Status of Air Quality and Related Values in Class I National Parks and Monuments of the Colorado Plateau

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Chapter 1. Introduction: Policy, Monitoring, and Synopsis of Air Quality on the Colorado Plateau

The National Parks (NP) and National Monuments (NM) of the Colorado Plateau receive millions of visitors each year, attracted by outstanding scenic vistas and ecosystems that approach pristine conditions for the American West. Air quality is fundamentally important; imposing scenery needs to be visible to be appreciated. The potential impacts of changing air quality on ecosystems may be more subtle, including changes in the physiology of sensitive species which could lead to changes in community composition.

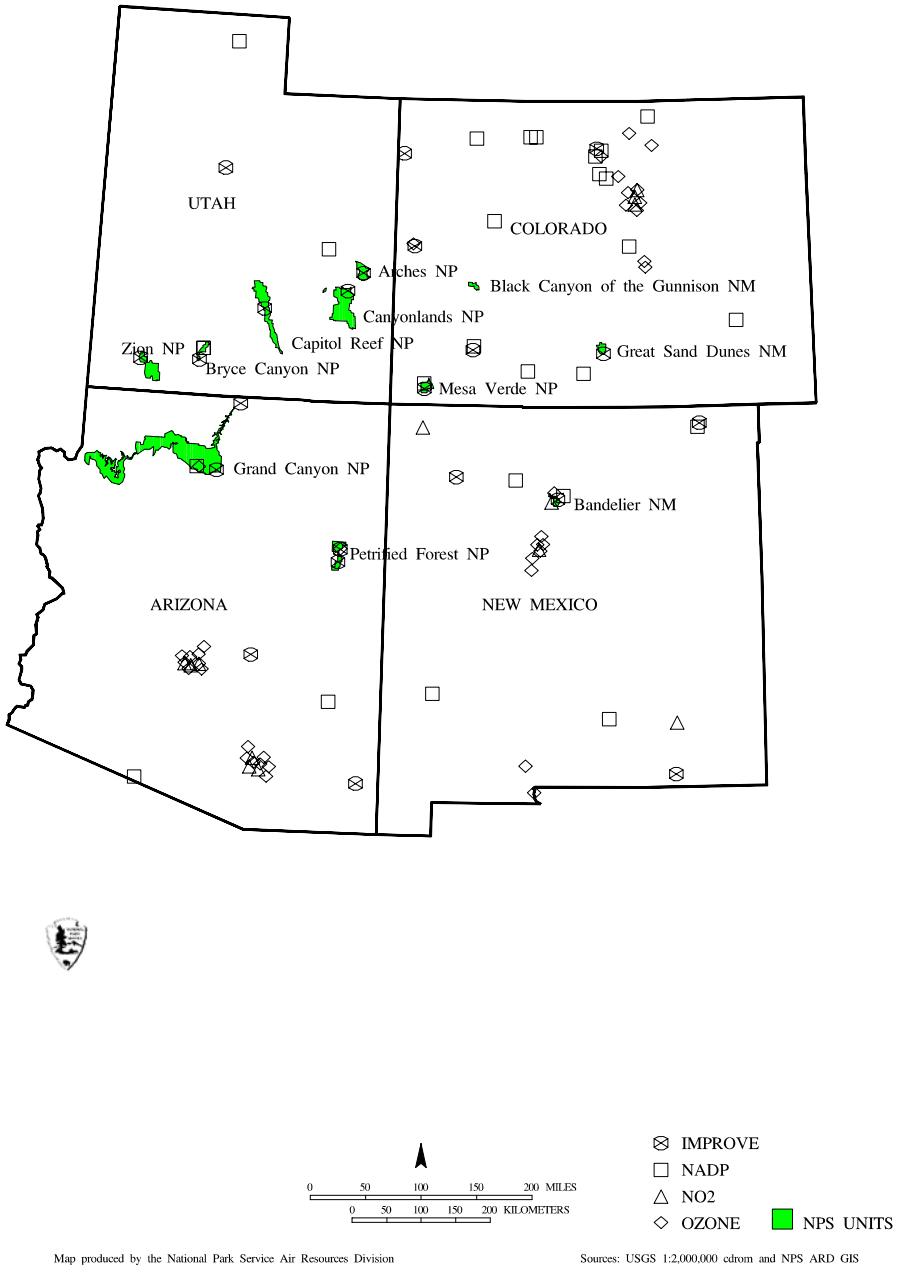
This project was initiated by the Air Resources Division (ARD) of the National Park Service (NPS), with the objectives of summarizing:

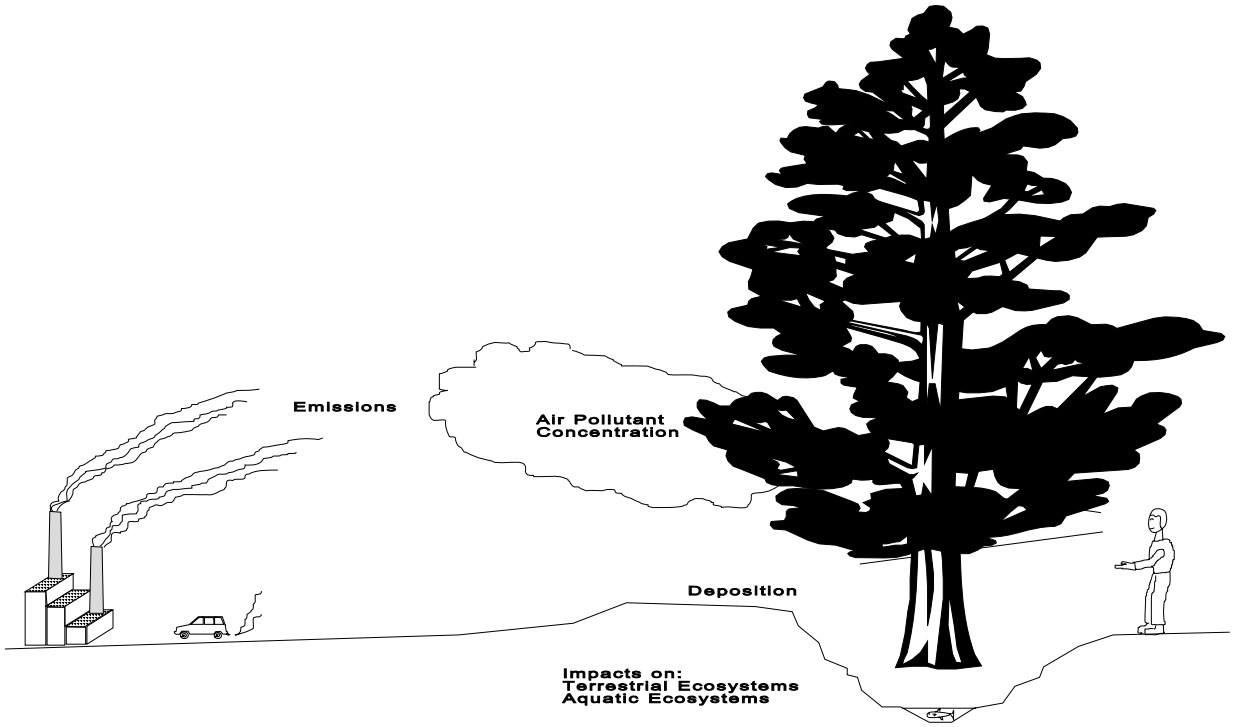
1) Air quality and atmospheric deposition;
2) Sensitivity of terrestrial and aquatic ecosystems;
3) Current status of air quality related values (AQRVs);
4) Likely future status of AQRVs based on potential future air quality and ecosystem sensitivity;
5) Key areas requiring further research to clarify current impacts or likely future impacts.

The NPS has responsibility for 9 Class I areas in the Colorado Plateau (Figure 1-1): Arches National Park (ARCH), Black Canyon of the Gunnison National Monument (BLCA), Bryce Canyon National Park (BRCA), Canyonlands National Park (CANY), Capitol Reef National Park (CARE), Grand Canyon National Park (GRCA), Mesa Verde National Park (MEVE), Petrified Forest National Park (PEFO) and Zion National Park (ZION). This report also covers two nearby areas that are not generally considered as part of the Colorado Plateau: Bandelier National Monument (BAND) and Great Sand Dunes National Monument (GRSA).

This assessment begins with an overview of the key features of air quality in the Colorado Plateau and the potential sensitivity of air quality related values. Individual chapters focus on each Class I area by following the flow of pollutants from emissions, to air concentrations (and effects on visibility), to deposition and effects on terrestrial and aquatic ecosystems (Figure 1-2). A final chapter synthesizes the overall picture for Class I areas of the Colorado Plateau (and nearby areas) administered by the NPS, and makes recommendations for future research.

