CHAPTER 7

Acid Deposition

http://www.epa.gov/oar/aqtrnd97/chapter7.pdf

Sulfur and nitrogen oxides are emitted into the atmosphere primarily from the burning of fossil fuels. These emissions react in the atmosphere to form compounds that are transported long distances and are subsequently deposited in the form of pollutants such as particulate matter (sulfates and nitrates), SO_2, NO_2, nitric acid and when reacted with volatile organic compounds (VOCs) form ozone. The effects of atmospheric deposition include acidification of lakes and streams, nutrient enrichment of coastal waters and large river basins, soil nutrient depletion and decline of sensitive forests, agricultural crop damage, and impacts on ecosystem biodiversity. Toxic pollutants and metals also can be transported and deposited through atmospheric processes. (See Chapter 5: Air Toxics.)

Both local and long-range emission sources contribute to atmospheric deposition. Total atmospheric deposition is determined using both wet and dry deposition measurements. Wet deposition is the portion dissolved in cloud droplets and is deposited during rain or other forms of precipitation. Dry deposition is the portion deposited on dry surfaces during periods of no precipitation as particles or in a gaseous form. Although the term "acid rain" is widely recognized, the dry deposition portion ranges from 20 to 60 percent of total deposition.

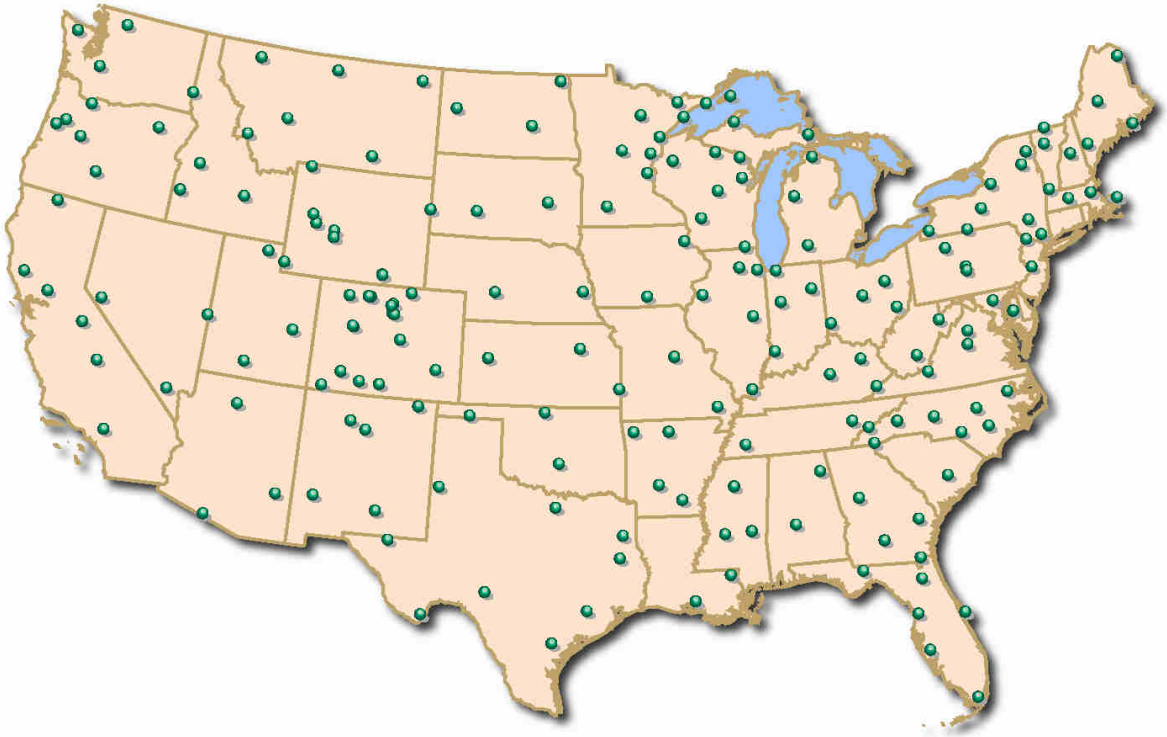
The United States Environmental Protection agency (EPA) is required by several Congressional and other mandates to assess the effectiveness of air pollution control efforts. These mandates include Title IX of the Clean Air Act Amendments (CAAA), the National Acid Precipitation Assessment Program (NAPAP), the Government Performance and Results Act, and the U.S. Canada Air Quality Agreement. One measure of effectiveness of these efforts is whether sustained reductions in the amount of atmospheric deposition over broad geographic regions are occurring. However, changes in the atmosphere happen very slowly and trends are often obscured by the wide variability of measurements and climate. Numerous years of continuous and consistent data are required to overcome this variability, making long-term monitoring networks especially critical for characterizing deposition levels and identifying relationships among emissions, atmospheric loadings, and effects on human health and the environment.

