

## 1997 AIR QUALITY STATUS AND TRENDS

Units of the National Park System are experiencing air pollution-related effects: reduced visibility, injury to vegetation, changes in lake and stream chemistry and deterioration of cultural resources. Under the Clean Air Act, the Organic Act, and other legislation, the Department of the Interior has a responsibility to protect resources within national park units from these effects.

### Background

Since the late 1970s the National Park Service has monitored visibility conditions and ambient levels of fine particles, ozone, sulfur dioxide, and wet deposition in national parks. Visibility monitoring, including photographic, optical and fine particle monitoring, is conducted as part of the Interagency Monitoring of Protected Visual Environments (IMPROVE)--a national visibility monitoring cooperative among the U.S. Environmental Protection Agency (EPA) and Federal land management agencies. Wet deposition monitoring is conducted as part of the Service's participation in the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). The Service has developed its own network for gaseous pollutant and meteorological monitoring, although a few States supplement NPS efforts at a few locations. These networks are essential to the understanding the impacts of air pollutants to park ecosystems previously presumed to be relatively free of anthropogenic stresses. Before the Service's networks were established, there was relatively little monitoring being conducted in national parks because EPA and States placed priority on health-related monitoring in urban areas. Additional funding provided by Congress in 1986 and 1987 allowed the Service to expand its monitoring network and establish a data center to process, validate, and archive NPS data. Ozone, sulfur dioxide, and meteorological data collected by NPS are entered into EPA's national database for use by EPA and State agencies and researchers. Visibility and wet deposition data are available via the Internet.

### Current Status

#### *Fine Particles and Visibility*

Until 1988 when the IMPROVE visibility monitoring network became operational, the NPS visibility monitoring program was the only source of visibility information in Class I areas (areas identified by the Clean Air Act as requiring special protection). NPS has maintained visibility monitoring in many of its parks since 1978. Visibility monitoring includes three types of monitoring: photographic monitoring, optical monitoring and fine particle sampling. Scene monitoring documents the condition of a scene(s) in a park three times a day using a 35-mm camera. Optical monitoring is performed using instruments that actually measure the visibility condition of the atmosphere. This monitoring provides a record of visibility conditions in parks on an hourly basis. Fine particle sampling allows the NPS to determine the causes of pollutants and their source types or source regions responsible for the observed impairment to visibility in our parks. Twenty-four hour average fine particle samples are collected twice weekly at each monitoring location.

## *Wet Deposition*

Wet deposition sampling in parks has been performed on a weekly basis since 1978 using wet/dry collectors. These collectors collect precipitation samples on an event basis, with the wet collector being open only when precipitation occurs. Samples are sent to a central laboratory for chemical analysis of important analytes, such as sulfate, nitrate, pH, sodium, calcium, and ammonium. There are twenty-nine wet deposition stations in national parks that are part of the NADP/NTN network (total of 200 stations in the U.S.). A recent NPS study showed that NPS stations make a very significant contribution to the overall NADP/NTN network in its ability to characterize spatial trends in precipitation chemistry across the U.S.

## *Gaseous pollutants*

Because of the toxicity of ozone and sulfur dioxide to park vegetation and other resources, NPS performs monitoring for these pollutants on a system-wide basis. Prior to 1983, NPS was reliant on state agencies to perform gaseous pollutant monitoring in its parks, however, only a few states actually monitored either ozone or sulfur dioxide in their parks. As a result, NPS had little or no data on the levels of these pollutants in parks. Since 1983, NPS has developed a nationwide network of gaseous pollutant and meteorological stations to assess the condition of the air resource in a selected number of parks. Using EPA protocols, ozone, and in some cases sulfur dioxide, are monitored on a continuous basis using sophisticated instrumentation housed in temperature controlled shelters. In a few special cases, ozone precursors (nitrogen oxides and volatile organic compounds) are also measured in this fashion. Sulfur dioxide is also measured on a time-integrated basis, with samples being collected either on a twenty-four hour basis twice per week or on a weekly basis. Recently, NPS has experimented with the use of passive samplers for the measurement of ozone, sulfur dioxide, and nitrogen oxides. These samplers provide integrated samples on a weekly basis although the samplers can be used for shorter duration. In late 1993, NPS formed a partnership with EPA to merge the western portion of the NPS gaseous pollutant network with EPA's National Dry Deposition Network. Although this will not increase the number of monitoring locations, it will provide for the measurement of additional pollutants in eighteen NPS areas and additional data analysis support to NPS.

Figures 1 through 8 show: 1) NPS locations where visibility (optical and fine particle), ozone, and wet deposition monitoring is currently being conducted by either the NPS or by other agencies as of 1997, 2) total fine particle and particulate sulfate concentrations and visibility conditions (displayed as deciviews) for the period 1992-1995, 3) wet deposition pH, sulfate and nitrate ion concentrations for 1996 and 4) 1994-1996 average ozone concentrations (displayed as a three-year average of the annual fourth highest daily maximum eight-hour concentration) at NPS monitoring sites.

## *Spatial Trends*

### *Fine Particles and Visibility*

Estimates of natural background concentrations for fine particles are 3.3 and 1.5  $\mu\text{g}/\text{m}^3$  in the east and west, respectively. Corresponding estimates of natural background sulfate concentrations are 0.2 and 0.1  $\mu\text{g}/\text{m}^3$ . Natural visibility conditions are estimated to be about 9.5

and 5.0 deciviews (dv) for the corresponding regions. The dv scale is chosen so that a value of zero represents excellent visibility, *i.e.*, visibility unimpaired by manmade or natural particles suspended in the air. The dv scale is a mathematical transform of the more traditional visual range and atmospheric indices. For example, 30dv and 10dv correspond to 19km and 144km standard visual, respectively.

Fine particle concentrations in the East are typically three to four times higher than in the West, but measurements from both regions, while well above the natural background estimates, are below the annual average EPA National Ambient Standard (NAAQS) for particulate matter of  $15 \mu\text{g}/\text{m}^3$ . This standard, with its companion twenty-four hour standard, if met, should protect the health of people from the adverse effects of fine particulate matter in the air. Though not shown here, all sites monitored appear to be in compliance with the twenty-four hour NAAQS as well.

Because of its important relationship to visibility impairment and acid deposition, sulfate concentrations are also shown (there is no NAAQS for sulfate). Observed sulfate concentrations are factors of six to ten and thirty to forty times natural background estimates in the West and East, respectively.

Visibility conditions display similar patterns to those just discussed. Much greater improvements in the East (about twenty deciviews) would be needed to improve conditions to those corresponding to natural background; the West would require about a four-deciview improvement (California excepted), on the average.

### *Wet Deposition*

Data from the NADP network for three major constituents (sulfate, nitrate, and pH) show the relatively high concentrations of acidic species in rain and snow in the northeastern U.S. and Ohio River valley. West of the Mississippi River the sulfate concentrations are generally low. There is a more variable pattern of nitrate concentrations in rain and snow. In the Northeast the nitrate deposition is still outweighed by sulfate. In the West nitrate concentrations often exceed sulfate. The pH of wet deposition is expressed on a logarithmic scale of hydrogen ion concentrations, with "natural rainfall" pH falling in the range of 5.2-5.8. A band of low pH rain is shown in the Northeast, with the lowest pH's being recorded in western Pennsylvania, New York, and Ohio. In the western U.S. wet deposition pHs are higher due to fewer acidifying emissions and the presence of buffering materials in the air (such as dust) that neutralize acidity. However, there are some hotspots of low pH deposition in the West.

The isopleths of wet deposition chemistry provide general information about distributions of pollutants. However, for park-specific assessments other methods of estimating total loading of chemicals to sensitive ecosystems are needed. For example, many of the sensitive lakes, streams, ponds, and watershed soils in Class I parks are located at high elevations, where much of the inputs are in the form of seasonal snow that is released during spring snowmelt. This temporal pattern of chemical inputs to poorly buffered systems is not captured in the annually averaged data and measurement of snow inputs requires different sampling methods and collection intervals.

## *Ozone*

The map of average ozone concentrations indicate that NPS monitoring sites in southern/central California, the Northeast and east-central U.S. generally record the highest ozone concentrations in the NPS network. The numbers plotted next to the bars on this map represent the 1994-1996 three year average of the fourth highest daily maximum eight-hour ozone concentration expressed in parts per billion (ppb). The EPA in the 1997 revision to the ozone National Ambient Air Quality Standard (NAAQS) adopted this particular measure of ozone levels. This standard, if met, should protect the health of people from the adverse effects of ozone. This standard is met when the three-year average concentration is less than 85 ppb. Acadia NP, Cape Cod NS, Great Smoky Mountains NP, and several park units in California had ozone levels in excess of the NAAQS.

## **Fine Particles and Visibility in Prototype Inventory and Monitoring Parks**

Three of the NPS units conducting prototype ecological monitoring are monitoring visibility: Denali National Park, Great Smoky Mountains National Park, and Shenandoah National Park. These three units, which are part of the IMPROVE visibility network, monitor particulate matter and the optical properties of the atmosphere that are important in understanding the effect that air pollutants have on visual air quality.

Figures 9, 10, and 11 present three-year average fine particulate matter concentrations in micrograms per cubic meter for the three parks. Fine particulate matter is characterized by particles with diameters less than 2.5 micrometers, and is referred to as PM-2.5. The graphs display the average concentrations associated with the best visibility days (marked as 10<sup>th</sup> percentile), average visibility days (50<sup>th</sup> percentile), and worst visibility days (90<sup>th</sup> percentile). The year indicated on the graph axis is the center year of a three-year period. Average PM-2.5 concentrations at Great Smoky Mountains and Shenandoah National Parks are approximately 20, 10 and 5 micrograms/cubic meter ( $\mu\text{g}/\text{m}^3$ ) on best, average and worst visibility days. The Denali PM-2.5 concentrations on worst visibility days (2-4  $\mu\text{g}/\text{m}^3$ ) are less than the concentrations on the best visibility days at the two eastern sites. Denali fine particle concentrations are generally the lowest of all those measured in the IMPROVE network.

The fine particulate matter collected in the IMPROVE network is analyzed to determine its chemical composition. The chemical species found at most IMPROVE sites can be categorized into five chemical types: sulfates, nitrates, mass associated with organic carbon, light absorbing carbon, and soil. In the East, sulfate is usually the greatest contributor to visibility impairment. On best, average and worst visibility days in the East sulfate contributes about 50%, 60% and 70% of the impairment, respectively. For western IMPROVE sites, sulfate contributes about 30%, 35%, and 30%, respectively. The next largest chemical contributors to impairment in both the East and West are organic carbon and light absorbing carbon. Nitrates contribute more towards visibility impairment in the West than in the East. Figures 12, 13, and 14 plot average winter and summer season sulfate concentrations at the three parks. The two eastern sites indicate a seasonal trend observed at most continental IMPROVE monitoring sites. Summer sulfate (as well as total fine particulate) concentrations are several times greater than those measured in the winter season. In Denali, winter sulfate concentrations exceed summer ones.

However, both summer and winter season sulfate concentrations at Denali are very low. Summer sulfate concentrations at the eastern sites are more than twenty times greater than those measured at Denali and more than ten times greater than those at western continental IMPROVE monitoring sites.

