Clean Air Status and Trends Network (CASTNET)

2006 Annual Report

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Clean Air Status and Trends Network

(CASTNET)

2006 Annual Report

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Prepared for:

U.S. Environmental Protection Agency
Office of Air and Radiation
Clean Air Markets Division
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Executive Summary

This report summarizes Clean Air Status and Trends Network (CASTNET) data collected during 2006 and examines trends in air quality and deposition on regional and national scales. CASTNET began operation in 1991 with the incorporation of the National Dry Deposition Network (NDDN), which had been in existence since 1987. CASTNET measures rural, regionally representative concentrations of sulfur and nitrogen species and ozone in order to evaluate the effectiveness of national and regional air pollution control programs.

Key Results through 2006

- Mean annual sulfur dioxide and particulate sulfate concentrations have declined significantly over the 17-year period 1990 through 2006. Sulfur dioxide levels have declined 37 percent while sulfate concentrations have declined 25 percent.

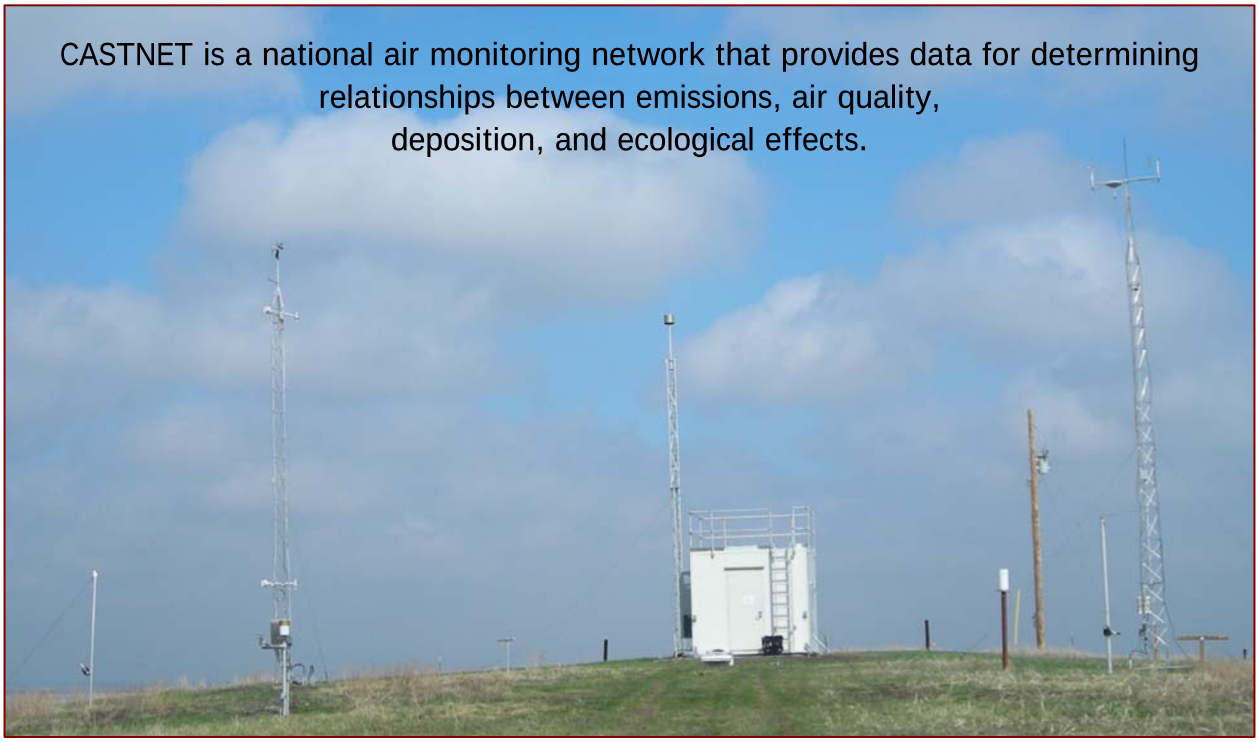
- Total sulfur deposition has declined by 28 percent from 1990 to 2006.

- Mean annual concentrations of total nitrate (nitric acid plus particulate nitrate) have declined by approximately 18 percent over the 17-year period.

- Total nitrogen deposition has declined by 12 percent from 1990 to 2006.

- Ozone levels measured in 2006 continue to show a downward trend that began after a peak in 2002. The median fourth highest daily maximum 8-hour ozone concentration for 2006 (72 ppb) was the second lowest in the history of the network. For the most recent 3-year period (2004-2006), only two eastern and four California sites recorded exceedances of the 8-hour standard. This 3-year period is notable as it had the fewest exceedances (six total) in the history of the network. The recent decline in rural ozone and nitrate levels has been attributed to the documented decline in nitrogen oxides emissions as well as changes in weather conditions.

Chapter 1: **CASTNET Overview**



CASTNET is a national air monitoring network that provides data for determining relationships between emissions, air quality, deposition, and ecological effects.

Santee Sioux, NE (SAN189)

Background

The United States Environmental Protection Agency (EPA) established the Clean Air Status and Trends Network (CASTNET) to provide data for determining relationships between changes in emissions and any subsequent changes in air quality, atmospheric deposition, and ecological effects. The rural monitoring network was mandated by the 1990 Clean Air Act Amendments (CAAA) to assess the effectiveness of requirements promulgated to reduce emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) as Congress recognized the need to track real-world environmental results as the Acid Rain Program was implemented.