Figure 1-1. Class I National Parks and Monuments of the Colorado Plateau.





This introductory chapter summarizes major features of air quality policy for Class I areas, and then provides a synoptic view of major features of air quality around the Colorado Plateau, with some comparisons with the nation as a whole. The presence of pollutants in the atmosphere directly influences visibility values of landscapes, and we describe the key aspects of visibility and how they have been monitored on the Colorado Plateau. Other pollutants, like ozone, directly damage vegetation; we describe the monitoring programs in the area and the regional scale information on concentrations of gaseous pollutants. The introductory chapter concludes by describing the monitoring efforts that gauge rates of deposition of pollutants from the atmosphere to ecosystems, and how they might affect terrestrial and aquatic ecosystems.

Air Quality Policy in National Parks and Monuments

One of the purposes of the 1977 Clean Air Act Amendments is to “preserve, protect, and enhance the air quality in national parks, national wilderness areas, national monuments, national seashores, and other areas of special national or regional natural, recreational, scenic, or historic value” (Section 160). The Act provides for greatest protection in “Class I" areas, defined as national parks over 2,430 ha and national wilderness areas over 2,020 ha that were in existence

before August of 1977. According to the Clean Air Act and its amendments, federal land managers have "...an affirmative responsibility to protect the air quality related values (AQRVs)...within class I areas" (Clean Air Act section 165(d)(2)(B); Eilers et al. 1994).

Human activities produce a wide variety of air pollutants, with various potential effects on humans and ecosystems. The U.S. Environmental Protection Agency (EPA) established National Ambient Air Quality Standards (NAAQS) to protect human health (primary) and public welfare (secondary). Some of these pollutants, such as carbon monoxide and lead, may have greater effects on human health than on wildland ecosystems. Other pollutants, such as ozone, may have substantial effects on ecosystems at thresholds below the human-health standards (see Chapter 2).

Table 1-1. National Ambient Air Quality Standards (NAAQS) in $\mu g/m^3$ (40 C.F.R. part 50), increments allowed above baseline in Class I areas, that may prevent significant deterioration (PSD), and proposed (July 23, 1996) significant levels that represent increments which would trigger a cumulative increment analysis.

Pollutant	Averaging time	Primary	Secondary	Increments	Significant levels
Sulfur dioxide	Annual arith.	80	none	2	0.1
	24-hour[1]	365	none	5	0.2
	3-hour[1]	none	1300	25	1.0
PM_{10}[2]	Annual arith.	50	same	4	0.2
	24-hour	150	same	8	0.3
Carbon monoxide	8 hour[1]	10000	same	none	none
	1-hour[1]	40000	same	none	none
Ozone	1-hour[3]	235	same	none	none
Nitrogen dioxide	Annual arith.	100	same	2.5	0.1
Lead	Calendar quarter	1.5	same	none	none

[1]Maximum concentration not to be exceeded more than once per year.

[2]PM_{10} = particulate matter with diameter < 10 μm.

[3]This standard is attained when the number of days per calendar year with the maximum hourly average concentrations above the standard is equal to or less than one.

Some revision of these primary standards are being considered. The EPA issued an announcement on November 27, 1996 of proposed revisions, including:

- a $PM_{2.5}$ (particulate matter < 2.5 μm) of 50 μg/m^3 for 24 hr average (annual mean of 15 μg/m^3);
- a primary ozone standard of 80 ppm for 8 hr average; and
- a secondary ozone standard of a seasonal SUM60 (sum of hourly ozone concentrations in excess of 60 ppb for 12 hr/day for 3 months) for protection of plants.

In addition to these "criteria" pollutants that may affect human health and welfare, ecosystems may be sensitive to deposition of acidity, sulfur (S) and nitrogen (N) compounds, and heavy metals, and visibility may be impaired by a variety of particulates. Areas that meet the standards may still experience substantial impacts from poor air quality. Therefore, air quality in Class I areas involves provisions of the Clean Air Act that aim to "prevent significant deterioration". The permitting process for new point sources of pollution, and major modification of existing point sources, requires that the new source will not violate state or national ambient air quality standards, will use the best available control technology to limit emissions, and will not harm AQRVs in any Class I area (Peterson et al. 1992, Bunyak 1993, Eilers et al. 1994).

Air quality related values include: visibility, plants, animals, soils, surface waters, historic and geologic resources, and virtually any other resource affected by air quality. The information base is strong for some AQRVs for Class I areas of the Colorado Plateau, but very weak in others. This assessment does not consider the effects of air quality on cultural values.

Air Quality Monitoring in Class I National Parks and Monuments of the Colorado Plateau

Across the United States (U.S.), many parameters of air quality have improved over the past two decades (EPA 1995). In the past 10 years, average national concentrations of lead declined by 86%, carbon monoxide (CO) by 28%, sulfur dioxide (SO_2) by 25%, and ozone (O_3) by 12%. The Colorado Plateau has typically experienced the best air quality in the continental United States. A wide range of monitoring, research, and case studies have measured levels of various pollutants across the Colorado Plateau for varying lengths of time (Figure 1-3). The length of record is variable

for these programs, but most of the active sites have records spanning from 5 to 8 years. The NPS monitors visibility conditions and supports studies to determine the causes of visibility impairment (haze and plumes) at many parks and wilderness areas nationwide. The purpose of this monitoring is to establish the spectrum of current visibility conditions, identify the specific chemical species and the emission sources that contribute to visibility impairment, and to document long-term trends to assess the effects of changes in emissions. The NPS cooperates and shares resources with other federal land managing agencies, states, and the EPA in the Interagency Monitoring of Protected Visual Environments (IMPROVE) program (Sisler et al. 1993). On the Plateau, IMPROVE monitoring is conducted at Arches NP, Bandelier NM, Bryce Canyon NP, Canyonlands NP, Grand Canyon NP, Great Sand Dunes NM, Mesa Verde NP, and Petrified Forest NP. The NPS also participates in the National Atmospheric Deposition Program (NADP) which monitors the chemistry and quantity of precipitation across the U.S., including 10 stations in the Colorado Plateau area. The NPS conducts routine monitoring of ozone in selected national parks and monuments, with data available from the Aerometric Information Retrieval System (AIRS), administered by the EPA.

Table 1-2. Air quality monitoring in Class I National Parks and Monuments of the Colorado Plateau.

National Park or Monument	Ozone	NADP (deposition)	SO_2 concentration	Visibility
Arches	88-92	Nearby (Green River, 1985-present)	1988-1992	Camera 1986-1991 IMPROVE sampler 1988-1992
Bandelier	90-94	1982-present[1]	1988-1992	Transmissometer 1988-present; Camera 1978-1995; IMPROVE sampler 1988-present
Black Canyon of the Gunnison	95-96 (passive)	No	No	Camera 1985-1993
Bryce Canyon	95-96 (passive)	1985-present	1988-1989, 1991-1992	Camera 1979-present IMPROVE sampler 1988-present
Canyonlands	92-present	Nearby (Green River, 1985-present)	1988-1989, 1991-present	Transmissometer 1987-present; Camera 1982-1995; IMPROVE sampler 1988-present

Capitol Reef	95-96 (passive)	Nearby (Green River, 1985-present)	No	Camera 1985-1991
Grand Canyon	83, 89-present	1981-present	1988-1989; 1991-present	Transmissometer 1986-present; camera 1979-present; IMPROVE sampler 1988-present
Great Sand Dunes	88-91	Nearby (Alamosa, 1980-present)	1988-1992	Camera 1987-1995; IMPROVE sampler 1988-present
Mesa Verde	93-present	1981-present	1991-1992	Transmissometer 1988-1993; camera 1979-1995 IMPROVE sampler 1988-present
Petrified Forest	87-91	No	1988	Transmissometer 1987-present; camera 1986-1995; IMPROVE sampler 1988-present
Zion	95-96 (passive)	No	No	Camera 1985-1991

[1]Present = 1996

IMPROVE Station Description and Rationale

Visibility impairment results from both absorption and scattering of light by particles suspended in the air. "Fine" particles < 2.5 μm and gases with molecular diameters on the order of 0.0001 μm are especially efficient at scattering light. Scattering of light by fine particles and gases accounts for the majority of visibility impairment in the Colorado Plateau. Scattering by "air" molecules (Rayleigh scattering) causes the sky to appear blue, and sets the limit on the best possible visibility for a specific geographic location.