Three-year average visibility conditions (expressed as deciview) in the three parks are displayed in Figures 15, 16, and 17. The NPS investigated trends in the three-year average deciview over the years 1988-1996. For the worst visibility days, the trend analysis indicated no or insignificant change in three-year average deciview at Shenandoah National Park, an improvement in visibility (about 0.2-0.4 dv/year) at Denali, and was statistically inconclusive for Great Smoky Mountains National Park. With respect to the average visibility days, all three parks showed an improvement in average visibility conditions. The estimated improvements were about 0.3-0.5 dv/year at Denali, 0.02-0.1 dv/year at Great Smoky Mountains, and 0.1-0.2 dv/year at Shenandoah. The trend for the best visibility days also indicated an improvement at each of the three sites. An improvement of about 0.3-0.4 dv/year, 0.1-0.2 dv/year, and 0.1-0.2 dv/year were estimated for Denali, Great Smoky Mountains, and Shenandoah National Parks, respectively.

#### Reference:

Sisler, J.F. and R. Damberg. In press. Interpretation of Trends of PM-2.5 and Reconstructed Visibility From the IMPROVE Network. Journal of the Air and Waste Management Association.

### **Wet Deposition in Prototype Inventory and Monitoring Parks**

Figures 18 through 21 show NADP wet deposition data for four of the Inventory and Monitoring prototype monitoring parks: Cape Cod National Seashore, Shenandoah National Park, Great Smoky Mountains National Park, and Denali National Park. The graphs focus on concentrations of three chemical species in rain and snow: sulfate, nitrate, and hydrogen ion (expressed as pH). These four parks have NADP data sets that extend from 1980-81 to the present, with time trend analysis available for the period of 1985-93 (Lynch et al., 1995). The effects of chemical deposition on surface waters, watersheds, and aquatic biota are the subjects of monitoring activities in the four parks.

#### *Wet Sulfate*

The three eastern parks (CACO, SHEN and GRSM) all show elevated sulfate in deposition, with these concentrations being about ½ of the highest concentrations found at sites in western New York and Pennsylvania. The maximum sulfate concentrations in these parks are between 2-3 mg/l over the period of record (1980-96), with the highest concentrations being measured in the 1980s. Sulfate values are comparable at CACO and SHEN, with lower values being measured at the low elevation site in GRSM. At the DENA site sulfate ranged as high as 0.52 mg/l, but was generally in the range of 0.1-0.25, comparable to other low deposition sites in the western U.S. Trend analysis for the period 1985-93 showed a statistically significant trend in sulfate only at SHEN, where the concentration of this chemical species declined through the period.



### *Wet Nitrate*

Nitrate concentrations in rain and snow at the three eastern parks (CACO, SHEN, and GRSM) ranged from 0.6-1.2 mg/l, with CACO showing the highest concentrations. Sulfate was always higher than nitrate in these samples. These numbers are about ½ the maximum concentration values for nitrate recorded at monitoring sites in Michigan, New York, and Pennsylvania. At DENA the nitrate concentrations were low, in the range of 0.06-0.26 mg/l, comparable to western U.S. sites. However, at DENA the nitrate to sulfate ratio approaches one, with nitrate being greater than sulfate in 1991. Time trend analysis for 1985-93 showed no significant patterns for the eastern parks; DENA nitrate concentrations showed a significant increase.

### *Hydrogen Ion*

Hydrogen ion or acidity of wet deposition is expressed as pH, which is the negative log of the hydrogen ion concentration. The pH values measured in the three eastern parks (CACO, SHEN, and GRSM) are considered to be acidic, with a range of 4.36-4.75. Only the deposition acidity “hotspots” in Pennsylvania and New York have lower pHs. DENA pH values range from 5.15-5.6, approaching the theoretical “unpolluted” rain pH of 5.6, and are comparable to western U.S. sites. No temporal trends in pH values were detected for the period of 1985-93 for any of these four sites.

### Reference:

Lynch, J. A., V.C. Bowersox, and C. Simmons. 1995. Precipitation Chemistry Trends in the United States: 1980-1993. Summary Report. National Atmospheric Deposition Program, National Resource Ecology Laboratory, Fort Collins, CO. 103 pp.

### **Ozone in Prototype Inventory and Monitoring Parks**

Figures 22-26 display three-year average ozone concentrations for five of the NPS units that are conducting prototype ecological monitoring: Cape Cod National Seashore, Channel Islands National Park, Denali National Park, Great Smoky Mountains National Park, and Shenandoah National Park. The concentrations plotted in these graphs represent three year averages for the three year period ending with the year indicated on the axis of the graphs. Thus, the concentration plotted on the graph associated with 1992 actually represents the three-year average for 1990-1992.

In the ozone National Ambient Air Quality Standard (NAAQS), the EPA uses a three-year average of the 4<sup>th</sup> highest daily maximum eight-hour ozone concentration as its measure for comparing ozone concentrations and determining attainment of the NAAQS. This measure is an eight-hour concentration that is determined by calculating the highest eight-hour concentration

for each day of the year, taking the fourth highest of those daily high values each year, and then averaging this fourth highest value over three consecutive years. Calculating ozone averages this way has the effect of smoothing out some of the shorter-term peak ozone concentrations that may result from atypical meteorological conditions. Three-year average ozone concentrations greater than or equal to 85 ppb exceed the NAAQS. Air pollution levels above the NAAQS can produce adverse effects on human health, particularly for children, the elderly, and people with respiratory diseases.

In the NPS ozone monitoring network, the 1994-1996 average of the fourth highest eight-hour concentration varied from forty-six parts per billion (ppb) at Olympic National Park to 105 ppb at Sequoia National Park. Of the five prototype parks with ozone monitoring, the three eastern sites recorded the highest 1994-1996 average concentrations. Cape Cod and Great Smoky Mountains (Look Rock site) levels exceeded the ozone NAAQS level for that period. Shenandoah, with 84 ppb was very close to the 85 ppb standard. Channel Island and Denali were below this new ozone standard. Denali's 1994-1996 average ozone concentration of 52 ppb was the second lowest concentration in the NPS network and well below the level of the EPA national standard. Eastern and southern California park monitoring sites have consistently recorded the highest concentrations in the NPS network. The lowest concentrations in the National Park System are typically observed in the northwest, Alaska, northern plains, and the Colorado Plateau.

Analysis of statistically significant long-term trends in ozone concentrations is in progress and is not available at this time. A qualitative inspection of the ozone charts suggests that three-year average ozone concentrations at Cape Cod have declined between 1989 and 1996, increased at Great Smoky Mountains (Look Rock site) between 1990 and 1996, and varied little at both Shenandoah and Denali between 1989 and 1996. (Ozone monitoring at Channel Islands National Park ended in 1992 and commenced again at a new site in 1996. No ozone data were collected during 1993-1995.) 1990 and 1991 three year averages at the eastern NPS sites include the influence of 1988 ozone levels which were unusually high because of the long, hot, and dry summer that enhanced the production of ozone.

Figure 1







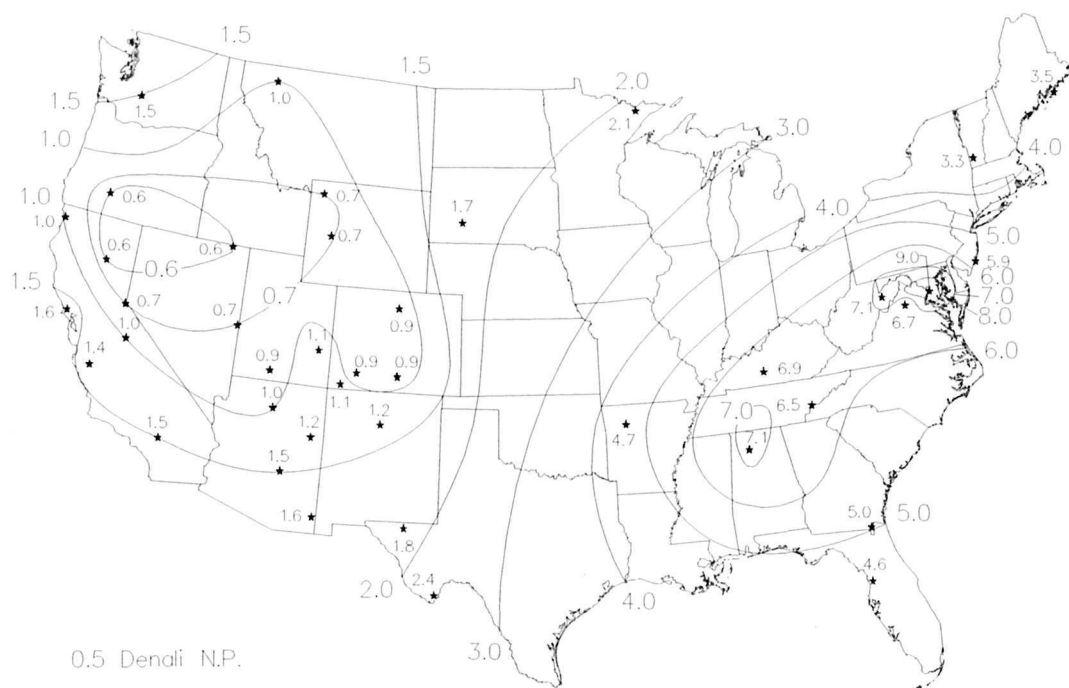


Figure 3 Average fine sulfate aerosol concentrations (in  $\mu\text{g}/\text{m}^3$ ) for each site in the IMPROVE network for March 1992 through February 1995.

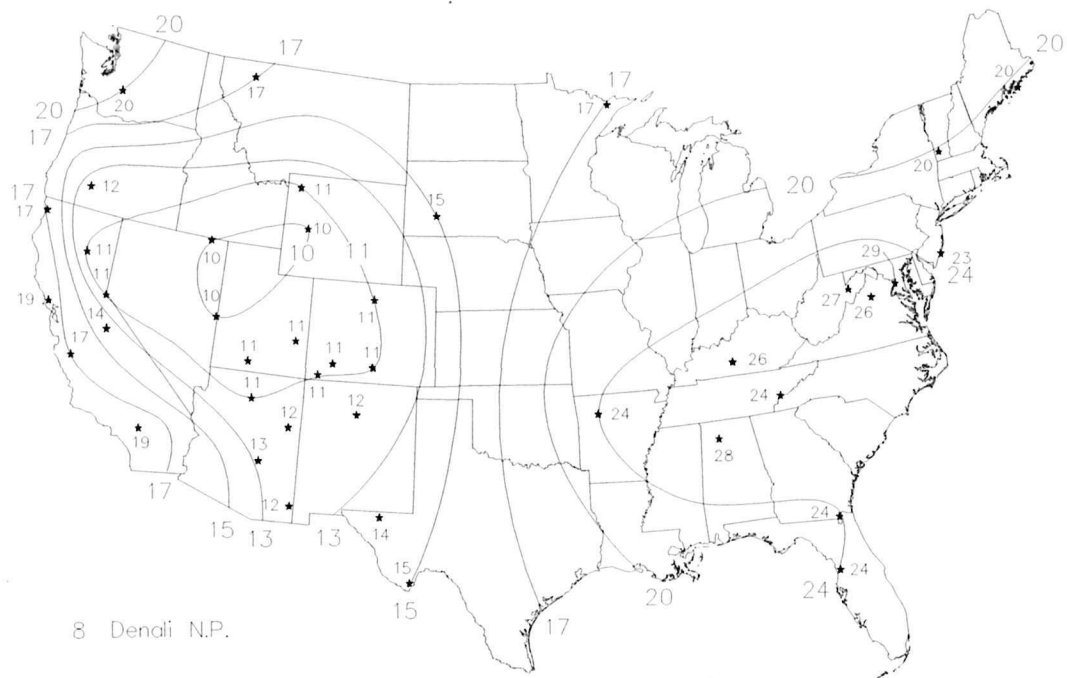
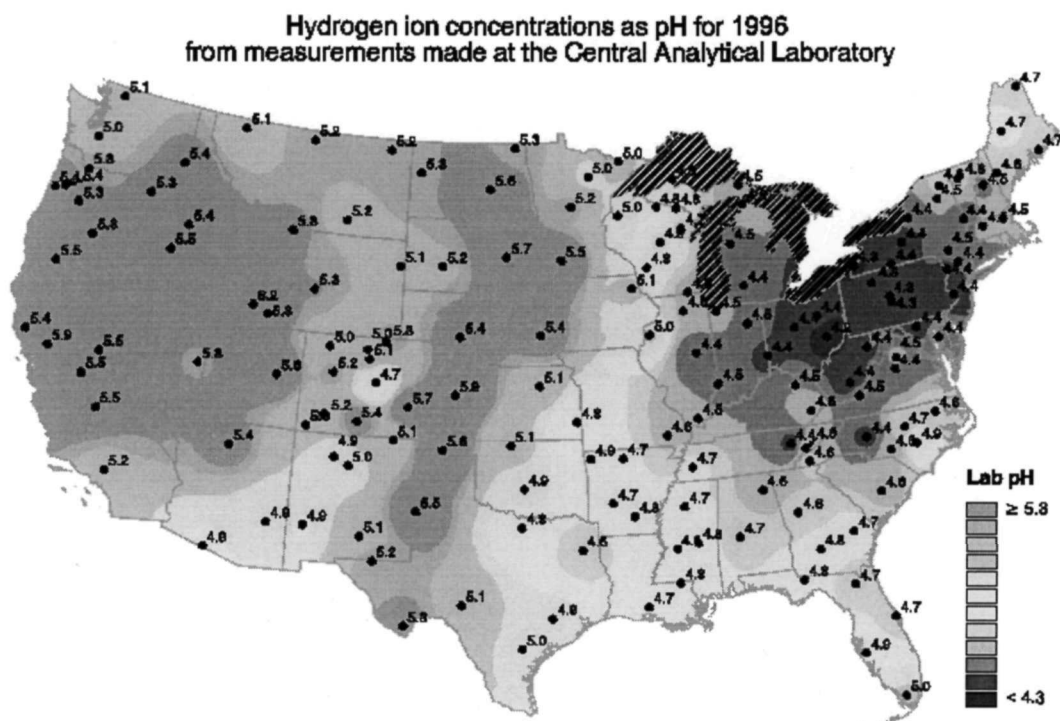