Under the CAAA, the Acid Rain Program has produced significant reductions in SO_2 and NO_x emissions from electric generating plants since 1995. More recent NO_x emission control programs also produced substantive declines in NO_x emissions in the eastern United States. These programs include the Ozone Transport Commission (OTC) NO_x Budget, NO_x State Implementation Plan (SIP) Call, and NO_x Budget Trading Program. EPA relies on CASTNET and other long-term monitoring networks to generate the data and information used to assess the effectiveness of these emission control programs under several different mandates including the Government Performance and Results Act, The National Acid Precipitation Assessment Program (NAPAP), Title IX of the CAAA, and the United States – Canada Air Quality Agreement. This report summarizes CASTNET monitoring activities and the resulting concentration and deposition data collected over the 17-year period from 1990 through 2006.

Additional information, previous annual reports, and other CASTNET documents can be found on the EPA Web site, http://www.epa.gov/castnet. The CASTNET database is also available to the public by accessing the "Data" link on EPA's CASTNET Web page. The Web site provides archives of the concentration and deposition data. Fully validated data are available approximately 10 months following collection.

Partnerships

CASTNET is sponsored by EPA and the National Park Service (NPS). NPS began its participation in CASTNET in 1994 under an agreement with EPA. NPS is responsible for the protection and enhancement of air quality and related values in national parks and wilderness areas. The CASTNET sites sponsored by NPS as of December 2006 numbered 27. In addition to EPA and NPS, the principal sponsors, CASTNET operates in partnership with other rural long-term monitoring networks:

- **National Atmospheric Deposition Program/National Trends Network (NADP/NTN)** operates monitoring stations with wet deposition samplers to measure the concentrations and deposition rates of air pollutants removed from the atmosphere by precipitation. NADP/NTN operates wet deposition samplers at or near virtually every CASTNET site.

- **Canadian Air and Precipitation Monitoring Network (CAPMoN)** operates 28 measurement sites throughout Canada and one in the United States. CASTNET and CAPMoN both operate samplers at monitoring stations in Ontario, Canada and at Pennsylvania State University.

- **Interagency Monitoring of Protected Visual Environments (IMPROVE)** measures aerosol pollutants near more than 30 CASTNET sites. IMPROVE measures particulate air pollutants that affect visibility and visual air quality.

- **AIRNow** is a Web site designed to allow the public to view air quality data for a specific area in real-time. Ten CASTNET sites send 1-hour ozone data to the AIRNow database. The data have not gone through the full quality assurance process and, therefore, should not be used for publication or regulation.

Although EPA and NPS are the primary sponsors of CASTNET, other organizations, tribes, universities, and government agencies play a role in sponsoring individual CASTNET sites. These groups, or co-sponsors, provide an in-kind service that supports the operation of a site. The types of assistance offered may include site operation, land use, or both. Table 1-1 lists all current co-sponsors for the network. All of the sites added during the recent expansion of the network (since 2001) have an associated co-sponsor. Some of the co-sponsors listed in Table 1-1 have maintained long-term relationships with CASTNET sites. For example, Pennsylvania State University, co-sponsor of PSU106, PA, and the University of Michigan, co-sponsor of ANA115, MI, have been involved with the network since the late 1980s.

Three CASTNET monitoring sites are located on tribal lands (Figure 1-1) as a result of a unique cooperative effort among EPA Headquarters, EPA Regions, tribal governments, and the Inter-Tribal Environmental Council (ITEC). This collaborative effort has resulted in monitoring sites operating on the tribal lands of the Cherokee Nation in eastern Oklahoma (CHE185), the Alabama-Coushatta in eastern Texas (ALC188), and the Santee Sioux in northern Nebraska (SAN189). State agencies also operate special purpose air pollutant measurement devices at some CASTNET sites.

