and wet deposition processes. The NPS has also shown sulfate particulates to be a major cause of visibility impairment in the West.

Nitrogen Oxides

Nitrogen oxide emissions are evenly split between transportation sources (about 45 percent) and fuel combustion and other industrial processes (55 percent). Nitrogen oxides play an important role in the formation of the phytotoxic gas, ozone. Nitrogen oxides can also transform in the atmosphere to nitric acid and nitrate particulate. The nitrate particulate can also degrade visibility and contribute to acidic deposition.

Volatile Organic Compounds

Volatile organic compounds (VOC) are emitted by a variety of source categories. However, the chief categories are transportation sources and industrial processes. These sources include automobiles, refineries, surface coating plants, furniture manufacturers, and any facility using solvents. VOCs may react with sunlight and other gases in the atmosphere to form ozone or organic particulates which affect visibility.

Ozone

There are few manmade sources that emit ozone directly. Most ozone, that results from man's activities, is formed by photochemical reactions involving nitrogen oxides and VOC. The Environmental Protection Agency (EPA) has shown ozone to be toxic to humans and vegetation. The EPA set an ambient standard of 0.12 ppm (1-hour average) to protect human health. Studies have also shown that some vegetation can be harmed by ozone concentrations as low as 0.06 ppm. The processes by which ozone is formed and accumulated in the atmosphere near the Earth's surface are shown in Figures 1 and 2, respectively.

Other Gaseous Pollutants

Other gaseous pollutants of concern that may be emitted in large quantities include fluorides, other photochemical oxidants (for example, peroxyacetyl nitrate), chlorine, hydrogen peroxide, and carbon monoxide.

Regulatory Mechanisms for Control

The EPA and State and local agencies have implemented measures to curb unlimited increases in pollutant emissions and to abate air pollutant problems where they exist. These measures have included the setting of emission and ambient standards. The former places a limit on the rate at which pollution can be emitted into the atmosphere. Regulatory authorities frequently express emission limits in tons per year, pounds per hour, or grams per second of pollutant emitted. The latter limits the concentration of pollutants (see Table 1) that can occur in the ambient air. Ambient limits (ambient standards) are usually specified in parts per million or micrograms per cubic meter. These limits are based on the levels needed to protect human health and welfare.

The Clean Air Act (CAA) contains different provisions for dealing with those areas of the country that are meeting the ambient standards and those that are not meeting them. In those areas meeting these standards, State Implementation Plans (SIPs) are in place to insure attainment and maintenance of the standards. In addition, the CAA as amended in 1977 established the Prevention of Significant Deterioration provisions which limit the incremental amount (concentration) to which an attainment area could be allowed to degrade (with the ambient standard being the net ceiling). In those same amendments Congress identified and provided for special protection of class I areas, which included national parks over 6,000 acres and wilderness areas over 5,000 acres.

For those areas not meeting the ambient standards (nonattainment areas) the provisions are significantly different. In these areas the State determines the control strategy (subject to approval by the EPA) it will use to attain the standards. This control strategy will target specific sources or mix of sources (for example, industrial versus transportation sources) for emission reductions. The strategy may include the retrofitting of existing sources with control devices, a change in operating practices, using substitute fuels, inspection and maintenance of automobiles, and the recovery/recycling of materials. If a State wishes to permit a new source to locate in such an area, or to let an existing one increase its emissions, the CAA requires the State to prepare a SIP revision. Until the EPA approves that SIP revision, emission offsets (emission reductions greater than the proposed increase) in the nonattainment area are required by law. It is possible that the approved SIP for a nonattainment area can accommodate growth. It is also possible that the approved SIP will require emission offsets to assure attainment and maintenance of the ambient standards.

Pollutant Monitoring

Existing Networks

The most extensive ambient monitoring network is probably the State/EPA network. This network includes equipment for continuous monitoring for ozone, sulfur dioxide, carbon monoxide, nitrogen dioxide, 24-hour sampling for particulate matter and fine particulate matter (less than 10 micrometers in diameter), and calendar quarterly averages for lead. While this network is extensive, it is primarily urban in focus and frequently not of direct benefit to NPS lands located in rural or remote settings.

National Park Service/Air Quality Division

The NPS Air Quality Division maintains a network of monitoring sites servicewide. Unlike the State/EPA network this network focuses on remote sites. The network includes continuous and integrated samples for sulfur dioxide, continuous sampling for ozone and meteorology, twice a week 24-hour average fine particle monitoring (including chemical speciation), and visibility monitoring. The specific parks where the NPS conducts monitoring and the configurations of each site are shown in Figures 3 and 4. These monitors are in place to determine the current state of air quality in the parks, to establish trends, and to support studies on the effects of air pollution on natural resources. Note that several of these sites are located in desert parks.

National Atmospheric Deposition Program (NADP)

As other authors have discussed elsewhere in these proceedings, several government entities (including the NPS) have participated in a nationwide precipitation chemistry monitoring network. This network includes several sites in desert parks.

EPA Dry Deposition Network

EPA has recently installed a nationwide dry deposition network (NDDN). The specific sites are shown in Figure 5. Each site includes a continuous ozone monitor, meteorology monitoring equipment, and a fine particle sampler. As you can see, this program has an eastern bias, with only nine sites located in the West.

Results from Gaseous Pollutant Monitoring in Western Parks

Ambient Concentrations

The results from monitoring conducted in NPS units through 1987 are characterized by low sulfur dioxide at most sites, but relatively high ozone concentrations at many sites. Sulfur dioxide concentrations are frequently below the minimum detectable limit of the monitors. The highest 24-hour concentration recorded in western parks was approximately 0.02 ppm (approximately 52 micrograms per cubic meter) at Saguaro NM. Weekly averages in 1986-1987 at Arches NP, Petrified Forest NP, and Guadalupe Mountains NM were 1.8, 3.8, and 4.2 micrograms per cubic meter, respectively. Ozone concentrations, however, are frequently above or at the level of the national ambient standards in many parks, including those in remote locations. For example,

hourly ozone concentrations have exceeded 0.15 ppm in Sequoia NP, 0.09 ppm at Saguaro NM, and 0.10 ppm Petrified Forest NP.

Spatial Patterns

The location of large stationary sources that emit sulfur dioxide determines the geographic distribution of ambient sulfur dioxide concentrations. The highest concentrations will occur near these sources, for example, near the large nonferrous smelters in the southwest. Long-range transport of sulfur dioxide usually does not occur because, as we have already seen, the sulfur dioxide readily transforms to particulate sulfate. Ozone concentrations are similarly high immediately downwind of major urban areas. However, because of the photochemical reactions of the precursors of ozone (that is, nitrogen oxides and hydrocarbons), which can be transported for long distances, high ozone concentrations have been found in remote locations throughout the country. As can be seen in Figure 6, the highest hourly ozone concentrations observed in 1987 occurred in the eastern part of the United States, southern California, and Arizona.

Temporal Patterns

Concentrations of sulfur dioxide measured in NPS units typically exhibit erratic diurnal and seasonal patterns. Concentrations are strongly affected by changes in emissions of local sources and local meteorology. Conversely, analyses of ozone data collected in NPS units has revealed regular geographic, diurnal, and seasonal patterns. Ozone typically displays a diurnal profile with highest concentrations occurring in the late afternoon and the lowest in the early morning. Annual maximum ozone concentrations usually occur in late spring, summer, or early fall (the "ozone season"). The minimum concentrations usually occur in the winter. The strongest diurnal patterns occur during the "ozone season." Parks with relatively low hourly concentrations year round, such as Denali, Voyageurs, and Grand Canyon NPs, usually have a much less dramatic diurnal profile than parks with higher hourly ozone concentrations such as Acadia, Shenandoah, and Guadalupe Mountains NPs, Saguaro and Joshua Tree NMs, and Santa Monica Mountains NRA. There is also some evidence that higher elevation sites may exhibit suppressed diurnal curves, but higher total ozone doses due to higher nighttime concentrations. Natural processes, such stratospheric intrusions and thunderstorms, may also lead to elevated ozone at the surface. However, these phenomena are highly localized and, further, the intrusions do not usually occur during the "ozone season," when the maximum concentration of anthropogenically-generated ozone usually occurs.

Summary

Desert parks are not immune from the effects of gaseous pollutants just because these parks are frequently located long distances from the sources of pollution. Ambient pollutant monitoring and data analyses conducted by the NPS has documented the long-range transport of pollutants into these remote parks.

TABLE 1. NATIONAL AMBIENT AIR QUALITY STANDARDS (MICROGRAMS PER CUBIC METER (PPM))

POLLUTANT	AVERAGING TIME	PRIMARY	SECONDARY	PSD INCREMENTS			SIGNIF. ***
				CLASS I	CLASS II	CLASS III	
SULFUR DIOXIDE	ANN. ARTH. 24-HOUR * 3-HOUR *	80 (0.03) 365 (0.14) NONE	NONE NONE 1300 (0.5)	2 5 25	20 91 512	40 182 700	1 5 25
TOTAL SUSPENDED PARTICULATE MATTER	ANN. GEO. 24-HOUR *	NONE NONE	NONE NONE	5 10	19 37	37 75	1 5
PM-10	ANN. ARTH. 24-HOUR *	50 150	SAME SAME	4 **** 8 ****	17 **** 30 ****	34 **** 60 ****	- -
CARBON MONOXIDE	8-HOUR * 1-HOUR *	10000 (9) 40000 (35)	SAME SAME	NONE NONE	NONE NONE	NONE NONE	500 2000
OZONE	1-HOUR **	235 (0.12)	SAME	NONE	NONE	NONE	NONE
NITROGEN DIOXIDE	ANN. ARTH.	100 (0.05)	SAME	2.5	25	50	1
LEAD	CALENDAR QUARTER	1.5	SAME	NONE	NONE	NONE	NONE

* MAXIMUM CONCENTRATION NOT TO BE EXCEEDED MORE THAN ONCE PER YEAR.

** THE STANDARD IS ATTAINED WHEN THE EXPECTED NUMBER OF DAYS PER CALENDAR YEAR WITH THE MAXIMUM HOURLY AVERAGE CONCENTRATIONS ABOVE THE STANDARD IS EQUAL TO OR LESS THAN ONE.