A fully complemented IMPROVE station includes monitoring of fine and coarse particle concentrations (particles with diameters < 10 μm, these particles do not scatter light well and therefore do not contribute much to visibility impairment) optical conditions, and view monitoring with photography. Water vapor in the air can affect visibility, so most stations also record temperature and relative humidity. Particle monitoring provides concentration measurements of

specific chemicals that contribute to visibility impairment and involves sets of four samplers that automatically collect two 24-hr samples each week (Wednesday and Saturday from midnight to midnight) by drawing air through filters. The filters capture suspended particles that are then sent for laboratory analyses to determine the mass and chemical composition of the particles. One sampler collects coarse particles and the other three collect fine particles with diameters <2.5 μm. The three fine particle samples are analyzed for elemental composition and mass, mass of sulfate and nitrate, and mass of carbon species. These masses and air flow information are used to determine concentrations and are reported quarterly.

Optical monitoring provides a quantitative measure of light extinction (light attenuation per unit distance) to represent visibility conditions. Optical monitoring uses long-path transmissometers and nephelometers. Transmissometers measure the amount of light transmitted through the atmosphere over a known distance (between 0.5 and 10 km) between a light source of known intensity (transmitter) and a light measurement device (receiver). The transmissometer measurements are electronically converted to hourly averaged light extinction (scattering plus absorption). Nephelometers draw air into a chamber and measure the scattering component of light extinction.

View monitoring provides a photographic record of visibility conditions. View monitoring is accomplished with automated 35-mm camera systems. These cameras take three shots a day at fixed times of selected scenes. The resulting slides are used to facilitate data interpretation, display anticipated changes in visibility, and form a photographic record of characteristic visibility conditions.

A more detailed description of the visibility and particle monitoring network may be found in Sisler et al. (1993).

Visibility Characterization

Visibility is usually characterized by visual range (the greatest distance that a large black object can be seen against the horizon sky background) or extinction (the attenuation of light per unit distance). These two characterizations are inversely related; a great visual distance relates to a very low light extinction. Visual range is useful for safety reasons such as to direct aircraft traffic near airports, but it is not particularly useful for assessing the quality of scenic vistas that include color, texture, and other details. Nonetheless, visual range remains a useful measure for describing overall visibility, especially for communication with visitors to parks and monuments.

Extinction (expressed as inverse megameters (Mm^{-1})) is a better characterization of visibility impairment and is more directly related to scenic quality. Extinction can be directly measured or derived from measured particle concentrations ("reconstructed extinction"). Also, "extinction budgets" can be prepared which show the relative contribution of each atmospheric constituent (particles and/or gases) to extinction. With these extinction budgets, one can display the relative importance of each constituent to impairment and estimate changes in visibility conditions due to changes in the concentrations of the constituents which may be caused by emission increases or decreases

A drawback to both of these extinction characterizations is that the effect of a specific change (such as 2 Mm^{-1}) may be small or large, depending on background conditions.

Another visibility characterization, the deciview, has been derived to index a constant fractional change in extinction or visual range (Pitchford and Malm 1994). The advantage of this characterization is that equal changes in deciview are equally perceptible across different baseline conditions.

Overview of Conditions Across the Colorado Plateau

The IMPROVE monitoring network currently has 55 sites, with 6 sites on the Colorado Plateau. Figure 1-3 shows isopleths of the total reconstructed light extinction (including Rayleigh, which is about 10 Mm^{-1}) for each of the reported sites in the IMPROVE network for the period March 1988 through February 1994. The highest reconstructed light extinction (>100 Mm^{-1}) occurs in the southeastern U.S. while the Colorado Plateau and the Great Basin have the lowest extinctions. Regionally averaged visual ranges are presented in Figure 1-4, and again the Colorado Plateau (along with the Great Basin and central Rockies) has the best visibility conditions in the continental U.S.

Figure 1-4. Transmissometer visibility monitoring sites for geographic regions.

Visibility Metric:

Average conditions...	Arithmetic mean of all visibility data for all regions (Visual Range = 78 km, b_{ext} = 50 Mm^{-1})
Best conditions...	Arithmetic mean of the 20% least impaired visibility data for all regions. (Visual Range = 145 km, b_{ext} = 27 Mm^{-1})
Worst conditions...	Arithmetic mean of the 20% most impaired visibility data for all regions. (Visual Range = 45 km, b_{ext} = 95 Mm^{-1})

Box Plot Key:

Columns - Represent Meteorological Seasons
- Column 1 - Winter (December, January, and February)
- Column 2 - Spring (March, April, and May)
- Column 3 - Summer (June, July, and August)
- Column 4 - Autumn (September, October, and November)

Rows - Represent Defined Visibility Ranges
- Row 1 - Average seasonal visibility is in the "Worst" visibility metric category.
- Row 2 - Average seasonal visibility is in the "Below Average" visibility metric category.
- Row 3 - Average seasonal visibility is in the "Above Average" visibility metric category.
- Row 4 - Average seasonal visibility is in the "Best" visibility metric category.

Example Box Plot:

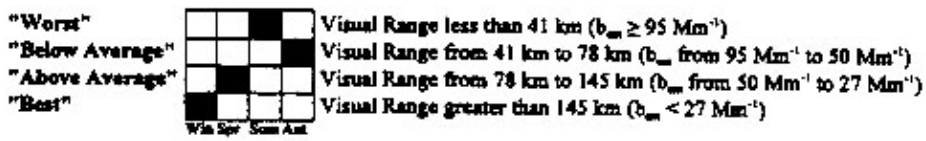


Table 1-3. Transmissometer visibility monitoring sites for geographic regions in Figure 1-4.

Region	Transmissometer Monitoring Sites
Appalachian Mountains	Shenandoah National Park - Virginia
Central Rocky Mountains	Bridger Wilderness - Wyoming Rocky Mountain National Park - Colorado Yellowstone National Park - Wyoming
Coastal Mountains	Pinnacles National Monument - California
Colorado Plateau	Bandelier National Monument - New Mexico Canyonlands National Park - Utah Grand Canyon National Park - Arizona Mesa Verde National Park - Colorado Petrified Forest National Park - Arizona
Great Basin	Great Basin National Park - Nevada
Northeast	Acadia National Park - Maine
Northern Great Plains	Badlands National Park - South Dakota
Northern Rocky Mountains	Glacier National Park - Montana
Sierra Nevada	Yosemite National Park - California
Sonoran Desert	Chiricahua National Monument - Arizona
Southern California	San Gorgonio Wilderness - California
West Texas	Big Bend National Park - Texas Guadalupe Mountains National Park - New Mexico

Light extinction on the Colorado Plateau derives primarily from scattering by fine particles (about 40% of total annual extinction, Table 1-4), and by natural Rayleigh scattering by atmospheric gases (32%). The remaining extinction results from scattering by coarse particles, and by absorption by particles and gases. The differences among seasons are small, with total extinction ranging from 29 Mm^{-1} in the spring to 33 and 34 Mm^{-1} during the summer and winter, respectively. As shown in Table 1-5, ammonium sulfate on the average, consistently accounts for about 30% of the particle extinction. Ammonium nitrate exhibits the strongest seasonal variation with its highest contribution being in the winter.

Table 1-4. Colorado Plateau extinction apportioned by general category (Mm^{-1})

Season	Total Extinction	Non-Rayleigh Extinction	Fine Scattering	Coarse Scattering	Absorption
Spring	29.3	19.3	10.3	4.1	4.9
Summer	33.0	23.0	12.4	4.3	6.3
Autumn	30.7	20.7	12.1	2.9	5.6
Winter	33.8	23.8	16.5	2.1	5.2
Annual	31.5	21.5	12.7	3.4	5.5

Table 1-5. Contributions of various types of fine particles to the total non-Rayleigh light extinction for the Colorado Plateau (Mm^{-1})

Season	Particle Extinction	Ammonium Sulfate	Ammonium Nitrate	Organics	Carbon (soot)	Soil & Coarse Material
Spring	19.3	5.1	1.2	3.9	4.9	4.1
Summer	23.0	6.0	0.8	5.6	6.3	4.3

Autumn	20.7	6.3	0.9	4.9	5.6	2.9
Winter	23.8	8.2	3.9	4.4	5.2	2.1
Annual	21.5	6.5	1.5	4.7	5.5	3.4

Sources

In the Colorado Plateau, the major sources of sulfate (SO_4^{2-}, a secondary pollutant formed in the atmosphere from sulfur oxides, SO_x) are coal and oil-fired power plants, and refining and smelting activities. The primary sources of nitrate (NO_3, also a secondary pollutant formed from nitrogen oxides, NO_x) are automobiles and all other combustion sources. Organic pollutants can substantially affect visibility, and they derive from both natural sources (bioemissions), and from smoke and industrial solvents. Soot particles come from diesel exhaust and smoke, and coarse particles come from wind-blown dust, smoke, and pollen.