Figure 1-1 Native American Participation in CASTNET Operations

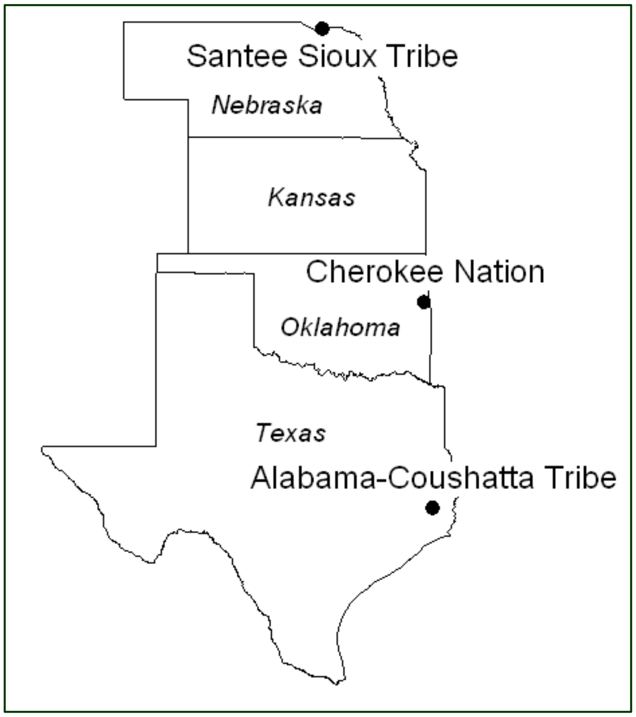


Table 1-1 Co-Sponsors for CASTNET

Site	Co-sponsor
ALC188, TX	Alabama-Coushatta Tribe of Texas
ANA115, MI	University of Michigan
CAD150, AR	United States Army
CHE185, OK	Cherokee Nation
CON186, CA	U.S. Department of Agriculture-Forest Service Pacific Southwest Research Laboratory
EGB181/ EGB281, ON	Environment Canada
EVE419, FL	Environmental Protection Agency
HWF187, NY	State University of New York
IRL141, FL	St. Johns River Water Management District
KNZ184, KS	Konza Prairie Long Term Ecological Research Program
PND165, WY	U. S. Department of Interior-Bureau of Land Management
PSU106, PA	Pennsylvania State University
SAN189, NE	Santee Sioux Tribe of Nebraska
SND152, AL	Tennessee Valley Authority

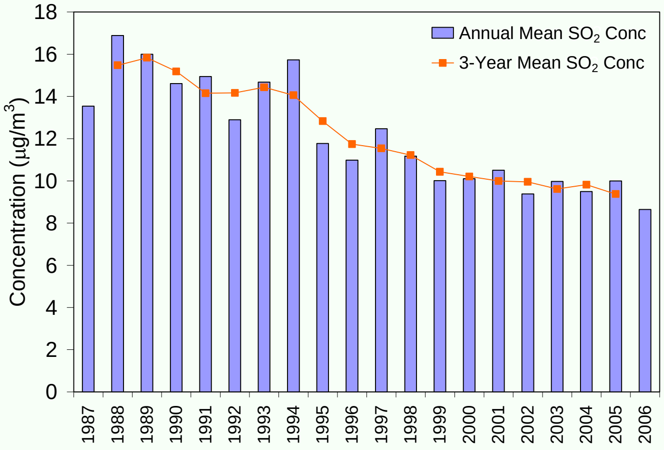
Twenty Years of Network Monitoring

PSU106, PA

CASTNET was designed primarily to measure seasonal and annual average concentrations and depositions over many years. Consequently, measurements of weekly average concentrations were selected as the basic sampling strategy. An open-face, three-stage filter pack was employed to measure gaseous and particulate sulfur and nitrogen pollutants as well as concentrations of other pollutant species. The filter pack technology and sampling protocol have been used consistently over the 20 years, providing a comparable data set each year and allowing for the analysis of long-term trends. Any future sampling methods will be examined with respect to comparability with the filter pack so the information obtained will continue to be available for long-term trends in pollutant species.

As of December 2006, the network included 87 monitoring stations at 84 site locations throughout the continental United States, Alaska, and Canada. CASTNET sites measure rural, regionally representative concentrations of sulfur and nitrogen species and ozone in order to detect and quantify trends, define the spatial distribution of rural pollutants, and estimate dry deposition fluxes. The goal of estimating dry deposition also requires the measurement of several meteorological parameters and information on vegetation and land use.

20-Year Trend in SO_2 Concentrations (µg/m^3) at PSU106, PA



Note: Annual mean SO_2 concentrations have declined by 39 percent at PSU106, PA over the 20 years.

CASTNET has its origins with the National Dry Deposition Network (NDDN), which was established in 1986 and began operation in 1987. Many of the original NDDN sites are still operational after 20 years and provide useful information on trends in air quality. The site at Pennsylvania State University, PA (PSU106) began collecting samples in January 1987 and is the longest running site.

NPS Air Monitoring Program

The NPS Air Resources Division administers an extensive air monitoring program that measures air pollution levels in national parks. The purpose of the program is to establish current air quality conditions and assess long-term trends of air pollutants that affect park resources. These data are also used to determine compliance with the National Ambient Air Quality Standards (NAAQS) and to assess the effectiveness of national and regional air pollution control programs. Measuring air pollution levels in parks is an essential part of the NPS air resource management program that provides vital information to Congress, air pollution control agencies, academia, and the public (NPS, 2007).

The NPS air monitoring program consists of an extensive network of air monitoring stations in almost 70 national parks across the country. Twenty-seven of these sites are also CASTNET sites. Several NPS sites have been in operation for over 20 years. The program has three primary components: visibility (IMPROVE), gaseous pollutants (mainly ozone), and atmospheric deposition (wet - NADP/NTN, NADP/MDN and dry - CASTNET). Meteorological monitoring is also conducted at most locations to aid in the interpretation of measured air pollution levels. In addition to long-term monitoring, NPS is involved in many special studies that tend to be short-term and more intensive in nature. These studies are often initiated to explore specific local and regional research topics, such as identifying sources of air pollution or assessing the potential risk to natural resources in parks (NPS, 2007).