*** SIGNIFICANT LEVELS SHOULD NOT BE USED FOR IMPACTS ON CLASS I AREAS.

**** PM-10 PROPOSED.

FIGURE 1. OZONE FORMATION

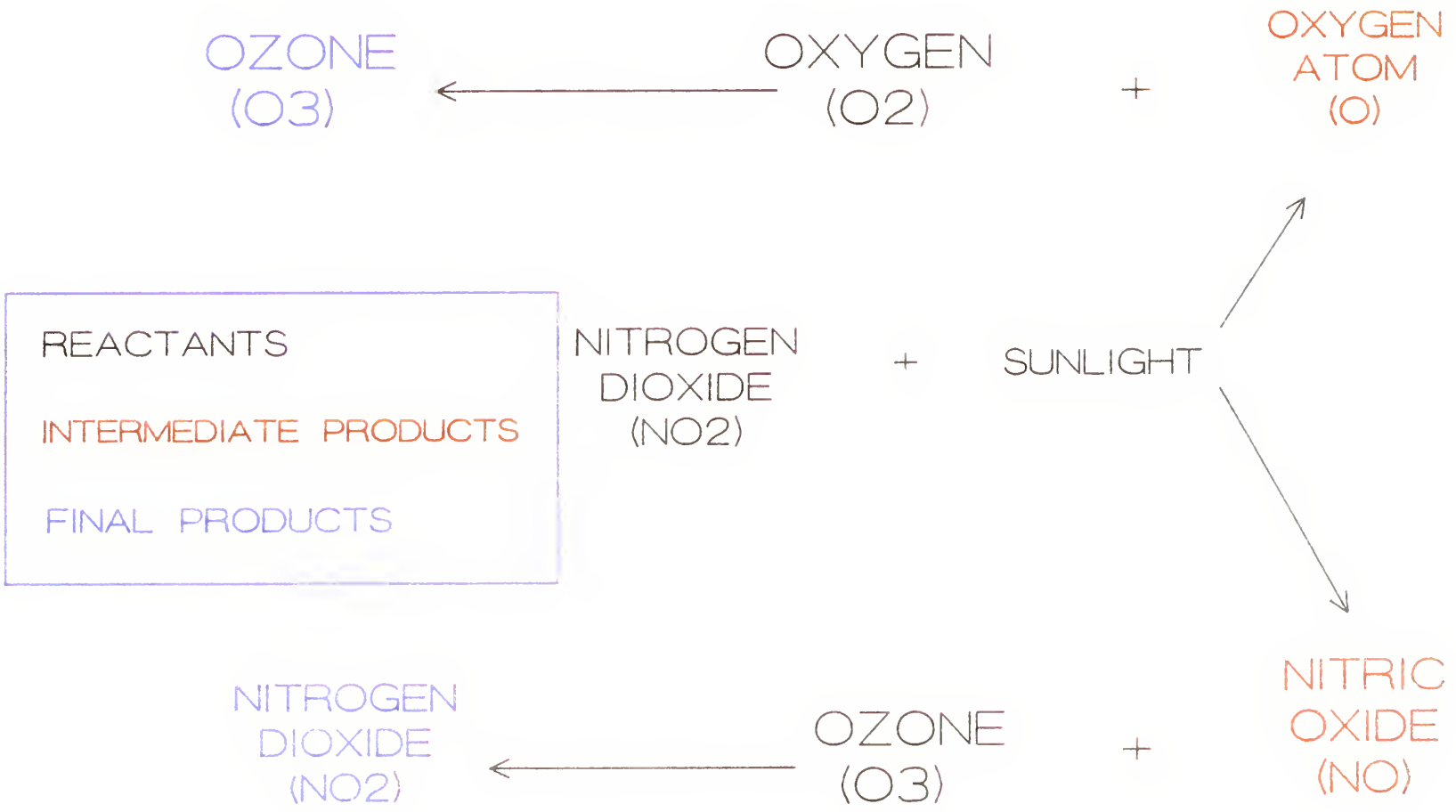


FIGURE 2. OZONE ACCUMULATION

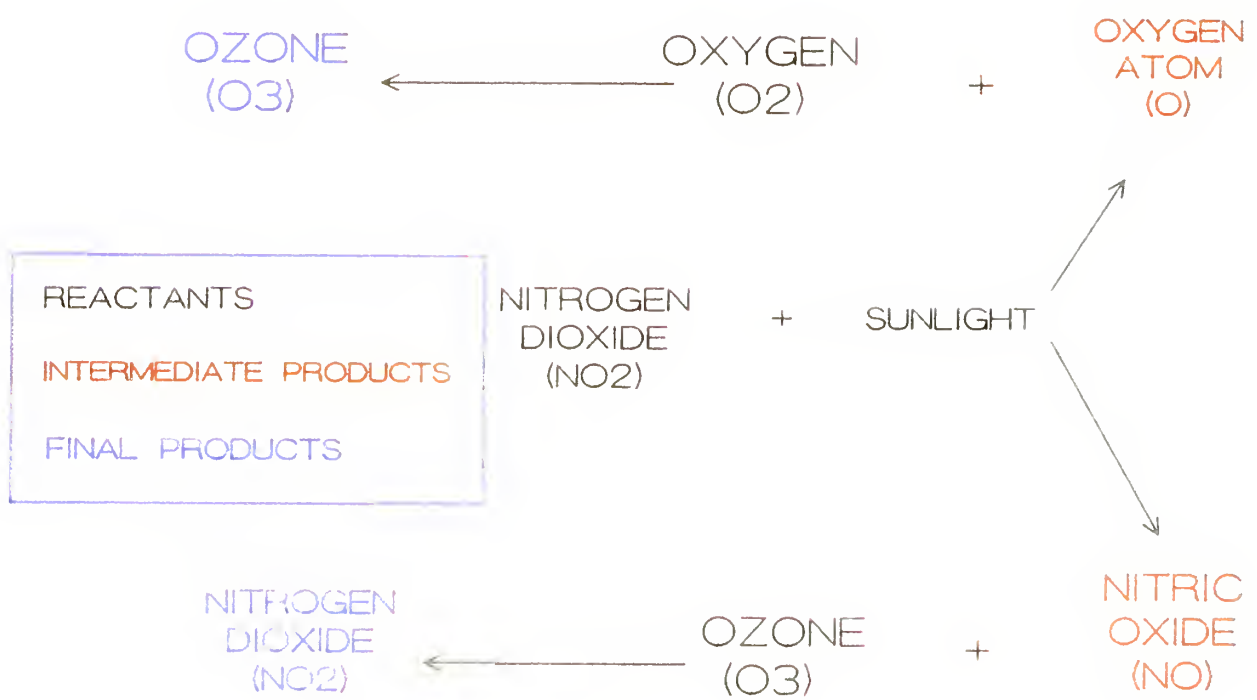


Figure 3. National Park Service Gaseous Pollutant Monitoring Network

Figure 4. IMPROVE and NPS Visibility Monitoring Sites

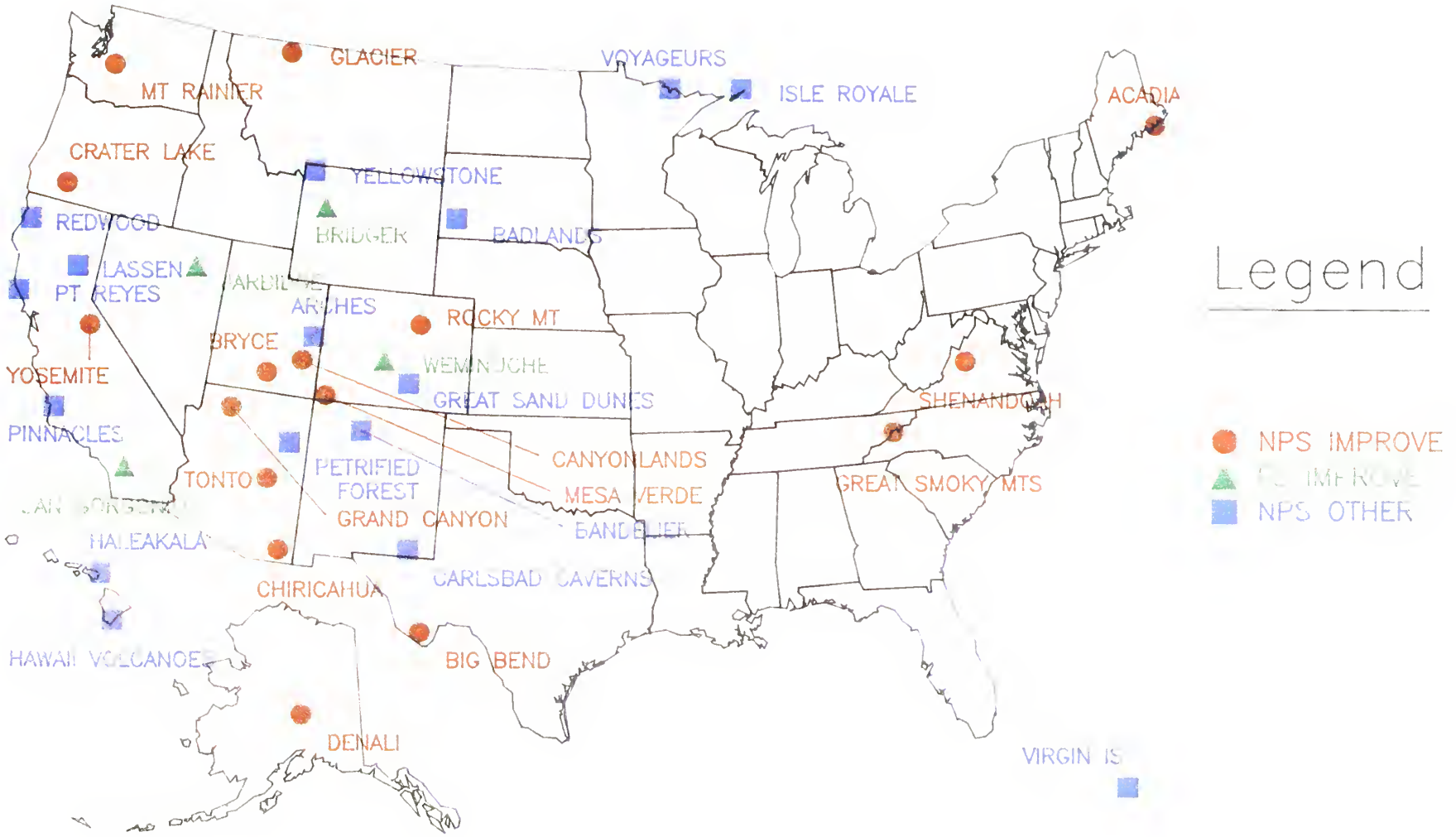


Figure 5. National Dry Deposition Network Monitoring Sites

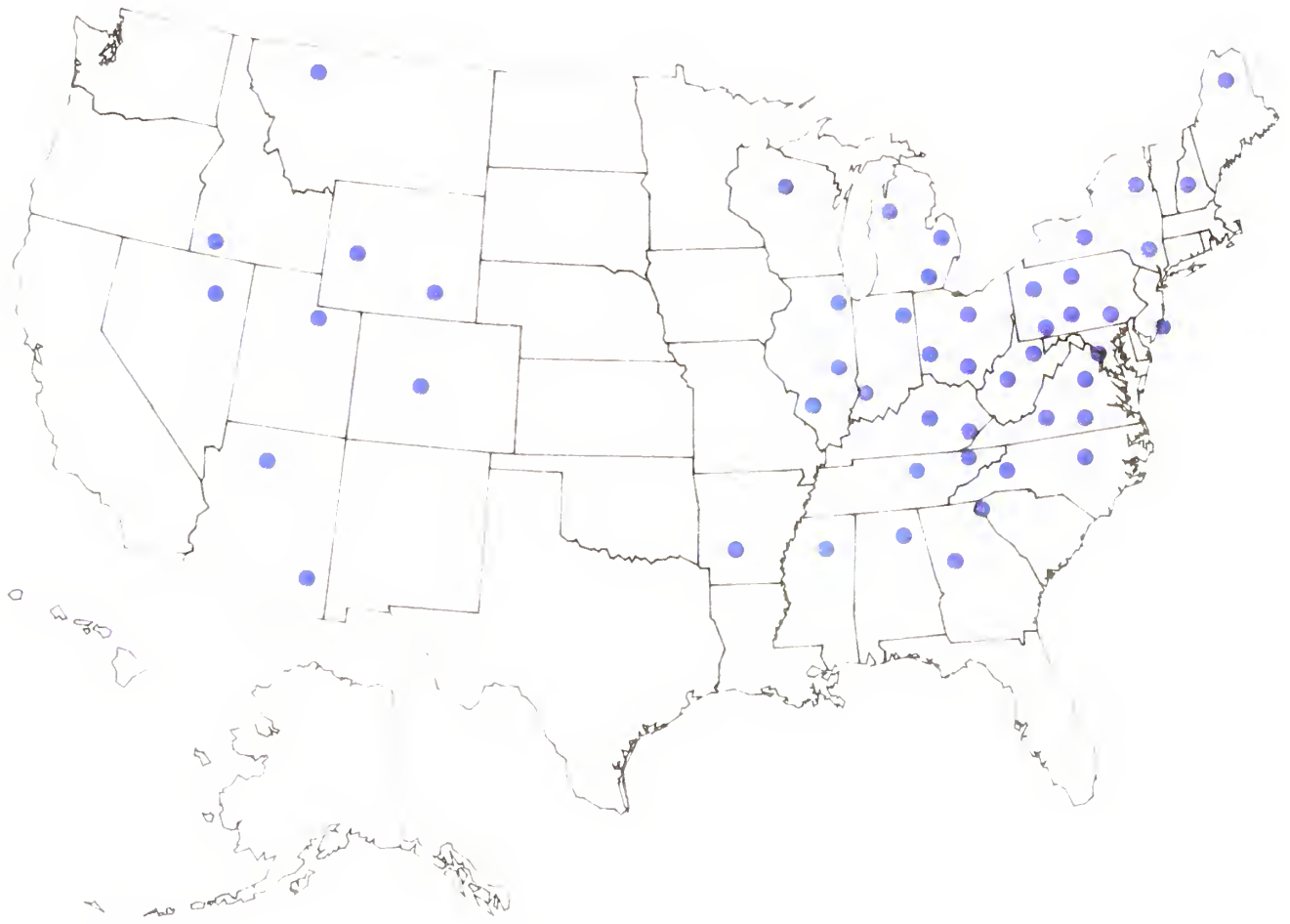
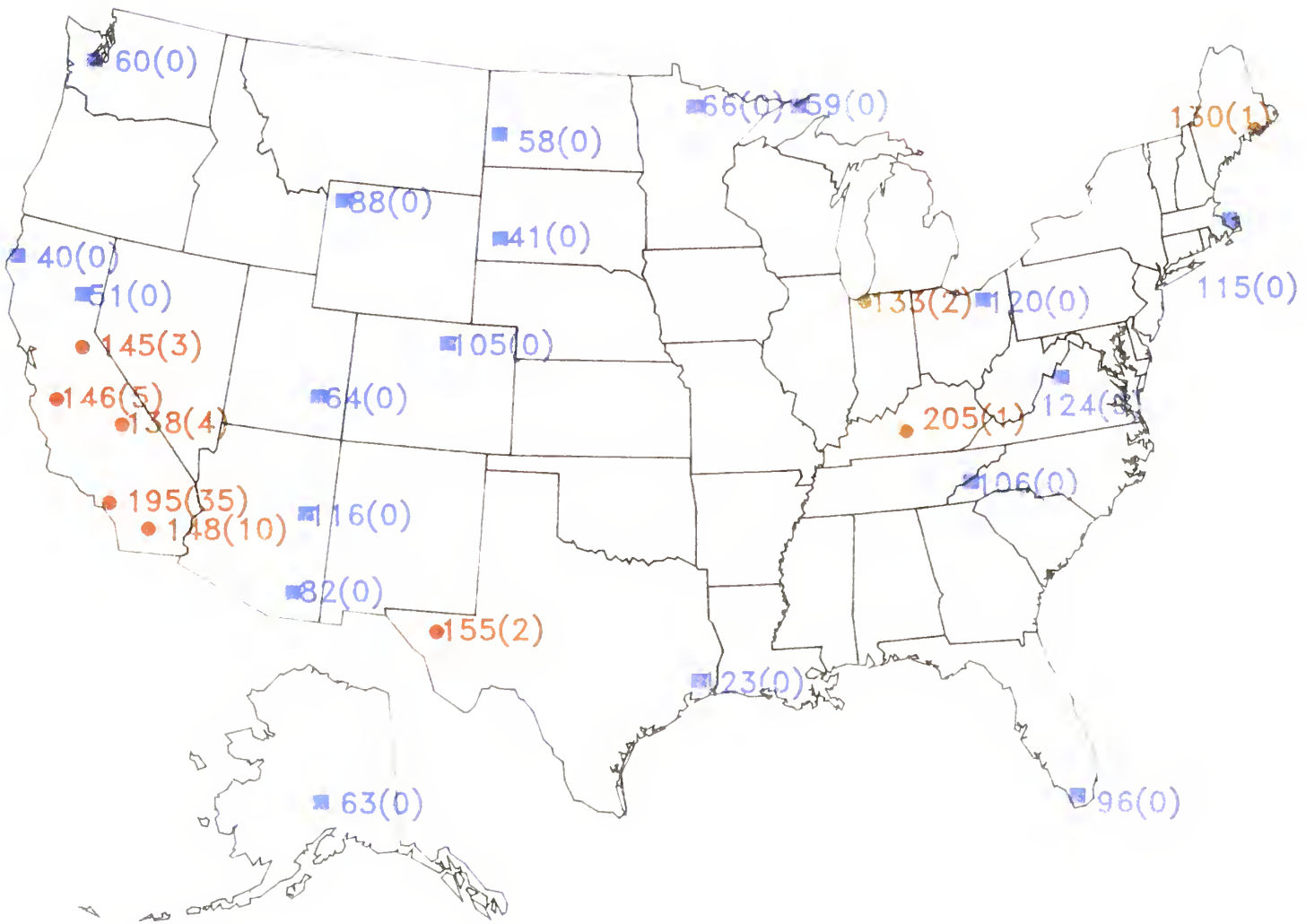


Figure 6. National Park Service Highest Ozone Concentrations 1987 - ppb
(No. of Days with Hourly Concentrations over 125)



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Sensitivity of Plant Ecosystems in Desert Areas to Gaseous Pollutants

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Abstract. Controlled fumigation exposures and field studies have shown that some desert species are susceptible to relatively low levels of ozone and sulfur oxide pollutants. Desert plant species are susceptible to gaseous pollutants only when elevated concentrations occur concurrently with periods of adequate soil moisture and high physiological activity. Susceptibility of desert species to gaseous pollutants is thought to be related to rates of stomatal conductance and external and internal foliar leaf morphology.

Desert annual wildflower species have been injured when exposed to relatively low concentrations of ozone and sulfur dioxide in fumigation experiments. Coniferous species in higher elevation montane ecosystems have been observed with visible foliar injury at ambient levels of ozone that have occurred in some southwestern National Parks. Desert shrubs that prefer mesic habitats in desert ecosystems show visible foliar injury in controlled exposure and in field studies in NPS units. Riparian tree species are sensitive to low levels of air pollutants, but no pollutant injury in NPS units has been recorded. Lichen species appear to be responsive to gaseous air pollutants when physiologically active, but because their period of susceptibility is greatly reduced in desert ecosystems due to low rainfall and humidity, they may be less responsive than similar species in more mesic environments.

Cacti species have not been extensively studied for their sensitivity to gaseous air pollutants, but some studies have indicated that cacti species are relatively tolerant of sulfur dioxide. Since most cacti species have crassulacean acid metabolism (CAM) and are physiologically not very active, toxic metals, organic pesticides, and herbicides, and other toxins that enter through roots are a greater threat to cacti than are gaseous pollutants.

Nitrogen oxides do not function as foliar phytotoxins, but may threaten the stability of desert ecosystems through effects on nitrogen cycling in nitrogen-poor communities. Field studies have shown that modest amounts of nitrogen fertilization (10 kg per hectare) can alter the composition of mesic plant

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communities and decrease species diversity. Nitrogen fertilization has sometimes been linked with phenological alterations (winter hardening) in conifers. There is concern about the potential for frost-sensitive cacti species to be more sensitive to freeze injury because of delays in winter-hardening/dehardening processes due to anthropogenic atmospheric fertilization with nitrogen compounds.

Limited information is available on the susceptibility of desert species to pollutants like hydrogen fluoride and organic aerosols (herbicides and pesticides). Additionally, few desert grass, annual, herb, shrub, tree, or lichen species have been evaluated for sensitivity to gaseous pollutants.

Introduction

Gaseous air pollutants are a threat to desert plant species depending on the nature of the pollutant, the nature of the species exposed to the pollutant, and the environmental conditions at the time of pollutant exposure. Ozone, sulfur dioxide, hydrogen fluoride, and other gaseous pollutants affect vascular plants by entering stomata in the normal gas exchange processes of photosynthesis. Lichens and other cryptogams can be injured by gaseous pollutants by direct absorption of the pollutant into the plant. Physiological processes, such as photosynthesis, respiration, and water use efficiency, can subsequently be affected, depending on the internal pollutant dose received and the inherent susceptibility of the organism. Physiological impacts can result in reductions in growth (root, shoots, and thalli), reproduction, and survivorship.

Environmental factors, such as temperature, relative humidity, soil moisture, and radiation, affect gas exchange in leaves and will affect the severity of pollutant injury to vascular plants. This is especially true of soil moisture in desert ecosystems. Biological factors also affect the severity of pollution injury. Species that have thin, mesophyllous leaves with high rates of gas exchange are generally more sensitive to gaseous pollutant injury than are species with thick, coriacious leaves with low levels of foliar gas exchange. However, one cannot infer species pollutant sensitivity or tolerance based on these physical and physiological factors alone, since not all species with thin, mesophyllous leaves are pollutant sensitive (Davis and Wilhour, 1976; Jacobsen and Hill, 1970) and species with thick, coriacious leaves are not all pollutant tolerant.

The determination of a species sensitivity to air pollutants can be accomplished through surveys of species at homogeneous sites along strong air pollution gradients that exist around point sources. More precise, but more costly, determinations of pollutant sensitivity can be accomplished through controlled fumigation studies conducted in situ to determine the relative sensitivity of species, the nature and magnitude of the biological response to the air pollutant, and the effect of increasing levels of pollution on the sensitive species. Field studies can be conducted to determine the variability in pollutant response of sensitive species, followed by short and/or long-term biomonitoring of the sensitive species under field conditions.

Gaseous Pollutants of Concern

Copper, zinc, and lead smelters and power plants emit sulfur oxides, nitrogen oxides, volatile organic compounds (VOCs), and toxic metals which may affect NPS units throughout the southwest. Acute (short duration, high concentration) exposures may cause obvious injury to

biological resources, and chronic (long duration, low concentration) exposures may cause subtle but cumulative impacts after many years of deposition. Urban areas adjacent to desert parks are sources of nitrogen oxides, VOCs, and ozone.

Ozone is a strong oxidant (phytotoxicity threshold around 80 ppb hourly average) and injures mesophyll cells of plants by reacting with cell wall components and altering the permeability of the cell wall. Solutes leak out of the injured cells, the chloroplasts aggregate within the cell, and the cell collapses and dies. The injurious effects of ozone on plants result from the degradation of photosynthetic cells and the subsequent effects on root and shoot growth, reproduction, and resistance to pathogens and environmental stresses. Although biochemical residues of ozone injury may be found, there is no residue unique to ozone and consequently there is no elemental diagnostic test for ozone. Ozone injury tends to occur on the upper leaf surface between veins of broadleaf species. Typically there is a red, white, purple, or tan stipple covering parts of the leaf that are physiologically most active. On conifers, ozone injury typically appears as a chlorotic mottling of the surface of the needles. In desert ecosystems the groups of plants most likely to be affected by ozone are spring and summer annuals (with C3 metabolism), high-elevation herbs and shrubs, and high-elevation conifers. Ozone at relatively low concentrations is known to injure the desert annuals Camissonia claviformis, C. hirtella, and Cryptantha nevadenses (Thompson et al., 1984).

Sulfur dioxide (SO_2) is a moderate oxidant that can be metabolized by leaves and used as a nutrient if the levels of ambient SO_2 are low. Toxicity occurs when conversion of SO_2 to sulphite and bisulphite and then sulphate is occurring too slowly relative to uptake of SO_2. Sulphite, which is more toxic than sulphate, begins to accumulate in the plant tissues. Injury on broadleaved plants is often bifacial and occurs either interveinally or at the leaf margins (Barrett and Benedict, 1970).

Hydrogen fluoride (HF) is phytotoxic when it enters the plant and is translocated to the margin of leaves. There is evidence that HF can be translocated to other plant organs, including the stem tissue and pollen. Injury tends to be bifacial and occurs at the tips or margin of leaves. Fluoride bioaccumulates in plants and in the herbivores that feed on the plants.

Nitrogen dioxide (NO_2) is a weak oxidant but can directly injure vegetation. The major problems associated with NO_2 are the acidification of rainfall, nitrogen fertilization of ecosystems, and subsequent effects on plant distribution (Tilman, 1987; Robertson et al., 1988), and the potential for nitrogen fertilization to alter phenological cycles and delay winter dormancy (Freidland et al., 1984; Freer-Smith and Mansfield, 1987).

Environmental Factors Affecting Species Response to Air Pollution

Environmental factors, such as temperature, relative humidity, soil moisture, wind speed, nutrients, and radiation affect the response of species to gaseous pollutants (Heck et al., 1965; Heck, 1968; Jacobsen and Hill, 1970; Huttunen, 1984). In general, environmental factors that reduce gas exchange between the atmosphere and plant foliage reduce sensitivity to pollutants. Low relative humidity, low soil moisture, low wind speed, high radiation, and high temperature reduce the sensitivity of species to gaseous air pollutants.

Desert Biological Resources Susceptible to Gaseous Pollutants

Desert annuals are particularly susceptible to injury from pollutants because of their short reproductive cycle. Factors that affect growth or seed production could have ecological impacts since the species survival is dependent on seeds produced each year. Pollutants can affect annual plant growth in a number of ways. Phytotoxic pollutants, such as ozone and sulfur dioxide, can hinder photosynthesis, resulting in reduced growth and seed production. Acid rain can affect seed germination by accelerating the scarification of the seed coat and triggering seed germination before adequate levels of soil moisture are available. Seed germination can be suppressed by acid rain. The addition of nitrogen oxides, in either wet or dry form, can change growth patterns among species resulting in changes in species competition and annual survivorship.

Examples of Gaseous Pollutant Effects On Desert Ecosystems

Thompson et al. (1984) exposed 47 species of annual plants to 0, .05, .10, .20, .30, and .40 ppm O_3 and 0, .20, .50, .60, .80, 1.0, 1.5 ppm SO_2 for 8 hours/day for 4-5 days. Response variables were visible injury (47 species) and sulfur accumulation (11 species exposed to .20 ppm SO_2). Camissonia claviformis, C. hirtella, and Cryptantha nevadensis were the most sensitive species. Visible injury occurred at .10 ppm O_3 and at .20 ppm SO_2. Eight of eleven species evaluated for sulfur accumulation had elevated sulfur concentrations in the foliage after exposure to .20 ppm SO_2. Baileya pleniradiata and Perityle emoryi accumulated the most sulfur.

Sheridan (1979) exposed the poikilohydric, terricolous lichens Collemia tenax and Lecidea sp. to a 5.3 : 1.0 solutions of NaF (0-10 ppm) and $PbCl_2$ (pH 6.5) and solutions of $NaHSO_3$ (pH 7.0) for 24 hours. Nitrogenase activity was measured using the acetylene reduction technique. Both species were affected by the lowest treatment concentrations of .01 ppm flouride. Nitrogen fixation rates of Collemia were reduced to 25 percent of controls and Lecidea nitrogen fixation rates were reduced to 70 percent of controls at .01 ppm flouride. A 0.10 ppm $NaHSO_3$ solution reduced the nitrogen fixation rate of Collemia by 50 percent and at 1.0 ppm reduced the nitrogen fixation rate of Collemia by 80 percent.

Marsh and Nash (1979) evaluated the diversity and abundance of 159 lichen species (40 genera) within a 40-mile radius of the Four Corners Power Plant. The growth form distribution of these species was 58 percent crustose, 38 percent foliose, and 4 percent fruticose. They reported no decreases in the number of species along the gradient out from the power plant. The lack of impact was attributed to the high proportion of crustose species (generally pollutant-resistant) and the short period of time when the lichens would be hydrated and consequently sensitive to air pollutants. Dawson and Nash (1980) suspected sulfur dioxide as the cause of acidification of the upper 2 cm of soil near the Inspiration copper smelter near Globe, Arizona. Twenty years of operation had lowered the pH of the surface soils to about 4.0 compared to a pH of 6.0 in the surface soils 8 km away. This increase in acidity can cause toxic elements, such as copper, to become more mobile and available for plant uptake.

Wood and Nash (1976) suspected sulfur dioxide as the cause of acidification of the upper soil horizons and the decreased abundance of Cercidium sp. near the copper smelter at Superior, Arizona. It was not possible to distinguish whether the decreases in cover and abundance of annual, perennials, or grasses were from the effects of sulfur dioxide or heavy metals (Cu, Zn, Pb, and Cd) or a combination of both.

Keller and Beda (1984) exposed the pollen of Abies alba, Pinus sylvestris, P. nigra, and P. mugo to .025 ppm, .075 ppm, and .225 ppm SO_2 for 16 and 24 hours. Significant reductions in pollen germination (about 40 percent) were observed for Pinus nigra after exposure to .025 ppm SO_2 for 24 hours. Significant pollen germination reductions were observed for Abies alba (about 50 percent) after exposure to .075 ppm SO_2 for 24 hours and for Pinus sylvestris and Pinus nigra (greater than 75 percent) at .075 ppm SO_2 for both 16 hour and 24 hour exposures. Pollen germination in all species was almost zero percent after exposure at .225 ppm SO_2 for 16 or 24 hours.

DuBay and Murdy (1983a) found that in vivo germination of pollen of Lepidium virginicum was reduced 50 percent from exposure to .60 ppm SO_2 for 2, 4, or 8 hours at 90 percent relative humidity. In a similar study, DuBay and Murdy (1983b) exposed flowers of Geranium carolinianum to .60 ppm SO_2 at 90 percent relative humidity during anthesis. The exposure reduced the number of germinmated pollen grains and the number of seed set per flower. Similar exposures at 70 percent and 80 percent relative humidity had no effect on seed set.

Olszyk (1988) fumigated the crassulacean acid metabolism (CAM) species Opuntia basilaris, Ananas comosus, Bryophyllum blossfeldiana, B. pinnata, B. pinnata, and Agave deserti with acute SO_2 exposures (0.5 - 3.0 ppm for 2 hours) and chronic SO_2 field exposures (0.35 and 0.9 ppm for 79 hours over a 7-day period). Visible injury (white necrotic band across fully expanded pads) was observed on O. basilaris in the acute exposure. In the chronic field study SO_2 had no effect on CO_2 uptake, transpiration, or tissue acidity.

Tilman (1987) added nitrogen to a native oak savannah community and three old fields. Response variables evaluated were plant biomass, height, light penetration, and species richness over a 4-year period. The rate of nitrogen addition was 1.0, 2.0, 3.4, 5.4, 9.5, 17.0, and 27.2 grams per square meter per year. In all nitrogen treatments, plant biomass and height increased significantly, and light penetration and species richness decreased significantly. In high nitrogen treatments, more than 60 percent of the species were displaced at the end of the 4-year period. There was a transitional period when some species initially increased in the high nitrogen treatments, but were eventually displaced after four years. Plots receiving high rates of nitrogen were dominated by long-lived herbaceous and woody species to the exclusion of early successional annuals and short-lived perennials.

Raynal et al. (1982) found that seeds of five tree species differed in their germination response to solutions of pH 5.6, 4.0, 3.0, and 2.4. Only hemlock and white pine were exposed to the pH 2.4 treatment. White pine seeds were stimulated in their germination response at low pHs (3.0 and 2.4), while germination of yellow birch was depressed at pH 3.0 treatment. Red maple germination was suppressed at pHs of 4.0 and 3.0. Sugar maple germination was not affected by any of the pH treatments. Hemlock germination was severely reduced at pH 2.4 but was not affected by any other pH treatments.

In Saguaro National Monument (SAGU), visible injury caused by ozone has been documented on ponderosa pine (Pinus ponderosa vars. scopulorum and Arizonica) (Duriscoe, 1989). No evaluation of the effects of ozone on cacti, small trees, shrubs, grasses or herbs has been made in the desert ecosystems of SAGU. Thompson et al. (1984) has shown that some desert annuals are injured by relatively low ozone levels (.10 ppm). Additionally Temple (1985) has shown that the desert shrub Rhus trilobata can be injured by .10 ppm ozone for short durations. The effects of other urban, industrial, or agricultural pollutants (nitrogen oxides, trace metals, and organics) on any of the biological resources of SAGU have not been determined. Tillman (1987) showed

that the addition of relatively low levels of nitrogen (1 gm per square meter per year) can cause significant changes in the cover, height, and importance of species in native ecosystems. Additionally, Freer-Smith and Mansfield (1987) indicate that exposure to mixtures of gaseous pollutants could lower the frost resistance of native species. Freidland et al. (1984) have indicated that fertilization of spruce trees with anthropogenic nitrogen could cause winter injury. Wicks et al. (circa 1969) has described the effects of herbicides on cacti species in rangelands. Kitchen et al. (1980) has described the effects of other organic compounds on species common to arid ecosystems.

Major Ecological Groups in Desert Ecosystems

Grasses

Grass species are important ecological components of desert ecosystems. They are a primary food source for herbivores and are important in stabilization of desert soils.

The susceptibility of desert grasses to gaseous air pollution is not well known. Hill et al. (1974) performed experimental exposures to determine the susceptibility of species of desert grasses to SO_2 and found that some species were susceptible at relatively low concentrations.

Shrubs

Shrub species, like the grasses, have not been extensively evaluated for susceptibility to gaseous air pollutants. Temple (1985) exposed the mesotrophic shrub Rhus trilobata to relatively low levels of ozone and found sensitive genotypes with foliar injury, but no growth effects were found. Heuston (1990) found that susceptible genotypes of Rhus trilobata in a biomonitoring garden and in field surveys had visible injury symptoms that were macroscopically similar to symptoms observed in the chamber fumigations. Thompson et al. (1980) exposed the xerophyllous desert shrub Larrea tridentata to acute and chronic doses of sulfur dioxide and found the shrub to be relatively tolerant to this pollutant.

Trees

Desert trees include desert wash and bajada species (palo verde, mesquite, and ironwood), riparian species (sycamores, poplars), mid-elevation shrub-woodland species (oaks, manzanitas, pinyons), and upper-elevation montane species (pines, firs, oaks, aspen). There appears to be a large difference in pollutant-susceptibility between mesic species (riparian and montane ecosystems) and the species adapted to more xeric conditions (foothill and desert wash/bajada ecosystems). Trujillo et al. (1991) fumigated pinyon pine seedlings with acute and chronic exposures of sulfur dioxide and ozone (greenhouse conditions) and found little response except at very high acute concentrations.

Controlled fumigation exposures (Miller et al., 1963; Harward and Treshow, 1975) and field studies (Duriscoe, 1987) have shown that tree species found in montane and riparian ecosystems in desert areas are sensitive to ozone and sulfur dioxide. Trees known to be sensitive to ambient concentrations of ozone and sulfur dioxide are listed in Table 1.