Case Studies of Visibility on the Colorado Plateau

In addition to the IMPROVE network, the Colorado Plateau has been the focus of a variety of studies that examined visibility, haze, and the sources of pollutants responsible for visibility impairment. These studies have included:

- basic principal component/back-trajectory analyses (Malm 1989) which have identified southern California and southeastern Arizona as major contributors to haze at the Grand Canyon and regions to the northwest of the park as sources of clear air.
- the SCENES visibility monitoring (Mueller et al. 1986) for the Colorado Plateau. This was a cooperative study to identify visibility conditions on the Colorado Plateau.
- the 1987 Winter Haze Intensive Tracer Experiment (WHITEX) (Malm et al. 1989) which characterized the effect of the Navajo Generating Station on visibility in the Grand Canyon and resulted in sulfur dioxide emissions at that facility being reduced by 90%.
- the National Academy of Sciences evaluation of WHITEX (National Research Council 1990).
- Project MOHAVE, an EPA-sponsored tracer study to quantify the contribution of the Mohave power plant and western urban sources to haze at the Grand Canyon. The field study was

completed in 1992, but study results are not available as of June 1997.

- Grand Canyon Visibility Transport Commission (GCVTC), formed as a result of the Clean Air Act of 1990, to recommend methods of improving visibility throughout the Colorado Plateau by considering all sources of emissions in the western States that may impact the Plateau region.

Visibility Projections

The 1990 Clean Air Act mandated the establishment of the GCVTC to advise the EPA on strategies for protecting visual air quality in national parks and wilderness areas on the Colorado Plateau. The Commission was composed of the governors of eight western states (Arizona, California, Colorado, New Mexico, Nevada, Oregon, Utah and Wyoming), leaders of four tribes (Acoma, Hopi, Hualapai, Navajo), representatives of four federal land management agencies [U.S. Bureau of Land Management (BLM), U.S. Fish and Wildlife Service (USFWS), U.S. Forest Service (USFS), and NPS], representatives of the Columbia River Inter-Tribal Fish Commission, and the EPA. The Commission issued its final report in June of 1996 (GCVTC 1996). The Commission reviewed available information, developed data bases, and simulated various features of air quality.

Recommendations of the Commission include:

- Setting regional targets in 2000 for SO_2 emissions from stationary sources; exceedances would invoke a yet-to-be developed regulatory program which might include a market trading program for emissions.
- The Commission's research and modeling showed a wide range of sources of air pollution reaching Class I areas of the Colorado Plateau, including emissions from urban areas.
- The Commission concluded that both prescribed fires and wildfires are likely to increase in the coming decades as a result of previous efforts at fire suppression.
- The Commission recommended establishment of an on-going body similar to itself for addressing the continuing issues of air quality on the Colorado Plateau.

The GCVTC (1996) performed extensive computer modeling to examine contributions of regional and local pollutants to visibility impairment. Results suggest that long-range transport (>160 km) substantially contributed to haze in Class I areas of the Colorado Plateau; Grand Canyon visibility was affected by pollution from Los Angeles, and visibility at Canyonlands NP was affected by pollution from Salt Lake City. The Commission also concluded that local sources may be more important to production of haze than previously thought, particularly in windless periods. However,

the report cautioned that years of technical work may be necessary before the relative visibility impacts of regional and local sources can be confirmed.

The Grand Canyon Visibility Transport Commission projected likely visibility for the Grand Canyon NP, Bryce Canyon NP, Canyonlands NP, and Mesa Verde NP through 2040, and the major species responsible for visibility impairment. Reduced emissions from utilities were projected to reduce light extinction by about approximately 1 Mm^{-1}. Light extinction caused by vehicle emissions was projected to decline until approximately 2005, and then increase through 2040. The dirtiest days have more than twice the visibility impairment of clean days with the bulk of the impairment resulting from human- related sources. Emissions from Mexico are increasing, contributing high quantities of sulfates to the air that reaches the Colorado Plateau.

The incidence of prescribed fires and wildfires is likely to increase in the coming decades as a result of past fire suppression, and fire-generated soot may substantially impair visibility. Historically, about 14 million ha of land burned annually across the region contributes to reduced visibility on the Colorado Plateau, with large variation among years. Current prescribed fire programs ignite only 0.5 million ha of land. Fire suppression for the past 80 years has resulted in large fuel accumulations, and millions of hectares of forests, shrublands and grasslands across the Colorado Plateau are at risk from catastrophic wildfire (GCVTC 1996). The Commission concluded that emissions from fire may represent the single most important change in air quality on the Colorado Plateau in the next 50 years.

The effects of fire on visibility are highly seasonal, with far greater effects for periods of days to weeks than on an annual average basis. Some of the best visibility occurs in winter on the Colorado Plateau, whereas fires occur in spring, summer and autumn. Therefore, increased fires would have little effect on the cleanest days, but would exacerbate visibility impairment on days that are already lower in visibility.

The Commission also evaluated the contributions of 95 source areas to visibility reduction at the Grand Canyon. They concluded that the greatest gains in visibility would come from reducing the tons of emissions from sources with large “transfer coefficients” (a relationship between the visibility impairment at a site and the magnitude of emission at the source).

Ozone

Ozone concentrations on the Colorado Plateau have been monitored at several National Parks and Monuments using continuous monitors by ultraviolet photometric methods. Some sites were

monitored in 1995 and 1996 by a passive ozone sampling system (see below).

The mean daily ozone concentrations for the growing season (May through September) are low across the Colorado Plateau (Table 1-6), typically falling between 40 and 50 ppb (24 hr mean). The “natural” concentration of ozone in the absence of pollution may have been between 30 and 50 ppb (Lefohn et al. 1990, EPA 1996), indicating modest increases over pre-industrial levels. No observations have exceeded the primary standard of 120 ppb, except for one occasion in 1991 in Petrified Forest, which recorded a value of 134 ppb. Across the Colorado Plateau, the cumulative exposures to ozone are relatively low. D. Joseph (NPS-ARD) calculated the “sum60" cumulative exposures for 3 month summer periods for 12 hr/day (Table 1-6). The cumulative exposures are commonly about 10000 ppb-hr or less, with notably higher concentrations for some years at Bandelier and Grand Canyon. The highest observed values came in 1991, reaching 28000 ppb-hr for Bandelier and 22000 ppb-hr for the Grand Canyon. These data indicate that peak concentrations of ozone are not likely to cause problems for plants, but that the possibility of damage from chronic exposure to moderate concentrations of ozone warrants examination (see Chapter 2).

Table 1-6. Ozone concentrations and exposures between May and September. Upper value is mean daily ozone concentration (ppb); middle number is the maximum 3-month “Sum60" exposure value (ppb in excess of 60, for 12 hr/day (ppb-hr)/yr; data provided by D. Joseph, ARD); and bottom number is the maximum 1-hr concentration observed each year (ppb). Percent of data capture varied among sites and years. Data from the NPS Air Resources Division’s Quick Look Annual Summary Statistics Reports.

Year	Arches	Bandelier	Canyonlands	Grand Canyon	Great Sand Dunes	Mesa Verde	Petrified Forest
1983 Mean Sum60 Max	--	--	--	 26 -- 66	--	--	--
1987 Mean Sum60 Max	--	--	--	--	--	--	 42 18207 116
1988 Mean Sum60 Max	 44 7597 70	--	--	--	 40 1863 76	--	 39 7611 101
1989 Mean Sum60 Max	 45 6117 87	--	--	 43 -- 68	 41 728 63	--	 43 20902 104

1990 Mean Sum60 Max	28 -- 56	48 15200 81	--	43 -- 74	42 4975 70	--	40 13427 97
1991 Mean Sum60 Max	36 -- 74	48 28265 87	--	46 21923 79	41 6598 77	--	41 14802 134
1992 Mean Sum60 Max	46 -- 76	46 13070 78	47 -- 65	44 10416 78	--	--	--
1993 Mean Sum60 Max	--	44 8490 77	47 4156 75	46 7228 73	--	41 3280 67	--
1994 Mean Sum60 Max	--	46 19160 90	51 16023 73	49 12542 79	--	45 7985 72	--

Ozone Sampling with Passive Samplers (1995 and 1996)

Given the low number (and high expense) of continuous ozone monitoring on the Colorado Plateau, several parks used Ogawa passive samplers in 1995 and 1996 (provided by J. D. Ray, ARD, Table 1-7). The passive samplers use nitrite-coated filter pads to collect ozone by diffusion to form nitrate. Exposed filters were returned to a commercial lab, and nitrate was determined by ion chromatography. These devices have an accuracy of about ±10% and a precision of better than 3% based on duplicate samples. Weekly values from the passive samplers in 1995 were divided by the number of hours of data collected to provide 1-hr average concentrations (Table 1-7). Comparable values were calculated for continuous ozone monitors at Mesa Verde and Grand Canyon. The average hourly ozone concentrations followed the weekly changes in regional weather. The parks where ozone was measured with the passive samplers were generally found to be slightly cleaner (41 to 46 ppb ozone) compared to the parks with continuous ozone monitors (49 to 54 ppb average). The ozone concentrations were strongly correlated among Capitol Reef, Black Canyon of the Gunnison, Grand Canyon, and Mesa Verde. Zion and Bryce Canyon correlated with each other, but not with the other parks.