For wet and dry deposition, these studies typically include measurement of concentration levels of key chemical components as well as precipitation amounts. For dry deposition, analyses also must include meteorological measurements that are used to estimate rate of the actual deposition, or "flux." Data representing total deposition loadings (e.g., total sulfate or nitrate) are what many environmental scientists use for integrated ecological assessments.

Primary Atmospheric Deposition Monitoring Networks

The National Atmospheric Deposition Program (NADP) and the Clean Air Status and Trends Network (CASTNet), described in detail below, were developed to monitor wet and dry acid deposition, respectively. Monitoring site locations are predominantly rural by design to assess the relationship between regional pollution and changes in regional patterns in deposition. CASTNet also includes measurements of rural ozone and the chemical constituents of $PM_{2.5}$. Rural monitoring sites of NADP and CASTNet provide data where sensitive ecosystems are located and provide insight into natural background levels of pollutants where urban influences are minimal. These data provide needed information to scientists and policy analysts to study and evaluate numerous environmental effects, particularly those caused by regional sources of emissions for which long range trans-

Figure 7-1. The NADP/NTN Network.



port plays an important role. Measurements from these networks are also important for understanding non-ecological impacts of air pollution such as visibility impairment and damage to materials, particularly those of cultural and historical importance.

National Atmospheric Deposition Network

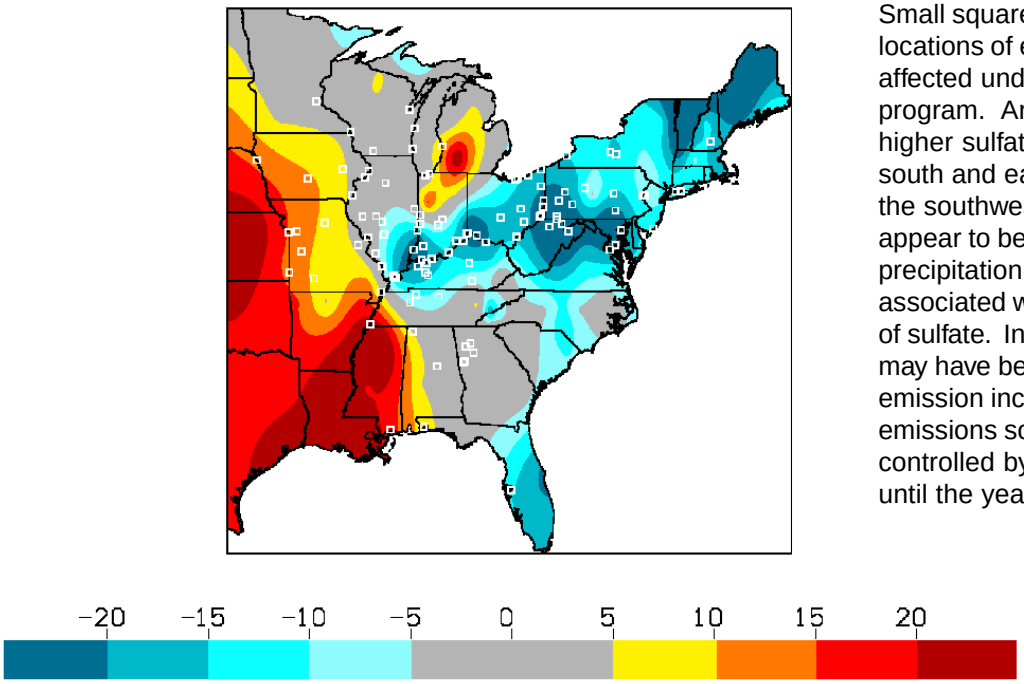
The NADP was initiated in the late 1970s as a cooperative program between federal and state agencies, universities, electric utilities, and other industries to determine geographical patterns and trends in precipitation chemistry in the United States. Collection of weekly wet deposition samples began in 1978. The size of the NADP Network grew rapidly in the early 1980s when the major research effort by the NAPAP called for characterization of acid deposition levels. At that time, the network became known as the NADP/NTN (National Trends Network). By the mid-1980s, the NADP had grown to nearly 200 sites where it stands today as the longest running national deposition monitoring network (see Figure 7-1).