Cacti

Desert cacti (opuntias, chollas, and columnar species) appear to be relatively tolerant to the gaseous pollutants ozone and sulfur dioxide. Although only a few experimental exposures of species with CAM metabolism have been conducted, in general the low gas exchange rates found in these species result in little injury. Effects of ozone and/or sulfur dioxide on the cuticles of cacti species may warrant some attention since the epicuticular waxes on the needles of some conifer species have been shown to be degraded by these pollutants.

Lichens

Lichens are often used as indicators of ambient air pollution (Marsh and Nash, 1979; Anderson and Treshow, 1984; McCune, 1988). They have been used on local, regional, and national levels to map the deposition of air pollutants. The sensitivity of lichens to air pollutants is related to the lack of a cuticle and the inability of these species to regulate the flow of gases into the tissues. Lichens are particularly sensitive to sulfur dioxide. Annual average concentrations of less than 30 micrograms per cubic meter have been demonstrated to cause the disappearance of sensitive species.

Soil Crusts

Organisms in soil crusts in desert ecosystems serve to control soil erosion, increase permeability of the soil to rainfall, and fix atmospheric nitrogen. There is evidence that they are also sensitive to air pollutants (Sheridan, 1979; Belnap, 1990). These cyanobacteria and lichens are most sensitive when ambient temperatures are low and the crusts are moist.

Recommendations

Controlled fumigation studies in NPS units exposing a variety of desert species to gaseous pollutants under natural conditions are needed. Controlled exposures to gradients of nitrogen added to field plots will help us to evaluate the effects of nitrogen fertilization on the phenological processes and community structure of ecologically important species. Field studies should be conducted for species shown to be sensitive during fumigation experiments to determine the nature, severity, incidence, and extent of injury. Long-term monitoring plots can then track spatial and temporal trends in injury and determine pollutant effects on individuals, communities, and ecosystems. These studies should be initiated in NPS desert units where pollutant monitoring data show that seasonal pollutant levels are highest when ecosystems components are physiologically active.

Table 1. Species found in desert ecosystems and their relative sensitivity to gaseous pollutants.

Plant Type	Species	Ozone			Sulfur Dioxide		
		Low	Mod	High	Low	Mod	High
Annual	Camissonia claviformis			X			X
	Camissonia hirtella			X			X
	Crypantha nevadensis			X			X
Grass	Orozypsis hymenoides						X
Herb							
Shrub	Rhus trilobata			X			
	Salix gooddingii		X				
	Encelia farinos		X			X	
Tree	Platanus sp.			X			
	Populus sp.			X			
	Pinus ponderosa			X			X
	Pinus strobiformis		X				
	Pinus edulis	X			X		
	Abies concolor		X				
	Pseudotsuga menziesii		X				X
Lichen	many species		X				X
Crusts	some species						X

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Origins and Effects of Dry-deposited Materials in Desert Ecosystems: Some Atmospheric Chemistry Considerations

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Abstract. The general principles of atmospheric chemistry and long-range transport of inorganic air pollutants are discussed. The use of these basic concepts and the double normalization Enrichment Factor scheme to the large quantity of data being produced for the NPS can materially assist in interpreting and assessing the impact of pollutant sources on NPS resource management areas. These concepts are applied to both the environmental materials being collected at the Saguaro National Monument and to particulates being analyzed under the NPS visibility monitoring program. Some limitations to the use of these interpretive tools in desert ecosystems are suggested.

This paper is intended as an introductory look at atmospheric chemistry for the scientific layman. The research and concepts that are discussed have evolved over the past 20 years of atmospheric chemistry research. My primary purpose is to illustrate some of the things one can do with the tremendous amounts of elemental information available to the NPS. In general, the atmosphere is composed of major gases (nitrogen and oxygen), trace gases (argon, methane, carbon dioxide, neon, and xenon), particles composed of inorganic elements (metals) or inorganic compounds (ammonium sulfate, calcium carbonate, silica, etc.), organic compounds (soot, terpenes, formaldehyde, etc.), or a combination of these matrices. These materials originate from a variety of sources, and the original source may have a great impact on the nature and toxicity of the materials released to the atmosphere (Stern, 1968; Hidy, 1984; Seinfeld, 1987). Source characterization has been an important area of research for many years. In general, one can divide sources into two categories: natural background and anthropogenic. Natural sources of gases and particulates consist of continental weathering products (soils, rocks), marine aerosols, volcanic materials injected during eruptions, meteoritic debris ablated during atmospheric entry, and trace gases from animals such as methane from termites (Woodcock, 1952; Duce et al., 1967; Duce, 1969; Duce and Woodcock, 1971; Wilkiniss and Bressan, 1971; Delany et al., 1973; Zoller et al., 1980; Sedlacek et al., 1983). We have learned a great deal about the "background" aerosol through research in remote areas of the Arctic, Antarctic, and open oceans (Zoller et al., 1974;

Berg et al., 1983; Berg et al., 1984; Duce et al., 1975; Maenhaut and Zoller, 1977). However, since the industrial revolution began about 200 years before the advent of atmospheric chemistry, there is continuing debate about how real the assessment of natural background can be today (Proch et al., 1970). Indeed, evidence for anthropogenic input of certain trace elements and gases (Pb, fluorocarbons) to the atmosphere seems to be found worldwide. Anthropogenic sources may be large "point-sources" such as smelters, specialized industries (microelectronics), energy conversion facilities (electric generation, coal gasification) and waste incineration (Gladney, 1974; Zoller et al., 1974; Gordon et al., 1974; Gladney et al., 1976; Gladney et al., 1978; Gallorini et al., 1981). They may also be widespread, non-point sources such as internal combustion engines, agricultural operations, or aircraft (Lee et al., 1971; Ondov et al., 1982).

These sources have some characteristic particle formation and atmospheric injection mechanisms which are useful in interpreting aerosol composition data. Particles can be formed by direct physical abrasion during erosion and injected into the lower atmosphere by wind action. Plant and animal communities also contribute to the weathering of continental materials (Delany et al., 1973). Marine aerosols are commonly formed through the injection of tiny droplets from bursting bubbles at the sea surface and their subsequent dehydration into "salt" particles (Woodcock, 1952; Duce et al., 1967; Duce and Woodcock, 1971). Particles are also formed directly in the lower atmosphere by a variety of gas-to-particle conversion processes (Duce, 1969; Berg et al., 1983). These processes include simple cold condensation processes (water vapor to form clouds) and hot condensation processes that occur in the elevated temperature zones of volcanos and industrial smokestacks (Sedlacek et al., 1983; Gladney et al., 1976). Other cold processes include chemical reactions that occur on gaseous species after they have been released to the atmosphere and cooled to ambient temperatures, such as the photolytic conversion of materials in urban atmospheres (the Brown Cloud) or the catalytic conversion of sulfur dioxide to form sulfuric acid (a component of acid rain) or ammonium sulfate. The chemical changes occurring as the aerosol ages can be accelerated by the presence of metallic catalysts on the particle surfaces (Lee et al., 1968).

The specifics of the formation and injection process influence both the chemical composition and the size distribution of the particles formed. Figure 1 is a highly generalized summary of the results of some of the major conversion processes and sources mentioned above. There are some useful generalizations that can be drawn from this information that apply directly to the interpretation of aerosol data collected for the NPS. Three different patterns of size distribution/composition have been shown. Most continental weathering processes yield particles of uniform composition, strongly skewed towards large particles. High temperature combustion processes, often with subsequent condensation from the gaseous state, result in particles of varying composition, strongly skewed towards the smallest particles (this is affected by the age of the aerosol). Condensation from the gaseous state is strongly influenced by the surface area available on particles and occurs preferentially on the smallest particles since they have the greatest relative surface area. Marine processes seem to yield particles that are intermediate in size distribution, with their number-distribution maxima in the mid-size range. This may be a result of the dehydration of the large particles that are injected through the bubble-bursting process.

One NPS network collects rough size-distribution information from dichotomous samplers. The data shown in Figure 1 are taken from seven-stage Cascade Impactors that sort particles into this larger number of groups that must then be analyzed separately. The larger number of size fractions yields more information but increases the analytical cost by a factor of 3 or more. The two size cuts obtained from the visibility monitoring system gives the NPS the most cost-effective

information for establishing overall trends rather than developing detailed investigations of air chemistry processes. As shown in Figure 1, two size cuts effectively separate many natural processes (large particles) from anthropogenic activities (primarily small particles).

An appreciation of elemental composition as a function of particle size is important for understanding the long range transport of atmospheric aerosols. Atmospheric transport over ranges of 1000 - 10,000 km is being used to interpret the results of air particulate filter composition studies. Rahn and Lowenthal (1984) have developed a seven-element tracer system (arsenic (As), antimony (Sb), manganese (Mn), vanadium (V), zinc (Zn), indium (In), and selenium (Se)) to assess source regions and long-range air pollution transport. Several of these elements are prominent in non-ferrous metal smelter emissions, and are being observed at elevated levels in some soils in the Tucson area (Kahn and Lowenthal, 1984; Landsberger, 1988).

Atmospheric concentrations of elements carried on particles are usually expressed in terms of the weight of the element per cubic meter of air. Total elemental concentrations are of prime interest from a public health point of view. However, they are difficult to use in identification of sources since they are affected strongly by wind speed and direction, precipitation, mixing heights, distance from local sources, etc. Emission inventories provide some information about sources but one must use models to predict down-wind elemental concentration patterns from these data.

Many of the uncertainties noted above can be removed by dividing the absolute concentrations of elements of interest by that of a reference element that is abundant in the aerosol and/or easily measured by the analytical method of choice with a high degree of precision and accuracy. This is shown in:

$$[X] / [R]$$

Where [X] = Concentration of element of interest
[R] = Concentration of reference element.

The concentrations of elements X and R must be in the same units (e.g., ug/g, ug/m^3, etc.) Such a normalization tends to remove variations caused by changes in total atmospheric particulate loading. The reference element should be a major constituent in material emitted from the source being studied.

One can obtain even more useful information by performing a second normalization to the elemental abundance pattern that has been established for individual sources of airborne materials. Enrichment factors can be calculated using the following equation:

$$EF = \frac{[X]a/[R]a}{[X]c/[R]c}$$

where [X]a = concentration of element X in atmospheric aerosol
[R]a = concentration of reference element R in atmospheric aerosol
[X]c = concentration of element X in average crustal material
[R]c = concentration of reference element R in average crustal material

The reference element for this calculation must be chosen with care. It is important that the one chosen have only one source in the atmosphere, be fairly abundant and/or easily measured with high precision and accuracy. The usual reference elements are silicon (Si), aluminum (Al), and scandium (Sc) for the soils component; sodium (Na) and chlorine (Cl) for the marine component; and lead (Pb) and bromine (Br) for the automotive component. If neutron activation is used as the analytical method, Si is eliminated since it is difficult to detect using this technique (Gordon et al., 1971; Gordon et al., 1973; Hopke et al., 1976).

Much suspended particulate matter is soil and rock dust injected by wind erosion. Relative concentrations of elements borne by dust are probably the same as that of the reference material used in the double normalization. Also, relative concentrations of many elements in several source materials are similar to those of crustal material. For example the alumino-silicate portion of coal (ash) has a concentration pattern much like that of average crustal material. Thus when an element has a large relative concentration after the double normalization, one must look to special sources to find explanations for the enrichments.

If the airborne material is primarily from the source from which the reference element is selected, the EF values should be close to one. For elements that display EF values strongly in excess of 1, the implication is that there are one or more additional sources that contribute significantly to the concentration of those elements. For example, near the coastline, EF values for Na and Cl relative to crustal materials show strong enrichments. This suggests that crustal weathering is not the primary source of these two elements in the atmospheric aerosol. In fact, the nearby ocean is the major source of these two elements, and if mean ocean water chemical data are used as the reference the recalculated EFs for Na and Cl approach unity. Situations where the EF is significantly less than unity require special care. This usually results from inappropriate choice of reference element or reference material composition. For example, if local soil dominates the local aerosol and has different composition than the crustal average normally used for the reference material data set, this may result in significant depression of the EF values. Calcium in the Tucson aerosol may be such a case.

These concepts are applied to atmospheric aerosol data measured in three major urban areas (Figure 2). Many of the common crustal elements have EF values of less than 10 and their airborne concentrations are primarily a result of suspended dust of crustal composition with little anthropogenic pollution component. Notice that Na and Cl show highly elevated EFs in Boston and San Francisco but have values near 1.0 for N.W. Indiana, illustrating the strong input from a natural marine source in coastal areas. Many of the elements with high EFs come from neither of these natural sources, and merit further investigation as potential indicators of anthropogenic air pollution (Gordon et al., 1971; Gladney et al., 1974).

The results of these approaches on two different soil groups near Saguaro National Monument (SAGU) are shown in Table 1-3. Table 1 lists mean elemental concentrations from four soils taken 0.5 - 1.0 km downwind of the San Manuel Smelter, located in the next major basin north of SAGU and thought to be a potential source of atmospheric input of trace element at the Monument. Table 1 also shows mean elemental content of 25 soil samples taken near the "Exclosure" in the Cactus Forest section of the Eastern unit of SAGU, as well as the mean crustal composition according to Wedepohl (1968). Evaluation of possible elevated levels of any elements in the San Manuel or SAGU soils from these data is not straightforward, nor is the determination of whether there are any significant differences in soil compositions between the two sites. Table 2 shows the results of applying the simple elemental ratio approach to the data in Table 1. The resulting data are probably even more difficult to interpret, because of the large

and varying number of leading zeros. However, the power of the enrichment factor approach is demonstrated in Table 3 after the double normalization technique is applied to the data in Table 2. Most of the elements in both soil source areas have EF values in the vicinity of one, can be assigned a natural crustal source with a high degree of confidence, and can be eliminated from further concern about anthropogenic impact in these two areas. This permits a rapid focus of attention on the few elements that are showing evidence of non-crustal sources (Cs, Hf, In, Sb, and Zn), since they have EF values that are significantly greater than one. Note that four elements (excluding Cs) also have higher EF values in the San Manuel samples than in the Exclosure, strongly suggesting that the San Manuel samples are from sites geographically closer to a local atmospheric source of these elements. The elevated levels of Cs in the Eastern unit of SAGU are difficult to understand and cannot be ascribed to San Manuel as a possible source, since the EF for Cs is much lower near the smelter.

Let's now apply this enrichment factor concept to the elemental data being generated by the NPS visibility monitoring system to see if it offers any opportunity to simplify this mass of data and permit the extraction of some conclusions. The elements being routinely reported on the fine-particle fraction, as measured by proton induced x-ray emission (PIXE), are shown in Table 4. Total mass is determined by the difference in weight of the filter before and after sampling. Mean enrichment factors for SAGU have been calculated for the fine-particle data relative to the exclosure soils and are shown in Table 5. Over 500 data points were reduced to produce this table. Immediately apparent is the fact that Zn, Br, Pb, S, and copper (Cu) in the fine-particle aerosol have large non-crustal sources. The data indicate that titanium (Ti), Mn, iron (Fe), Al, and potassium (K) can be ascribed largely to local soil materials. The EF values for magnesium (Mg), Na, and Ca are in an intermediate range where there is difficulty drawing hard conclusions. Possible alternatives are that there may be important non-crustal sources, or that there is some incompatibility between the data since different analytical methods were used to measure elemental concentrations in the soils and the fine particulates.

Let me illustrate one further mechanism to use to interpret the PIXE aerosol data. Pattern-recognition techniques can be used to investigate the potential sources of the aerosols observed in parks. There are some assumptions that can be applied to the PIXE data to see if they are internally consistent for the elements reported. Table 6 shows some calculations that can be used to calculate the total mass of the aerosol from individual elemental components. Table 7 summarizes the calculations applied to aerosol data from four representative dates in April 1986 at SAGU. The calculated mass of the aerosol compares with the observed total mass, suggesting that these three sources may be used to account for the vast bulk of the park's airborne material. A similar relationship was observed for almost all fine-particle filter data taken daily during March and April 1986. Whether the organic and sulfate components are natural or anthropogenic must be determined through other methods, since this approach cannot distinguish between different sources for the same materials. This latter function is partially performed with the enrichment factor calculations discussed earlier for inorganic materials such, as sulfate. The organic component requires more sophisticated analysis using gas chromatography/mass spectrometry to identify specific compounds. With this information, sources for the organic material may be inferred.

One must be alert to the interpretive problems that are introduced by desert environments into these simple aerosol resolution techniques. Natural salt concentrations are often much higher in dry ecosystems, and erosional exposure of caliche layers may affect the assumptions about sulfur sources. Furthermore, unusual sources of toxic metals (e.g., As, Sb, etc. in desert hot

springs) need to be evaluated before assuming that high enrichment factors for certain elements imply anthropogenic sources.

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Table 1: Elemental concentrations of selected Saguaro NM and Wedepohl's crustal data

Element (units)	Smelter	Exclosure	Wedepohl's Crust
Al (%)	6.0	8.6	7.83
Ba (ug/g)	560	650	590
Ca (%)	0.98	0.51	2.87
Ce (ug/g)	87	95	75
Co (ug/g)	19	12	12
Cr (ug/g)	63	62	70
Cs (ug/g)	7.5	25	2.7
Dy (ug/g)	7.4	6.9	6.1
Eu (ug/g)	1.6	1.4	1.4
Fe (%)	8.1	4.1	3.54
Hf (ug/g)	20	7.8	3.0
In (ug/g)	0.53	< 0.1	0.070
K (%)	2.7	3.6	2.82
Mg (%)	0.56	0.66	1.39
Mn (ug/g)	1270	570	690
Na (%)	1.16	0.84	2.45
Rb (ug/g)	126	220	120
Sb (ug/g)	6.3	1.8	0.20
Sc (ug/g)	13	14	14
Si (%)	31.0	32.0	30.54
Sm (ug/g)	8.1	7.6	6.6
Ta (ug/g)	2.4	1.3	3.4
Tb (ug/g)	1.0	0.9	1.4
Th (ug/g)	23	15	11
Ti (%)	115	0.36	0.47
U (ug/g)	3.7	4.3	3.5
V (ug/g)	169	80	95
Yb (ug/g)	4.9	3.9	3.4
Zn (ug/g)	240	104	60

Table 2: Elemental ratios of selected Saguaro NM and Wedepohl's crustal data to silicon

Element	Smelter	Exclosure	Wedepohl's Crust
Al	0.19	0.27	0.26
Ba	0.0018	0.0020	0.0019
Ca	0.03	0.02	0.09
Ce	0.00028	0.00030	0.00024
Co	0.000061	0.000036	0.000039
Cr	0.00020	0.00019	0.00023
Cs	0.000024	0.000077	0.0000088
Dy	0.000024	0.000021	0.000020
Eu	0.0000052	0.0000045	0.0000046
Fe	0.26	0.13	0.12
Hf	0.000065	0.000024	0.000010
In	0.0000017	< 0.0000003	0.0000002
K	0.09	0.11	0.09
Mg	0.02	0.02	0.05
Mn	0.0041	0.0018	0.0022
Na	0.04	0.03	0.08
Rb	0.00041	0.00069	0.00039
Sb	0.0000200	0.0000056	0.0000065
Sc	0.000042	0.000045	0.000046
Si	1.0	1.0	1.0
Sm	0.000026	0.000024	0.000022
Ta	0.0000076	0.0000039	0.0000110
Tb	0.0000033	0.0000030	0.0000029
Th	0.000074	0.000048	0.000036
Ti	0.04	0.01	0.02
U	0.000012	0.000013	0.000011
V	0.00054	0.00025	0.00031
Yb	0.000016	0.000012	0.000011
Zn	0.00078	0.00032	0.00020

Table 3: Enrichment factors relative to Wedepohl's crustal abundances for selected Saguaro NM data using silicon as the reference element

Element	Smelter	Exclosure	
Al	0.71.0		
Ba	1.01.0		
Ca	0.30.2		
Ce	1.21.2		
Co	1.61.0		
Cr	0.90.8		
Cs	2.78.8		
Dy	1.21.0		
Eu	1.11.0		
Fe	2.21.1		
Hf	6.52.4		
In	8.5	< 1.5	
K	1.01.2		
Mg	0.40.4		
Mn	1.90.8		
Na	0.50.4		
Rb	1.01.8		
Sb	318.6		
Sc	0.91.0		
Sm	1.21.1		
Ta	0.70.4		
Tb	1.11.0		
Th	2.11.3		
Ti	2.00.5		
U	1.11.2		
V	1.70.8		
Yb	1.41.1		
Zn	3.91.6		

Table 4: Fine particulate monitoring data Saguaro National Monument: Elements measured by PIXE

Na	Mg	Al
Si	K	Ca
Ti	Fe	
V	Cr	Ni
Cu	Mn	Zn
Br	Pb	
	S	
	H	

Table 5: Fine particulate monitoring data Saguaro National Monument: Enrichment Factors relative to SAGU Exclosure soil

Ti	0.7
Mn	0.7
Fe	1.0
Al	1.1
K	1.8
Mg	3.0
Na	8.0
Ca	9.0
Zn	40
Br	400
Pb	500
S	1100
Cu	1500

Table 6: Fine particulate monitoring data Saguaro National Monument: Aerosol Component Calculation

Convert [Si] to soil component

Convert [H] to CH_4 for organic component

Convert [S] to NH_4SO_4 for sulfate component

Soil mass = 4 x [Si]

Organic mass = 7 x [H]

Sulfate mass = 4 x [S]

Table 7: Fine particulate monitoring data Saguaro National Monument: Aerosol Component Calculation

Date	(ng/m3) [H]	[Si]	[S]
04/08/86	167	504	297
04/12/86	181	438	302
04/15/86	185	468	341
04/19/86	202	432	410

Date	Soil	Organic	Sulfate
04/08/86	2016	1169	1188
04/12/86	1752	1267	1208
04/15/86	1872	1295	1364
04/19/86	1728	1414	1640

Date	Total Mass		Cal/Obs
	Calculated	Observed	
04/08/86	4373	3900	1.12
04/12/86	4227	4200	1.00
04/15/86	4531	4500	1.00
04/19/86	4782	4500	1.0