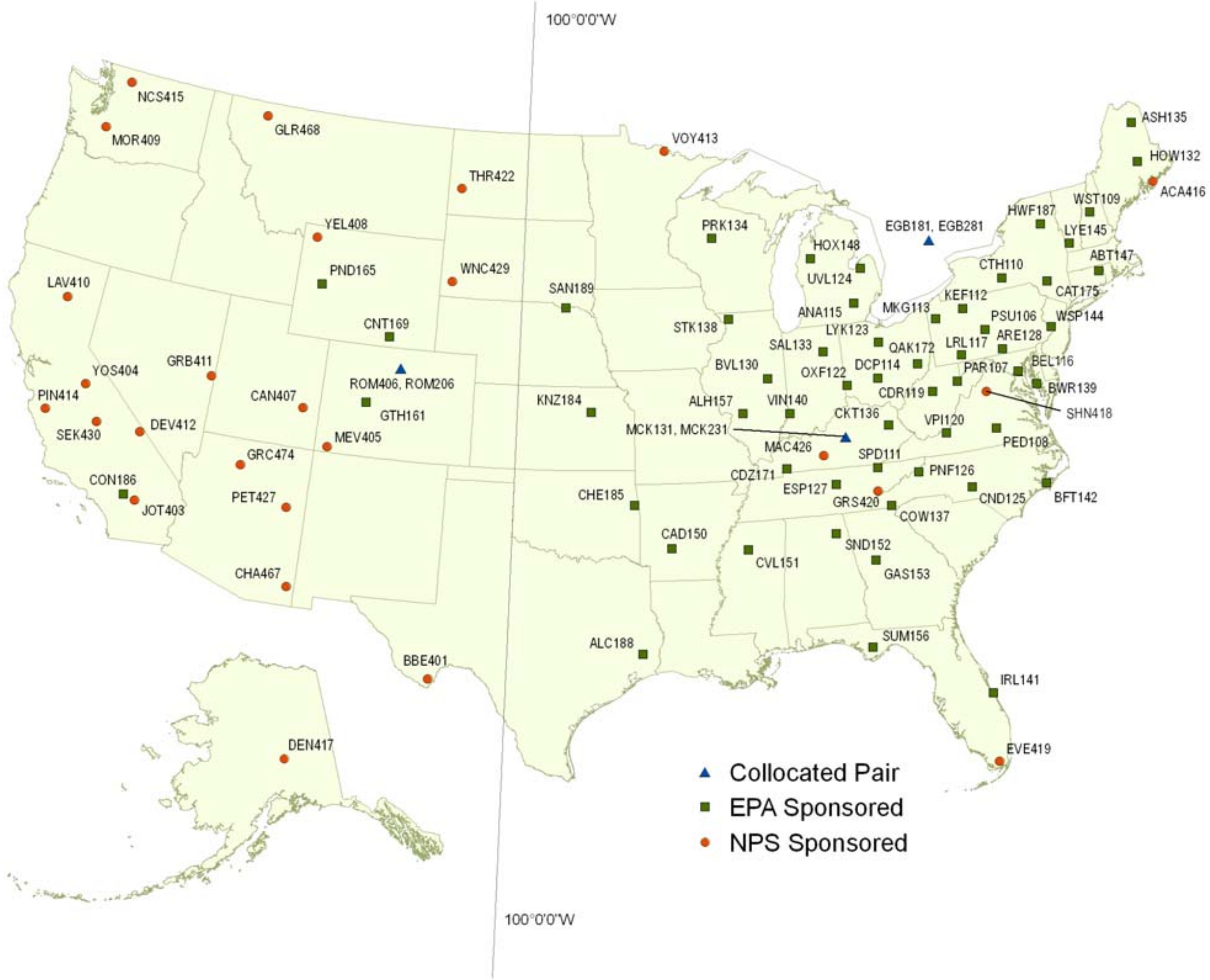
Assessing how air quality is changing is a prime function of the NPS air monitoring program. Monitoring data on visibility, ozone, and atmospheric deposition show that air pollution is affecting some park resources nationwide. Consistent with the Government Performance and Results Act, NPS has established the air quality goal of stable or improved air quality in 70 percent of reporting park areas by September 30, 2008. An area meets the goal if it does not show statistically significant deterioration in any of the performance indicators (NPS, 2007).

Additional information on the NPS Air Monitoring program can be found on the Web site: http://www2.nature.nps.gov/air/monitoring/.

Locations of Monitoring Sites

Figure 1-2 shows the locations of CASTNET monitoring sites as of December 2006. Eighty-seven sites were operational at 84 distinct locations. Most CASTNET sites are located in rural or remote locations away from pollutant emission sources and heavily populated areas. Appendix A provides the location and operational characteristics of each site by state including information on start date, latitude, longitude, elevation, and the types of measurements taken at each site. For the purposes of this report, CASTNET sites are called "western" or "eastern" depending on whether they are west or east of 100 degrees west longitude. In general, sample flow rates are set to 1.5 liters per minute (lpm) in the east and at a higher rate of 3.0 lpm in the west due to lower pollutant concentrations in the western United States.