The NADP analyzes the constituents important in precipitation chemistry, including those affecting rainfall acidity and those that may have ecological effects. The Network measures sulfate, nitrate, hydrogen ion (measure of acidity), ammonia, chloride, and base cations (calcium, magnesium, potassium). To ensure comparability of results, laboratory analyses for all samples are conducted by the NADP's Central Analytical Lab at the Illinois State Water Survey. A new subnetwork of the NADP, the Mercury Deposition Network (MDN) measures mercury in precipitation. The MDN is discussed in Chapter 5 of this report.

TRENDS ANALYSES FOR SULFATE AND NITRATE CONCENTRATIONS IN WET DEPOSITION

Sulfate concentrations in precipitation have decreased over the past two decades.[1] The reductions were relatively large in the early 1980s followed by more moderate declines until 1995. These reductions in sulfates are similar to changes in SO_2 emissions. In 1995, however, concentrations of sulfates in precipitation over a large area of the Eastern United States exhibited a dramatic and unprecedented reduction.[2] In 1995 and continued in 1996, sulfates have been estimated to be 10–25 percent lower than levels expected with a continuation of 1983–1994 trends (see Figure 7-2). This important reduction in acid precipitation is directly related to the large regional decreases in SO_2 emis-

Figure 7-2. Percent differences in mean annual measured sulfate concentrations as compared to projected concentrations for 1995–1996 for the Eastern United States (from NADP/NTN).



Small squares on the map show locations of electric utility plants affected under Phase I of the acid rain program. Areas on the map depicting higher sulfate concentrations (e.g., south and east of Lake Michigan and the southwestern portion of map) appear to be due to below average precipitation volumes, which are associated with higher concentrations of sulfate. In addition, these results may have been affected by SO_2 emission increases at some Phase II emissions sources that will not be controlled by the acid rain program until the year 2000.

sions resulting from Phase I of the acid rain program (see the SO_2 section in Chapter 2). The largest reductions in sulfate concentrations occurred along the Ohio River Valley and in states immediately downwind of this region. For example, the average reduction in sulfate concentrations in Ohio was approximately 21 percent, in Maryland, 27 percent, and in Pennsylvania, 15 percent. The largest decrease (32 percent) occurred in the northern portion of West Virginia. Reductions in hydrogen ion concentrations (H^+) in the East, the primary indicator of precipitation acidity, were very similar to those of sulfate concentrations, both in magnitude and location. Nitrate concentrations at NADP/NTN sites were not appreciably different in 1995–1996 from historical levels.[3] Analyses based on the 1997 data are not yet available.

The dense network of NADP/NTN sites facilitate the development of concentration and wet deposition maps to describe the trends and spatial patterns in the constituents of acid precipitation. Figures 7-3 and 7-4 show sulfate and nitrate concentrations in precipitation levels for 1997. Sulfate concentrations in precipitation are highest in the Great Lake States and areas extending eastward. Nitrates in precipitation are more regionally uniform. The highest nitrate levels in precipitation are in the vicinity of the Great Lakes, with relatively high concentrations extending from the Plains States to the Northeast.