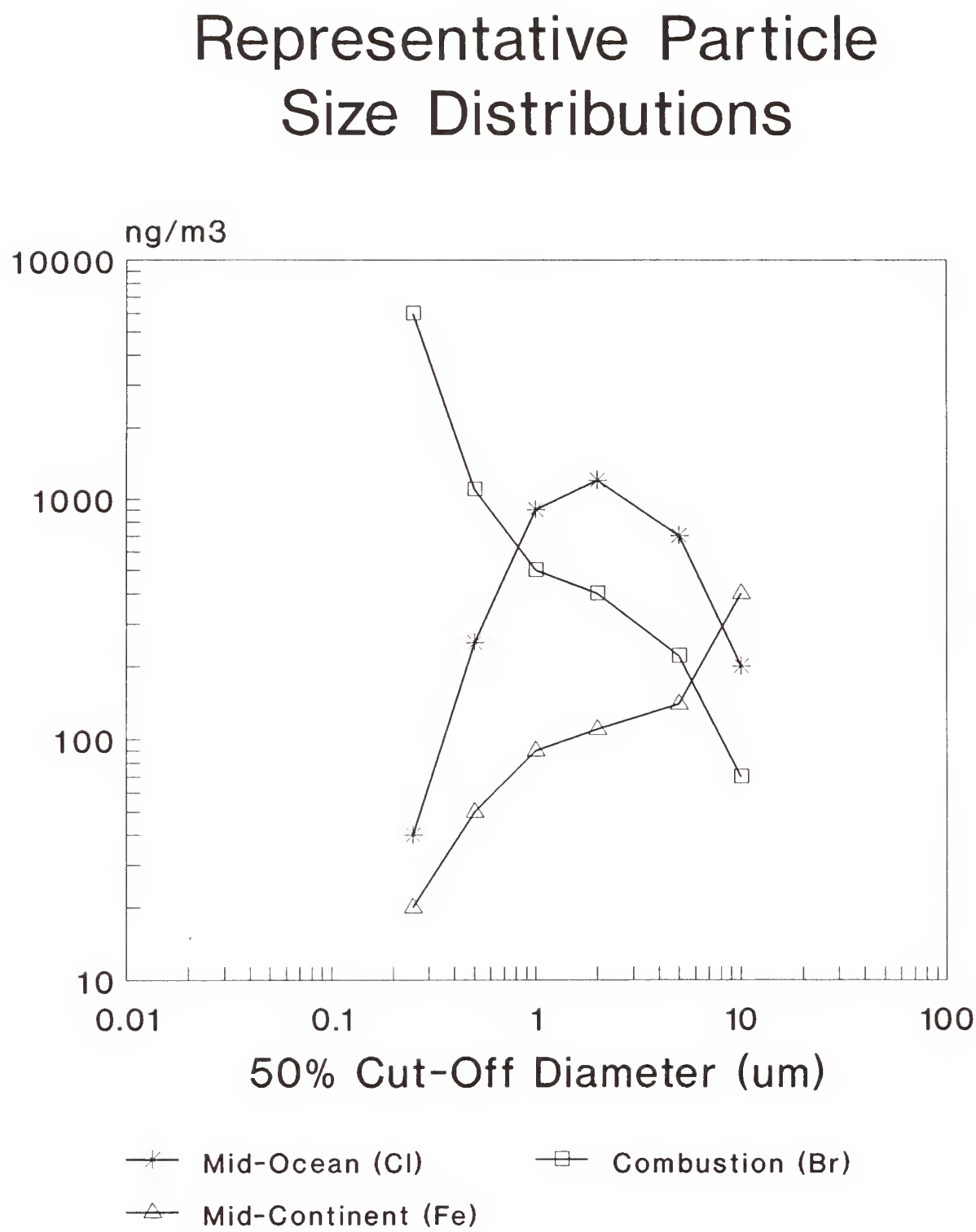
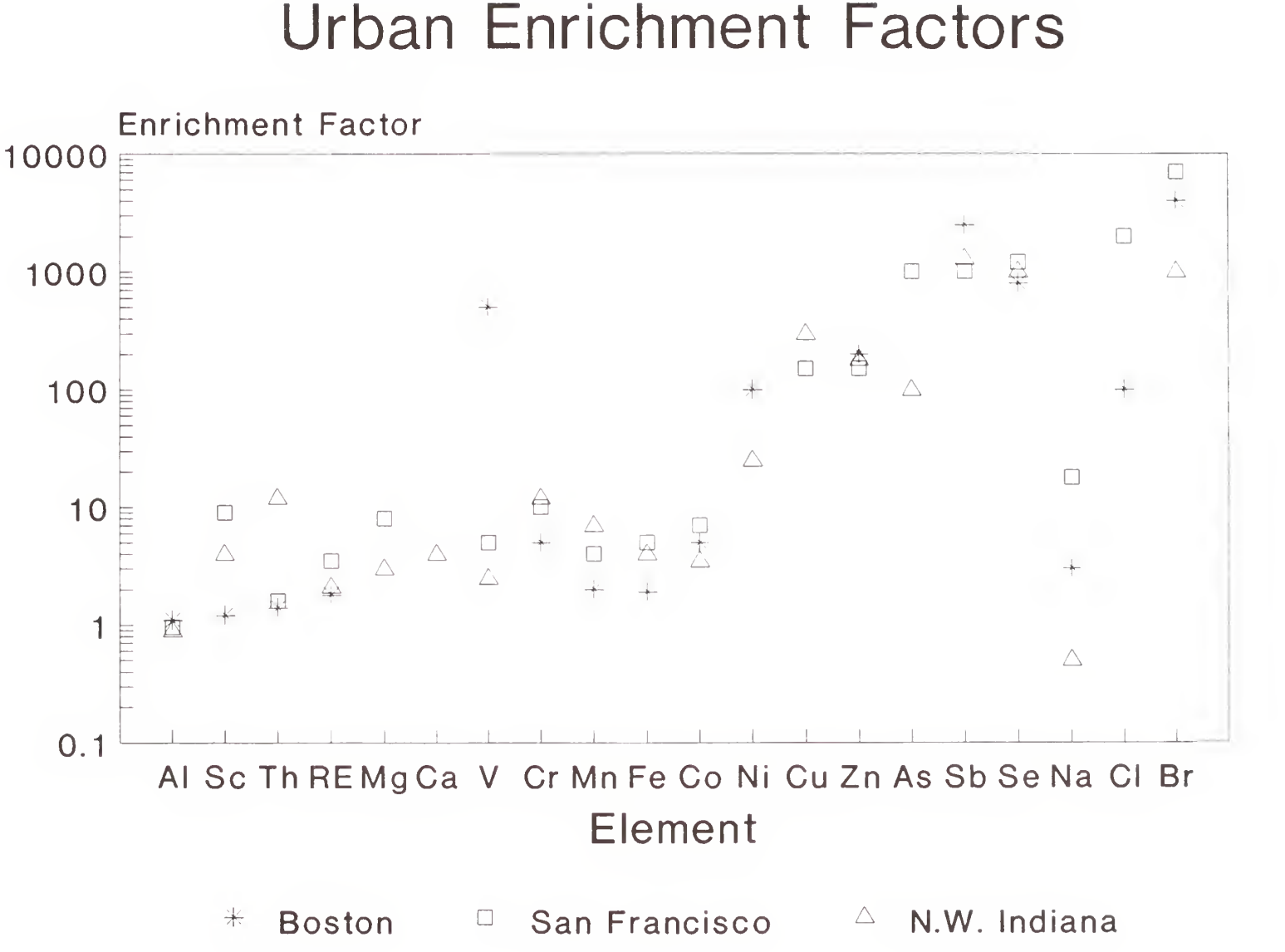


Figure 1. Typical size distributions for continental dust in remote areas observed by Rahn (1971) with an Andersen sampler, for marine aerosols observed in Hawaii by Duce et al. (1967) with a Scientific Advances cascade impactor.



RE = Rare Earth Elements

Figure 2.

Origins and Effects of Dry-Deposited Materials in Desert Ecosystems: Ecophysiological Effects

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Abstract. For many years, the concern over acid deposition was thought to be irrelevant in desert settings because of the lack of moisture and relatively pristine atmospheric environment found in these areas. However, as the general understanding of acid deposition has increased, there is a realization that, even in the absence of moisture, dry deposition of particulate matter can result in the formation of acidic solutions when the particulate matter subsequently dissolves in dew or reacts with the moisture in plant tissues. Furthermore, studies are now showing that acid deposition does occur in desert environs (Roth et al., 1985; Young et al., 1988). The following discussion outlines some of the potential effects of deposition of particulate matter and its subsequent dissolution.

Effects on Vegetation

Particulate Effects

Temperature and Light Effects - Deposition of particulate matter on the surface of plant leaves or other plant parts forms an insulative layer that can impede the transfer of heat from the plant to the environment (Anda, 1986; Eller, 1977). In a desert setting, this can result in an internal temperature increase that could affect biochemical reactions or other physiological processes. A layer of particulate matter also can affect photosynthesis by reducing the amount of light internally available to chloroplasts (Manning, 1971; Thompson et al., 1984).

Stomatal Effects - Small diameter particulate matter can lodge in open stomates and interfere with subsequent closure (Eveling and Bataille, 1984; Ricks and Williams, 1974). In a desert environment, where stomatal control is critical to maintaining a favorable moisture balance within the plant, loss of stomatal control can result in desiccation and, ultimately, death. Water loss also can be accelerated by increased leaf temperature, as discussed previously (Anda, 1986).

Surface Microbiological Effects - The surface of a leaf is a microcosm, with microfloral, -faunal, and -fungal populations that are regulated, in part, by inputs to the system from the atmosphere

and from the plant leaf. Changes in the chemical input to the microcosm, such as those caused by pollution-mediated changes in atmospheric deposition, can result in shifts in numbers of microorganisms or in changes in species composition (Helander and Rantio-Lehtimaki, 1990; Khanna, 1986; Magan and McLeod, 1988; Singh and Rai, 1990). Beneficial populations of microorganisms can disappear or even be replaced by pathogens, with subsequent detrimental effects to the host plant (Manning, 1971). Shriner (1977) found that effects of acid deposition on pathogenic fungi could decrease or enhance the effects of the pathogen, depending upon when in the life cycle of the pathogen exposure to acid deposition occurred.

Acid Effects (subsequent to dissolution)

Morphological and Anatomical Effects - Plants, because of their indeterminate growth pattern, retain undifferentiated, meristematic tissue throughout their lives. This tissue is relatively susceptible to attack by acidic substances, especially in situations where the growth form of the plant is conducive to accumulation of acidic materials in proximity to meristematic tissue. An example of a situation in which actual morphological effects were observed is the accumulation of acids in fascicle sheaths surrounding the meristematic tissue at the base of pine needle bundles (Gordon, 1972). The corrosive action of the acid resulted in necrosis of the meristematic tissue, with concomitant reduction in needle growth, producing needle clusters on the order of one-quarter to three-eighths inch in length. This effect was aggravated by the presence of particulate matter, which lodged under the fascicle sheath and allowed acidic substances to more readily penetrate to the meristematic tissue. Percy (1986) also noted reductions in needle and leaf initiation in forest tree species and reductions in needle length in conifers. Other effects that have been noted include necrosis of tissue at the bases of clasping leaves of oat plants (Ferenbaugh, 1974) and extreme stunting of growth in bean plants at high acid concentrations (pH < 2) (Ferenbaugh, 1976; Norby and Luxmoore, 1983). In desert plants, morphological and anatomical effects could be enhanced because of the accumulation of acidic particulate matter on the plant as a result of hirsute surfaces or structures such as leaf rosettes. Upon exposure to dew or rain, the accumulated acidic particulate matter would dissolve to form a highly concentrated acid solution.

Reproductive Effects - Reproductive structures are extremely susceptible to chemical attack. In the case of acidic deposition, direct effects on seed production can result from interference with pollination, fertilization, or seed development (Craker and Waldron, 1989; DuBay, 1989; Feret et al., 1990); Holub and Ostrolucka, 1988; Kratky et al., 1974; Van Ryn et al., 1988). Seed production also can be affected through a general reduction in productivity, as will be addressed later in the discussion on photosynthesis.

Seeds and seedlings of most plants are more sensitive to environmental stresses than are mature plants. In a study on the effects of acid deposition on germinative capacity of seeds of eleven forest tree species, Percy (1986) found that four of the eleven species were adversely affected. Lee and Weber (1979) and Raynal et al. (1982) have reported both adverse effects and enhancement of germinative capacity. Adverse effects are generally reported at pH values below 3. Enhancement at higher, but still acidic, pH values is not surprising, as acid scarification is sometimes used as an aid in breaking seed dormancy. Percy (1986) also reported that seeding survival was reduced in five of the eleven species studied.

Cuticular Penetration - The effect of acid deposition on plants is dependent on the extent to which the acid penetrates to the interior of the plant. Penetration is affected both by the cuticular morphology of the plant and by the type of acid involved (Evans, 1984). Although no

definitive results have been reported, there is some indication that the type of acid (i.e., organic versus inorganic) may affect the extent to which the acid is able to penetrate the plant cuticle. Evans (1984) indicates that non-polar molecules should penetrate the cuticle faster than polar molecules.

Xerophytic plants, by their very nature, are more resistant to acid penetration than are mesophytic plants. The cuticles of xerophytic plants are adapted for reduction of water loss and thus are relatively impermeable to penetration of aqueous solutions. Many desert plants have thick cuticles and, for this reason, are afforded some protection against acidic deposition. Other plants are protected by various types of surface structures that repel water. A non-desert example is *Chenopodium quinoa* (lambs quarters). The leaves and reproductive structures of this plant are covered with multiple layers of spherical glandular structures (Brian and Cattlin, 1968), that do not allow penetration of water or inorganic acid solutions. Acid solutions of low pH (1.0-2.0) have virtually no effect on *Chenopodium* plants (Ferenbaugh, 1974), although the same solutions have extremely corrosive and detrimental effects on unprotected leaves such as those of *Phaseolus vulgaris* (common bean) (Ferenbaugh, 1976). Cuticular penetration also is affected by chemical erosion of epicuticular wax coatings (Cape, 1986; Karhu and Huttunen, 1986; Mengel et al., 1989; Shriner, 1977).

Cation Leaching - One immediate effect of cuticular penetration is the leaching of nutrient cations (e.g., K, Ca, Na) from plant surfaces. Measurement of nutrient concentrations in acidic throughfall or stemflow has shown that cations may be leached from the plant surfaces through replacement by hydrogen ions from the acidic throughfall (Fairfax and Lepp, 1975; Joslin, et al., 1988; Kelly and Strickland, 1986; Muir, 1990; Scherbatskoy and Klein, 1983; Wood and Bormann, 1974).

Physiological Effects - Physiological processes, including biochemical reactions, require that intracellular parameters (e.g., pH, temperature) be within certain limits for these processes to proceed normally. If the parameters are not within acceptable limits, processes may proceed abnormally or not proceed at all. Two areas that have been investigated with respect to acid effects are photosynthesis and enzymatic reactions.

Various aspects of photosynthesis have been examined to determine the effects of acid on this process. Several studies have shown that acid may be detrimental to plant productivity (Evans and Lewin, 1981; Ferenbaugh, 1976; Hindawi et al., 1980; Irving, 1985; Johnston et al., 1982; Norby and Luxmoore, 1983). More specific investigation has shown that internal sugar and starch concentrations may be adversely affected by exposure to acid (Evans, 1984; Ferenbaugh, 1976). Although the specific mechanisms by which this occurs have not been elucidated, various studies have indicated that the light and dark reactions of photosynthesis may be uncoupled (Ferenbaugh, 1974) or that photosynthetic enzymes may be affected. *In vitro* studies have shown that acid reduces chlorophyll to a photosynthetically inactive derivative called phaeophytin (Schanderl et al., 1962), but there are conflicting reports as to whether this occurs *in vivo*. A few studies on intact plants show some reduction in chlorophyll, but mostly only at low pH values (less than 3) (Abouguendia and Baschak, 1987; Ferenbaugh, 1976; Hindawi et al., 1980) or in susceptible plants such as lichens (Sheridan and Rosenstreter, 1973). Other studies show either no effects or anomolous results (Heagle et al., 1983; Scherbatskoy and Klein, 1983).

Several studies have investigated the effects of acid treatment on enzymes. Because enzyme function is dependent upon conformance (structure, configuration), any change in physiological conditions, such as pH, may change enzyme conformance and thus interfere with proper enzyme

function. Although change of enzyme conformance (denaturization) upon application of acid is easily demonstrated *in vitro, in vivo* studies are not conclusive. Acid effects on *in vivo* enzyme function have been reported, but the mechanism of action has not been defined.

Anion Effects

Although the primary effects that are associated with acid deposition result from the hydrogen ion moiety, there also may be effects associated with the anions that are present. The primary anionic constituents of anthropogenic acid deposition are sulfate and nitrate. Sulfur and nitrogen are plant macronutrients, and the sulfate and nitrate from acidic deposition may enter into the internal plant biochemical processes. At low concentrations, this is harmless or even beneficial; but, if the capacity of the plant to accommodate the additional sulfate or nitrate is overloaded, toxic concentrations can accumulate (Thomas and Hill, 1937). Other emission sources also may have localized anionic effects. For example, near aluminum plants, the fluoride from hydrogen fluoride emissions is extremely toxic to plants (Weinstein, 1977).

Effects on Soil Systems

Nutrient Effects

In temperate soils, acidic precipitation can have a leaching effect, as hydrogen ions replace nutrient cations on the soil matrix and the nutrient ions subsequently are washed away (Abrahamsen and Dollard, 1979; Kelly and Strickland, 1987; Skiba and Cresser, 1986; Tomlinson, 1985). This type of leaching normally does not occur in desert ecosystems, where acidic deposition consists primarily of dry deposition and where the precipitation/evaporation ratio is less than one. Nevertheless, dry deposition can accumulate in or on the soil and release a "flood" of acidity when rainfall does occur. This may result in an accelerated transport of nutrient ions to the caliche layer of the soil. Acidic deposition also may affect plant nutrition through detrimental effects on mycorrhizal associations (Stroo and Alexander, 1985).

From an anionic standpoint, the argument can be made that acid deposition actually may have a beneficial effect. Many soils are sulfur deficient (Coleman, 1966), and neither sulfate nor nitrate are retained in soils by the electrostatic attraction forces that bind cations. Dry deposition of sulfates and nitrates may thus represent a continual nutrient input (Grennard and Ross, 1974; Kamprath, 1972; Prince and Ross, 1972).

Another potentially beneficial effect of acidic deposition results from the fact that many desert soils are calcareous, with plant nutrients bound in relatively insoluble forms. Experiments have shown that small amounts of acid may aid in the dissolution of these calcareous materials, with subsequent release of bound nutrients (Cates et al., 1982; Ryan et al., 1973).

Soil Ecology

Many soil microorganisms and soil invertebrates have relatively narrow pH tolerance ranges. Acidic deposition may affect soil ecology by changing soil pH in such a way that species composition of microorganisms or invertebrates changes. While desert soils may not be as susceptible to these types of changes as temperate soils, the following effects potentially could occur.

Nutrient cycling in soils frequently is dependent on a series of microbially-mediated chemical transformations. For example, nitrate goes through a series of reactions before transformation into a compound that can be taken up by plants. If the organism required for one of these transformations can no longer survive because of a change in soil pH, or if growth simply is inhibited, the whole process will come to a halt, with the possible accumulation of some intermediate at the point where the series of reactions is interrupted (Cohen and Ruston, 1925; Oden, 1968; Persson et al., 1989; Skiba and Cresser, 1986; Thompson et al., 1987). Nitrogen fixation and nitrogen mineralization, in particular, have been studied (Abrahamsen and Dollard, 1979; Denison et al, 1977; Klein and Alexander, 1986). Microbial decay processes, in general, seem to be retarded under acidic conditions. A natural example of this is the thick detritus accumulation that occurs in coniferous forest soils ("mor" soils). These soils are acidified by the organic acids leached from fallen pine needles, and decomposition is reduced to relatively slow, fungally-mediated decay processes (Wielgolaski, 1969).

Soil invertebrates are important in nutrient cycling because they break detritus particles into smaller and smaller fragments, thus facilitating dissolution, nutrient cycling, and microbial transformation processes. If the soil invertebrate population is depleted, the decay process will be retarded because size reduction of detritus particles will take longer. While there is some indication that earthworms are sensitive to acidic conditions and that decomposition proceeds more slowly under these conditions (as indicated by the scarcity of earthworms in acid coniferous forest soils) (Wielgolaski, 1969), other studies indicate that decomposition and invertebrate populations are affected only at very low soil pH values (Abrahamsen and Dollard, 1979).

Effects on Ecosystems

The effects that particulate deposition may have on ecosystems are essentially secondary effects, including effects on community composition and effects on food chains (Brandt and Rhoades, 1972; Schreiber and Newman, 1988). In both cases, the effects result from differential susceptibility of species to the pollutant deposition, which depends on how each individual species reacts to all of the potential effects discussed previously. Those species for which the combination of effects is severe will disappear or diminish in importance. Other species may tolerate the change in conditions, and new species may move in to fill the niches vacated by the species that disappear. There are two overall adverse effects that can potentially result from these changes. One is that the new species moving in under these conditions may be weedy or opportunistic species that tolerate harsher environmental conditions but have less desirable characteristics than the species that they replaced. The other is that a species that disappears may be a vital link in a food chain. Disappearance of a species in this situation has a ripple effect in that other species higher in the food chain will be adversely affected even though they may not have suffered any direct effects from the pollutant.

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Aquatic Resources at Risk

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Abstract. The diversity and ecology of aquatic habitats in desert habitats is poorly known. Flora and fauna of desert rock pools are probably least known and most sensitive to acid deposition and air pollution. The distribution and abundance of aquatic organisms can potentially be affected by air borne inorganic nutrients, heavy metals, toxic organic compounds, and acidity.

Introduction

The Congressional mandate creating the NPS says the purpose of the national parks "is to conserve the scenery and the natural and historic objects and the wildlife therein and to provide for the same...in such manner...as will leave them unimpaired for the enjoyment of future generations". This suggests to me that we need, 1) to know a great deal more about what animals (mostly invertebrates) are in the desert parks, and 2) to have long-term planning (on the same scale as the ecology of the aquatic organisms: several years to decades) so that we can respond to changes in the fauna that occur as air pollution affects aquatic habitats.

There are many types of aquatic systems found in desert areas of the Southwest United States. These include streams, ponds, playas, reservoirs, and rock pools. Some of these, such as playas and rock pools, are ephemeral, depending upon rainfall as their only source of water. These aquatic habitats harbor diverse communities of organisms. Some of these organisms are endangered (e.g., desert pupfish) by changes in land use. Others could be endangered or already affected by agricultural or rangeland effluent, which in many cases serves to fertilize aquatic systems. Agricultural runoff may also include toxic organic compounds such as herbicides and pesticides. All aquatic systems are susceptible to airborne pollutants which may include heavy metals, toxic organic compounds, and acids from either wet or dry deposition. This paper presents a very brief summary of desert aquatic habitats and threats to their well-being.

Aquatic habitats are vulnerable to toxic organic compounds. Additionally, most aquatic habitats will respond to inputs of nutrients such as nitrogen and phosphorous that enter either as runoff or from atmospheric deposition. The effects of metals and acids, however, are dependent on the bedrock mineralogy underlying the water body. Most aquatic systems of the southwest desert

areas are situated on sedimentary rocks, rich in carbonates and basic cations. These may provide for alkaline and well-buffered aquatic habitats.

Metals, such as aluminum, lead, cadmium, copper, or zinc, are unlikely to be a biological problem in well-buffered areas because the metals tend to be insoluble in neutral or alkaline water, and they are chelated and precipitated by organic material. Where non-calcareous rocks or leached sandstones are the substrate for pools or streams, one expects low buffering capacity. The possibility exists that acid deposition will cause heavy metals to remain in solution upon deposition, or will solubilize from the sediments.

This same argument holds true for susceptibility of desert aquatic systems to direct acid deposition. Many aquatic systems are situated on well-buffered substrate, such as playas and reservoirs; these systems are not threatened by acidic deposition. Streams may have a groundwater source, which again, might buffer their communities against acidification. This should not be taken for granted, however. Surveys of stream chemistry are highly recommended before final conclusions are drawn.