Figure 4 Average visibility impairment in deciviews calculated from total (Rayleigh included) reconstructed light extinction for three years of IMPROVE, March 1992 through February 1995.

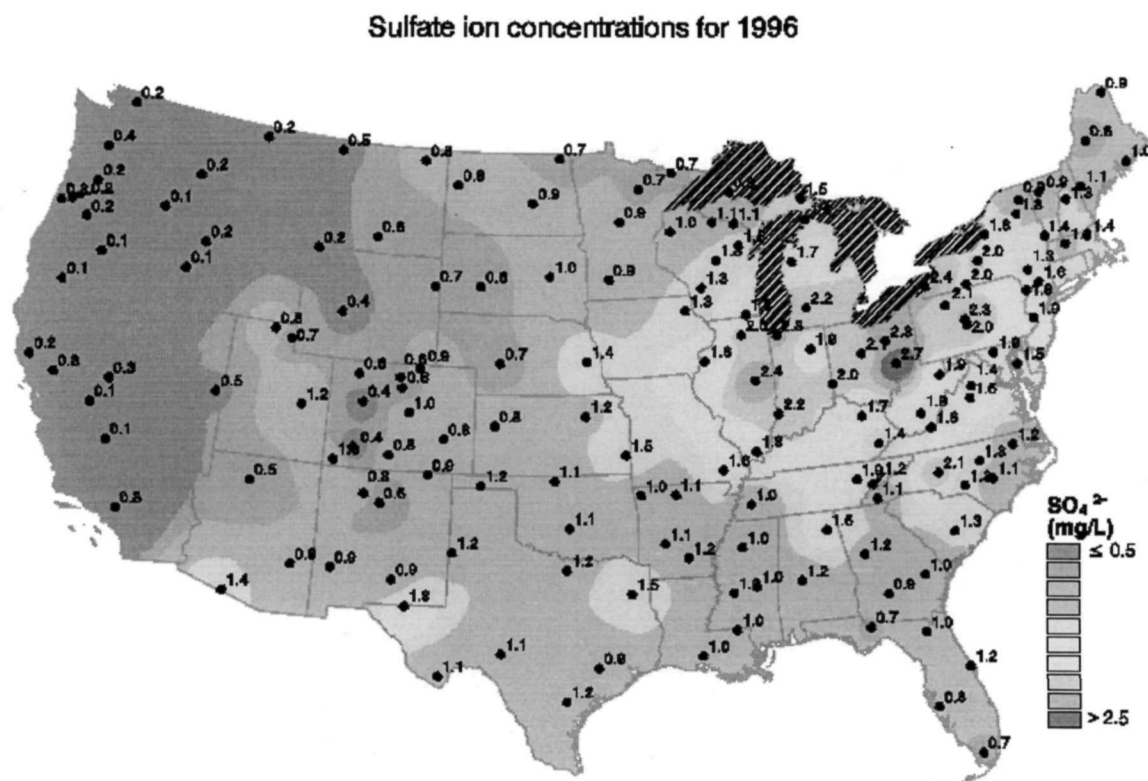
Figure 5



National Atmospheric Deposition Program/National Trends Network

Printed: 09/01/97

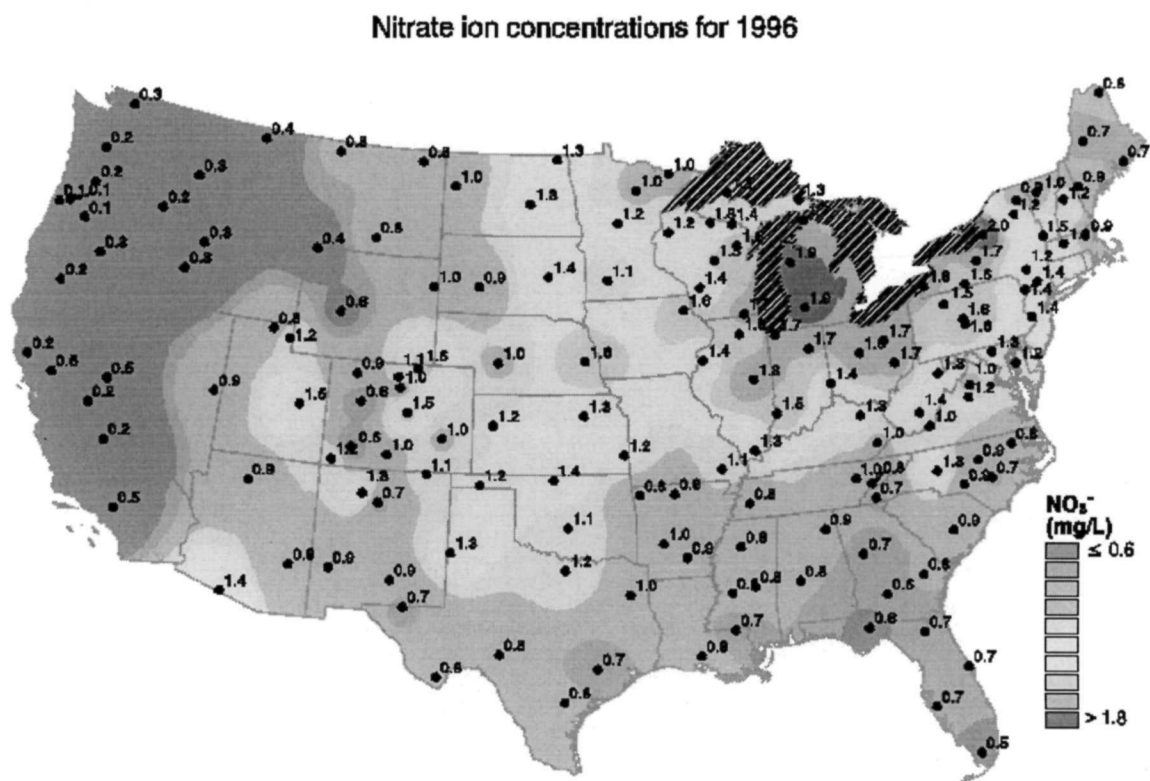
Figure 6



National Atmospheric Deposition Program/National Trends Network

Printed: 09/01/97

Figure 7



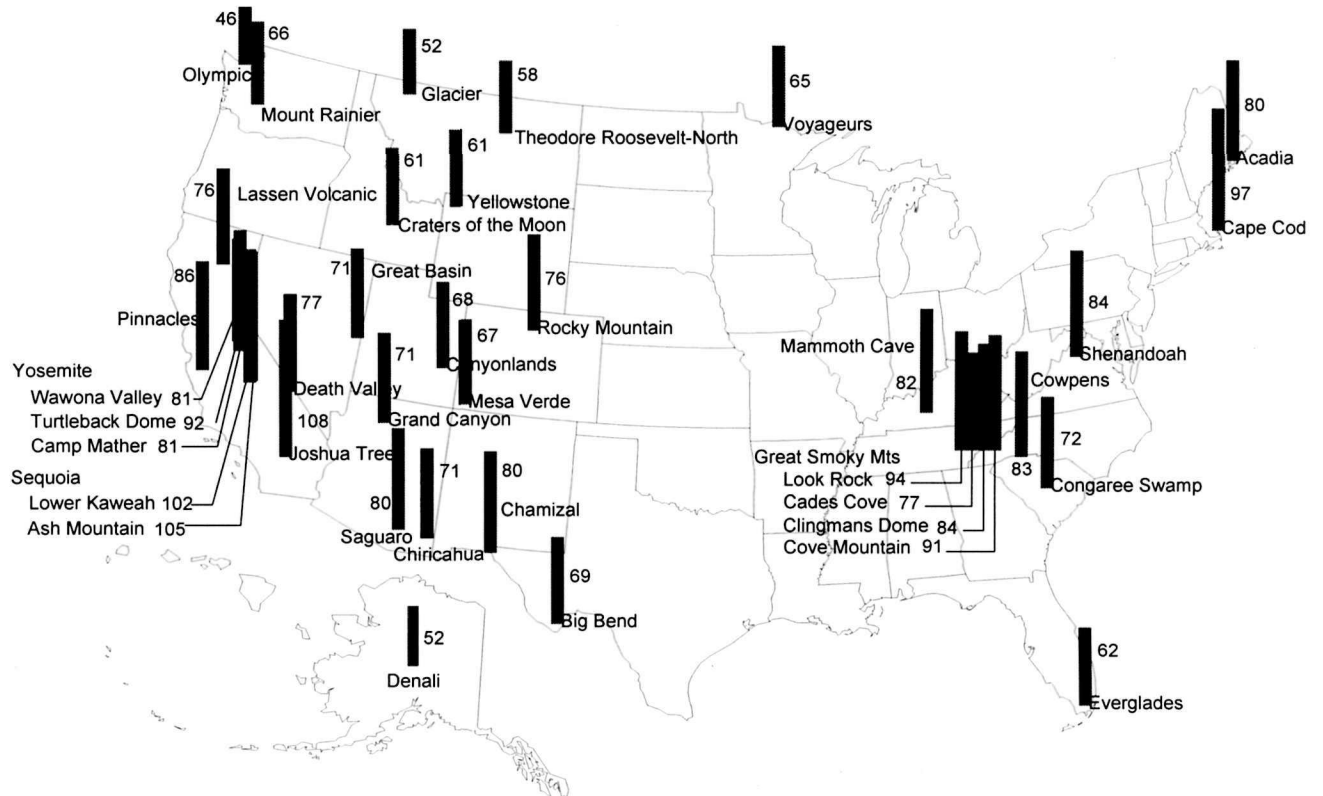
National Atmospheric Deposition Program/National Trends Network