Reported concentrations and total wet deposition are both dependent on the amount of precipitation in a particular year. While larger amounts of precipitation can dilute the measured pollutant concentration, it also can contribute to higher levels of wet deposition. Figures 7-5 and 7-6 present estimates for total wet deposition of sulfates and nitrates respectively, by multiplying concentration by the total amount of precipitation. During 1997, the highest sulfate wet deposition occurred in western New York State extending southward through the Ohio Valley and along the Appalachian ridge. Nitrate deposition shows a similar pattern.

Clean Air Status and Trends Network

The CASTNet provides atmospheric data on the dry deposition component of total acid deposition, ground-level ozone and other forms of atmospheric pollution. CASTNet is considered the nation's primary source for atmospheric data to estimate dry acidic deposition and to

Figure 7-3. Sulfate concentration in precipitation, 1997.

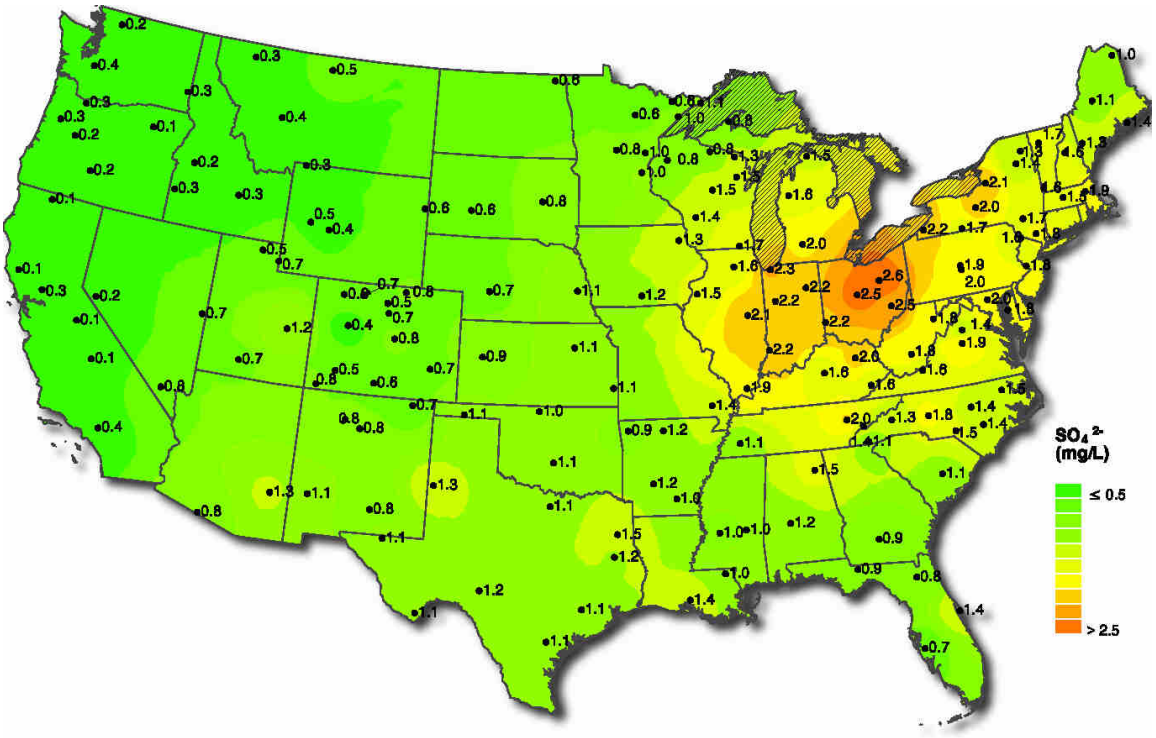


Figure 7-4. Nitrate concentration in precipitation, 1997.