Table 1-7. Average hourly ozone for weekly samples (ppb) based on weekly sample periods for 1995 (data from J. Ray, NPS-ARD).

Month	Week	Black Canyon	Bryce Canyon	Capitol Reef	Zion	Mesa Verde mean[1]	Mesa Verde maximum[2]	Grand Canyon mean[1]	Grand Canyon maximum[2]
		Passive monitoring				Continuous monitoring			
May	1	45.7	39.8	42.3	42.5	49.7	58	53.1	74
	2	46.0	42.4	41.7	44.8	49.6	61	53.1	75
	3	47.9	46.3	46.1	54.6	54.1	66	58.5	73
	4	44.4	36.5	42.3	35.3	50.3	67	53.3	68
	5	41.0	37.1	41.3	44.9	48.0	67	53.4	69
June	1	45.5	48.2	46.2	46.0	51.1	71	56.2	68
	2	46.3	49.9	39.7	43.4	51.0	67	51.6	75
	3	48.5	49.9	43.9	48.5	51.3	61	54.2	69
	4	37.8	43.9	- -	41.3	43.9	57	53.8	72
July	1	47.1	49.9	43.5	45.5	50.8	67	55.7	69
	2	36.6	43.4	37.5	44.0	41.9	56	47.5	65
	3	40.3	49.3	41.3	51.6	46.1	56	54.3	73
	4	47.7	50.6	46.1	52.4	50.4	63	56.4	67
Aug	1	53.0	55.2	- -	46.8	- -	- -	- -	- -
	2	45.5	47.8	- -	39.5	- -	- -	- -	- -
	3	41.7	45.4	- -	46.0	- -	- -	- -	- -
	4	45.0	44.1	- -	- -	- -	- -	- -	- -
	5	48.7	49.6	- -	44.0	- -	- -	- -	- -
Sept	1	42.0	44.0	30.0	- -	- -	- -	- -	- -

	2	45.5	49.5	- -	42.1	- -	- -	- -	- -
	3	40.0	45.0	- -	44.8	- -	- -	- -	- -
	4	37.3	40.2	37.8	44.4	- -	- -	- -	- -
Oct	1	- -	- -	36.5	40.0	- -	- -	- -	- -
Maximum		53.0	55.2	46.2	54.6	54.1	71	58.5	75
Mean		44.2	45.8	41.1	44.9	49.1	- -	53.9	- -

[1] Hourly mean calculated from weekly sample.

[2] Maximum 1-hr observation.

Sulfur Dioxide

Sulfur dioxide pollution is produced during combustion of materials (such as oil and coal) that contained reduced sulfur compounds. A variety of natural processes also produce SO_2, including volcanic eruptions, sea-spray, and microbial activity (Wellburn 1988). Burning of coal to produce electricity accounts for about half of the human-made emissions, with substantial contributions from refining and burning of oil. Controls on point-sources of sulfur have led to declining emission of SO_2 across the US; emissions have also dropped in the Southwest as a result of reduced copper smelting. The estimated emissions of SO_2 by state for 1990 were: 559 tons/day for Arizona, 297 tons/day for Colorado, 482 tons/day for New Mexico, and 271 tons/day for Utah (Radian 1994).

Sulfur dioxide reacts readily with water to form sulfuric acid, which may fall as “acid rain” or may react with particles to form sulfate salts. The residence time of SO_2 in the atmosphere is on the order of days to weeks, allowing substantial transport away from point sources before deposition as sulfuric acid or sulfate salt (Graedel and Crutzen 1989). Sulfur dioxide enters plants primarily through stomata, forming sulphite (SO_3^{2-}) and bisulfite (HSO_3^-). Although these anions are not free radicals, they are relatively reactive and can damage a variety of biochemicals either directly or after partial oxidation to form free radicals (such as sulphoxyl and superoxide radicals). Damage from SO_2 may include disruption of disulphide bridges that are critical in maintaining the 3-dimensional shapes of enzymes and proteins, and interference in photosynthesis (either C fixation or photophosphorylation of adenosine diphosphate (ADP) to adenosine triphosphate (ATP), Wellburn 1988). Documenting the long-term effects of SO_2 exposure on plants

has been very difficult, owing to a variety of factors such as exposure regimes, presence of other chemicals in the air, features of controlled environment chambers, genetics of test plants, and type of response measured (visible injury, growth, etc.). Wellburn (1988) concluded that yields of agricultural crops will not be impaired at SO_2 levels of 60 parts per billion or less.

Observed Concentrations of Sulfur Dioxide (1988 - 1994)

Sulfur dioxide concentrations have been measured as part of the sampling protocol for the IMPROVE monitoring program. The concentrations are measured for 24-hrs, twice weekly. The samples are collected on carbonate-coated filters, and then analyzed by ion chromatography in a certified laboratory. Both the maximum and the mean concentrations are given because the maximum is often many times larger than the mean and represents a few events during the year. The timing and size of peak concentrations are not correlated across the Colorado Plateau, suggesting that localized plumes do not affect all of the region. The 24-hr average concentrations of SO_2 were much lower than the primary standard (Table 1-8), and about two orders of magnitude below levels that are expected to affect plants. For example, the maximum observed value of 7.2 $\mu g/m^3$ (for the Grand Canyon in 1993) is less than 3 ppb, more than an order of magnitude below threshold values that may affect the most sensitive species of lichens and vascular plants (see Chapter 2).

Table 1-8. Sulfur dioxide measured by IMPROVE filter samplers ($\mu g/m^3$) (1 $\mu g/m^3$ equals approximately 0.38 parts per billion by volume).

	Grand Canyon		Sand Dunes		Bryce		Canyonlands		Petr. For.		Mesa Verde		Arches		Bandelier	
Year	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean
88	3.0	0.6	0.7	0.2	0.7	0.2	0.7	0.5	2.1	0.6	- -	- -	1.5	0.4	1.9	0.1
89	2.6	0.4	0.8	0.2	1.2	0.3	3.0	0.5	- -	- -	- -	- -	2.5	0.6	1.2	0.2
90	- -	- -	3.0	0.3	- -	- -	- -	- -	- -	- -	- -	- -	3.1	0.4	1.3	0.2
91	2.8	0.5	0.6	0.2	2.2	0.5	2.3	0.7	- -	- -	2.6	0.4	1.5	0.4	1.6	0.1
92	1.7	0.3	0.0	0.0	1.4	0.3	0.8	0.3	- -	- -	5.1	0.9	1.4	0.4	0.9	0.2
93	7.2	0.4	- -	- -	- -	- -	2.9	0.6	- -	- -	- -	- -	- -	- -	- -	- -
94	2.3	0.3	- -	- -	- -	- -	1.1	0.5	- -	- -	- -	- -	- -	- -	- -	- -

24-hour samples taken twice per week

Although the mean SO_2 concentrations show some consistency from year to year, the maximum concentrations varied so much between 1988 and 1994 that no meaningful trend was apparent. Grand Canyon, Canyonlands, Arches, and Mesa Verde had higher maximum values, more often, than the other parks. These parks may be hit by plumes that follow the Colorado River drainage,

or by more localized sources.