Printed: 09/01/97



**Figure 8**

**1994-1996 Average of the 4th Highest Daily Maximum  
8-hour Ozone Concentration (parts per billion, ppb)**



**Figure 9**

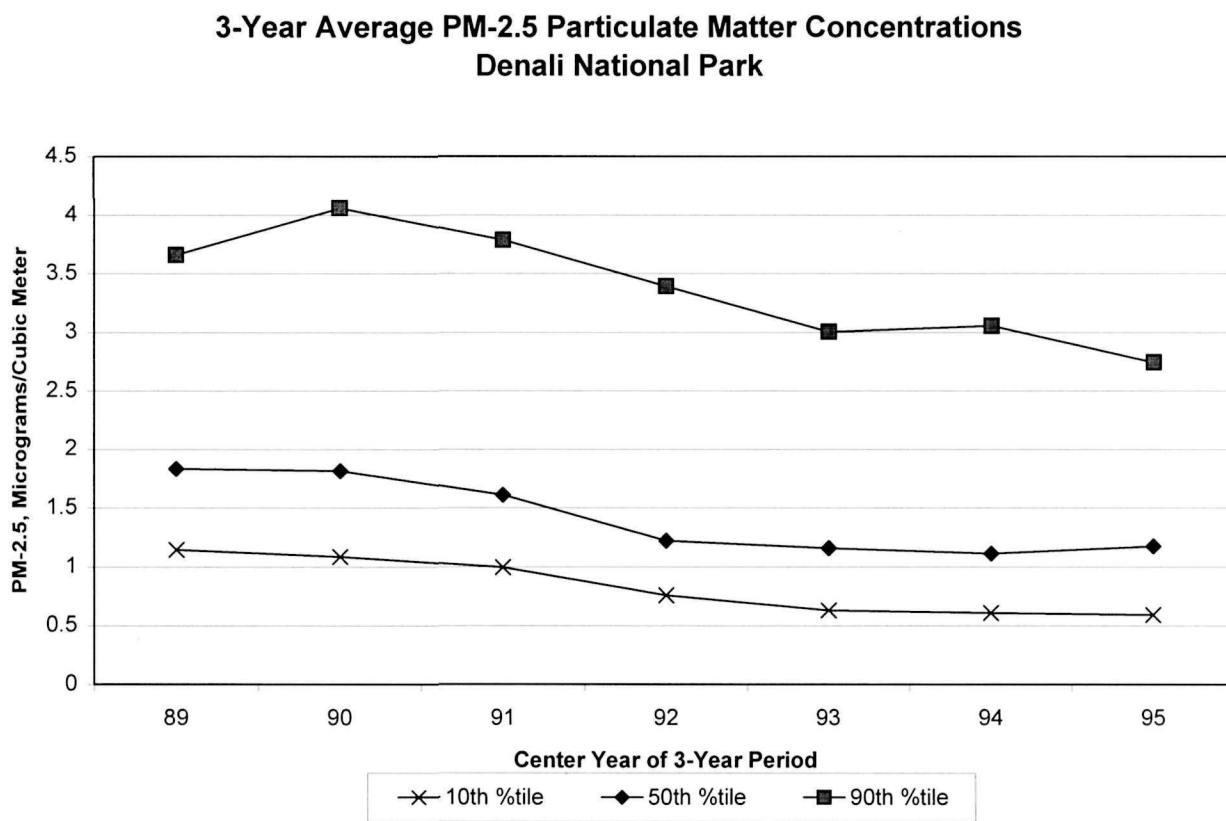


Figure 10

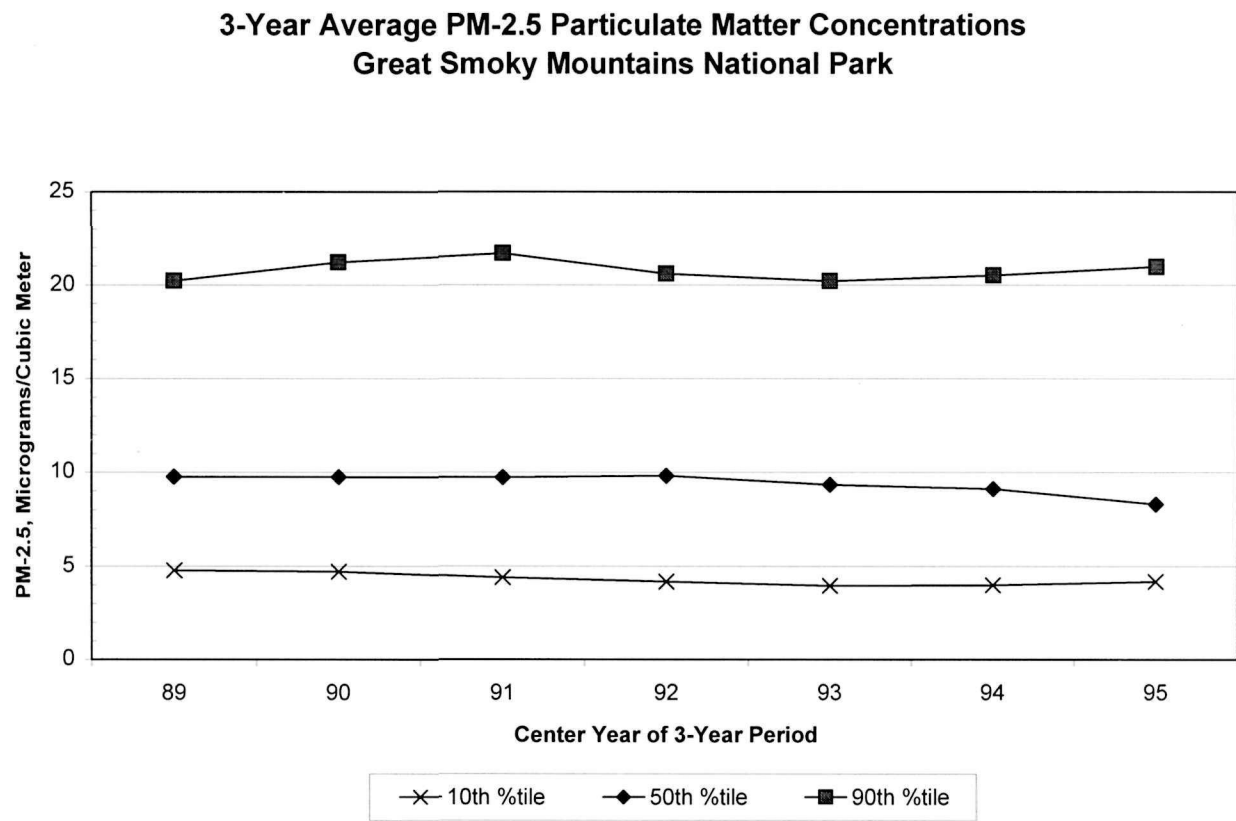


Figure 11