Figure 1-2 CASTNET Sites as of December 2006



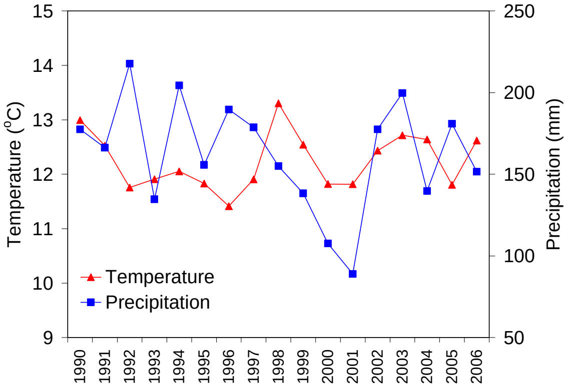
CASTNET Monitoring at Long Term Ecological Research Sites

The National Science Foundation's (NSF) Long Term Ecological Research (LTER) Program was established in 1980 to support research on long-term ecological phenomena across a wide range of geographical scales. The network consists of 26 field sites representing diverse ecosystems in continental North America, the Caribbean, the Pacific, and Antarctica. The sites represent most of the Earth's major ecosystems and include forests, grasslands, deserts, urban areas, tundra, agricultural systems, freshwater lakes, coastal estuaries and salt marshes, coral reefs, and coastal ocean zones. Disturbances often shape ecosystems by periodically reorganizing or destroying them, providing opportunities for significant changes in plant and animal populations and communities. Disturbances include, for example, hurricanes, land use changes, changes in climate and atmospheric chemistry, or forest harvesting (NSF, 2005).

Three CASTNET monitoring systems are located on LTER field sites. CASTNET provided early support to LTER by establishing sites at Coweeta, NC (COW137) in 1987 and Hubbard Brook, NH (WST109) in 1988. The third LTER CASTNET site was established at Konza Prairie, KS (KNZ184) in 2002. CASTNET monitors are also located near other LTER sites, e.g., Florida Coastal Everglades, Baltimore Ecosystem Study, Niwot Ridge in Colorado, and North Temperate Lakes in Wisconsin.

The Coweeta LTER research program centers on the effects of disturbances and environmental gradients on biogeochemical cycling and the underlying watershed ecosystem processes that regulate and respond to those cycles. It now represents one of the longest continuous environmental studies in North America (LTER, 2004a). This LTER research project is a continuing long-term study concentrating on recovery from phenomena that are of major consequence in the southern Appalachians, such as drought, weather (Figure 1-3), and altered atmospheric deposition.

Figure 1-3 Annual Mean Temperature (°C) and Precipitation (mm) Data for COW137, NC



The Hubbard Brook Experimental Forest was established by the U.S. Department of Agriculture Forest Service, Northeastern Research Station in 1955 as a major center for hydrologic research in New England. In 1963, the Hubbard Brook Ecosystem Study was initiated in order to use the small watershed approach at Hubbard Brook to study linkages between hydrologic processes and nutrient flux and cycling in response to natural and human disturbances such as air pollution, forest cutting, land-use changes, increases in insect populations, and climatic factors (LTER, 2004b).

The Konza Prairie Biological Station was founded in 1971. The Konza Prairie LTER Program is a comprehensive, interdisciplinary research program designed to provide an understanding of ecological processes in mesic grasslands, particularly tallgrass prairie, and to contribute to conceptual and theoretical advances in the field of ecology (LTER, 2004c). Some current areas of research include grassland ecology and the effects of fire, grazing, and climatic variability on the structure and function of mesic grass-land ecosystems.


WST109, NH

CASTNET supports the three LTER sites by providing information on air pollutant concentrations, dry deposition fluxes of pollutants to the ecosystems, and meteorological conditions. These data contribute to an assessment of disturbances related to air pollution, atmospheric deposition, and climate change.


KNZ184, KS

LONG TERM ECOLOGICAL RESEARCH NETWORK

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Measurements Collected at CASTNET Sites

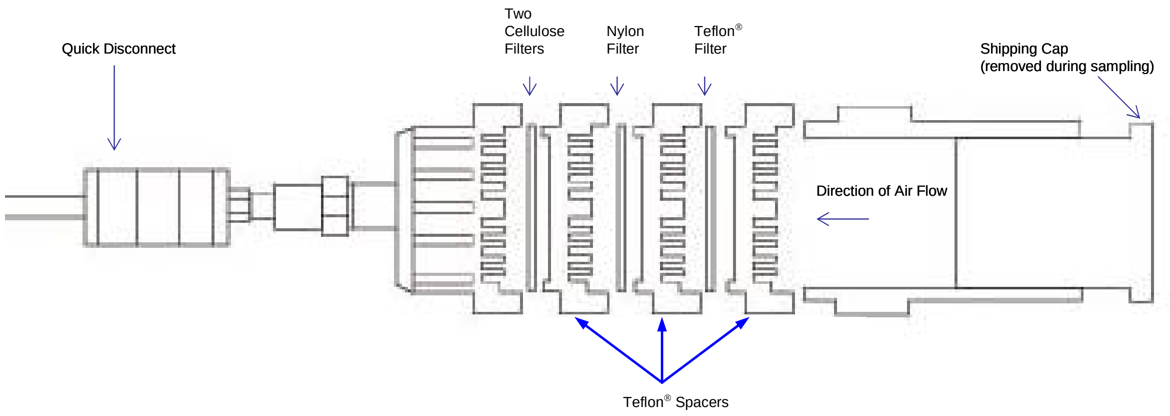
CASTNET was designed primarily to measure trends in seasonal and annual average concentrations and depositions over many years. Consequently, measurement of weekly average concentrations was selected as the basic sampling strategy. Over the course of the week, air is drawn at a controlled flow rate through a three-stage filter pack (Figure 1-4) mounted atop a 10 meter tower to collect air pollutants in the form of gases and particles. The first stage of the filter pack encloses a Teflon® filter, the second a nylon filter, and the third holds two potassium carbonate (K_2CO_3)-impregnated cellulose filters. The filter pack is changed out each Tuesday and shipped to the analytical chemistry laboratory for analysis.