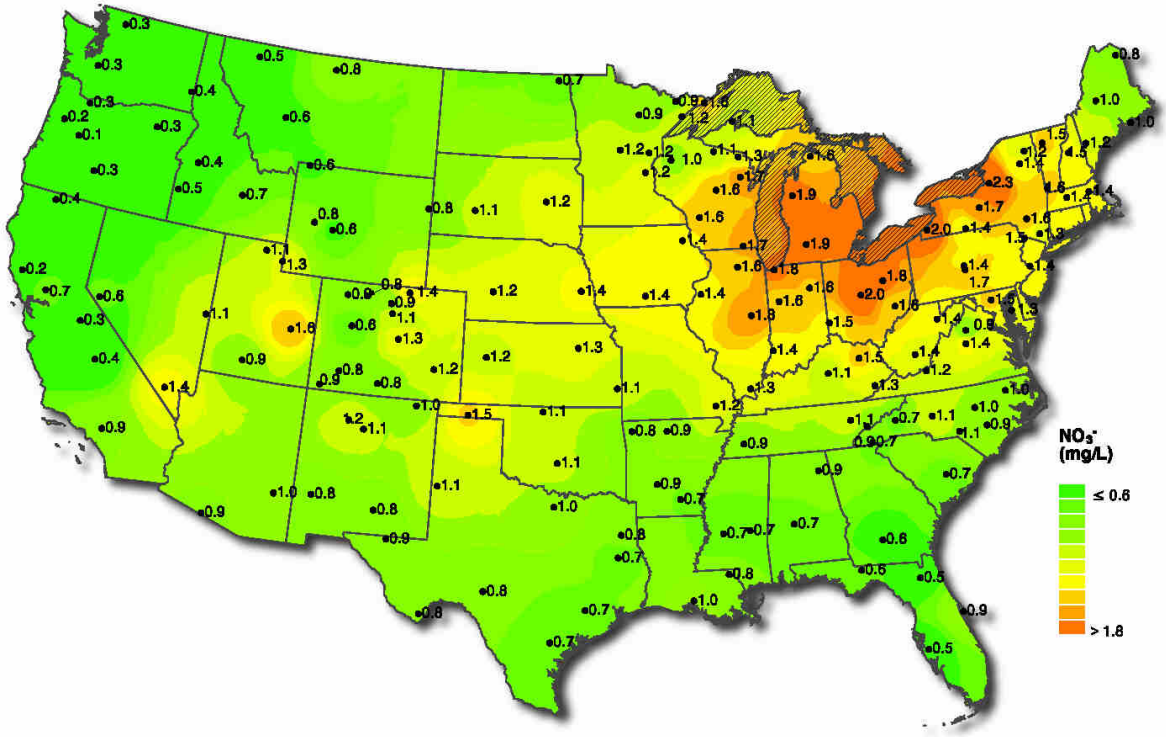


Figure 7-5. Wet deposition of sulfate, 1997.