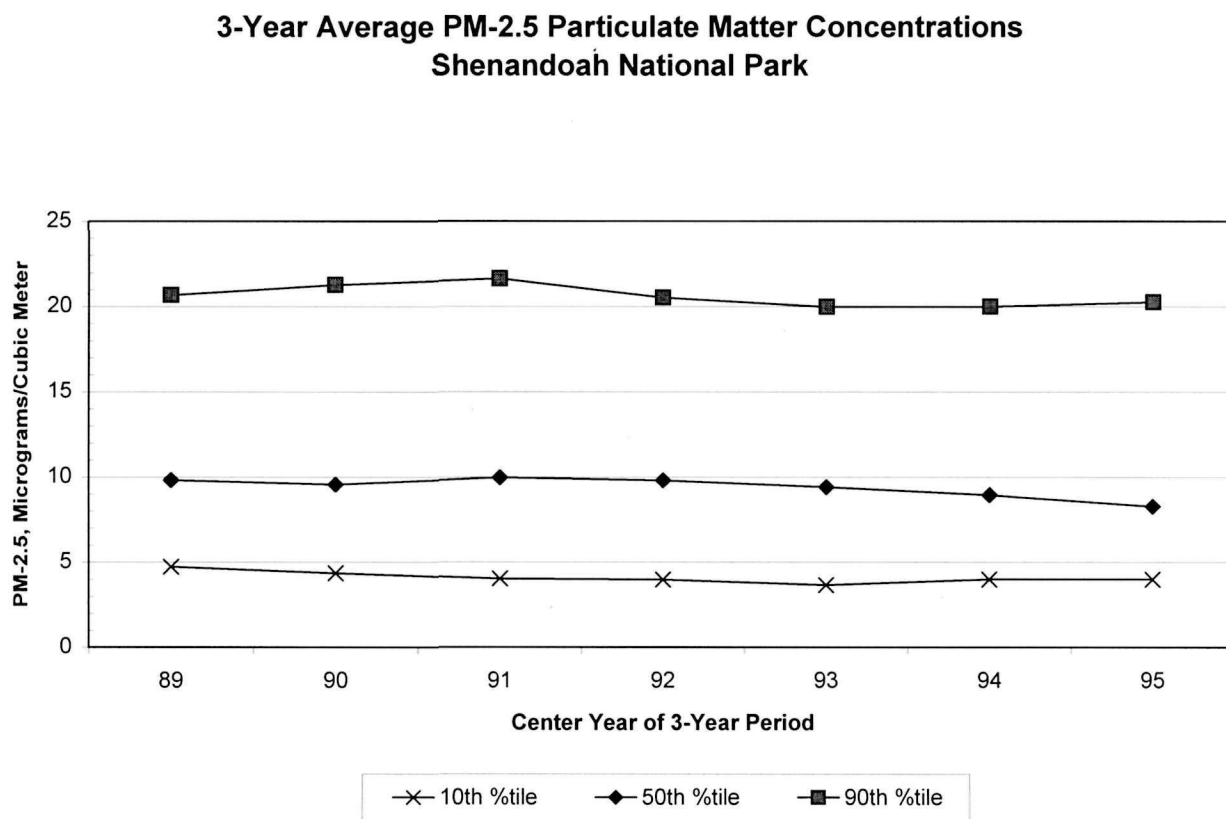


Figure 12

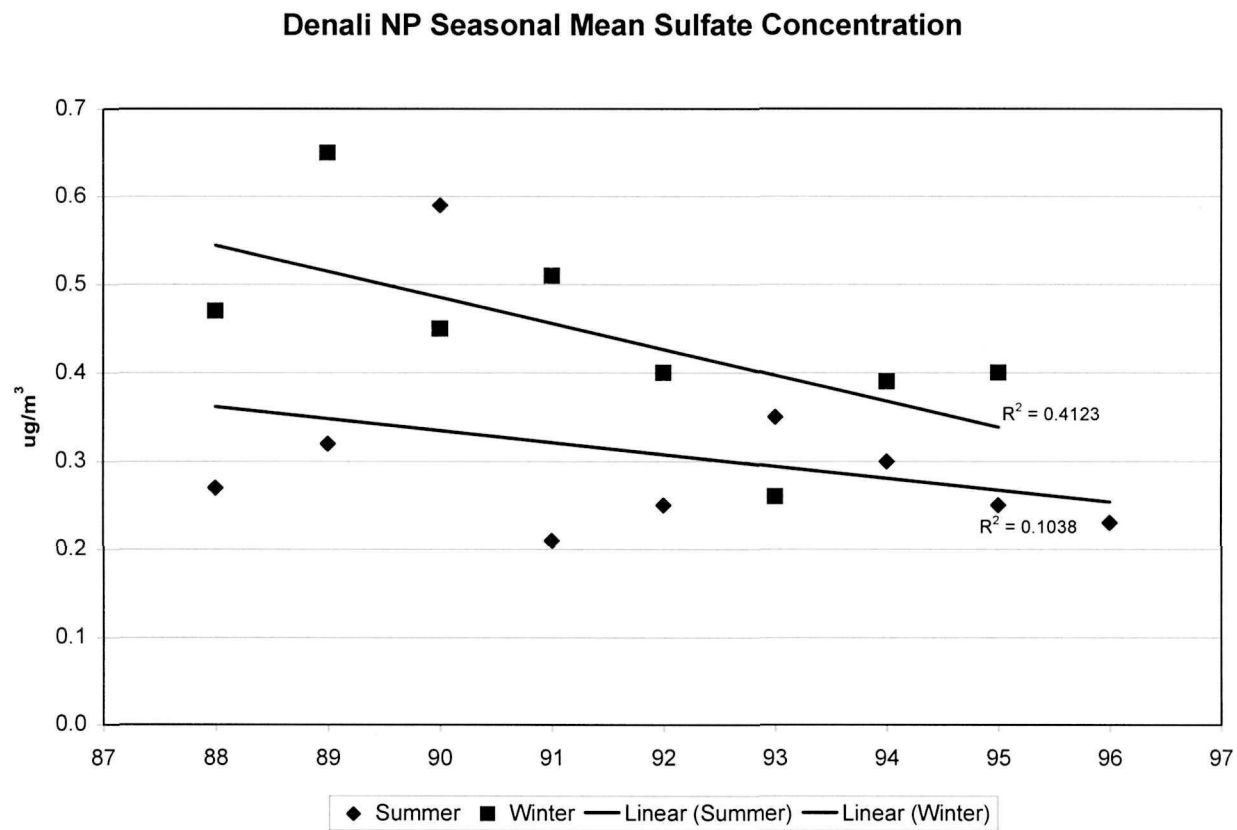


Figure 13

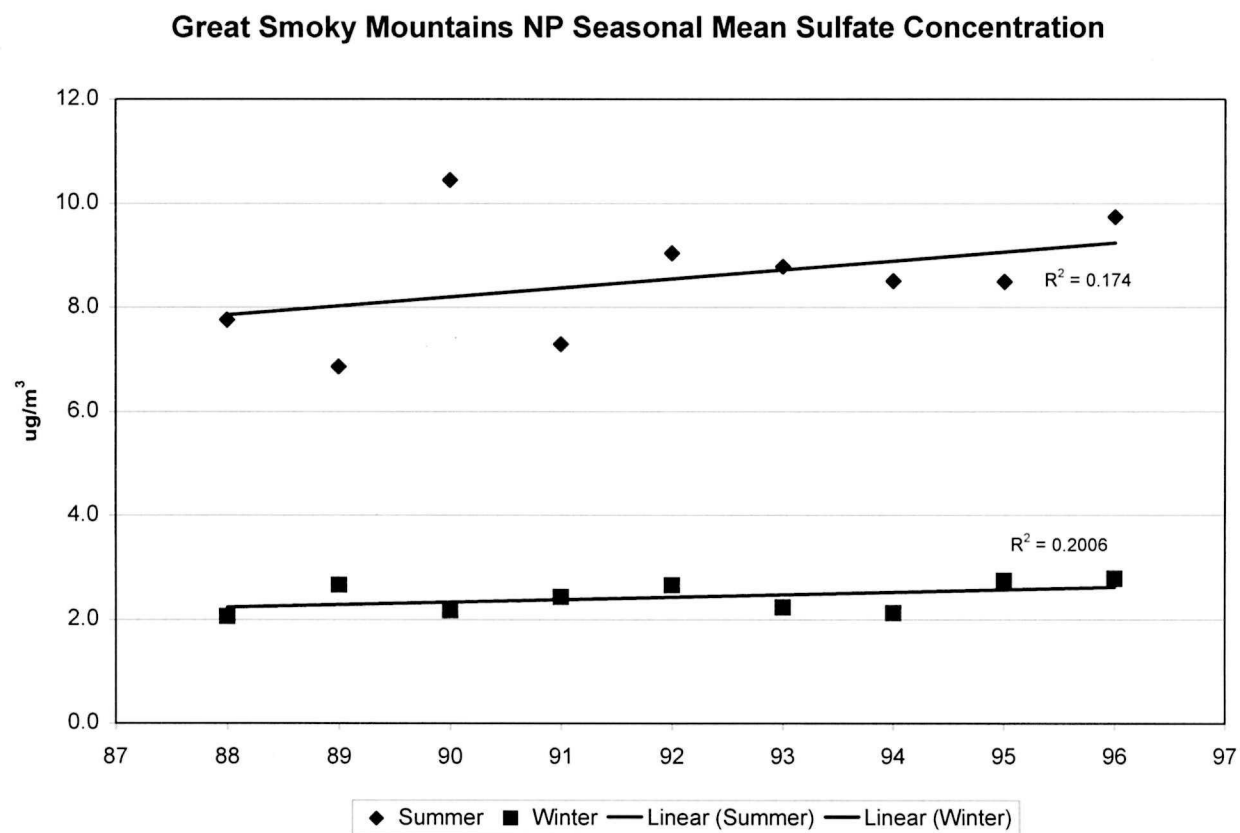




Figure 14

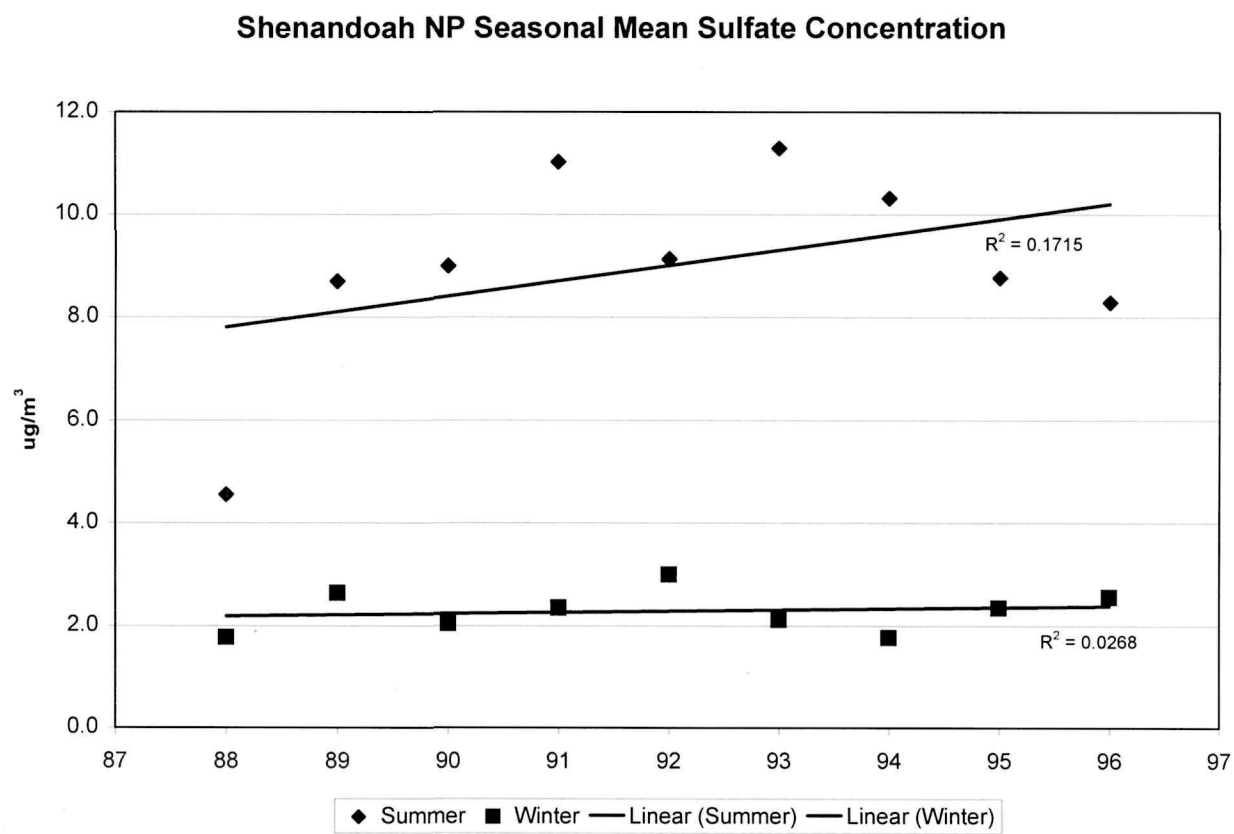
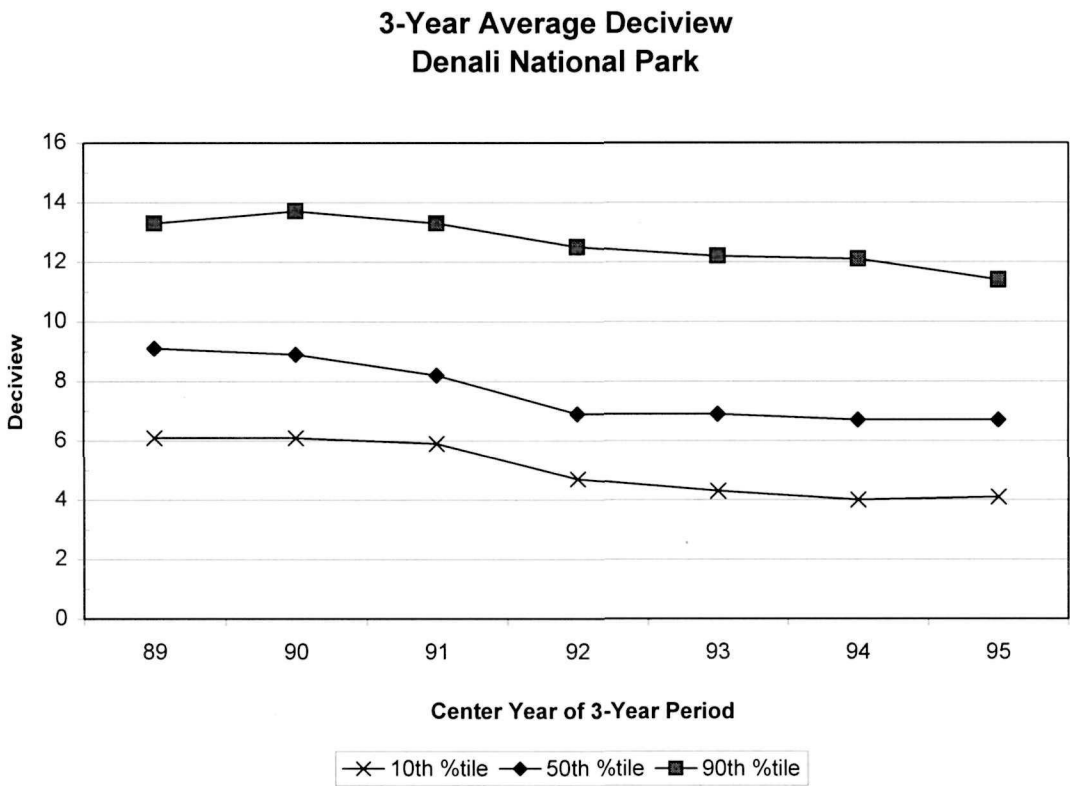
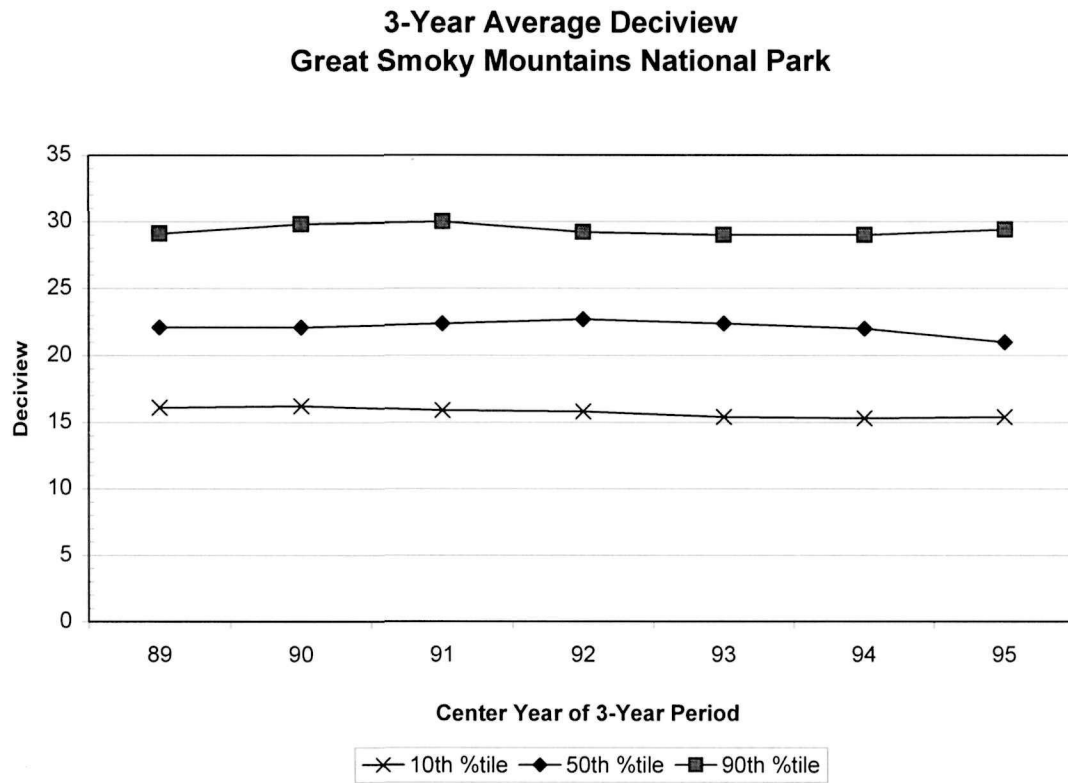