The major habitat that could potentially be acidified are rock pools, which may be poorly buffered and are filled directly by rainwater. Very little is currently known about the chemical and biological dynamics of these pools. They can be an important source of water for terrestrial desert animals (Brown and Johnson, 1983). They may be located on metamorphic rock types which do not supply acid neutralizing capacity. Some rock pools may have a groundwater source. Others may receive water as direct precipitation falling on the pool, depending on the size of their watersheds. Still others may be fed by runoff from rainfall flowing down the sides of the watershed into the pools. Most desert rock pools are ephemeral, wetting up with rains, and drying after the rainy season. This has created very unusual chemical dynamics in these pools. Pool water starts out relatively dilute as the pool fills with water. Evaporation over the course of a season causes these waters to become progressively more concentrated, until brines may actually develop. Organisms that can survive such variability must either have very rapid life cycles, to live their lives at the most appropriate concentrations, or specialized adaptations.

Sources and Effects of Pollutants to Desert Aquatic Systems

Acidic Deposition and Effects

Precipitation and fog currently contains biologically significant amounts of inorganic acids (Bormann and Likens, 1970; Dodson, 1982; NADP, 1987; Blanchard and Stromberg, 1987; Glotfelty, 1987). In addition, biologically significant amounts of acids are deposited as dryfall from the atmosphere. Acid deposition can be carried long distances and then dropped by thunderstorms (Dickerson et al., 1987).

Studies of poorly-buffered lakes in the northeastern United States, in the upper Midwest, and in the Rockies and Sierra Nevada provide characteristics of acidification (Sprules, 1975; Cronin and Schofield, 1979; Harte and Hoffman, 1989). Acidification down to a pH of about 5.5-5.1 results in:

- decrease in biological diversity (Harte and Hoffman, 1989).
- establishment of a few acid-resistent species, which may not have previously occurred in the lake (Sprules, 1975).

- o a decrease in productivity of the lake.
- o possible mobilization of ions such as aluminum (Hooper and Shoemaker, 1985) or lead.

The desert rock pools may be poorly-buffered. A preliminary study in Utah suggests these pools may be susceptible to acid deposition (Dobson, 1987), but more needs to be learned about the water chemistry. The chemistry of rock pools water may also be affected by: 1) dry deposition washed off the rocks, so that the chemistry of precipitation itself is relatively unimportant, and 2) weathering of carbonates from rocks in the watershed (Hooper and Shoemaker, 1985), such that animals in pools may receive a pulse of pollution washed in during the first few hours after a pool is filled.

Results of the study of Utah rock pools (Dodson, 1987) suggest that at least three sorts of communities occur in the pools:

- o Gnats, mosquitos, and frog tadpoles occur in the most ephemeral pools, or at the beginning and end of pool existence,
- o fairy shrimps occur in slightly longer-lived pools,
- o insects, cladocerans, copepods, and salamander larvae occur in permanent pools.

The biology of many of these animals is poorly known. We do not know how many species there are, what their life histories are, or how they fit into the community. The preliminary study suggests that the duration of the pool is important, but that biological interactions, especially predation, are also important. Both the species diversity and biological interactions can be affected by acid deposition and air pollution.

Acidification of water is associated most often with the failure of reproduction. Adult vertebrates or invertebrates are able to persist down to pH levels of 5.5-5.0, but often their eggs will not develop. This suggests that in habitats with declining pH, it would also be useful to track reproductive rates of common animals. This can be done by estimating the recruitment each generation, or by looking for changes in the age structure of the populations.

Metal Deposition

As much as 10 percent of the annual inputs of metals in the Great Lakes is from the atmosphere (Eisenreich, 1980; also see articles in Schmidtke, 1988, and Nriagu and Simmons, 1984). The southwest desert parks are in or near mineralized areas with the associated mining, near the smelters of Arizona and northern Mexico, and near southern California, with its sources of atmospheric pollution from transportation, industry, incineration, and power generation. Precipitation or wind containing smelter smoke is characteristically acidic and has high concentrations of sulfate and several metals (Blanchard and Stromberg, 1987). Thus, it is possible that aquatic habitats receive relatively large amounts of metals from anthropogenic sources.

Toxic Organic Compounds

Many studies on lakes, especially the Great Lakes, have shown that toxic organic compounds come into the lake via air pollution (Manchester-Neesvig and Andren, 1989). Photochemical smog can be carried long distances (Dickerson et al., 1987). Toxaphene is not used in the watershed of the Great Lakes (used for cotton in the South), but occurs in Great Lakes fish

(Rice et al., 1986). DDT, supposedly not used in the United States, is being transported from Mexico and Central America. The "new" DDT added to the Upper Midwest is 10-20 percent of the peak accumulations around 1960. PCBs continue to be added to the Great Lakes via a number of paths, including atmospheric deposition. Establishment of trash or toxic waste incinerators increases the deposition of toxic compounds like dioxin.

Studies of the effects of low concentrations of toxic organics on the biology of aquatic animals have shown one or more of the following (Colborn et al., 1990): population declines; reduced recruitment due to reproductive failure; metabolic changes, such as wasting away of adults; developmental deformities; increased tumor frequency; specific changes in specific organs (such as the liver); behavioral changes; hormonal changes; immune suppression; and changes in enzyme concentrations or enzyme induction.

We need to study population size, life history, physiology, and behavior of desert aquatic animals, in order to establish the response of organisms to air pollution.

Nutrient Fertilization and Effects

Nitrogen compounds are important nutrients for plants, but if present in too great concentrations, they can lead to nuisance plant growth and anoxic water which greatly reduces the species richness of desert waters. Animal droppings, which add nitrates and phosphates, can be considered a natural input of nutrients (Ganning and Wulff, 1969). This input may be greater here than in non-desert areas, because the scarcity of standing water tends to concentrate animals. These nutrients stimulate the growth of algae and macrophytes in standing water, which in turn serve as the base of the food chain. When desert areas are used for grazing, the input of nitrogen (and other growth nutrients) can easily be excessive. This leads to nuisance algae and plant growth and results in stinking, unpalatable water. Algal blooms may cause loss of oxygen in water.

Studies in Chesapeake Bay and numerous other stations across the United States (NADP, 1987) show that a significant portion (up to 1/2) of the nitrogen budget of an aquatic habitat can come from the atmosphere. The same phenomenon is likely in desert aquatic habitats, especially those downwind of urban areas.

Suggested Inventory and Monitoring

Very little is known about the chemistry of aquatic systems in deserts. Both temporal and spatial stream surveys are needed, with an emphasis on temporary rock pools. This survey should start with maps of geologic substrate overlain with water bodies. Reconnaissance surveys of all water bodies should be undertaken to determine size, depth, and current state of the water body. The water bodies can then be classified and stratified according to watershed size, geology, and a number of other characteristics, and a subset chosen for more intensive investigation. It is strongly recommended that a geo-referenced computer data management system (GIS) be used for data storage and retrieval. Physical, chemical, and biological sampling should be carried out frequently (once per week) throughout several seasons to determine the temporal variability of these systems.

Physical parameters that should be sampled in pools include temperature, depth to bottom of pool, light attenuation (secchi depth), and total dissolved solids.

Chemical parameters that should be measured include specific conductance, pH, dissolved organic carbon, and major cations and anions (Ca, Mg, Na, K, NH_4, H, SO_4, NO_3, Cl, PO_4, HCO_3). Heavy metals and toxic organic compounds are more easily sampled from the sediments at the bottom of the pool. A collection from the surface 2 or 3 cm can be used to determine whether the pools are enriched in these pollutants (organic compounds, especially, have no known natural source; their detection is evidence of pollution). More detail can be obtained from a carefully collected sediment core from which metals and organics are extracted by depth; these can be used to reconstruct rates of deposition over time.

Since the desert park aquatic habitats are close to sources of toxic organic compounds, they may be affected by these compounds, and any increase in production of organic toxins could have a devastating effect on desert aquatic habitats. Sampling for these compounds, while expensive, may be necessary.

Taxonomic surveys, assessments of primary productivity, biomass, and seasonal succession are needed to characterize rock pool communities. Algal community composition can be used to characterize the trophic state (sensitivity to fertilization) and stage of acidification. It is also suggested that reproductive rates of vertebrate and invertebrate organisms be qualitatively assessed each season by estimating recruitment or by looking for changes in the age structure of population suspected of vulnerability to pollutants. Caution must be exercised in interpreting these results, however, as many factors in addition to pollution contribute to the population dynamics.

Some Final Words on Monitoring Programs

To solve a management problem, routine sampling of aquatic habitats may be initiated by federal agencies. However, such programs are going to tell us little about the biology of aquatic habitats. This approach is often taken in place of a well-designed study, but is wasteful of research money and time.

Biological data collected in a large, routine sampling program are rarely analyzed and published. Many samples are never analyzed. Large-scale sampling can also be wasteful because the animals are not identified to species. Most journals do not accept papers based on data from monitoring programs. Since the first priority of many agency research projects is to produce a report for a supervisor, the data are all too often stored away in reports of limited distribution. Thus the results of the study are lost to other scientists, and cannot be used for comparisons.

If published papers are to be produced from monitoring programs, it is necessary to develop a careful design for data collection and analysis. The design should be based on one or more interesting biological questions. The question must come first, before the design of the monitoring program. When the question comes first, it is often possible to design an efficient sampling program. The answers to questions such as "How often to sample", "How many samples should be taken", "How many replicate samples should be taken" become obvious once the biological question is carefully articulated. It is often best to state the question in the form of a testable (null) hypothesis, such as: "acid deposition has no effect on the pH of desert rock pools in the Capitol Reef National Park", or "variation in rock pool pH has no effect on growth and reproduction of fairy shrimp".

In order to find out the most about the biology of aquatic organisms in deserts, I feel that instead of large monitoring programs, it would be much better, at least until we know more about the

animals, to fund smaller projects, with more limited goals, that are carried to completion, and whose results are published in a scientific journal.

Would it be possible to encourage Master's and PhD research on a small scale? Even a very small program would greatly add to our knowledge of the biology of desert aquatic habitats. Such a program would be particularly effective if funding were based on published preliminary work, and continued funding was based on publication record. Even grants for graduate study on the order of a few thousand dollars each could produce a steady flow of new information about desert aquatic habitats. In order for this sort of research program to be effective, the funding must be on a 2- to 3-year cycle.

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Effects of Acid Rain and Air Pollution to Desert Parks

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Abstract. The cultural resources in NPS units in desert areas (where annual precipitation is less than 25 cm) (Figure 1) are for the most part associated with ancient indigenous cultures and the Spanish colonization. The materials range from relatively durable stone and masonry remains (e.g., masonry structures of stone and/or adobe, petroglyphs, pictographs, ceramics, lithics) to the more difficult to conserve organic materials (baskets, textiles, leather artifacts).

The role airborne pollution plays in accelerating the decay of these resources depends on several factors: the reactivity of the material type with the pollutant species, the exposure of the resource to the ambient atmosphere; i.e. the concentration of pollutants, the thermal environment, and the presence of moisture on the surface. Conventional wisdom identifies water as the primary culprit of materials deterioration; therefore, one should expect that from a broad perspective, resources in desert parks will weather more slowly than in more humid environments. On the other hand, in arid areas, other weathering agents, such as pollution, may play a relatively more important role in resource decay than in humid areas, because moisture as an agent of decay is limited. The quantity of pollution is an extremely important factor; compared to urban areas, concentrations of airborne pollutants tend to be as much as 50 times lower in the desert, and in comparison with areas east of the Mississippi, the precipitation tends to be less acidic, by perhaps as much as 1-2 pH units.

Chemical Susceptibility of Cultural Materials

Minerals

Stone weathering occurs by several processes: chemical, mechanical, and biological, and pollutants can alter the rate of these three weathering phenomena. Dragovich (1981) provides an excellent review of decay as it relates to the preservation of petroglyphs.

Some biological weathering agents use sulfur or nitrogen oxides as nutrients; thus the presence of pollutants provides a viable environment for bacteria and lichen growth; acids can be excreted

on to rock surfaces of cultural interest. Wetting and drying of lichen tissue on rock surfaces could be responsible for small scale flaking. (Meinke et al., 1990)

Pollution's role in mechanical weathering of rocks is to provide soluble salts (e.g., gypsum or calcium sulfate dihydrate, ammonia-bearing salts) which crystallize and re-crystallize within the pore structure, exerting pressure that weakens the stone matrix, and ultimately can lead to spalling and exfoliation (Roth, 1968; Schumm and Chorley, 1978; Cooke and Smalley, 1968; Wellman and Wilson, 1965). The various forms of hydrated and anhydrous calcium sulfates are widely occurring in desert environments. Cooke and Warren (1973) propose a weathering mechanism that involves sulfate deposition to the rock surface, followed by slow hydration at high desert temperatures, which is followed by sudden wetting, such as from condensation, causing rapid hydration with produces tensile stresses within the rock matrix.

Perhaps the most direct effect of pollution is to provide reactants to the chemical weathering process. Sulfur oxides and nitrogen oxides react readily with carbonate minerals, forming alteration products, which in most cases, are much less resistant to weathering than the original mineral. Hydrogen ion (or acidity) substantially increases the solubility of carbonate minerals (Figure 2; Plummer et al., 1979). Silicate minerals are far less reactive with acids than carbonate minerals (Figure 3; Loughnan, 1969). However, hydrogen ions released through the hydrolysis of silicate minerals can easily penetrate and disrupt the charge balance of crystal lattices because of their high charge:radius ratio. At above ambient concentrations, acids can etch quartz, which results in a frosty appearance but relatively insignificant chemical or physical change.

The reactivities and mobilities of iron, manganese, and other pigmenting chemical species (either naturally occurring as in desert varnish or man-made pigments as used in pictographs) with pollutants has not been extensively reported. However, inferences about domains of mineral pigment stability can be made from Figure 3 (Loughnan, 1969). Laboratory experiments and field surveys (Elvidge, 1979) indicate that manganese-based pigments form and persist under alkaline desert conditions, where the input of alkalinity exceeds the input of acidity in precipitation. Increasing acidic conditions on rock surfaces are likely to increase the mobility of the manganese ions, thus causing the pigment to erode or to bleed.

Organic Polymers

Most of the cultural artifacts made from organic polymers (textiles, baskets, leather and feather objects, and associated colorants) are generally exposed in indoor environments. As is beginning to be more fully understood (Brimblecombe, 1990; Cass et al., 1989), the indoor museum environment is not pollutant-free. Perhaps the most dramatic effect is the fading of pigments in the absence of ultraviolet light and in the presence of ozone (Cass et al., 1989). Ozone penetrates indoor spaces efficiently; and in the absence of activated carbon filters in the HVAC stream, interior concentrations are likely to be as high or higher than outside. Sulfur oxides can embrittle leather and feather materials, through chain scissoring of double bonds in the carbon chain. Nitric acid vapor is highly reactive with almost any type of surface. While nitric acid concentrations are thought to be low, their impact is relatively high in that the deposition process is highly efficient. Particles are of concern because of their potential reactivity (sulfates, nitrates), as well as the soiling from carbon- and crustal element-containing particles, which increases deterioration from increased cleaning/dusting requirements.

Table 1 summarizes potential effects on cultural materials of different pollutants.

Deposition Considerations in the Desert Environment

Nocturnal dewfall and frost are signatures of the desert environment. Figure 4 maps occurrences of frost; Table 2 lists representative temperature and relative humidity data for the southwest arid region. As the elevation increases and the temperature decreases, the ability of air to hold moisture decreases, and the probability of condensation increases (Figure 5). Nocturnal cooling, unmodulated by vegetative cover as occurs in other climates, causes the air to deposit its accumulated moisture on solid surfaces at ground level. As the salt content of the surface increases, its ability to extract moisture from the air also increases. Thus, the relative humidity at which water will condense from the air, is often less than that predicted by the curve in Figure 5.

The phenomena of dewfall and night frost may significantly enhance the impact of airborne pollutants on cultural materials. Soluble gases and particles, notably SO_2 and particulate $SO_4^=$, deposit much more efficiently to moist surfaces than to dry surfaces. Given the typical diurnal moisture cycle in deserts, exposed material surfaces are highly likely to be wet with dew or frost in the early morning hours. During this period, the stable nocturnal structure of the atmosphere breaks up, and upper air masses are transported to ground level through the warming action of solar radiation. If pollutant plumes are present in the air aloft, then the sulfur oxides will be delivered to the material surfaces, which if wet with condensation or frost, will readily take up the pollutant. In short, the presence of surface moisture in the early morning hours can maximize the effect of relatively small concentrations of pollutants, by enhancing the surface's ability to capture the airborne trace gases and particles.

The delivery of insoluble pollutant species (e.g., HNO_3 and neutral particles) is not affected by the presence or absence of surface moisture. The deposition of these species depends entirely on the concentration in the air and the aerodynamic conditions of the exposed cultural resource.

Another aspect is deposition of pollutant species to dry surfaces that are moistened by nocturnal moisture deposits. Depending on the level of antecedent deposition, it may be possible to generate pockets of highly concentrated acidic conditions by adding a small quantity of moisture to a relatively large quantity of acidic species.

The microclimate of caves and caverns, which can contain structural ruins and artifacts, is more moderate than the surrounding atmosphere (Dragovich, 1981; Dolske and Petuskey, 1987). The temperature variations are substantially less, and the probability of condensation reduced. Thus, deposition of gaseous pollutants from the atmosphere is less likely to affect these resources. The presence of a water source within the cavern would serve to enhance deposition of pollutants, and perhaps to increase salt weathering, depending on the humidity of the cavern air and the hygroscopic character of the masonry salts.

Field Measurements of Pollutants and Sandstone Erosion at Mesa Verde National Park

Aerometric and sandstone erosion measurements have been made at Spruce Tree House Ruin in Mesa Verde National Park from 1985-1987. Sulfur dioxide, particulate sulfate, and total nitrate (gaseous and particulate) levels were measured over weekly periods using filter-pack techniques (Dolske and Petuskey, 1987). The researchers report levels ranging from about 20

nanograms/cubic meter to 680 ng/m^3 for sulfur dioxide and 20-250 ng/m^3 for total nitrate. These levels are quite low, in part because the copper smelters which encircle the park were not in high level production during the study period. Precipitation acidity for the study period averaged pH 4.4 on an annual basis.

The erosion rates measured on the sandstone blocks within the protected area of the cliff dwelling were essentially zero; for the test wall exposed to rain and snow, erosion rates on the order of .2 - 1 microns/year. The researchers concluded that while the sandstones in the Mesa Verde locale were susceptible to chemical attack, the stones selected by the Anasazi for use in building the cliff dwellings represent some of the most chemically resistant materials in the area. They speculate that the ancients preferential selection of stones with desirable fracture properties resulted in selection of chemically resistant material.

Summary

Stone and artifact weathering occurs in desert areas. In the case of cultural resources carved into native stone surfaces, weathering processes (erosion, salt weathering, pigmentation loss) are irreversible, but relatively slow, although the rates can be accelerated by pollutants. Cut stone, built into walls and free-standing structures, experiences thermal stresses. The relative moisture cycles (and hence deposition, erosion, and salt weathering rates) between stone in outcrops and stone in structures depends to a large extent on the proximity to groundwater and the degree of exposure to the open sky, which tends to increase condensation.

Management actions to assess the potential problem include: mapping of stone types, ranking in sensitivity as calcitic sandstone, limestone, siliceous sandstone, or granites. White mineral pigments may be subject to accelerated deterioration from sulfur oxides and atmospheric acidity; iron pigments may change color or mobilize, depending on the acidity of the surface environment. Rock art documentation is recommended. For organic materials, appropriate storage (with desiccatants if needed) is an appropriate management strategy. Consideration should be made to install filters and/or ventilation systems if ozone/nitric acid levels are documented to exceed background levels, where collections include pigmented textiles and baskets.

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TABLE 1: Resource decay processes in which pollutants can play a role

Precipitation Acidity:

- o increased weathering of carbonate or clay containing rock types
- o potential mobilization of desert varnish
- o erosion of mineral pigments

Sulfur oxides (either gaseous or particulate):

- o increased weathering of carbonate or clay containing rock types
- o salt weathering of sandstones and limestones
- o potential discoloration of desert varnish
- o discoloration of mineral pigments
- o embrittlement of leather

Nitrogen oxides (either gaseous or particulate):

- o increased weathering of carbonate or clay containing rock types
- o salt weathering of sandstones and limestones
- o fading of vegetable pigments
- o loss of strength of textile fibers

Ozone:

- o fading of vegetable pigments
- o loss of strength of textile fibers

Organic acids are suspected to play some role in deterioration of both stone and organic materials, but the evidence is at present weak.