Nitrogen Oxides

Molecular nitrogen (N_2) comprises about 78% of the atmosphere, and combustion reactions and some microbial reactions produce various oxides of nitrogen. The major oxides of nitrogen are: nitrous oxide (N_2O), nitrogen dioxide (NO_2), nitric oxide (NO), and nitric acid (HNO_3), and nitrate (NO_3^-) salt. Some N may be present as ammonia (NH_3) or ammonium (NH_4^+). Nitrous oxide is relatively unreactive (with a residence time in the atmosphere of centuries; Graedel and Crutzen 1989) and has little effect on plants, although it may play a role in generation of other N oxides and ozone.

Nitrogen dioxide and nitric oxide are often lumped together as NO_x, where the x denotes one or two oxygen atoms. NO_x compounds are relatively reactive, with residence times of just a few days in the atmosphere. Most of the damage to plants from NO_x probably derives from the conversion to nitrite (NO_2^-). A variety of biochemicals and processes may be affected by toxic concentrations of nitrite in cells, including photosynthesis, respiration, and photorespiration (Wellburn 1988). However, most plants in natural ecosystems are N-limited, and nitrite can be reduced to form amino-N for plant use. Levels of NO_x below 300 ppb have shown no effects on plants, and most species show no effects up to 1000 ppb or higher (Wellburn 1988). Concentrations of NO_x are quite low across the Colorado Plateau, representing no threat to AQRVs.

Atmospheric Deposition

Rain water is a dilute solution of carbonic acid and salts in unpolluted areas, while rain water in polluted areas also has substantial concentrations of nitric acid (HNO_3) and sulfuric acid (H_2SO_4). The concentration of an ion, such as H^+, may directly affect an organism or a chemical reaction. The concentration of an ion multiplied by the total amount of precipitation water provides the quantity of an ion deposited, and this may be most important for ions such as nitrate which can act as fertilizers. In addition, some atmospheric deposition comes between precipitation events; this dry deposition includes the fall-out of particulates and deposition of gases.

The concentration of H^+ is commonly expressed on the pH scale, where pH is the negative of the logarithm of the H^+ activity (similar to concentration). A pH of 7.0 has equal quantities of H^+

and OH^-, and is considered neutral. Normal atmospheric concentrations of carbon dioxide lead to production of carbonic acid in rain water, and the normal pH for unpolluted rain may be near 5.6. The actual pH may be higher in the presence of alkaline dust particles, or lower with the presence of natural (or man-made) acids. Deposition of acid could be important from a number of perspectives. Aquatic ecosystems may be poorly buffered with respect to acidity, and input of low-pH (= high acidity) solutions may lead to high inputs of aluminum ions leached from the soil (inorganic aluminum ions are more soluble at low-pH levels) and direct damage to aquatic biota.

The deposition rates of ammonium and nitrate represent no toxic threat *per se*, but may offer the opportunity for N-deficient plants to increase growth, and perhaps shift dominance and composition of plant communities and aquatic communities. No observations or experimental information is available for the Colorado Plateau on the possible responses of plant communities to very low, chronic additions of N.

Deposition of sulfuric and nitric acid is primarily a concern for acidic soils, where movement of sulfate through the soil can lead to mobilization and transport of potentially toxic aluminum into aquatic ecosystems. In the northeastern U.S., and in some high elevation ecosystems in the west, depressions in pH and temporary loss of acid neutralizing capacity (ANC) in streams have been associated with elevated levels of nitrate. These episodes may affect native fish species and aquatic insects.

The National Atmospheric Deposition Program (NADP) was established in 1978 to document patterns in deposition across the U.S., and over time. The network currently has more than 200 sites, where uniform protocols for sampling and analysis provide comparable data by geographic regions. Precipitation samples are collected weekly at each site with an AeroChem Metrics model 301 wet/dry sampler. Personnel at each site collect water from the wet collector, and send samples to a central laboratory for analysis of major ions (sulfate, nitrate, chloride, phosphate, sodium, potassium, calcium, magnesium, ammonium, and hydrogen ion and total conductivity). Precipitation amounts at NADP sites are measured with a Belfort Model 5-780 dual-traverse recording rain gauge. The NADP protocols do not assess dry deposition rates. Estimates of dry inputs of N and S at Grand Canyon were developed as part of the National Dry Deposition Network (NDDN) for 1990 and 1991, and rates were very low (0.05 kg-N ha^{-1} yr^{-1} as nitrate, and 0.2 kg-S ha^{-1} yr^{-1} as sulfate; Clarke and Edgerton 1993).

The sites of the NADP across the Colorado Plateau show annual average pH values of 4.9 to 5.5 (Figure 1-5). These values are relatively high compared to the rest of the U.S. (Figure 1-6). The wet deposition of N is also relatively low, ranging from about 1.1 kg N ha^{-1} yr^{-1} at the Grand

Canyon to 2.5 kg N ha^{-1} yr^{-1} in parts of southern Colorado (Figures 1-7, 1-9), compared with > 6 kg N ha^{-1} yr^{-1} for much of the northeastern U.S. (Figures 1-8, 1-10). Fox et al. (1989) suggested that no forests would be affected by rates of N deposition between 3 and 10 kg N ha^{-1} yr^{-1}, and we think that rates less than 3 kg N ha^{-1} yr^{-1} likely pose no threat to desert, shrub, or forest ecosystems. Deposition of S as sulfate is also low, ranging from 0.7 to 2.4 kg S ha^{-1} yr^{-1} (Figure 1-11), again much lower than for the northeastern U.S. (Figure 1-12). The current deposition rates of S probably have no effect on air quality related values, especially given the high concentrations of sulfate in the arid and semi-arid soils of the Plateau. Fox et al. (1989) suggested that deposition rate less than 3 kg S ha^{-1} yr^{-1} could not threaten forests even on very sensitive soils.

Critical loads of S deposition have been set by the Canadians in the range of 2.7-6.7 kg S ha^{-1} yr^{-1} to protect low-ANC, oligotrophic (nutrient poor) lakes and streams. The NADP maximum value of wet S in deposition on the Colorado Plateau (2.4 kg ha^{-1} yr^{-1}) probably represents more than half of the total deposition. Accounting for both wet and dry deposition, S inputs on the Colorado Plateau probably fall below the critical range suggested for Canadian systems; additional information may be needed on dry deposition rates, however; too little direct information is available for gauging the sensitivity of unique aquatic resources such as potholes or tinajas that may be oligotrophic and low-ANC. Also, these critical loading estimates were developed for eastern aquatic systems, and are of limited value in this semi-arid environment. One study suggested that 10 kg N ha^{-1} yr^{-1} may be a critical load for protecting aquatic ecosystems in northern Europe (Dise and Wright 1995). Maximum loads of wet N deposition on the Colorado Plateau are 2.5 kg N ha^{-1} yr^{-1}, (or perhaps slightly higher if dry deposition is included; Clarke and Edgerton 1993). This is notably lower than published suggestions for critical loads for affecting air quality related values, though we note again that these loads were generally developed for different types of ecosystems than those occurring over much of the Colorado Plateau.

Figure 1-6. Rainfall pH (laboratory values) for the U.S. for 1995 (map from NADP, Colorado State University).