Figure 15



**Figure 16**



**Figure 17**

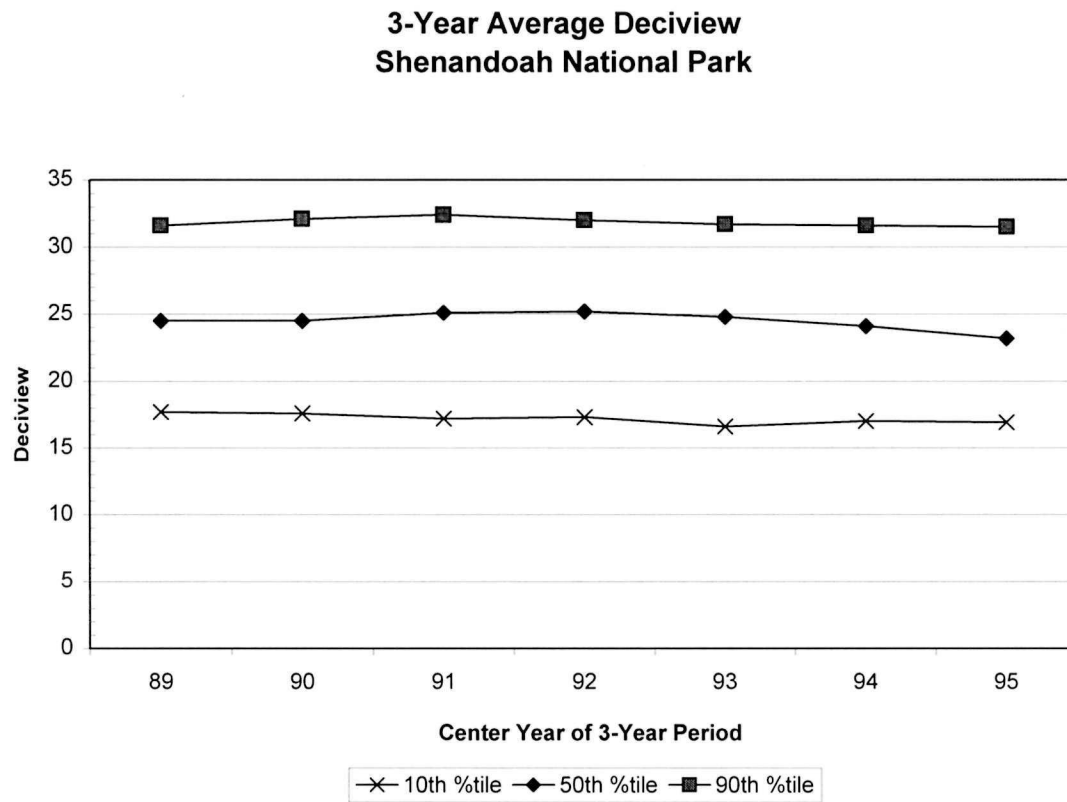


Figure 18

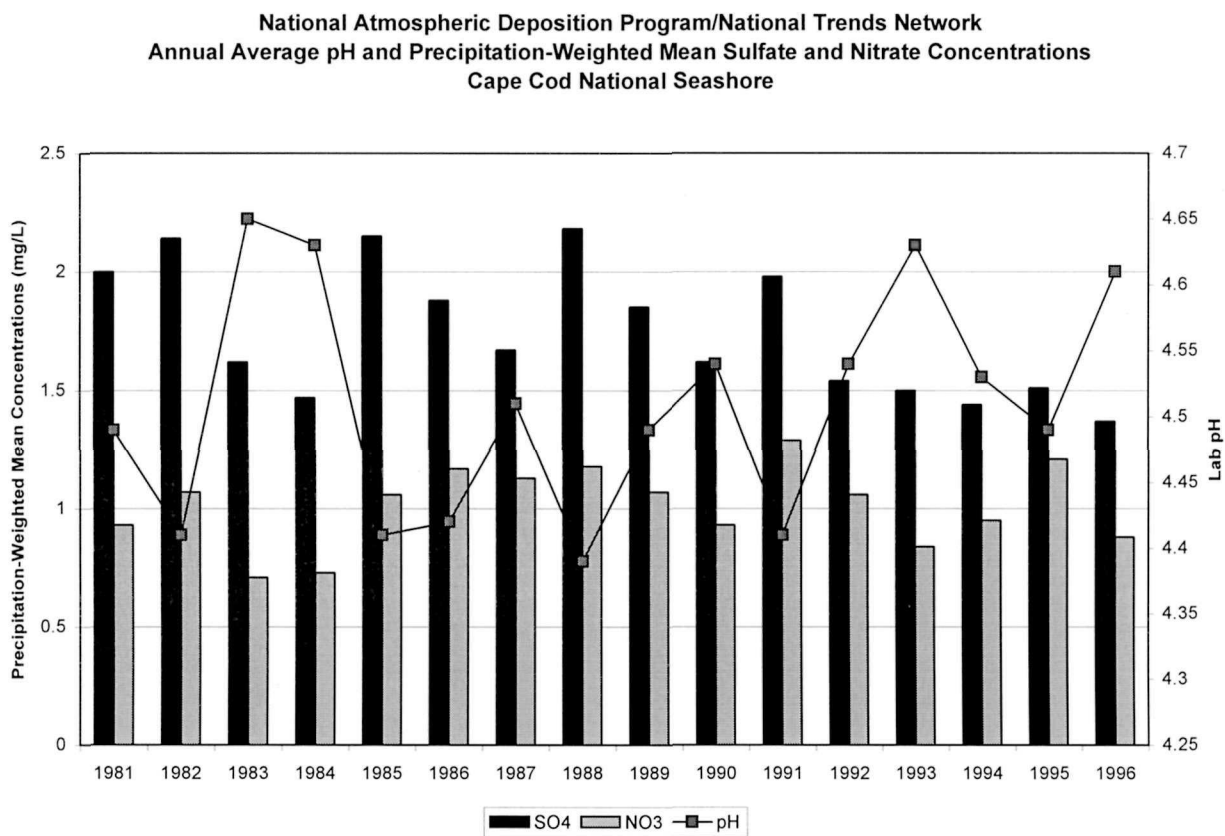


Figure 19