TABLE 2: Temperature and Moisture Data from Arid Regions in the Southwestern US

	TEMPERATURE Max/Min/Avg	MOISTURE Rain/RH 5am ann.avg/max.mo.avg.
Yuma, AZ	89/59/74	3"/47%/55%
Tucson, AZ	81/54/68	11"/52%/66%
Winslow, AZ	71/40/55	7"/63%/79%
Flagstaff, AZ	61/30/46	18"/73%/78%
Phoenix, AZ	85/53/69	7"/53%/68%
Reno, NV	68/31/50	7"/77%/83%
Las Vegas, NV	80/53/67	4"/41%/61%
Albuquerque, NM	69/44/57	8"/57%/69%
Clayton, NM	67/40/53	14"/68%/79%
Roswell, NM	77/40/59	12"/69%/82%

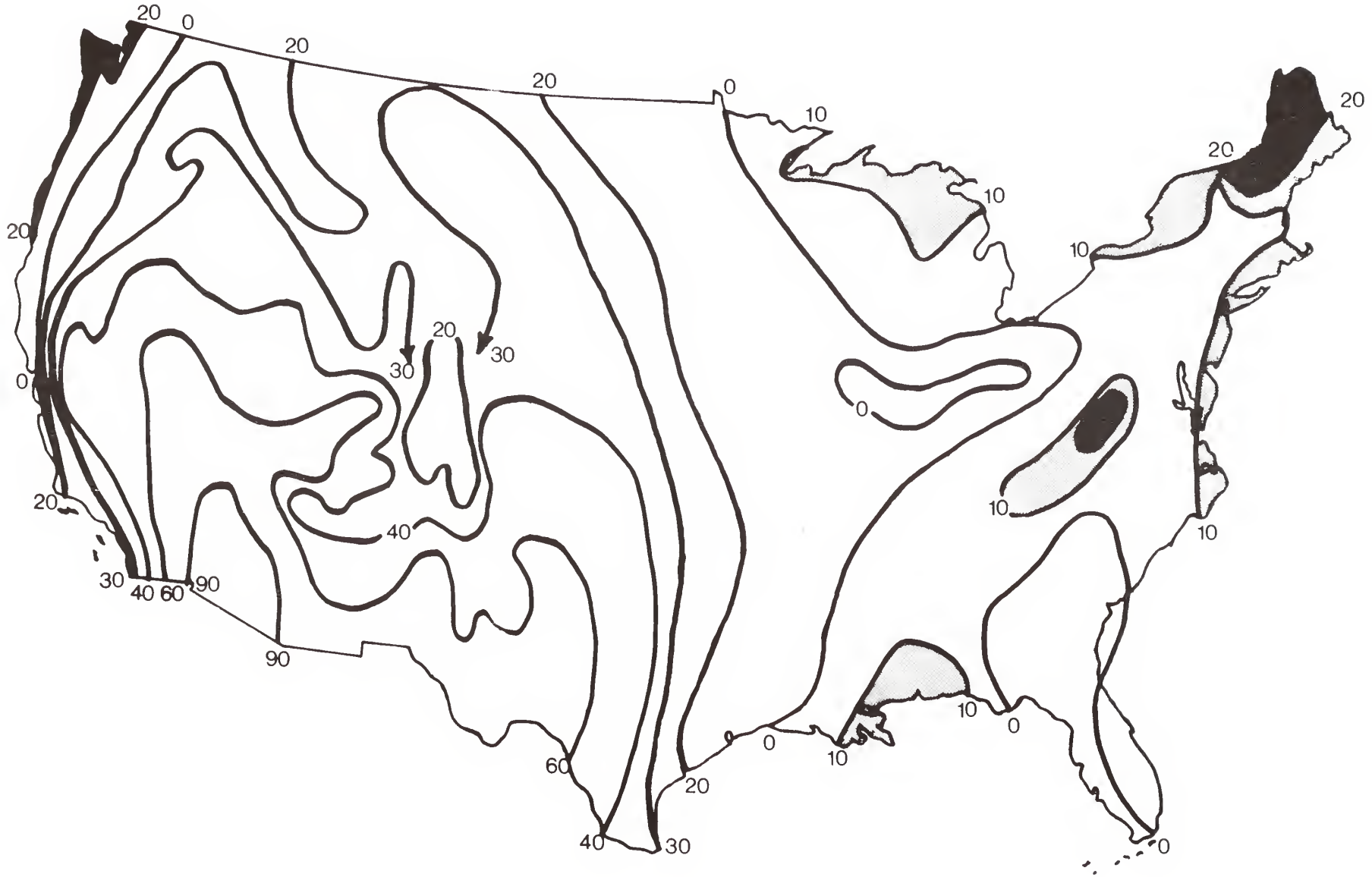


Figure 1. Differences between annual average precipitation and evaporation. Evaporation in excess, horizontally lined; precipitation in excess, vertically lined; in inches.

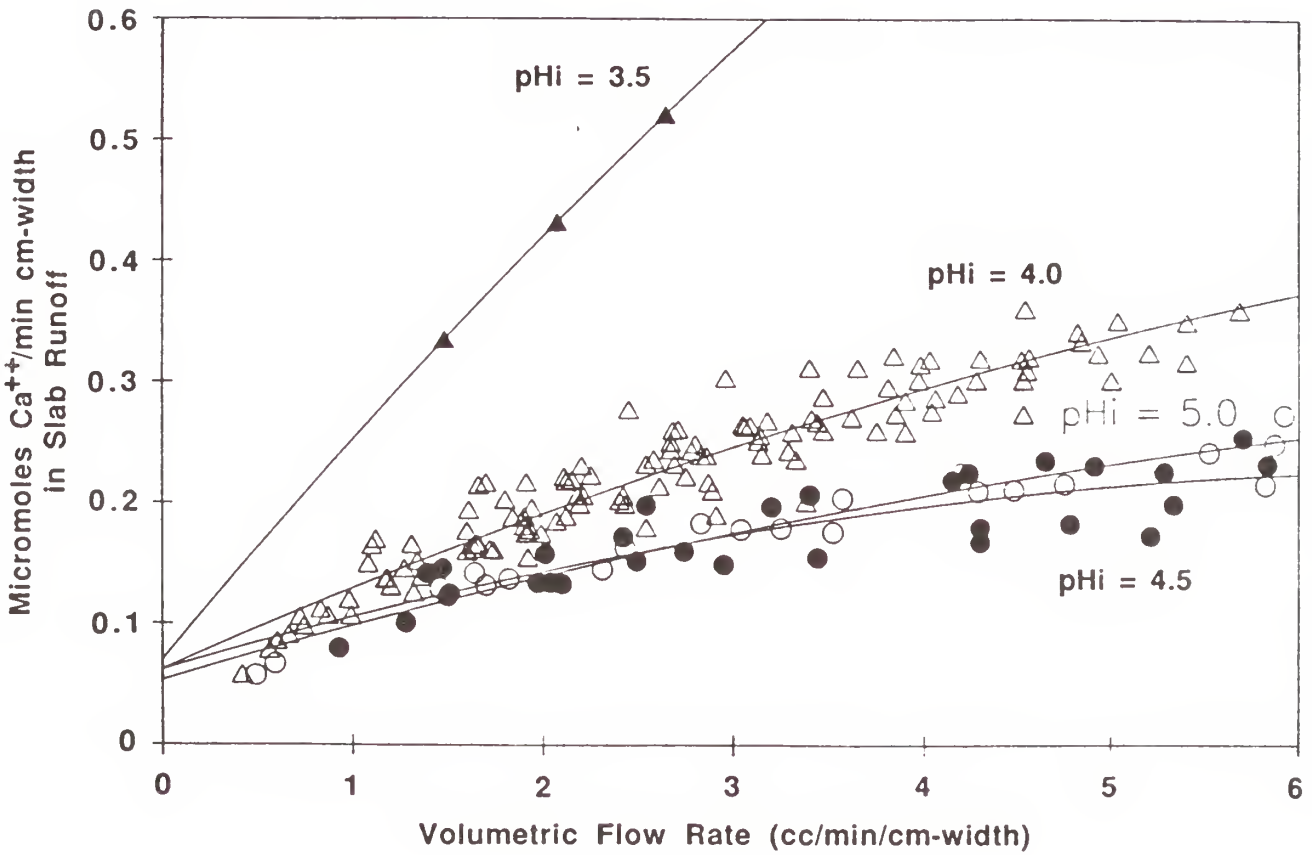


Figure 2. Calcite dissolution rate as a function of pH calculated using Plummer et al. (1979) forward rate constants. Solid curves represent overall rates: A for log $^{P}CO_2$ = -3.5 atm; B for log $^{P}CO_2$ = -1 atm. (Langmuir et al., 1989).

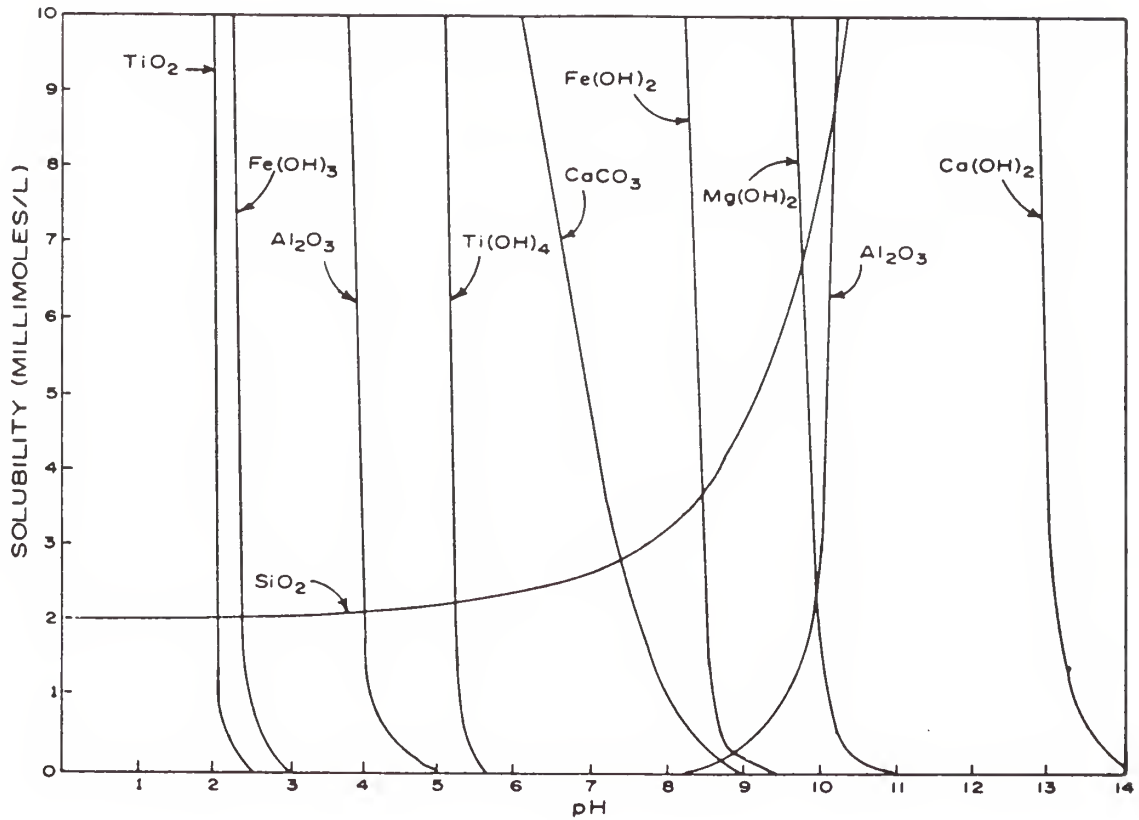


Figure 3. Solubility in relation to pH for some components released by chemical weathering.

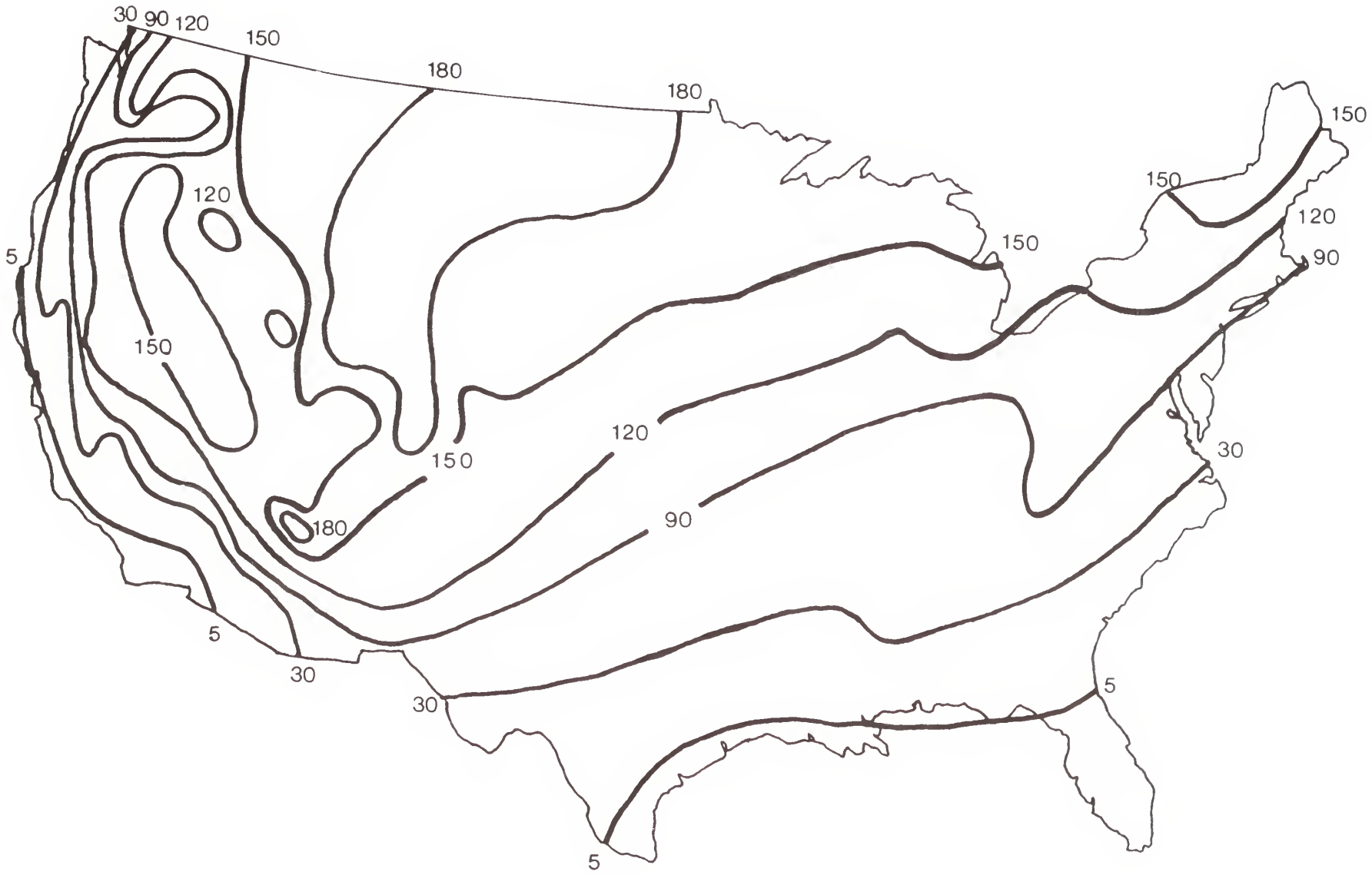
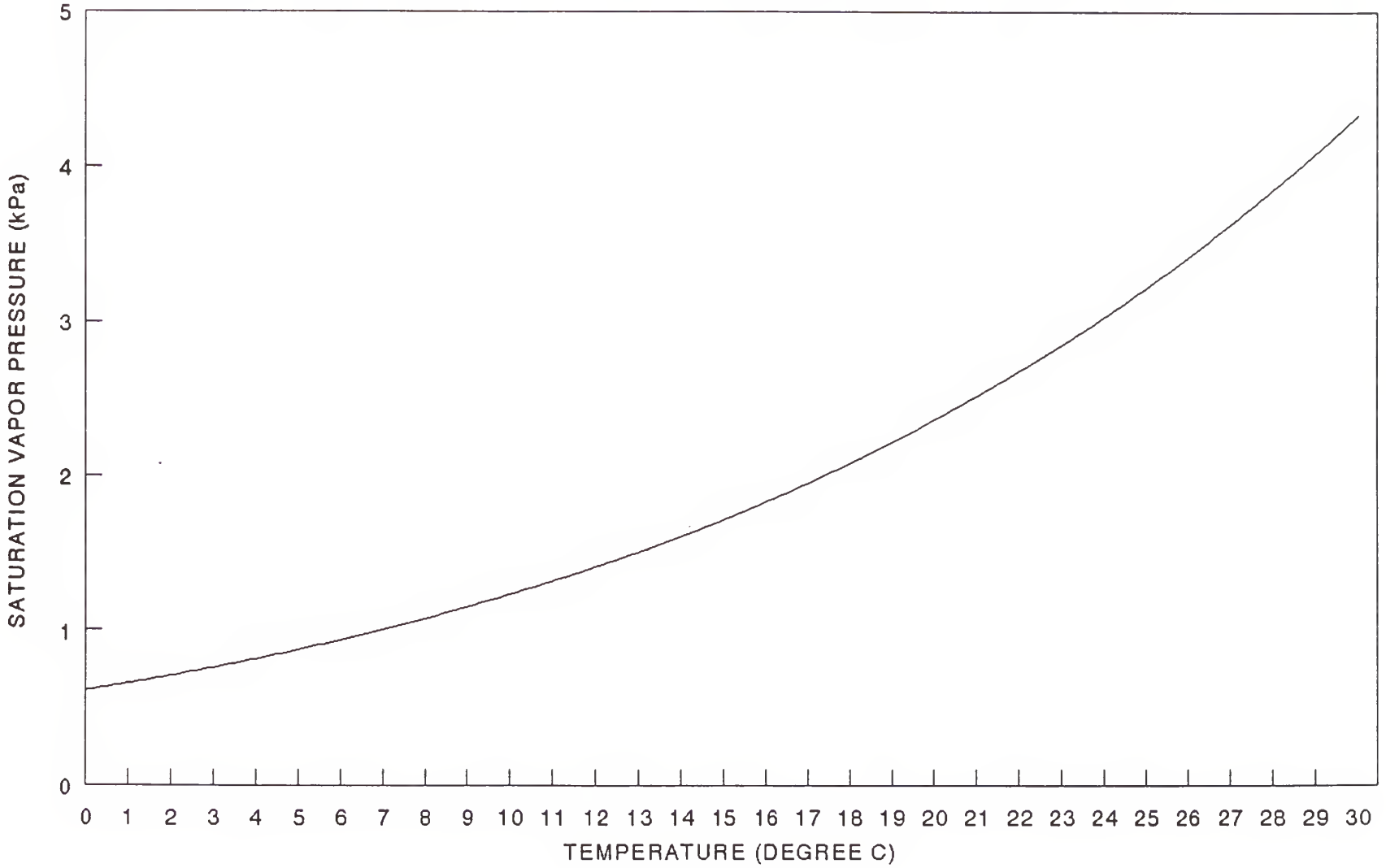


Figure 4. Frost at night, average number of times per year

FIGURE 5. SATURATION VAPOR PRESSURE VS. TEMPERATURE



Ways to Use Air Pollution and Acid Rain Information

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Abstract. We can collect all of the information we want on pollutants and their effects on park resources. However, unless we use the information to reduce existing pollution, or stop proposed pollution sources, the information has not helped us preserve and protect our park resources. This paper discusses ways in which the NPS can use air pollution and acid rain information to effect control of pollution sources, influence regulatory and policy decisions, and educate individuals about air pollution and its effects.

During this workshop we talked about pollutants that can affect the arid west, where they come from, and how they can degrade aquatic, cultural, and terrestrial resources. We need to use this information to protect our resources from existing and future pollution.

This paper will discuss how to use this information. Ways to use the information include: at the park level in park planning documents; at the local, state, regional, national, and international levels through such tools as land management/zoning decisions, affecting regulatory decisions and policy which control pollution sources, international agreements, interpretive programs, and informing people who make policy decisions.

First, we must collect good data. These data may form the basis for court hearings, testimony, setting standards, etc. As such, it must withstand the rigors of scientific and legal scrutiny. Experimental designs need to be peer-reviewed, and the results of the experiments should be published in peer-reviewed journals. Before spending time and money on collecting data, make sure the results will answer a question, and the experiment has been set up in such a way to yield useful information. The Environmental Protection Agency (EPA) will use the data in setting national standards only if it is published in peer-reviewed journals. For managers, this means that the project is not complete until the manuscript has been submitted for publication. For park scientists and technicians this means educating managers that the project should include time to write up the results and submit them to a journal, or one of the park publication series.

Air quality concerns should be addressed in park planning documents if it is an issue for your park. Such a plan will help to secure funding for air quality projects, and if the importance of air quality is included in park documents it can be used in federal, state, and local dealings to insure air quality. It is the responsibility of park staff to ensure that air resource management

is adequately addressed in NPS planning documents. It is much easier if enabling legislation or park management documents mention that air quality concerns are of primary importance. There are three main park planning documents which can be used to address air quality issues. These are the Statement for Management, the General Management Plan, and the Resources Management Plan.

The Statement for Management (SFM) is the first opportunity to address air resource issues. It is prepared by the superintendent and park staff. The SFM identifies issues, problems, and management objectives related to the park and is to be updated every two years. Sections of the SFM in which air quality issues may be addressed are: (a) the inventory and analysis of influences, (b) land uses and trends, (c) major issues, and (d) management objectives.

The General Management Plan (GMP) provides park-wide strategies for resolving issues and meeting management objectives over a 10- to 15-year period. The GMP is developed by an interdisciplinary team comprised of park, regional, Denver Service Center, and Washington office personnel. It is reviewed by the public and other agencies. The GMP does not address air quality issues in detail. The details are left for the action plans. Technical support is available from the Air Quality and Water Resources Divisions. While the details are not addressed, it is important to list air quality issues in the General Management Plan.

Air resource management issues can be addressed in detail in the Resources Management Plan (RMP). The project statements may address problems arising from air pollution. It is important to address air pollution issues in the RMP that are of concern to your park because funding requests are based on the issues listed in this document.

Many small sources of pollution will never come to the attention of the Air Quality and Water Resources Divisions. The park can influence local land use and land zoning decisions, if the park has information to bring to public hearings. By working with the developers of a housing project near Saguaro National Monument, the superintendent got concessions that will ease the impact on the park. County commissions and commissioners need to be informed of the effects of their decisions. Staff of Sequoia National Park testified at hearings in Hanford on the effects of a proposed coal-burning cogeneration facility. This involvement by park staff contributed to the defeat of this energy facility. By working with local groups, sources of local pollution can be reduced or eliminated.

Information collected by parks can be used by staff of the Air Quality and Water Resources Divisions in reviewing Environmental Impact Statements, and land use plans for agencies such as the Bureau of Land Management and the U.S. Forest Service. This information is also used to support EPA and states in setting air quality regulations.

The major tool we have to regulate existing and future sources of pollution is the Federal Clean Air Act (CAA). The goals of the CAA are to have safe and acceptable air quality through the attainment and maintenance of National Ambient Air Quality Standards (NAAQS). The CAA is implemented mainly through State Implementation Plans. The State Implementation Plan is most effective at addressing injury and impairment in Class II areas, and injury and impairment caused by existing sources, minor sources, multiple sources, and regional/long range transport of air pollutants. The AQD works with states on their plans, using data collected in local parks.

There are currently NAAQS for six criteria pollutants: sulfur dioxide, carbon monoxide, ozone, lead, nitrogen oxides, and total suspended particulates. Primary standards are designed to protect

human health, and secondary standards protect public welfare. Effects on vegetation, and other natural resources, fall under the secondary standard.

The Clean Air Act contains the framework for air pollution control in the United States. As such, it provides direction to federal, state, and local governments, as well as the private sector. It spells out both procedural and substantive requirements to assure protection of air quality and values that are dependent upon good air quality. The National Park Service is affected by the requirements of the Clean Air Act. NPS activities which generate air pollution may be subject to state, local, and/or EPA regulation. These regulated activities might include use of prescribed fire, construction and operation of a boiler within a park, or other activities which may directly or indirectly produce air pollution. In addition, the Clean Air Act establishes a strong air quality protection program for many national parks, national wilderness areas, and other special natural areas. As a part of this regulatory program, Congress stated that federal land managers, including the National Park Service, have "an affirmative responsibility to protect the air quality related values (including visibility) on any such lands..." Thus, not only is the NPS subject to regulations under the Clean Air Act, but the Service also has a key role to play in the regulatory process established under the Act which is designed to protect national parks, wilderness areas, and other lands.

The Clean Air Act establishes an interlocking set of federal, state, and local government responsibilities for air pollution control. The Environmental Protection Agency (EPA) must promulgate:

(1) National Ambient Air Quality Standards (NAAQS) - primary to protect public health; secondary - to protect public welfare (includes effects on natural resources),

(2) New Source Performance Standards (NSPS) - National emission control standards for new power plants, and new energy and industrial processes, and,

(3) National Motor Vehicle Emission Control Standards - National emission control standards for new cars, trucks, and buses.