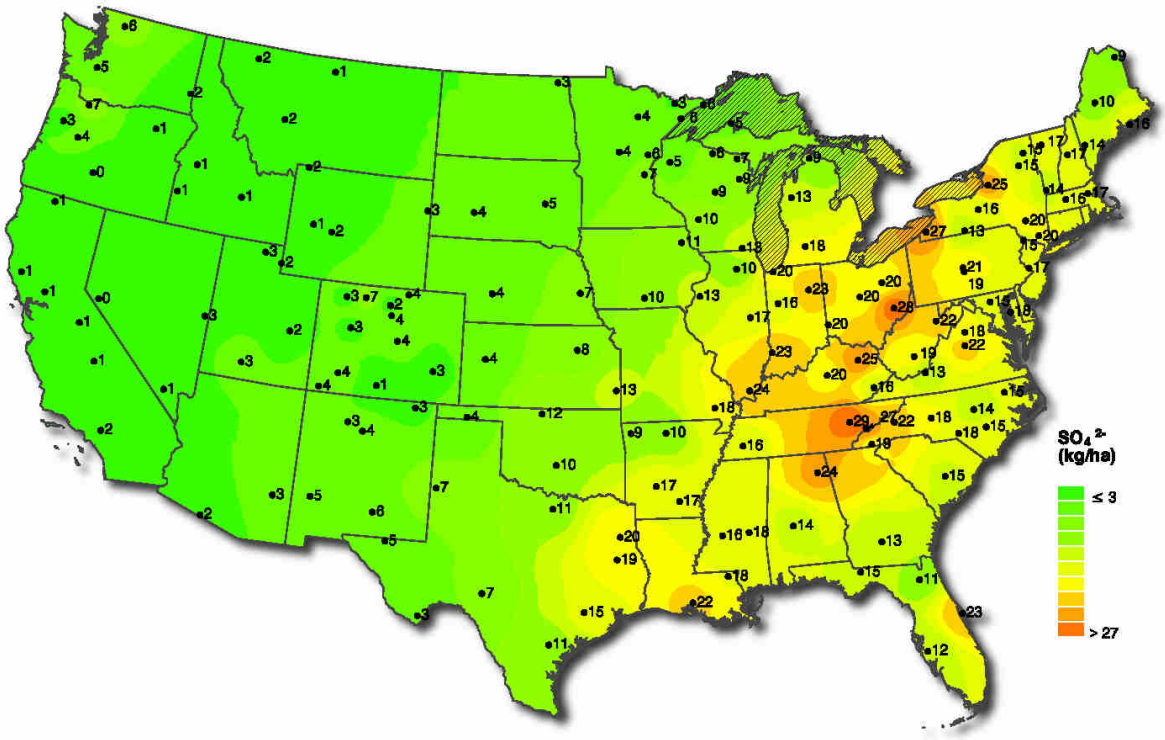


Figure 7-6. Wet deposition of nitrate, 1997.