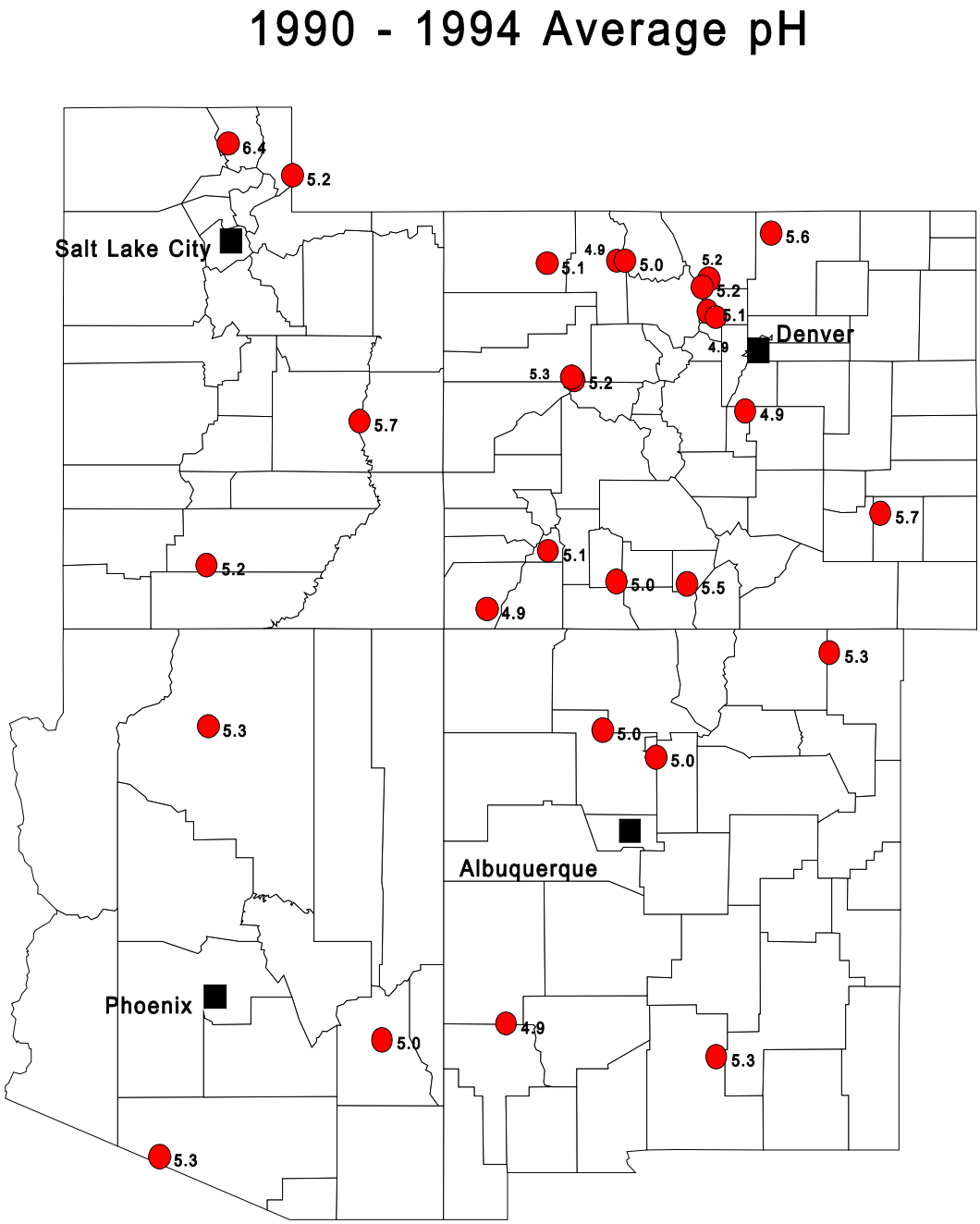


Figure 1-8. Ammonium deposition (NH_4^+; multiply by 0.778 for N only) for the U.S. for 1995 (map provided by NADP, Colorado State University.

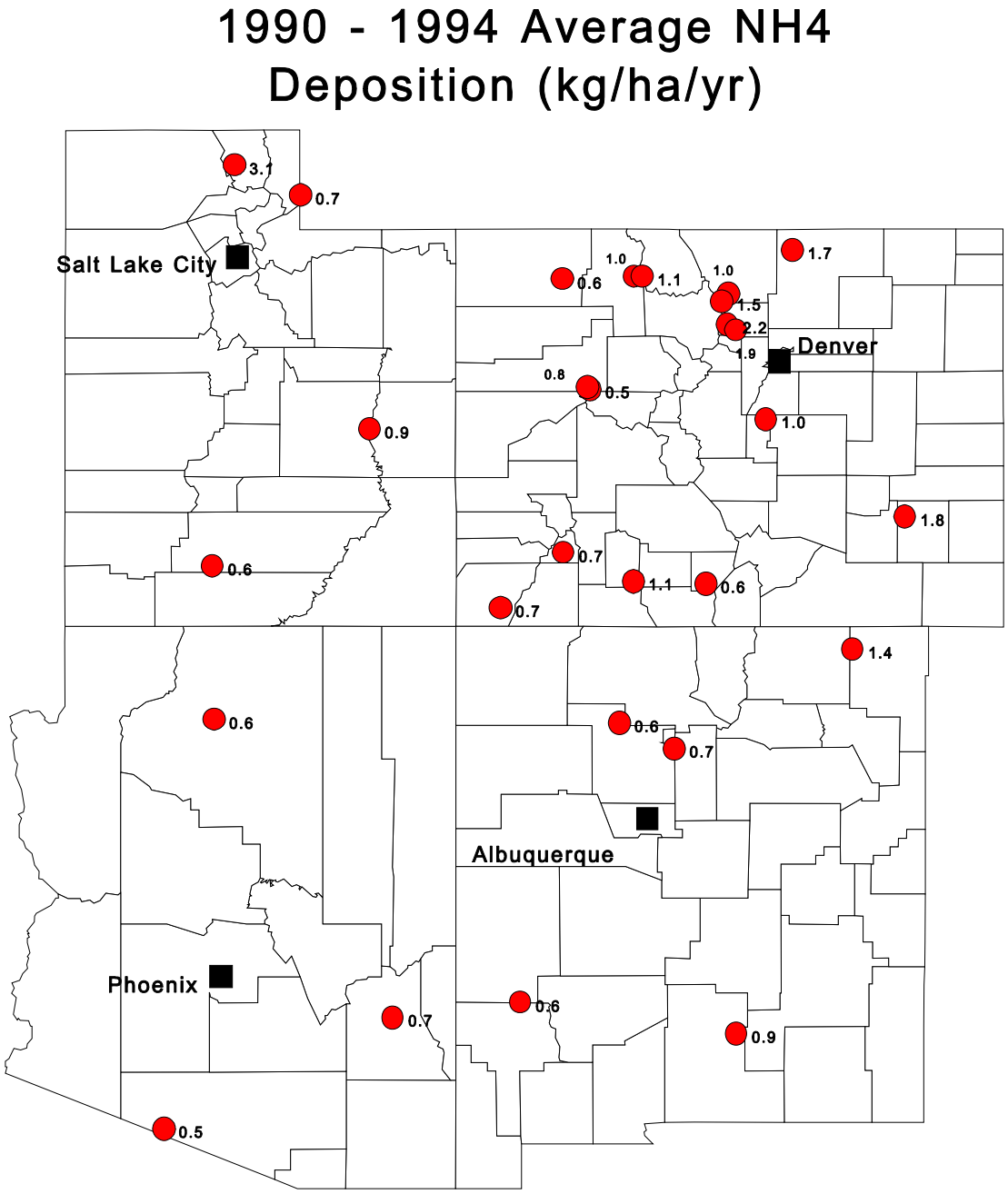


Figure 1-10. Nitrate deposition (NO_3^-; multiply by 0.226 for N only) for the U.S. for 1995 (map from NADP, Colorado State University.