States have primary responsibility for implementing and enforcing federally established air pollution requirements. However, where a state or local agency fails to adequately implement or enforce Clean Air Act requirements, EPA must step in and carry out those responsibilities.

The principal planning tool to achieve the federal standards is the State Implementation Plan, (SIP). The SIP must assure the timely attainment and maintenance of all federal air pollution control requirements. The public and other federal, state, and local agencies must be given the opportunity to provide input on the proposed SIP.

After preparing its SIP, each state must submit it to EPA for review and approval. If EPA disapproves it, the state must revise and resubmit the plan to EPA. Once a SIP has been approved, it becomes enforceable by EPA and by federal court as if it were part of federal law. Moreover, if at any time the state or local agency fails to adequately enforce the plan, EPA is required to step in and enforce it.

The importance of the SIP is two-fold. First, it is a state-prepared document describing how federal regulations will be applied within that particular state. If an interested party, including the federal land manager (FLM), wants a particular provision included to protect resources

within a park, that requirement must be included in the SIP. Second, once a requirement is included in a SIP, it is considered to have the force of federal law. Therefore, if NPS lands are to be protected from air pollution damage, requirements for the protection of air quality related values within an NPS-managed area must be included in the SIP.

One of the most important pathways for National Park Service involvement in the air quality regulatory activities is through participation in states' SIP development and review processes. NPS personnel can review proposals and plans, but can also provide research and monitoring data. During SIP development and revision, the NPS should become involved in public hearings held by the state. When the EPA reviews a SIP, the NPS can: (1) review and comment on EPA's revisions to the SIP, or (2) and review and comment on EPA regulations proposed in place of disapproved state regulations. Lead technical responsibility for reviewing proposed state plans and plan revisions rests with AQD, with the final approval and filing of comments with the state or with EPA being the responsibility of the regional director. AQD staff need to work with park staff to evaluate the effects of proposed regulations on the air quality of that park.

The Clean Air Act Amendments of 1977 established a program to prevent any significant deterioration of air quality in clean air regions of the country. The requirements of the "Prevention of Significant Deterioration" (PSD) program are designed to protect air quality in relatively unaffected regions.

The PSD rules establish a classification system for the areas of the country, designated as class I, class II, or class III. This classification is not a measure of the present quality of the air in an area, rather it indicates the additional "increment" of air quality degradation that will be allowed in that area. Thus, a class I area generally is to be subjected to only a very small addition of new pollution and a class II area to a moderate amount, while the class III increments provide for substantial air pollution increases.

The PSD rules generally are applicable only to major new or expanding facilities seeking to locate or expand operations in clean air areas. The program is implemented through the PSD new source review process, a preconstruction review and permitting program. Of particular relevance to the NPS are those provisions of this program relating to the federal park and wilderness areas which have been set aside for their natural, scenic, recreational, or historic values, since these values may be affected by air pollution. Any facility seeking a new source permit for location or expansion in a clean air area has several "standards" or "tests" which it must meet. Such a proposed facility cannot violate: National Ambient Air Quality Standards or Prevention of Significant Deterioration classes I, II, and III air pollution increments.

When a air pollution source wants to expand or when a new source wishes to locate in a clean air area, regardless of whether it is class I, II, or II, that source must receive a permit from the state. The permitting authority examines the plans for the facility, its proposed location, general design, projected air pollution emissions, to determine whether it (along with other emitting sources located in the area) will likely cause either the national ambient standards or the PSD increments to be exceeded. During this review process, the law requires the permitting authority to consult with the federal land manager whenever emissions from a proposed new source may adversely impact a class I area. The law also requires the federal land manager to exercise his "affirmative responsibility" to assure that the emissions from the proposed facility will not adversely affect the special air quality related values of that area. The AQD staff reviews these applications to determine the impact on the NPS unit involved. It is at this point that information collected in the parks, and relevant effects data collected in similar areas are used

to determine the impacts of the proposed source on resources of the NPS unit. These data must be of sufficient quality to withstand court scrutiny.

Air Pollution and Desert Systems at Risk: The Susceptibility of Pothole Ecosystems on the Colorado Plateau to Acid Deposition

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Abstract. Potholes are ephemeral rain pools in rock. These pools contain an aquatic fauna unique to temporary environments. Some species found in potholes are related to organisms that have been shown sensitive to reduced pHs. The ability to neutralize added acids, or buffering capacity, is low in potholes. These qualities indicate that potholes may be at risk from acid deposition. Results from this study show that while pothole water has low alkalinity, sediments in the basins have buffering capacity that can be mobilized to neutralize added acids. More study is needed to determine the extent of this buffering. Chemical analyses of pothole water in and near Arches National Park show little evidence of pollution. These findings indicate that pothole ecosystems studied are not at risk from acid deposition at this time. Pools nearer pollution sources on the Colorado Plateau, and potholes in non-calcareous rocks, should be studied to determine if these systems are good candidates for biomonitoring.

Introduction

Acid deposition in the arid Southwest has received little attention in the past for a number of reasons. Sources of acidic pollutants are not as concentrated as in the eastern United States. Pollutants were thought to be diluted and dispersed during scarce and infrequent precipitation events in deserts. The alkaline soils of the Southwest have high buffering capacity, and most surface and ground waters are alkaline (Roth et al., 1985). Any acidic deposition in the Southwest was thought to be quickly neutralized, preventing damage to desert organisms.

These generalizations do not hold for all ecosystems in arid and semi-arid parts of the Southwest. Acidic pollutants may actually accumulate over time via dry deposition. During a small precipitation event, the resultant solution could be much more acidic than the rainfall itself.

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Specific desert systems (e.g., potholes, cryptogams, desert mountain aquatic systems) may not have the buffering capacity of surrounding rock and soil, and thus may be at risk to damage from acid deposition.

The Southwest is dotted with power plants and industrial facilities that add pollutants to the atmosphere. The Colorado Plateau region, of particular interest for this study, is surrounded by coal- and oil-fired power plants (Figure 1), and new sources are likely over the next 20-50 years. Wind patterns carry air masses from industrial areas (e.g., Southern Arizona and Mexican smelters, the Los Angeles Basin, etc.) across the Colorado Plateau (Malm and Joseph, 1985). NADP stations on or near the Colorado Plateau (Figure 1) have recorded pHs of less than 5 for many weekly precipitation averages in the past eight years, the lowest being 3.84 at Mesa Verde National Park for the week of 30 August 1983 (NADP/NTN, 1989).

Aquatic organisms are particularly susceptible to decreased pHs (Arvola et al., 1986; Ormerod et al., 1987; Pierce and Sikand, 1985; Weatherley and Ormerod, 1987). Research on sensitivity to acid deposition should include studies of aquatic systems predicted to be at risk. Biomonitoring can then be used to indicate changes in precipitation chemistry.

Potholes are depressions in bedrock that are not in active drainages. Precipitation collected in these basins creates small, ephemeral aquatic environments. These pools contain fauna unique to temporary aquatic systems. Some organisms inhabiting potholes are related to species known to be sensitive to decreased pH (Sprules, 1975; West, 1980; Schindler and Turner, 1982; Eilers et al., 1984; Keller and Pitblado, 1984; Pierce and Sikand, 1985; Stokes et al., 1989). Alkalinity measurements in potholes have generally been low. Changes in pH would be more rapid in potholes in response to acid rain than in other aquatic systems in the Southwest. For this reason potholes are good candidates for biomonitoring acid deposition rates in the Southwest.

A study was initiated in 1988 to answer some of the questions concerning sensitivity of pothole ecosystems to acid deposition. Research focused on two areas: basic ecological questions of pothole species, community structure, and ecosystem functioning, and sensitivity of pothole species and systems to acidification. Acid sensitivity studies included three areas: 1) sensitivity of individual species' reproduction to low pH, 2) bioassays of pothole organisms to determine whether any species can be used as biomonitors, and 3) in situ acidification of potholes. Chemical analysis of precipitation collected in potholes was conducted periodically during the study. Potholes included in the study are in Navajo Sandstone in Arches National Park, and Grand Resource Area, Moab District, Bureau of Land Management, Utah.

Ecology of Potholes

Few studies have been made of pothole ecology on the Colorado Plateau (Romney, 1971; Findley, 1975; Dodson, 1987). Environmental tolerance ranges are unknown for most species inhabiting Colorado Plateau potholes, as are hatching and mating cues. Little is known about determinants of community structure, what drives ecosystem functions, or what roles potholes play in surrounding terrestrial ecosystems. Before we can assess the impacts of air pollution on potholes, we need to learn more about the basic ecology of pothole species, communities, and ecosystems.

Characterization of pothole basins and communities were conducted in 1988. Over 120 potholes have been examined, and more than 80 were used in parts of this study. Surface areas and volumes were estimated, and surface area/depth and surface area/volume ratios calculated to

categorize the physical environment of the basins. Pool size (=longevity) has been reported to structure pothole communities (Dodson, 1987). The range of volumes are shown in Figure 2.

Species composition was determined periodically during 1988 in a qualitative manner. Quantitative sampling was done in 1990. Season and random precipitation patterns appeared to be the primary factors influencing occurrence. Some groups, such as copepods and the ostracod Cypridopsis sp., were present in great numbers in May and early June, but were absent from the same pools in the summer. They reappeared in late September or October, 1988. Copepods were present in fall of 1989 and 1990, but Cypridopsis has not been observed since 1988. Aquatic insects were generally less common in 1988 than in previous years.

Community respiration/production was measured in 1989 in a few pools by measuring dissolved oxygen at dusk-dawn-dusk for three days. Smaller pools appeared to be heterotrophic (O_2 content dropped over time), while larger pools experienced an increase in O_2. Precipitation was too low to repeat this experiment using more pools to test the generality of the 1989 results.

Sensitivity of pothole species and systems to acidification.

Potholes appear to be more susceptible to acid deposition than most desert aquatic systems (Dodson, 1991). Effects of low pH on ephemeral rock pools should be studied now, as these will probably be among the first systems affected by increasing pollution levels in the Southwest. Pothole communities and/or individual pothole-dwelling species may make good biological indicators of increased acid deposition. In order to use these systems in this capacity we need to know how they respond to lowered pHs.

A. Sensitivity of individual species' reproduction to low pH. Response to lowered pH varies among species, age classes, and type of response (Bell, 1970, 1971; Schindler, 1980; Confer et al., 1983; Pierce, 1985, 1987; Watras and Frost, 1989). Adults of many aquatic species may be able to tolerate quite low pHs, but reproduction and/or larval development may be seriously affected at higher pHs (Hendrey et al., 1976). Studies of impacts of acid deposition should include efforts to determine the effects of lowered pH on egg production, fertilization, egg hatching, and larval development.

   Eilers et al. (1984) state that amphibians, mollusks, and leeches are groups that are most sensitive to acid conditions. Amphibian egg and larval development at low pHs were examined to determine the sensitivity of these stages to acidification. Because toads and frogs use external fertilization, both sperm and eggs are exposed to low pHs in acidified waters. Thus, there is a greater opportunity for impacts of low pH on reproduction in amphibians (Pierce, 1985). The opportunistic breeding behavior of the species inhabiting potholes (Bufo punctatus and Scaphiopus intermontanus) makes it almost impossible to examine the effects of low pH on fertilization itself. Studies were conducted on the effects of acid on hatching of fertilized eggs, and on early larval development.

   Hatching success of ephemeral pool crustaceans in acid solutions was studied by adding different H_2SO_4 solutions to dry pothole sediment. Numbers of tadpole, fairy, and clam shrimp, and ostracods were counted after 24 hours. Results indicate a trend toward reduced hatching at lower pHs. Fairy shrimp and tadpole shrimp showed the strongest response. Clam shrimp and ostracods hatch more slowly, and it was difficult to get enough of these taxa to generate a pattern of sensitivity or resistance.

Response of these species to acid solutions is affected by interactions between solution and sediment. Acid solutions used in the hatching experiments were buffered by the sediment--pH of solutions increased by as much as 2 pH units in 5 hours (Graham, 1990). Buffering occurs within the time that hatchlings were first observed in the above experiments. I do not know whether the weak response to the acidic solutions is due to rapid buffering, or because these species are relatively acid tolerant. Experiments are needed where the pH remains constant at each treatment level.

The sediment-solution reaction appears to provide a measure of protection for pothole systems from acid deposition. Acidic precipitation falling on potholes in Navajo Sandstone would probably be buffered before organisms became active and thus susceptible to lowered pH conditions. Additional work is needed to determine the mechanism involved in the buffering interaction. A cation and anion analysis of pothole sediments should show what chemical species could be acting as buffers.

B. Bioassays of pothole organisms to determine whether any species can be used as biomonitors. Sensitivity to increased acidity can be very precise for many aquatic organisms (Eilers et al., 1984). Monitoring presence/absence, population shifts, and/or shifts in community structure of sensitive species can be used to indicate degradation of the pothole environment. Bioassays can determine which species will make good biomonitors (Cairns, 1983; Kimball and Levins, 1985).

Considerable work has been done on sensitivity of aquatic species in eastern North America (e.g., Schindler, 1988; Stokes et al., 1989; Vangenechten et al., 1989), but little has been done in western North America (Roth et al., 1985; Corn et al., 1989; Harte and Hoffman, 1989). Three types of bioassay studies of pothole organisms will be done: a) LC_{50} tests of adult crustaceans and snails, b) LC_{50} studies of crustaceans, using newly hatched larvae, and c) measurements of metabolic heat production by pothole inhabitants under different pH conditions in a microcalorimeter.

1. Bioassays of adult crustaceans and snails will be done to determine LC_{50} pH levels for each of the major macroinvertebrate species in potholes. These studies will provide information on how these species would be affected if an acidic precipitation event occurred after previous rains had filled the potholes, and the organisms had been active for a week or more. The pH gradually increases in a pothole over time after a rain. There is little chance that a precipitation event that occurred a week or more after initial filling would be acidic enough to drop the pool pH to the experimental levels (e.g., pH 5.0 or 4.5). These bioassays are useful, however, in determining which species are sensitive to acidic conditions. Some of these species (e.g., Bufo punctatus, Triops longicaudatus, Fossaria sp.) are common throughout the Southwest. The LC_{50} data can be used to identify potentially sensitive species in areas receiving more acidic precipitation and with less buffering capacity available in sediments and rock.

2. Similar bioassay studies will be done on newly hatched crustacean larvae, amphibian embryos and larvae, and gnat larvae. Many species show increased sensitivity to low pHs in early developmental stages (Pierce 1985, 1987; Schindler et al., 1985; Watras and Frost, 1989). In pothole systems, it would be possible for invertebrates to begin hatching, and amphibians to breed in response to a small rain event of normal pH, and then be inundated by a large volume storm dropping

acidic precipitation. This could drop the pH of the pool rapidly, affecting eggs and larvae of sensitive species. These studies will help identify species that are susceptible to acid deposition from such a scenario.

3. Measurements of metabolic heat production from pothole organisms in acidic solutions will be made. A microcalorimeter (Hansen et al., 1989) will be used to measure metabolic response of pothole organisms to reduced pHs. A slight shift in pH may not be fatal, but could stress the organism, affecting metabolic rate. One of three general responses is expected: metabolic rates will increase, decrease, or remain unchanged.

   The pothole environment has a short-lived wet phase. Pothole organisms must be able to survive the dry pothole environment in some way, and to develop rapidly during the wet phase to the stage that can survive the dry pothole (e.g., egg, adult leaves dry pothole, etc.). Metabolic rates of pothole inhabitants have not been measured, but it is predicted that rates for most species will be high because of the need to grow rapidly to complete life cycles before the pools dry up.

   Changes in metabolic rate in response to lowered pH can have drastic effects on reproduction. If metabolic rate is reduced, time needed to reach maturity and reproduce will increase, perhaps requiring more time than is available before a given pool dries up. An increase in metabolic rate could occur if the organism responds to damage from acidic water by repairing the damage. Metabolic activity and resources would have to go toward repairs rather than growth and reproduction, again increasing development time. Metabolic rate studies are needed, as are growth rate studies under different pH solutions.

C. In situ acidification of potholes. Behavior of species under controlled conditions may be quite different from responses under natural conditions (Cairns, 1983; Kimball and Levins, 1985; Likens, 1985; Brezonik et al., 1986; Carpenter et al., 1989). For example, Eilers et al. (1984) found in their extensive literature review that in laboratory studies minimum pH tolerances were one pH unit or more lower than field studies with the same taxonomic groups.

   To assess how pothole ecosystems respond to acidification, nine potholes were acidified, three each to pH 5.5, 5.0, and 4.5. Each pothole was studied for 6 days before acidification; pH, alkalinity, and temperature were measured at three locations in each pool three times each day, and pool volume and invertebrate populations were estimated once each day. Where possible, total number of tadpole shrimp were counted in each pool. An additional three pools were studied but were not acidified, to act as control pools. The same data were collected from all 12 pools following acidification until the pools dried up (four days).

   Potholes that were acidified had pHs return to near normal within 24 hours of acidification, probably as a result of buffering by sediment. Despite this rapid return to normal conditions, at least tadpole shrimp and fairy shrimp populations experienced significant mortality (Graham, 1990). Mortality of clam shrimp and ostracods was also observed, but significant differences between pre- and post-acidification populations were not measured. Dipteran larvae and pupae (Culicidae and Ceratopogonidae) did not appear to be affected by acidification.

Chemical analyses of pothole water collected shortly after rains fell in 1988 and 1989 have shown remarkably low levels of heavy metals and other elements that would indicate the air was not carrying a significant pollution load. These results, in conjunction with the finding that pothole sediment may play an active role in buffering added acids, may mean that Colorado Plateau potholes are not at a high risk from acid deposition at the present time. Further study is needed to determine the potential for future risk. Research is also needed to examine pothole ecosystems and communities in other National Park units, such as Glen Canyon and Lake Mead National Recreation Areas, which are closer to pollution sources (Navajo and Mojave Generating Stations, respectively), and Joshua Tree National Monument, where the pollution load is greater, and the buffering capacity may be lower because of different rock types.

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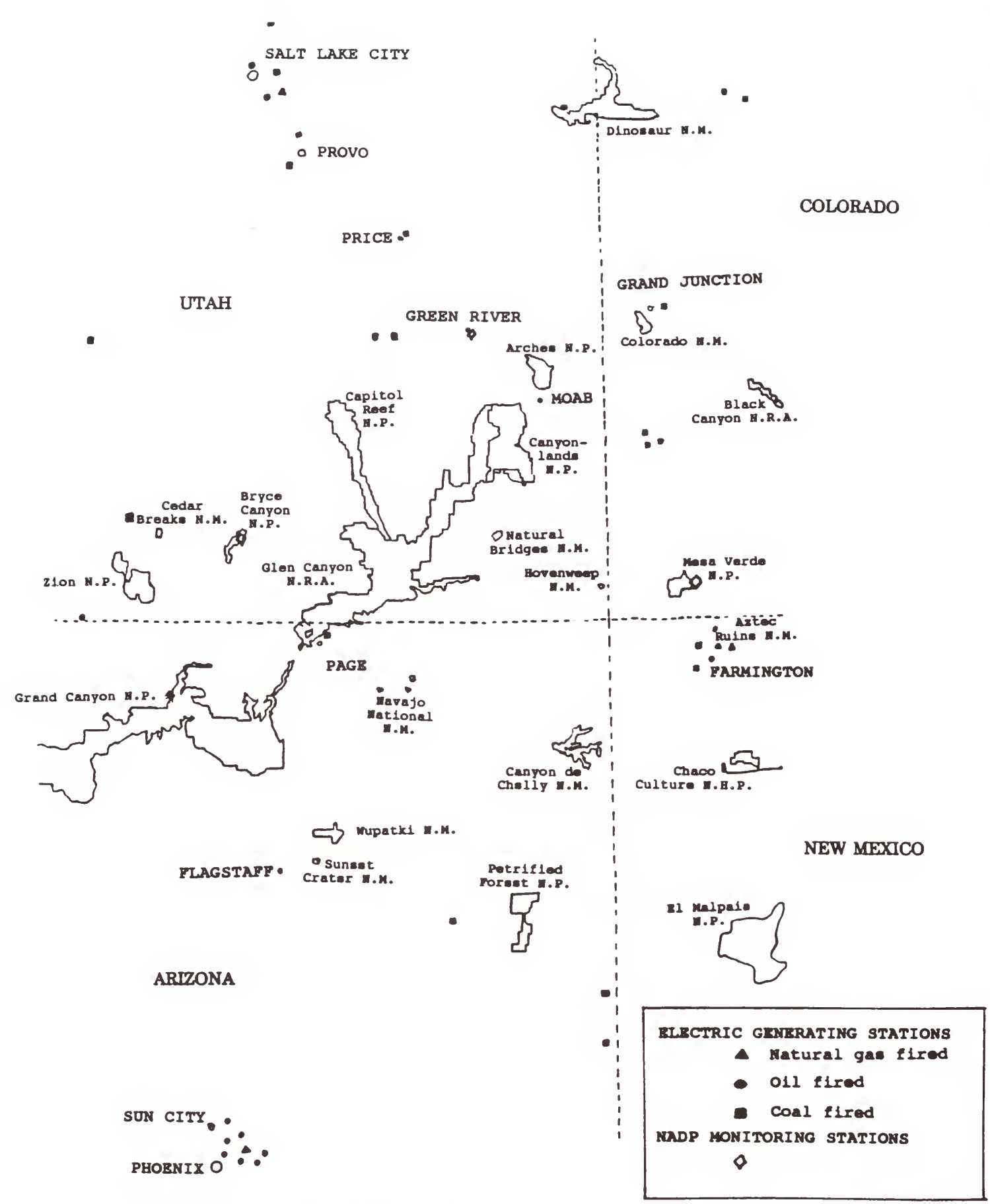

Figure 1. National Park Service units, electric generating stations, and NADP monitoring stations on or near the Colorado Plateau. Map information compiled by Jayne Belnap.