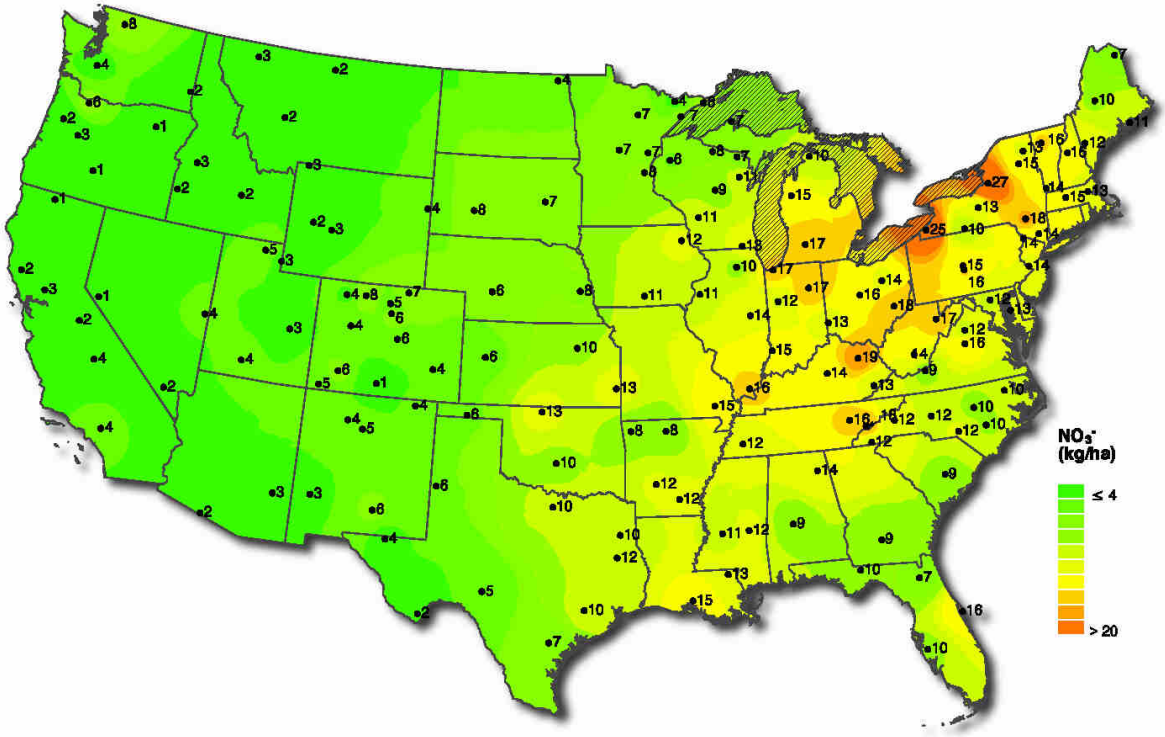
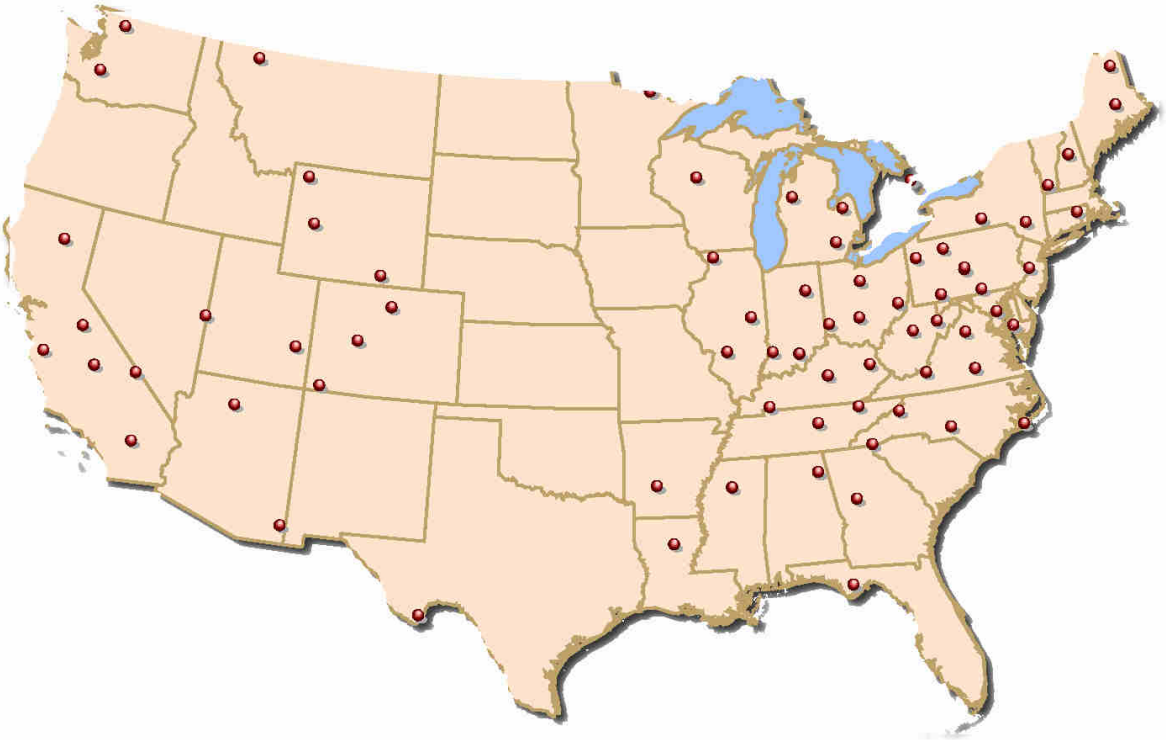


Figure 7-7. The CASTNet Network.



provide data on rural ozone levels. Used in conjunction with other national monitoring networks, CASTNet is used to determine the effectiveness of national emission control programs. Established in 1987, CASTNet now comprises 72 monitoring stations across the United States, as shown in Figure 7-7. The longest data records are primarily at eastern sites. The majority of the monitoring stations are operated by EPA's Office of Air and Radiation; however, 19 stations are operated by the National Park Service in cooperation with EPA. Of the total number of sites, 67 measure dry-deposition; 18 measure wet-deposition; 68 measure ozone; and 8 measure aerosols for visibility assessment.

Each CASTNet dry deposition station measures:

- weekly average atmospheric concentrations of sulfate, nitrate, ammonium, sulfur dioxide, and nitric acid.
- hourly concentrations of ambient ozone levels.
- meteorological conditions required for calculating dry deposition rates.