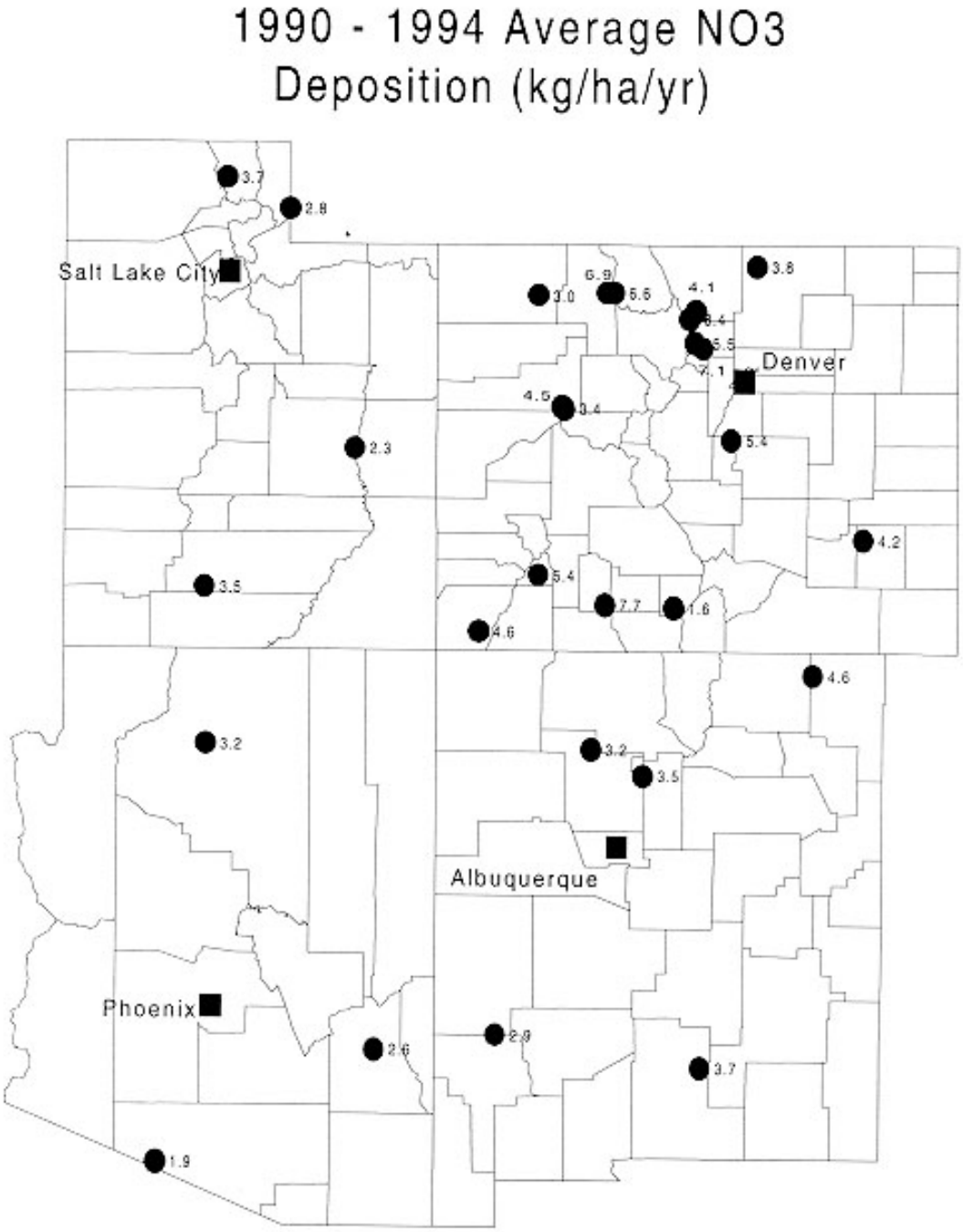
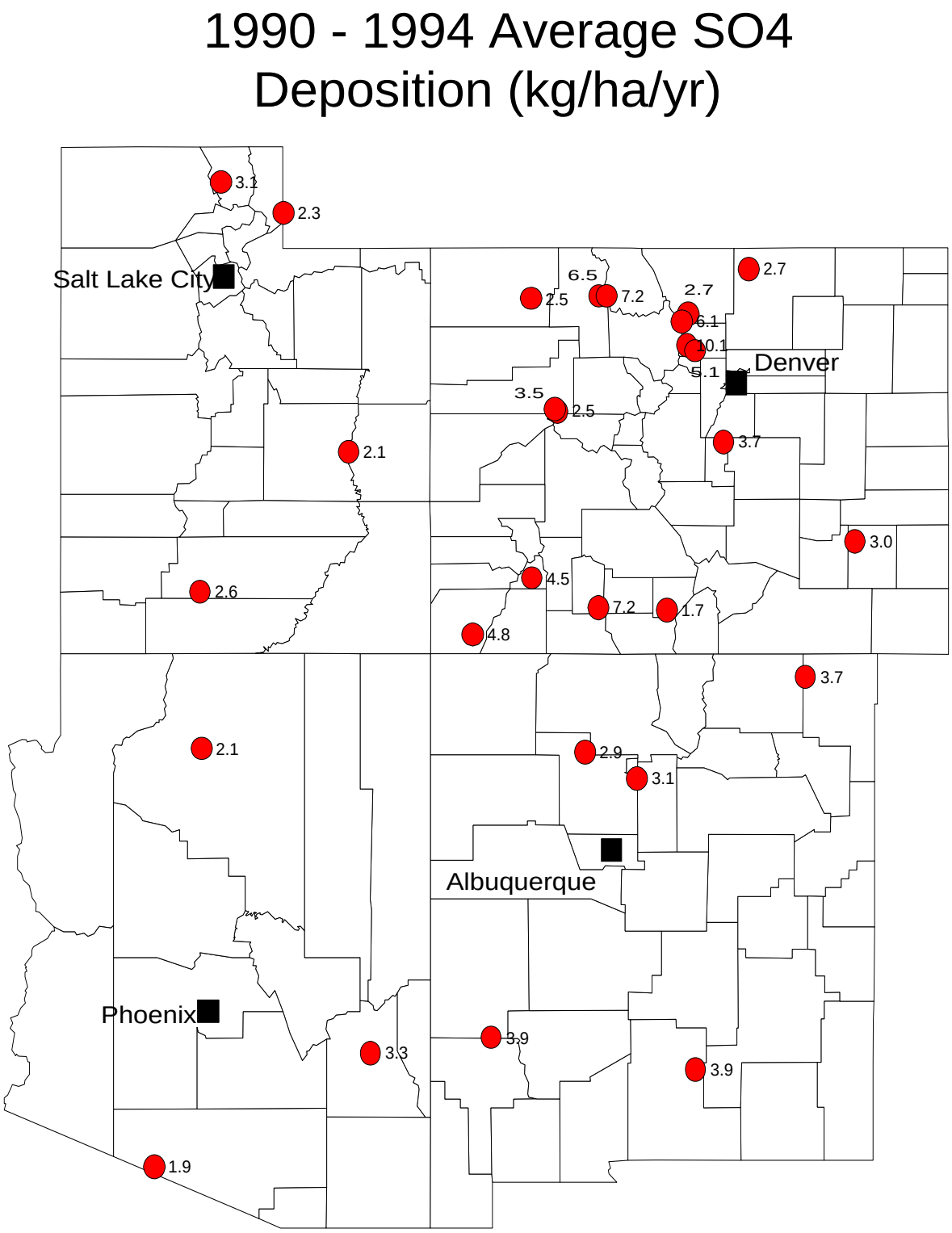


Figure 1-9. Nitrate deposition (NO_3^-; multiply by 0.226 for N only) for the Colorado Plateau and surrounding areas. Dots represent NADP monitoring sites, squares are major cities (data from NADP, Colorado State University).

Figure 1-12. Sulfate deposition (SO_4^{2-}; multiply by 0.333 for S only) for the U.S. for 1995 (map from NADP, Colorado State University).



Other Oxidants, Toxics, Heavy Metals, Radioactive Nuclides

A wide variety of other air pollutants may affect ecological systems, including oxidants [such as PAN (peroxylacyl nitrate)], organic pesticides, heavy metals (such as cadmium), and radioactive nuclides. Almost no information is available relevant to these chemicals and AQRVs on the Colorado Plateau. The State of Arizona is conducting some monitoring of radioactive particles in the air at Grand Canyon (see Chapter 9), and the levels are too low to pose a concern. The only likely importance of any of these would involve either naturally occurring soils with high concentrations of heavy metals (such as selenium), point-source spills of contaminants, or resumption of widespread mining of uranium.

Aquatic Systems and AQRVs

The parameters related to aquatic ecosystems include water quality, aquatic species populations (flora and fauna, both vertebrate and invertebrate), community structure, and process rates (e.g. nutrient cycling). These AQRVs can be affected by atmospheric deposition of nitrogen, sulfur, and acidity, resulting in acidification, nitrogen saturation, eutrophication, and nuisance algae blooms.

Aquatic AQRVs are usually described in broad terms, with the focus of surface water chemistry measurements on pH, ANC, and nutrients. Assessment of both chemical and biological parameters needs to consider the seasonal and interannual variability in these measurements that are due to natural variation.

Biological populations and ecosystem processes that may be affected by deposition of acidity and nutrients include:

1) phytoplankton and periphyton (especially diatoms and blue-green alga);
2) zooplankton (especially *Daphnia* species);
3) stream invertebrates (especially *Baetis* species)
4) aquatic vertebrates, including different life history stages of fish and amphibians;
5) nitrogen cycling in watershed soils and surface waters.

A summary of the possible effects of deposition on water chemistry and aquatic biota is included in the 1991 State-of-Science documents from the National Acid Precipitation Assessment

Program (NAPAP) (Baker et al. 1990, Baker et al. 1990, Thornton et al. 1990, Turner et al. 1990, Wigington et al. 1990). In our discussions of the "sensitivity" of aquatic systems on the Colorado Plateau, we are primarily concerned with the change in pH and ANC of low conductivity waters. When acid deposition falls on watersheds with bedrock that resists weathering, ANC and pH decline in the surface waters and sulfate or nitrate concentrations may rise. The organisms most likely to respond to such changes in the chemistry of surface waters include: native fish species (such as trout, dace, and minnows), aquatic insects, and amphibian larvae. The most common aquatic systems found on the Colorado Plateau are large rivers (e.g. the Colorado River) or high ANC feeder streams. Although these systems do not fall in the "sensitive" category, it is important to consider whether small, low conductivity systems might respond to increases in deposition of hydrogen, sulfur or nitrogen under increased atmospheric loading rates.

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