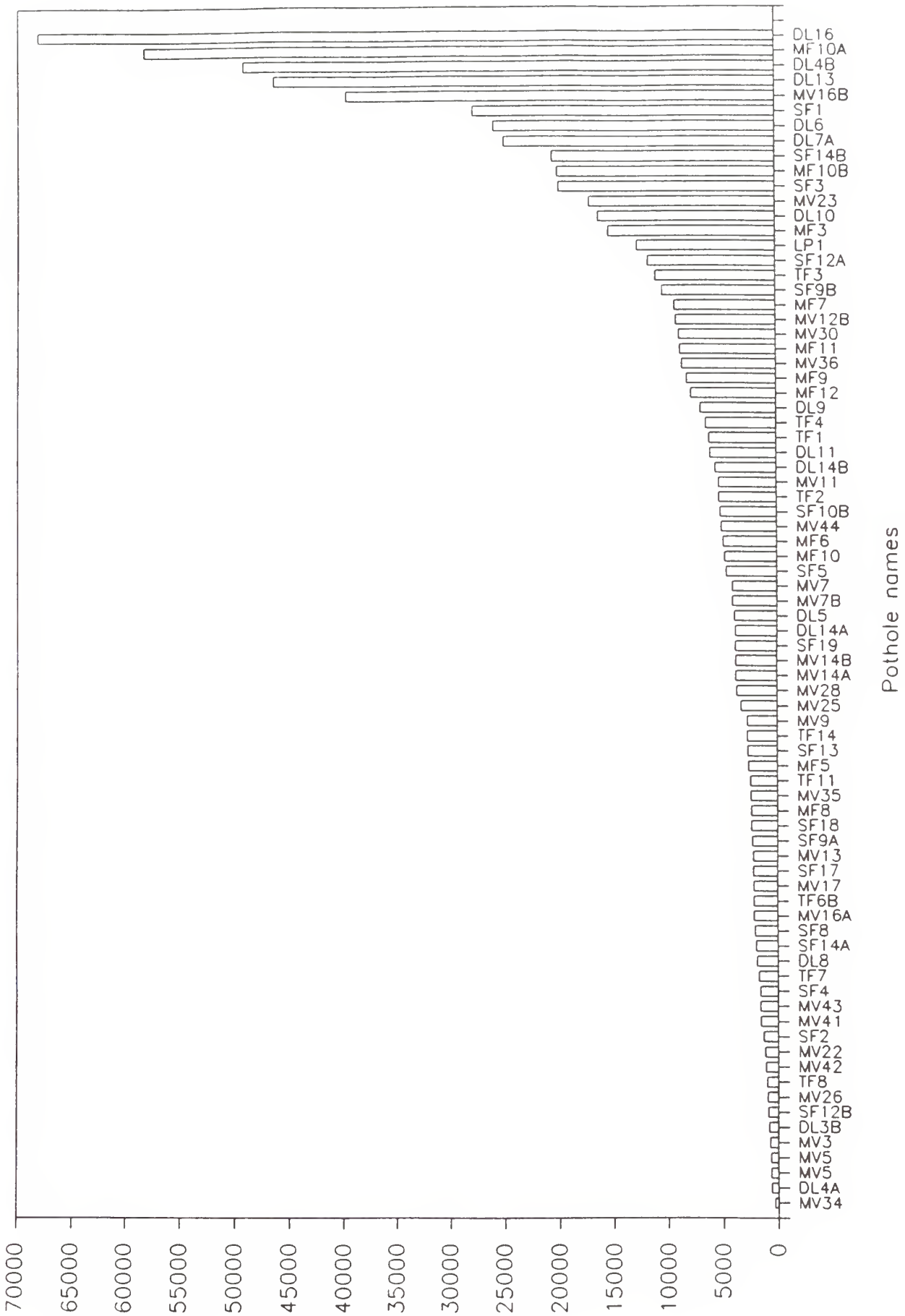

Figure 2. Estimated pothole volumes (liters) for 79 potholes in or near Arches National Park, Utah.

Sensitivity of Desert Cryptogams to Air Pollutants: Soil Crusts and Rock Lichens

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Abstract. Parks throughout the West are being faced with increasing air pollution threats from current or proposed industries near their boundaries. For this reason, it is important to understand the effects these industries may have on desert ecosystems. Rock lichens can be excellent biomonitors, acting as early warning systems of impending damage to other components of the desert ecosystem. Cryptogamic crusts, consisting mostly of cyanobacteria and lichens, may not only be excellent bioindicators, but also are an essential part of the desert ecosystem. Their presence is critical for soil stability as well as for the contribution of nitrogen to the ecosystem in a form available to higher plants. Air pollutants, such as emissions from coal-fired power plants, may threaten the healthy functioning of these non-vascular plants. The purpose of this study is to determine if, in fact, air pollutants do have an impact on the physiological functioning of cryptogamic crusts or rock lichens in desert systems and, if so, to what extent.

Some results have already been obtained. Both rock lichens and cryptogamic crusts exhibit physiological damage in the vicinity of the Navajo Generating Station in Page, Arizona. Increased electrolyte leakage and chlorophyll degradation, along with reduced nitrogen fixation, have been found. Preliminary studies comparing sensitivity between substrates indicate that crusts on limestone and sandstone substrates may be more sensitive than those on gypsum.

Introduction

Parks throughout the West are being threatened by ever-increasing pressures to locate polluting types of industries, such as coal-fired power plants, smelters and toxic waste incinerators, near their boundaries. For example, Zion and Bryce are located near the Intermountain Power Project, soon to be the largest coal-fired plant in the world, and the Allen Warner plant near Las Vegas. Glen Canyon National Recreation Area is adjacent to the Navajo Generating Station in Page, Arizona. Mesa Verde and Hovenweep are close to the Four Corners area, home of two very large, coal-fired plants. Parks in southern Arizona and California are threatened by urban

pollution and smelter activity. This situation makes it critical that the biological effects of such industries on desert ecosystems be evaluated, and that long-term monitoring efforts be initiated.

Non-vascular plants, most notably lichens, have long been used as indicators of air pollution (Ferry et al., 1973), especially those with fruticose growth forms. In the deserts of the Southwest, however, the majority of the non-vascular flora is crustose or foliose, forms generally regarded as more resistant to pollutants (Fenton, 1964; Nash, 1974). This, along with the aridity of the environment which results in less metabolically active time for the soil crusts and rock lichens, has led some researchers to conclude that desert species may not be as useful as indicators of air pollution (Marsh and Nash, 1979).

Field studies using non-vascular plants as indicators of pollutants have generally utilized species composition and/or cover values of lichens to measure pollution impacts (LeBlanc, et al., 1972; Marsh and Nash, 1979; Nash, 1974; Nash, 1975; Nash and Sommerfeld, 1981). No known studies have examined the effects of pollutants on soil crusts. If crustose and foliose species are more resistant to pollutants, it may be that in the arid West air pollution levels are not high enough or that the non-vascular plants are not metabolically active often or long enough to result in mortality. Nevertheless, the impacts may be enough to measurably impair physiological functioning of these crusts or rock lichens.

Cryptogamic soil crusts are found throughout the deserts of the world. They are especially well-developed in the deserts of the southwestern United States. These crusts are a very diverse microcosm, consisting of bacteria, green algae, cyanobacteria, microfungi and lichens, with cyanobacteria being the most prevalent component. These crusts play a vital role in the health of the desert ecosystem. Not only do they act to stabilize topsoil in an environment that combines otherwise loose sand with torrential rains, but they also contribute fixed nitrogen to a fairly nitrogen-poor system (MacGregor and Johnson, 1971; Snyder and Wullstein, 1973; Terry and Burns, 1986; Lynn and Vogelsberg, 1974). Rock lichens can be very sensitive biomonitors, acting as early indicators of impending damage to other components of the desert ecosystem. The purpose of this study is to determine the physiological sensitivity of desert soil crusts and some rock lichens found on the Colorado Plateau to air pollutants, as well as to assess their potential as biomonitors for these desert ecosystems.

There are three major areas of focus in this study: field transects, controlled fumigation studies, and documentation of some physiological baseline values in parks throughout the Colorado Plateau. Physiological measurements being used are chlorophyll degradation ratios (chlorophyll a to phaeophytin a), electrolyte leakage, and levels of nitrogenase activity (acetylene reduction). Elemental content of the lichens and crusts will be obtained as well. Three major crustal substrates found in parks on the Colorado Plateau will be examined: limestone from Bryce NP, sandstone from Canyonlands NP, and gypsum from Arches NP.

Field Transects

Field transects are located in the area surrounding the 2250 megawatt, coal-burning Navajo Generating Station near Page, Arizona. This power plant was chosen because of its proximity to Glen Canyon National Recreation Area. Transects run northeast of the plant, with sites located at increasing distances from the plant. Physiological measurements of rock lichens and soil crusts are being made at each site. Also, crusts will be transplanted from less polluted areas

(Canyonlands, Bryce and Arches NP) to these sites to be monitored for any long-term, physiological effects of being placed in the Page basin.

Some results from field transects have already been obtained. Rhizoplaca melanopthalma, a fairly common desert rock lichen, has been shown to exhibit significantly higher chlorophyll damage at sites near the Navajo Generating Station (7 and 12 km) when compared to sites further away (21 and 42 km). Degradation is calculated by the ratio of chlorophyll a (435 nm) to the degraded product phaeophytin a (415 nm). Consequently, a lower value for 435/415 indicates greater damage. Parallel results have been obtained for electrolyte leakage in this same lichen, with significantly higher leakage ($p < .001$) occurring at the closer stations than the two further out. Regression of chlorophyll degradation ratios and electrolyte leakage on distance from the plant is also highly significant ($r = .79$ and .92, respectively; $p < .001$: Fig.1 and 2). Electrolyte leakage values showed a much greater difference between sites near and those further removed from the Navajo plant than chlorophyll degradation, suggesting that electrolyte leakage may be a more sensitive measure of damage (Belnap and Harper, 1990). A similar conclusion was drawn by Fields and St. Clair (1984) when they compared methods of measuring SO_2 damage in lichens.

Nitrogenase activity in crusts and the lichen Collema tenax has also been measured at varying distances from the plant at three different times of year: mid-spring (March), early winter (November), and mid-winter (January). In March, nitrogenase activity in the Page basin was compared with values from Canyonlands NP and Grand Canyon NP. Activity within the Page area was an order of magnitude lower than that measured in Canyonlands and Grand Canyon ($F = 25.1$, $p < .001$, using analysis of variance and Duncan's multiple range test). In November and January, linear regression of site means on distance from the plant showed that increases in nitrogenase activity are significantly correlated with increases in distance from the plant ($p < .001$, Fig. 3; Belnap and Terry, in prep).

Weather factors may play an important role in influencing damage to the lichens. November through April are months with greater precipitation and lower temperatures than average (Sellers and Hill, 1986), generally resulting in longer periods available for photosynthetic activity in lichens since thalli would dry less rapidly (Nash and Moser, 1982), and winter daytime temperatures in the Page area are well within the range for photosynthetic activity in desert lichens tested (Nash and Moser, 1982; Kershaw, 1983; Nash et al., 1982; Lange, 1969). Winter months are also the time when ground fumigation events from the power plant are most likely to occur, given the greater atmospheric stability and the frequent temperature inversions experienced in winter in the Page basin during these months (Anonymous, 1975). These factors, combined with a greater relative humidity from Lake Powell that may increase time available for metabolic activity of lichens in this area, could result in greater of damage to lichens in the study area than at sites outside the Page basin.

It is not clear what pollutants are causing the observed damage. Coal-fired power plants are known sources of sulfur dioxide, nitrogen dioxide, and heavy metals. Exposure of lichens to sulfur dioxide and nitrogen dioxide have been previously implicated in degradation of chlorophyll (Garty et al, 1985; LeBlanc and Rao, 1973; Nash, 1976; Nash, 1973), reduction of photosynthetic rates (Pearson and Skye, 1965; Hallgren and Huss, 1975; Moser et al, 1982; Sheridan and Rosentreter, 1973) and electrolyte leakage (Fields and St. Clair, 1984; Henriksson and Pearson, 1981; Pearson and Rodgers, 1982). High concentrations of some trace metals have been shown to cause chlorophyll degradation, chlorosis, and reduced photosynthetic activity (Garty et al., 1985; LeBlanc and Rao, 1973; Nash, 1971, 1975). This study demonstrates that some particular

pollutant, or combination of pollutants, is affecting both chlorophyll degradation and electrolyte leakage, which may be a clue in pinpointing the causal agent.

Fumigation Chambers

Crusts were taken to dry fumigation chambers in Riverside, CA, where they were exposed for eight weeks. Treatments included ambient air, charcoal filtered ambient air with 95 percent of particulates scrubbed, ambient air with 95 percent of particulates scrubbed, and ambient air with 60 percent of particulates scrubbed. Preliminary results on the effects of dry deposition on these crusts indicate that while crusts on the different substrates seem to experience some fertilization effects, perhaps due to increased nitrates, chlorophyll degradation is significantly higher only on limestone substrates. Sandstone crusts were very close to demonstrating a significant amount of damage ($p = .06$). Gypsiferous crusts, on the other hand, showed a decrease in degradation when compared to controls. Metabolic rates were significantly higher on gypsiferous crusts than controls, while sandstone and limestone crusts showed increases that were not statistically significant. It may be that gypsum is able to buffer the effects of the pollutants more effectively than the limestone or sandstone. These treatments will be repeated, and the effects of wet deposition on crusts and rock lichens will be examined.

Efforts so far have answered some questions, and raised many more. The more pressing ones center around obtaining a more complete picture of the types of damage being done to lichens and cyanobacteria around the Navajo Generating Station. It would be of great value to examine other non-vascular plant species to see if, in fact, the observed damage to Rhizplaca melanopthalma and cryptogamic crusts is prevalent throughout the non-vascular plant community, and if other species in the area could act as even more sensitive biological monitors. Another important area of inquiry would be an examination of which pollutants are responsible for the damage observed, using chronic low levels of fumigation in controlled chambers.

Continued efforts in these directions give us an excellent opportunity to obtain information relevant to the management of public and private lands throughout the desert Southwest. This information is critical in providing land managers a basis from which to make informed decisions regarding on-going or proposed activities that would affect public lands, as well as to provide data with which to evaluate the alternatives and options presented.

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Table 1. Electrolyte leakage values and chlorophyll degradation ratios for Rhizoplaca melanopthalma at different distances from the Navajo Generating Station. Differences between means was analyzed using Duncan's multiple range test.

SITE NO.	DISTANCE FROM PLANT (km)	ELECTROLYTE LEAKAGE (umhos/mg/ml) x ± S.D.	OD 435/415 (nm) x ± S.D.
1	7	1.38 ± .89 a	0.794 ± .100 a
2	12	1.24 ± .20 a	0.715 ± .061 a
3	21	0.17 ± .09 b	0.957 ± .144 b
4	42	0.13 ± .17 b	1.07 ± .039 b
5	225	0.28 ± .17 b	

*a: Values are significantly different from sites 3, 4, and 5 in the same column at the .01 level
*b: Values are significantly different from sites 1 and 2 in the same column at the .01 level

A History of the Air Quality Program at Saguaro National Monument

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Saguaro National Monument, with 71,400 acres of legislated wilderness, is a mandatory Class I airshed. This area was established in 1933 to protect lands "...of outstanding scientific interest because of the exceptional growth thereon of various species of cacti, including the so-called giant cactus...". An interpretive slide program and video on air quality have been produced by the staff at the Monument. These programs provide an education for visitors on the need for preserving air quality to protect NPS resources.

The history of air quality monitoring in the monument goes back to the years 1975 through 1977 when some short-duration monitoring for ozone and sulfur dioxide was carried out (Hutchinson et al., 1984). An inventory was done to evaluate integral vistas as part of proposed visibility impairment determination (Coss, 1980). Photos taken in 1982 revealed a smoke plume entering the monument through Reddington Pass, which lies some 12 miles northeast of the visitor center in the Rincon Mountain District. The most probable source of this plume was a copper smelter located approximately 30 miles from the monument's boundary.

The Pima County Air Quality Control District began a three-month monitoring project for ozone in June, 1982. This monitoring was to determine summer ozone levels to make an assessment of the effect of this pollutant on the Class I airshed. Nighttime ozone levels in the monument were higher than those found at any other monitoring station in the Tucson metropolitan area (Mount, 1982). Subsequently, the NPS decided to continue this monitoring through September, 1983. This led to the signing of a cooperative agreement between the NPS and Pima County to continue monitoring for ozone indefinitely.

A report on air pollution sources, transport, and concentrations near the Rincon Mountain District was produced by Hutchinson, Rydout, and Matthias (1984). Conclusions reached in this study pointed toward increasing pollution effects in the monument as a result of increased growth in the area.

In 1985 monitoring of airborne pollutants in Saguaro began in earnest. Under a contract with the University of California at Davis, Saguaro became part of the western fine particulate monitoring network. The fall of this same year began with surveys conducted to determine if there was any ozone damage to ponderosa pine in the Rincon Mountains. A draft report resulting from this work stated that there appeared to be extensive damage as nearly 85 percent of the trees surveyed were affected by ozone pollution (Duriscoe, 1985). In cooperation with the Pima County Air Quality Control District, an air quality trailer was set up in December. For the

first time since continuous monitoring began in 1982, all air pollution monitoring was done at the same site. Prior to this time the ozone monitor was located in the visitor center and the particulate monitor in the tack room at the horse corral.

In the spring of 1986, Pima County supplied a sulfur-dioxide monitor, which was set up in the air quality trailer. Field work was carried out in the summer to determine if pollution levels were sufficient to damage sensitive lichen species. Conclusions reached as a result of this study were that no abnormal accumulations of polluting elements were present in any lichens collected (Wetmore, 1987). A second survey of ponderosa pine in the Rincon Mountains was conducted in the fall, and estimates of severity and quantity of damage were revised downward (Duriscoe, 1987). Just after this second survey was completed, automated equipment was installed in trailer. This included a datalogger, computer, printer, and calibrator to run checks on the monitoring equipment. The sulfur-dioxide monitor was put on line with the other equipment and the data gathered from it were logged along with the ozone information.

Climatological monitoring equipment was installed at the air quality site in February of 1987. A biomonitoring garden was laid out and a greenhouse was erected. The intent here was to grow native plants, transplant them to the garden, and begin monitoring these plants for any visible signs of pollution damage. A permanent position, for a Resource Management Technician devoted principally to air quality monitoring, was filled in June. December saw the beginning of studies of soils, histological, and elemental analyses of tissues of saguaro and of growth patterns of ponderosa pine.

Saguaro's Resource Management Technician went through air quality monitoring training in the early spring of 1988, SOPs for site operations were finalized, and the site began operating to NPS standards. Plants for the biomonitoring garden were produced as a result of the greenhouse operation. Studies were begun on cactus growth in various soils.

We were notified in May 1988 that an automated camera would be installed for visibility monitoring and that the monument was to get an IMPROVE sampler.

What does the future hold for air quality monitoring in Saguaro National Monument? Our goals, not in priority order, are as follows:

1. Begin monitoring of ozone and sulfur dioxide at a high elevation site in the Rincon Mountains.

2. Begin monitoring of wet precipitation for acidity.

3. Establish air pollutant monitoring (ozone and sulfur dioxide) in the Tucson Mountain District.

4. Work with the Pima Association of Governments to reestablish the Interagency Air Pollution Monitoring Committee to cover monitoring and other air quality issues for the Tucson basin.

5. Finalize the studies on saguaros aimed at assessing air pollution effects.

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Workshop Recommendations

Introduction

Individual park units can make significant contributions to understanding air pollution stress on biological and cultural resources by increasing their awareness of air quality issues in their areas. The formation of desert air quality research and management groups to jointly address issues germane to desert park units will consolidate resources in dealing with air quality issues. Once issues have been identified, we strongly recommend the initiation of a research program that makes use of rigorous scientific techniques and practices (QA/QC, peer review, publications). It is important that air quality and air pollution effects data are good enough to stand up in court.

Research and Monitoring Recommendations

There is a need to monitor wet and dry deposition at parks located near major urban or industrial sources of pollutants. While the current NADP network is sufficient to characterize regional levels of deposition, this is not specific enough to be of use to parks adjacent to major pollution sources, such as Joshua Tree and Saguaro National Monuments.

Little information is available regarding chemical or biological characteristics of desert potholes. They need to be surveyed for both species and chemical variability on a regular, and probably intensive, basis for several years before we can assess their potential response to combined wet and dry deposition.

Not enough is known yet about specific source-receptor relationships between air pollutants and desert plant species. In general, however, elevated pollutant levels coincident with periods of plant physiological activity have caused injury to sensitive species. It is recommended, therefore, that a systematic program of research be initiated in desert parks where elevated levels of pollutants have been recorded. Controlled exposure and field plot gradient studies need to be initiated to identify pollutant sensitive species, the nature and severity of the biological response to the pollutant, and the environmental conditions that influence the receptor response. Field surveys need to performed on species identified as pollutant sensitive to determine the incidence, severity, spatial trends, and biological ramifications of pollution injury. The establishment of long-term monitoring plots is needed to determine temporal trends in injury and ecological ramifications of chronic pollution injury.

Cultural resource research has identified sensitive receptors that can be degraded by air pollutants. Expanded research is needed to evaluate rocks, pigments, and other cultural resources sensitivity to diverse air pollutants. While this research may be beyond the expertise of NPS personnel, desert parks with cliff dwellings, pictographs, and petroglyphs need to stay current with research progress in materials effects.

Air pollution monitoring needs to be expanded to include additional class II airsheds and to represent ecosystems that are not near convenient power sources, such as montane coniferous ecosystems. Mandated quality assurance/quality control procedures need to be developed to

insure the reliability of air monitoring data and enable comparisons of air quality in different park units.

Management Recommendations

The Air Quality and Water Resources Divisions of the NPS Washington Office are available to assist with data collection and interpretation in parks. For the results of pollutant loads or their effects to be used properly for policy making, resource management, or legal action, studies must be well-designed, work plans must be reviewed by experts in the field, adequate QA/QC procedures must be implemented, and all results should be published.

List of Abbreviations

Al	aluminum
As	arsenic
Br	bromine
Ca	calcium
$CaCO_3$	calcium carbonate (lime)
CAM	Crassulacean Acid Metabolism
Cd	cadmium
Cl	chloride
CO_2	carbon dioxide
cm	centimeter
Cs	cesium
Cu	copper
EF	enrichment factor
F	fluoride
g/m^2	grams per meter squared
Hf	hafnium
H_2O	water
HF	hydrogen fluoride
In	indium
JOTR	Joshua Tree National Monument
K	potassium
kg	kilogram
km	kilometer
Mg	magnesium
Mn	manganese
N-fixation	nitrogen fixation
NADP	National Atmospheric Deposition Program
NAPAP	National Acid Precipitation Assessment Program
Na	sodium
NaF	sodium fluoride
$NaHSO_3$	sodium sulfite
N_2	nitrogen gas
NH_4SO_4	ammonium sulfate
NO_2	nitrogen dioxide
NO_x	nitrogen oxides
NO_3	nitrate
NPS	National Park Service
O_2	oxygen
O_3	ozone
Pb	lead
$PbCl_2$	lead chloride
pH	a measure of acidity (-log $[H^+]$)
PIXE	proton-induced, x-ray emission
ppb	parts per billion
ppm	parts per million
QA/QC	quality assurance/quality control
SAGU	Saguaro National Monument
Sb	antimony

Sc	scandium
Se	selenium
Si	silica (elemental)
SiO_2	silica (crystalline)
SO_2	sulfur dioxide
SO_4	sulfate
Ti	titanium
ueq/l	microequivalents per liter
ug/g	micrograms per gram
ug/m_3	micrograms per cubic meter
V	vanadium
VOC	volatile organic compounds
WASO-AQD	NPS Air Quality Division
Zn	zinc

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As the nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural and cultural resources. This includes fostering wise use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for enjoyment of life through outdoor recreation. The department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people. The department also promotes the goals of the Take Pride in America campaign by encouraging stewardship and citizen responsibility for the public lands and promoting citizen participation in their care. The department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

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