CASTNET Ambient Measurements

- Sulfur dioxide (SO_2)
- Particulate sulfate (SO_4^{2-})
- Particulate nitrate (NO_3^-)
- Nitric acid (HNO_3)
- Particulate ammonium (NH_4^+)
- Particulate calcium (Ca^{2+})
- Particulate sodium (Na^+)
- Particulate magnesium (Mg^{2+})
- Particulate potassium (K^+)
- Particulate chloride (Cl^-)
- Ozone (O_3)
- Meteorological variables and information on land use and vegetation

Figure 1-4 Three-Stage Filter Pack

Cellulose (2)	**Nylon**	**Teflon®**
Gaseous	Gaseous	Particulate
• SO_2	• HNO_3 • SO_2	• SO_4^{2-} • NO_3^- • NH_4^+ • K^+ • Ca^{2+} • Mg^{2+} • Na^+ • Cl^-



CASTNET measures concentrations of sulfur in the form of sulfur dioxide (SO_2) and sulfate (SO_4^{2-}) and nitrogen as nitrate (NO_3^-), nitric acid (HNO_3), and ammonium (NH_4^+). In addition, it measures concentrations of chloride (Cl^-), calcium (Ca^{2+}), sodium (Na^+), magnesium (Mg^{2+}), and potassium (K^+). Sulfate, NH_4^+, NO_3^-, Cl^-, and the earth metals are collected on the Teflon® filter. The nylon filter collects HNO_3 and some SO_2. The cellulose filters collect the remaining SO_2.

CASTNET also measures ozone, one of the major components of smog. In addition to the air pollutants, CASTNET sites record meteorological measurements of temperature, solar radiation, relative humidity, precipitation, wind speed and direction, standard deviation of wind direction (sigma theta), and surface wetness. These meteorological measurements are used to gauge the transport of air pollutants and as input to the Multi-Layer Model (MLM), a mathematical model used for estimating dry deposition to ecosystems in the atmospheric boundary layer. The ozone and meteorological measurements are recorded continuously and archived as hourly averages.

Calculating Dry Deposition

Dry deposition processes are modeled as resistances to deposition. The original network design was based on the assumption that dry deposition or flux could be estimated as the linear product of measured pollutant concentration (C) and modeled deposition velocity (V_d). Measured atmospheric concentrations are calculated based on the mass of each analyte in each filter extract and the volume of air sampled. The rate of deposition of a pollutant, also known as deposition velocity, is influenced by meteorological conditions, vegetation, and atmospheric and plant chemistry. The deposition velocity values are calculated for each hour of each year using the MLM. The MLM was described by Meyers *et al.* (1998) and Finkelstein *et al.* (2000). The data used in the MLM to estimate dry deposition are derived from meteorological measurements and pollutant concentrations taken at the site together with an estimation of the vegetation leaf-out and leaf area index (LAI).

The schematic of the MLM in Figure 1-5 shows the relationships among the various resistances and illustrates the meteorological and other data that are required as model input. An improved version of the MLM (Schwede, 2006) was delivered by EPA's Office of Research and Development (ORD) to MACTEC during 2006. This version includes changes to the soil moisture factor, which affects the stomatal and soil resistances, and to the radiation algorithm, which also affects the stomatal resistance. All deposition velocities and fluxes for the entire network were recalculated using the updated model.

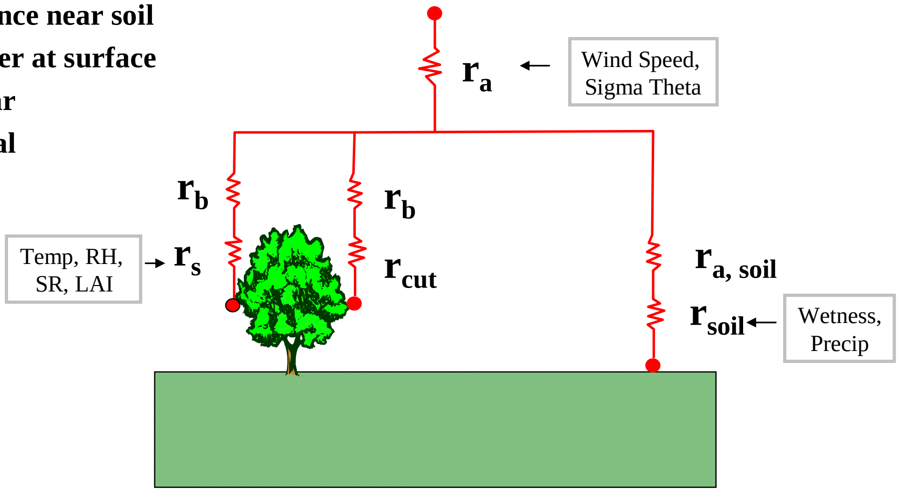
Indian River Lagoon, FL (IRL141)