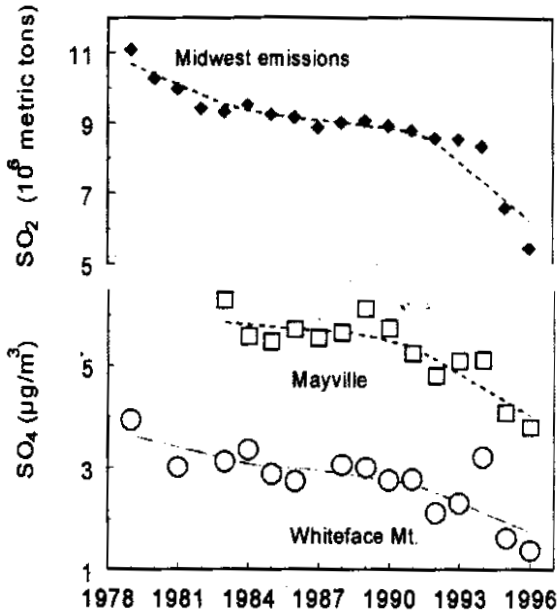
Dry Deposition

Dry deposition rates are calculated using atmospheric concentrations, meteorological data, and information on land use, vegetation, and surface conditions. CASTNet complements the database compiled by NADP. Because of the interdependence of wet and dry deposition, CASTNet also collects wet deposition data at the 18 sites where there are no NADP/NTN stations within a 50 km radius. Together, these two long-term databases provide the necessary data to estimate trends and spatial patterns in total atmospheric deposition. National Oceanic and Atmospheric Administration (NOAA) also operates a smaller dry deposition network called Atmospheric Integrated Assessment Monitoring Network (AIRMoN) focused on addressing research issues specifically related to dry deposition measurement.

Concentration Trends Analysis at CASTNet Sites

CASTNet data were analyzed for the period 1989–1995. During this 7-year period, atmospheric concentrations of sulfur dioxide and sulfate at 34 eastern CASTNet sites showed statistically-significant declining trends. The average reduction in sulfur dioxide concentrations for all sites was 35

Figure 7-8. Trends in annual mean aerosol sulfate concentrations at Whiteface Mountain and Mayville, 1978–1996.



Also shown are annual SO_2 emissions for the Midwest as explained in the text. Lines through the points are the result of multiple regression and smoothing and are only added to aid the eye.

percent and in sulfate concentrations was 26 percent. Trends in total nitrate concentrations (nitrates plus nitric acid) were not as pronounced, with an average reduction of 8 percent. A regional estimate for a cluster of sites in the Ohio River Valley showed a close correspondence between declining sulfur dioxide concentration (35 percent) and declining sulfur dioxide emissions (32 percent) in this region.[4]

The relationship between regional SO_2 emissions and sulfate air quality is graphically illustrated in Figure 7-8. This recently published graph compares long-term trends (1978–1996) in annual mean aerosol sulfate concentrations at two rural locations in New York State with upwind SO_2 emissions for the Midwest region (MN, WI, IL, MI, IN, OH, WV, KY and Western PA). Although average air quality fluctuates from year to year, the underlying trend in annual sulfate concentrations tracks emissions with both trends exhibiting a small decrease. Then, sulfates declined sharply in 1995, corresponding to a 36 percent reduction in regional emissions. During 1995, emissions from this region accounted for 38 percent of the national emission inventory. The air quality improvement (~1 µg/m^3) was approximately 30 percent for Mayville and an impressive 47 percent for the more distant Whiteface Mountain location.[4]

Rural Ozone

Ozone data collected by CASTNet are complementary to the larger ozone data sets gathered by the State and Local Air Monitoring Stations (SLAMS) and National Air Monitoring Stations (NAMS) networks. Most air quality samples at SLAMS/NAMS sites are located in urban areas, while CASTNet sites are in rural locations. Hourly ozone measurements are taken at each of the 50 sites operated by EPA. Data from these sites provide information to help characterize ozone transport issues and ozone exposure levels. Future trend reports will present information on rural O_3 concentrations measured at CASTNet sites.

References

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