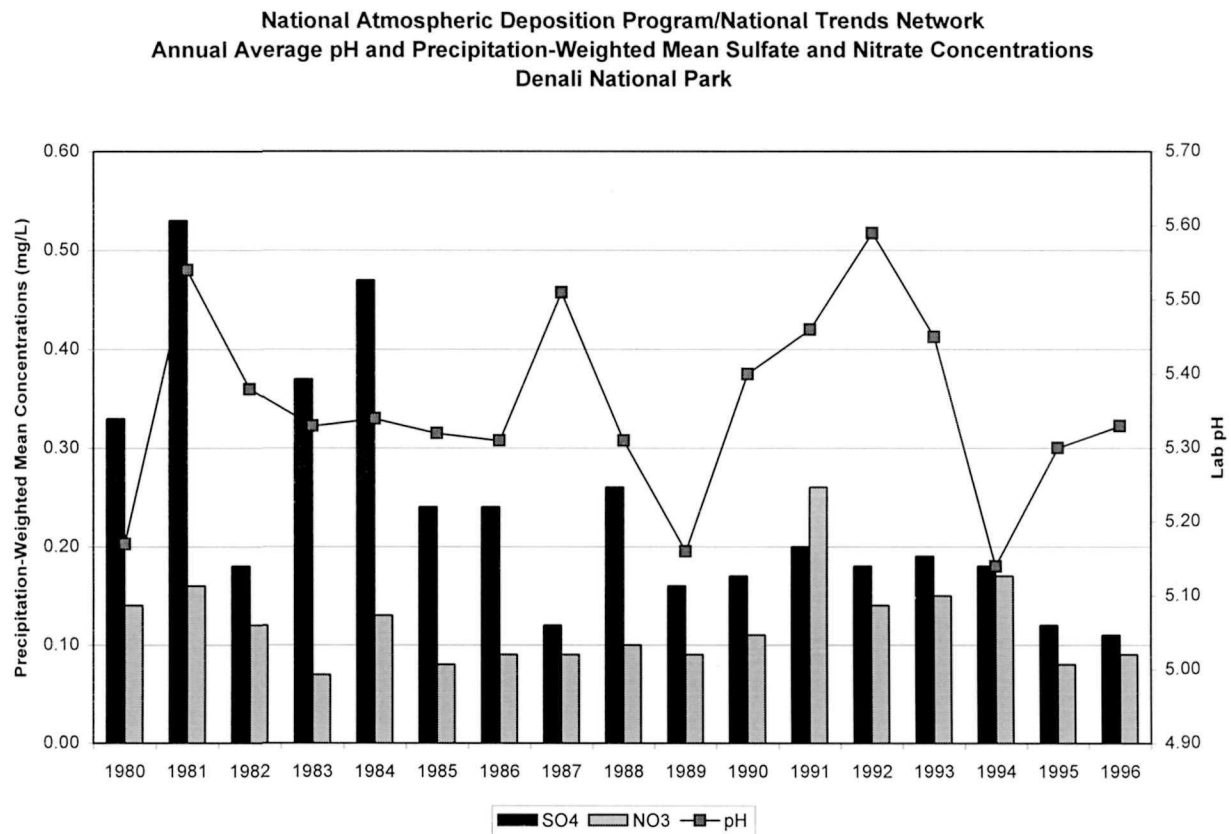




Figure 20

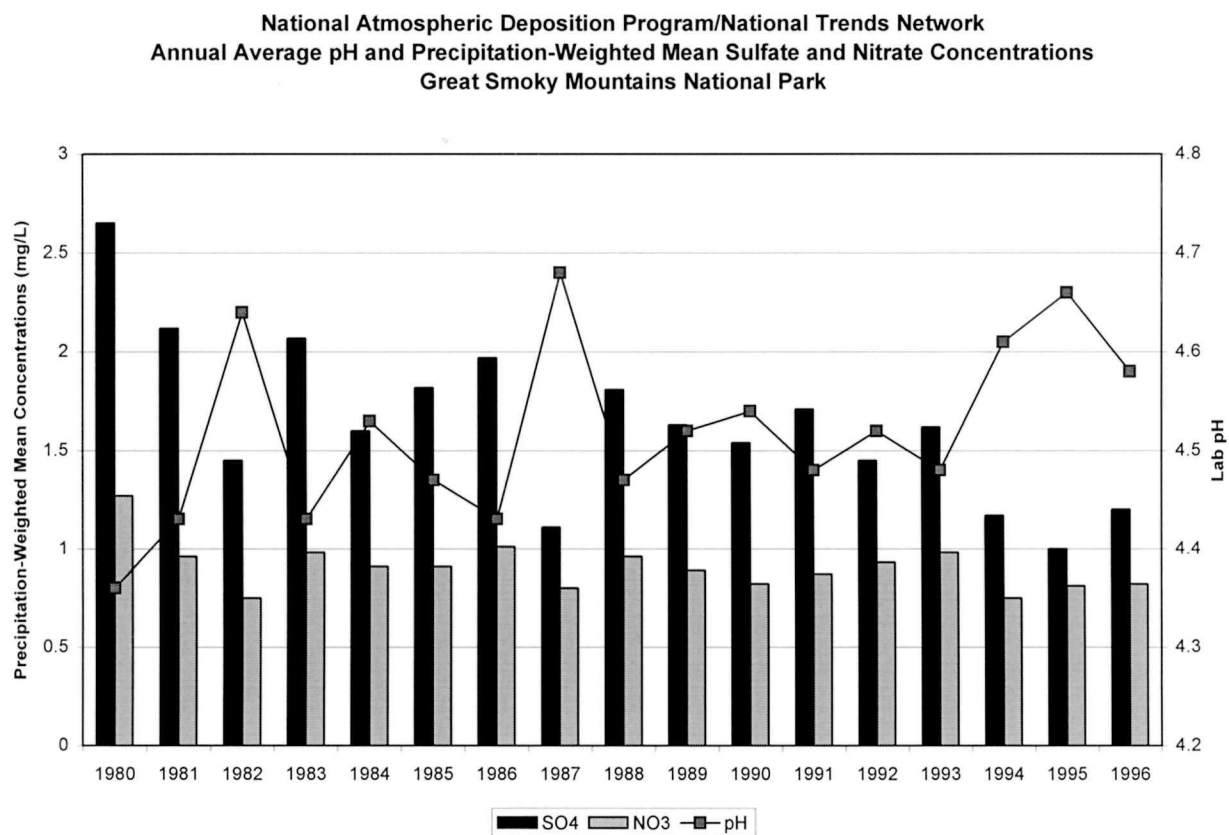
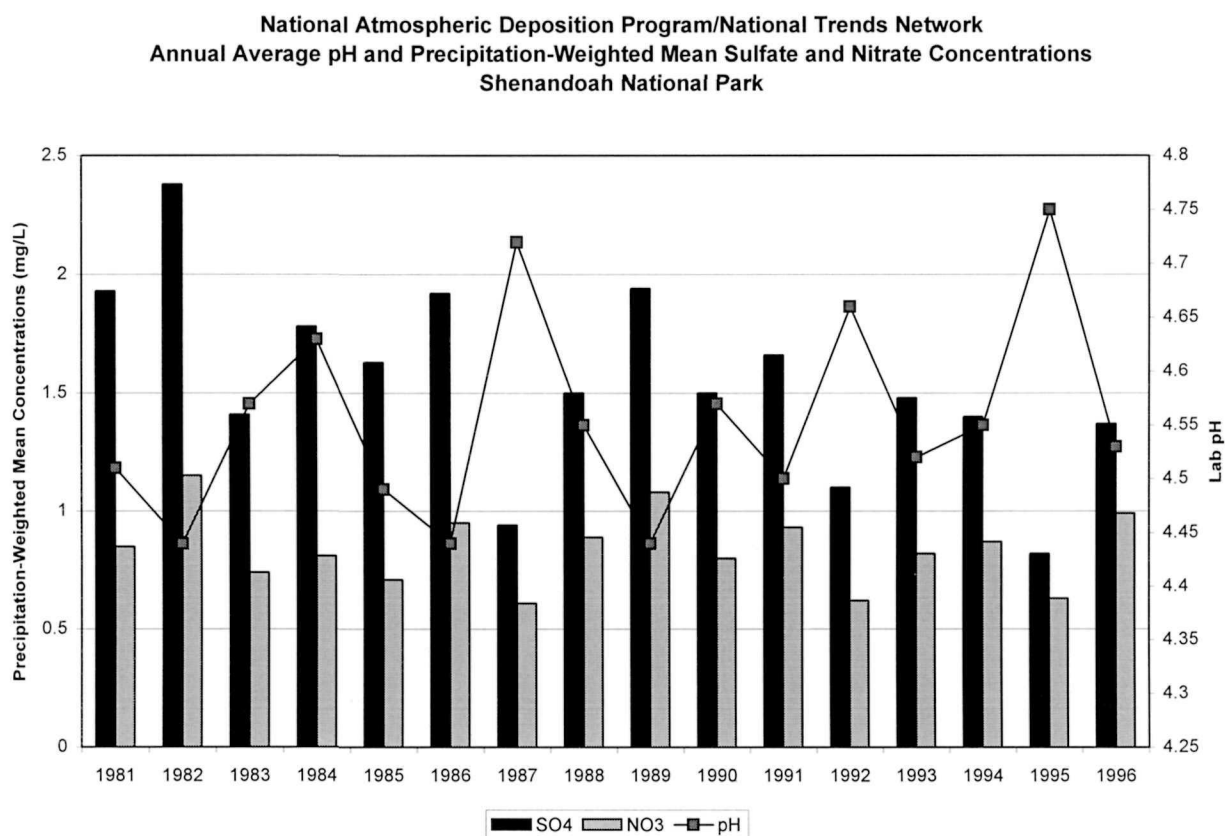
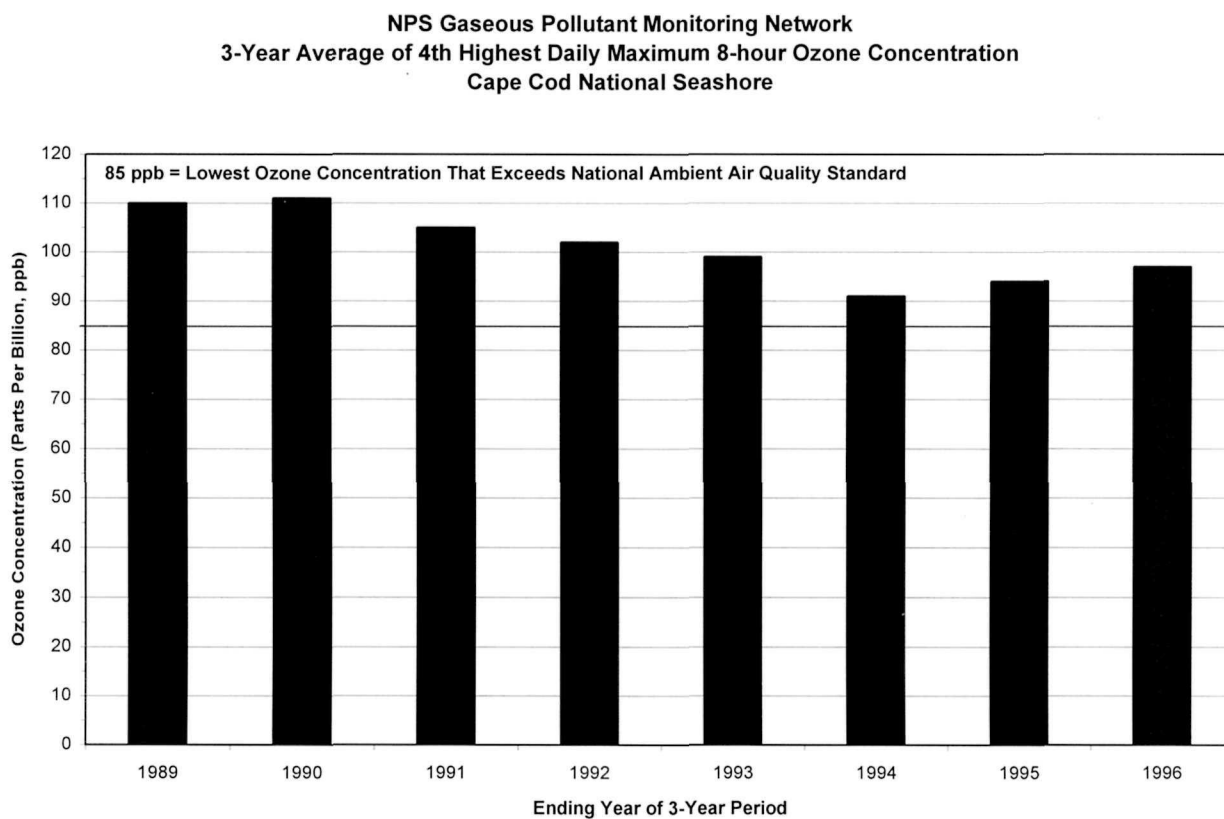