Figure 1-5 Multi-Layer Model

$$\textbf{Flux} = \overline{C} \, x \, \overline{V_d}$$

$$\mathbf{1/V_d} = \frac{1}{\dfrac{1}{r_s + r_b} + \dfrac{1}{r_{cut} + r_b} + \dfrac{1}{r_{a,soil} + r_{soil}}} + r_a$$

r_a = turbulence
$r_{a,\,soil}$ = turbulence near soil
r_b = thin layer at surface
r_{cut} = cuticular
r_s = stomatal
r_{soil} = soil



CASTNET Reference Sites

Chapters 2 through 4 present maps illustrating the magnitude of pollutant concentrations and deposition fluxes across the United States. In addition, measurements from 34 CASTNET reference sites (Figure 1-6) were analyzed for each pollutant in order to determine trends in concentrations and trends in rates of dry, wet, and total deposition. These 34 sites have been reporting CASTNET measurements since at least 1990 and are used for determining long-term trends. The reference sites were selected using criteria similar to those used by EPA in its *National Air Quality and Emissions Trends Report* (2000). The criteria include site longevity and data completeness. EPA's procedures to interpolate and extrapolate quarterly mean data were also used. In chapters 2 through 4, the data from the 34 reference sites were aggregated and then presented using box plots for the period 1990 through 2006.

Figure 1-6 CASTNET Reference Sites

SO_2 and NO_x Emissions

The Acid Rain Program (ARP), established under Title IV of the 1990 Clean Air Act Amendments, requires major reductions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions from the electric power industry. Under the Acid Rain Program, SO_2 reductions are achieved using a cap and trade program that sets a permanent cap on the total amount of SO_2 that may be emitted by all regulated electric generating units in the contiguous United States. The program began in 1995 and is being phased in with the final 2010 SO_2 cap set at 8.95 million tons, a level equal to about one-half of the emissions from the power sector in 1980.

Using a market-based cap and trade mechanism to reduce SO_2 emissions allows flexibility for individual combustion units to select their own methods of compliance. Currently, one allowance provides a regulated unit limited authorization to emit one ton of SO_2. The Clean Air Act Amendments of 1990 allocate allowances to regulated units based on historic fuel consumption and specific emission rates prior to the start of the program. The total allowances allocated for each year equal the SO_2 emission cap. The program encourages early reductions by allowing sources to bank unused allowances in one year and use them in a later year.

The ARP uses a more traditional approach to achieve NO_x emission reductions. Rate-based limits apply to most of the coal-fired electric utility boilers subject to the ARP. No nationwide cap has been placed on NO_x emissions. Other NO_x emission control programs have resulted in significant reductions in NO_x emissions during the ozone season (see Chapter 4). Two prominent control programs are the Ozone Transport Commission NO_x Budget (1999-2002) and the NO_x State Implementation Plan Call, which began in 2003 and will continue through 2007.

The ARP is comprised of two phases for the reduction of SO_2 and NO_x. Phase I applied primarily to the largest coal-fired electric generation sources from 1995 through 1999 for SO_2 and from 1996 through 1999 for NO_x. Phase II for both pollutants began in 2000. In 2005, the SO_2 Phase II requirements affected 3,391 operating units; the Phase II NO_x requirements applied to 989 of those operating units that exceed 25 megawatts and burned coal between 1990 and 1995 (EPA, 2005a).

The recently promulgated Clean Air Interstate Rule (CAIR) (EPA, 2007b) will establish regional caps on SO_2 and NO_x emissions for affected generating units. Annual SO_2 emissions will be capped at 3.7 million tons in 2010 and NO_x emissions will be capped at 1.5 million tons in 2009. CASTNET will be used to assess baseline and program milestones.

Figure 1-7 presents state-by-state total annual SO_2 emissions for Phase I and Phase II electric utility plants for four years (1990, 1995, 2000, and 2006). The heaviest emissions occurred in the eastern United States with major SO_2 sources centered around the Ohio River Valley. The most significant reduction in SO_2 emissions occurred in 1995 when the ARP began. Many of the states with the highest SO_2 emissions realized the largest reductions in emissions. For example, Ohio emitted 2,212 tons in 2000. This total dropped to 962 tons in 2006, a 57 percent reduction. Annual NO_x emissions by state are depicted in Figure 1-8 for the same four years. States with the higher NO_x emissions also produced significant declines.

Figure 1-7 Annual Utility SO_2 Emissions (Phase I and Phase II Plants only)