Figure 21



**Figure 22**



**Figure 23**

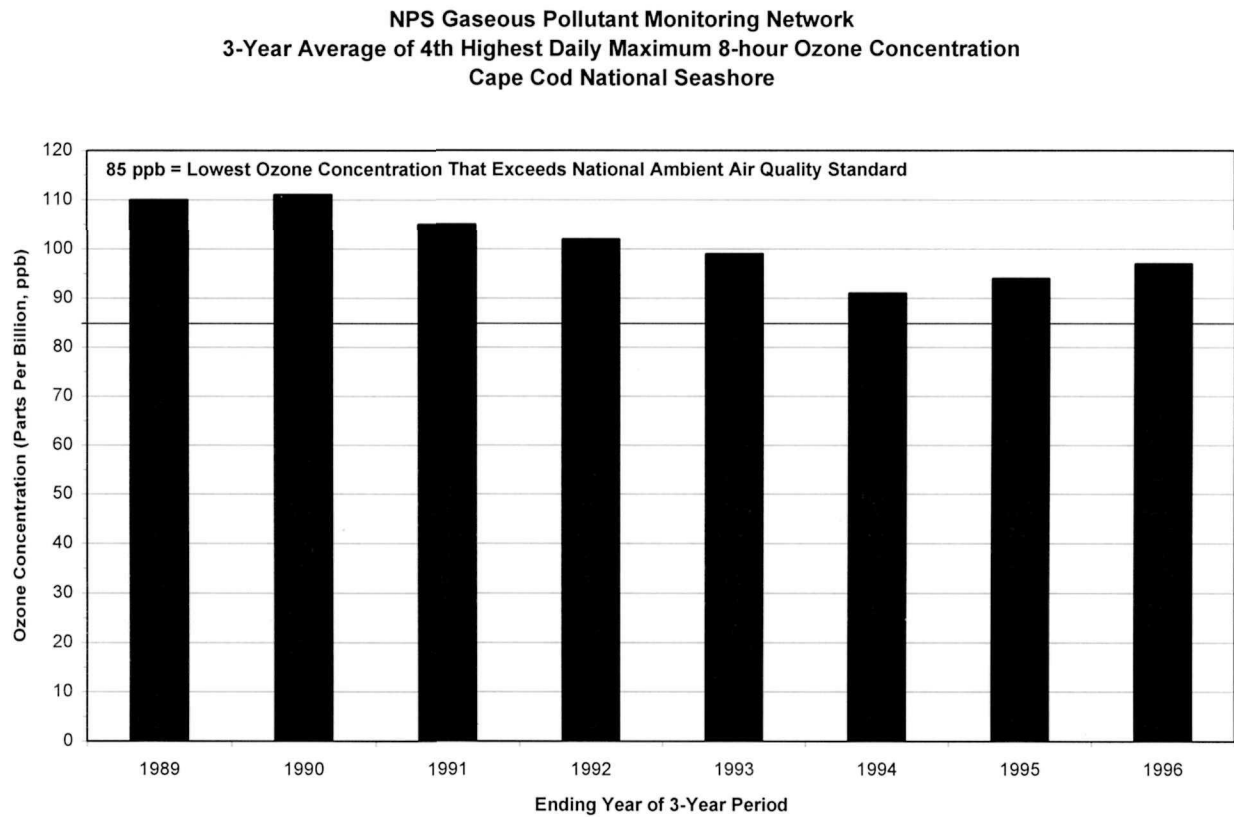
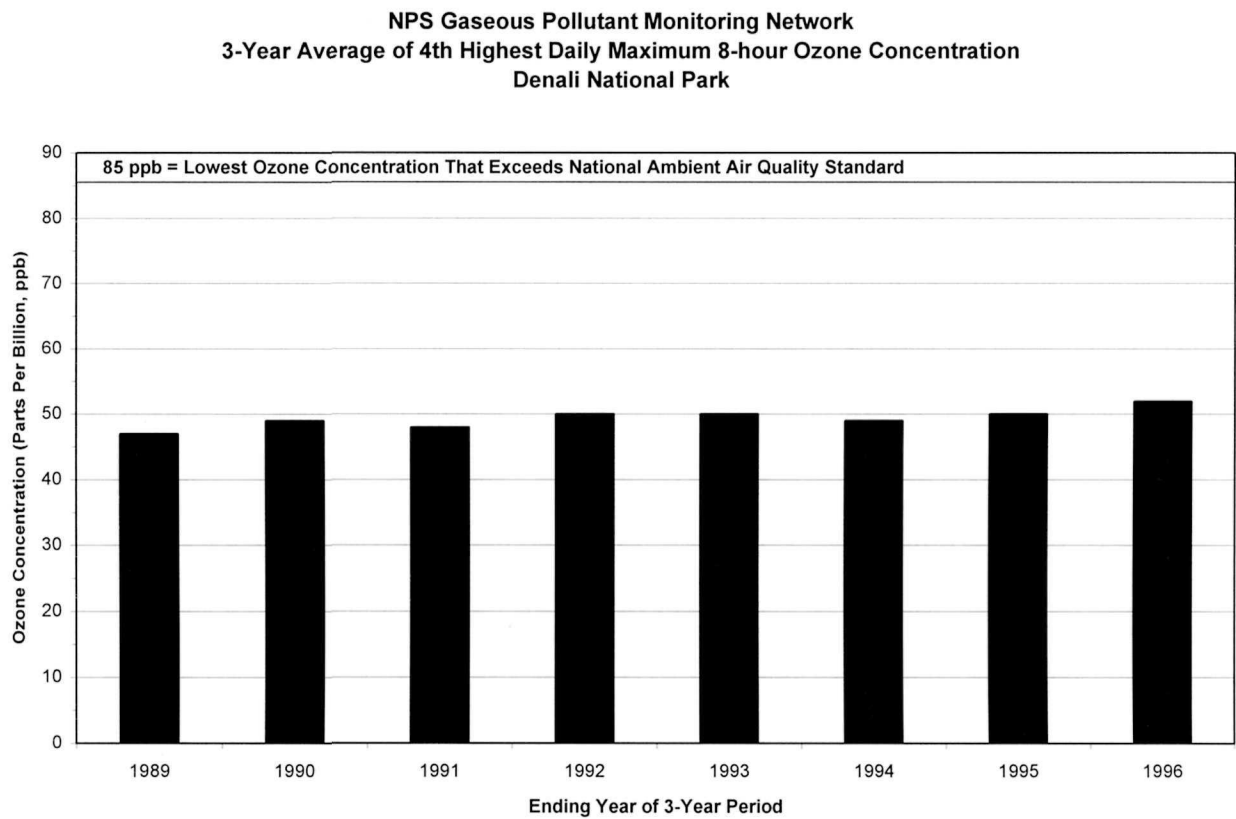


Figure 24



**Figure 25**

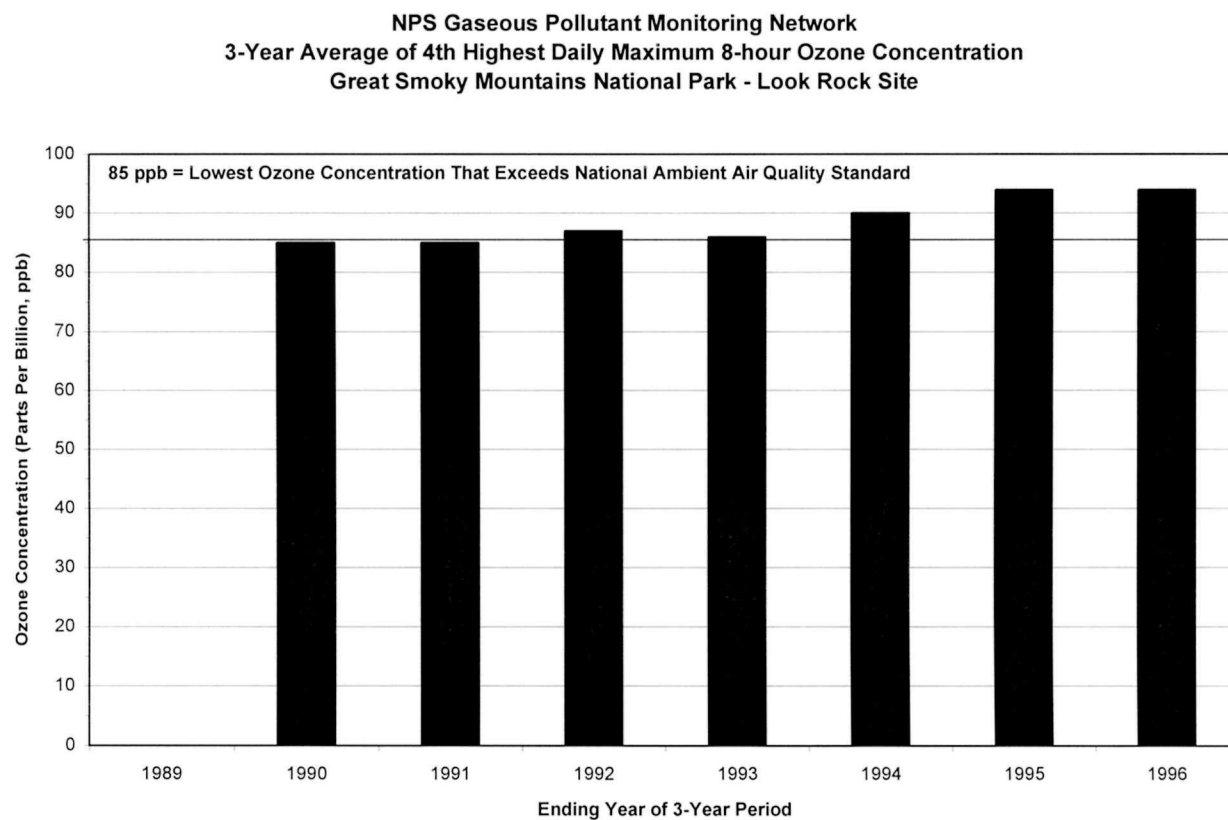
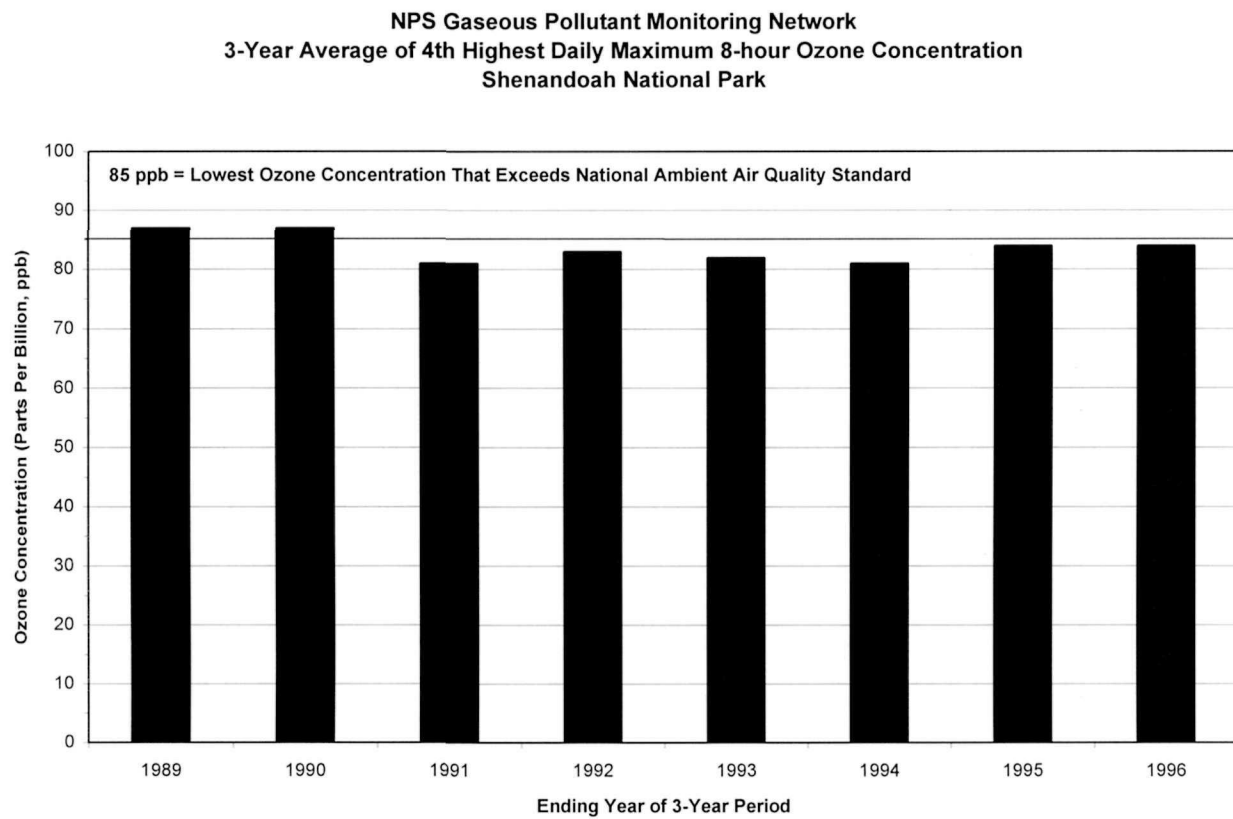




Figure 26



SOURCE: Air Resources Division, National Park Service, U.S. Department of the Interior

Entered: 1999