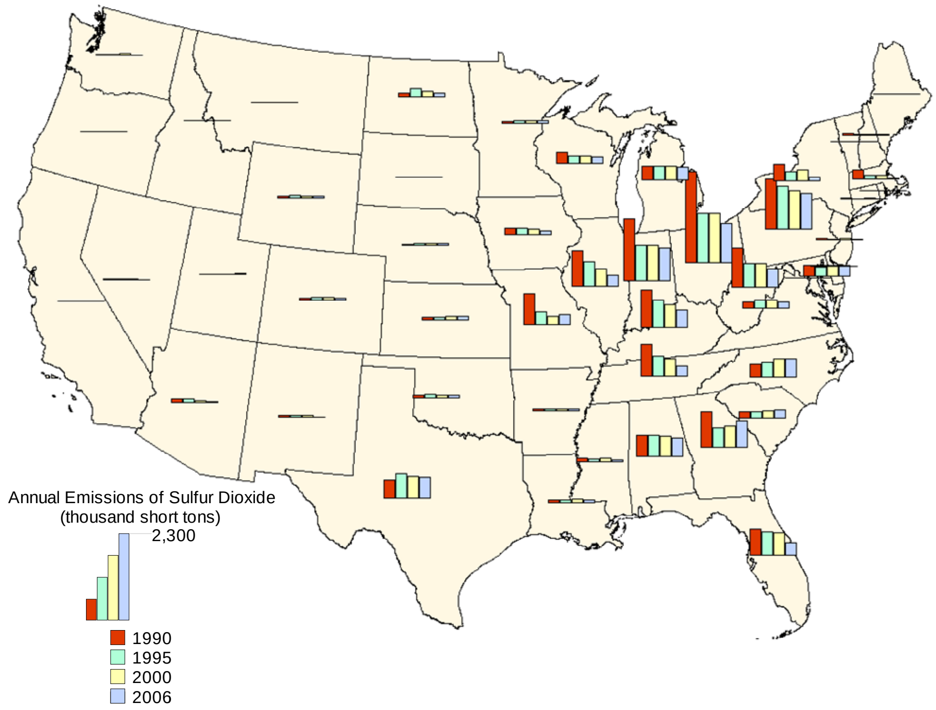
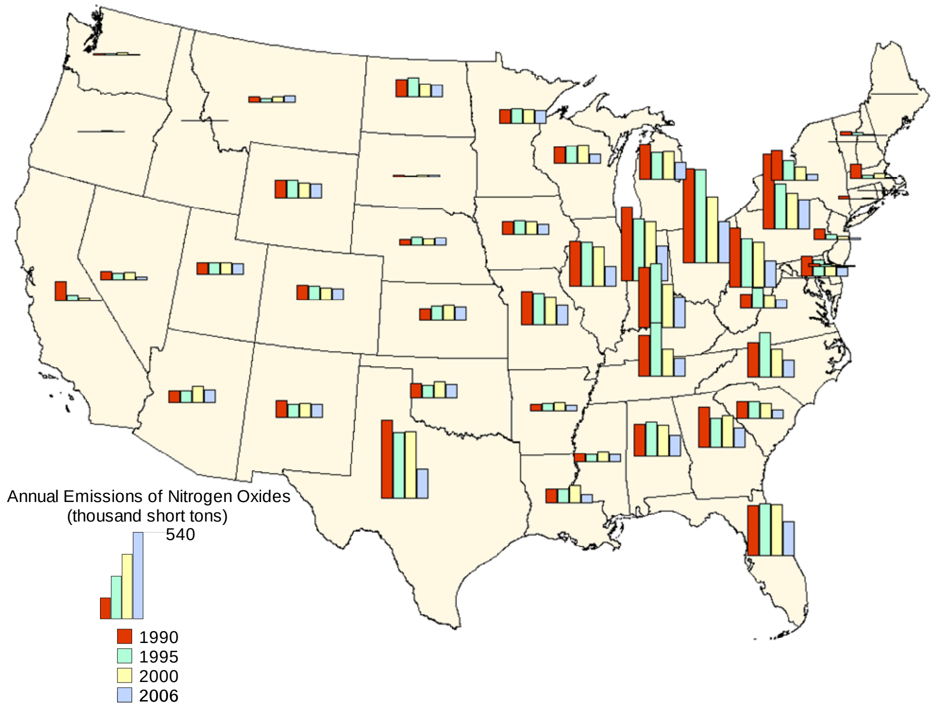


Figure 1-8 Annual Utility NO_x Emissions (Phase I and Phase II Plants only)



Significant Events during 2006

January

Element DataSystem™ replaced Chemical Laboratory Analysis and Scheduling System (CLASS™) as the laboratory information management system used for CASTNET.

March

EPA approved the CASTNET Quality Assurance Project Plan (QAPP), Revision 3.0 on March 6.

EPA and the Tennessee Valley Authority began operating collocated ozone monitors at the EPA-sponsored CASTNET site Cadiz, KY (CDZ171).

A field study began at three CASTNET sites to determine the size and distribution of particulate nitrate collected by the CASTNET open-face filter pack sampling system.

July

A new EPA-sponsored site, Santee Sioux, NE (SAN189), began collecting samples on July 5. The site is operated in cooperation with the Santee Sioux Tribe, part of the Great Sioux Nation.

Use of a routine laboratory control sample (LCS) with all analyses was implemented as an additional quality assurance/quality control mechanism to monitor for potential sample handling artifacts and possible analyte loss between extractions.

The annual “floor-to-ceiling” audit of CASTNET property was conducted by EPA and the Defense Contract Management Agency at MACTEC’s Gainesville, FL location. The property management system was approved by the audit.

MACTEC conducted a two-day site operator refresher training course for 10 site operators/backup operators from seven sites. The training session took place in Somerset, PA and at the nearby CASTNET site Laurel Hill State Park, PA (LRL117).

August

New Thermo Fisher Scientific Model 49i ozone analyzers were purchased for replacement of the older analyzers.

September

Field calibrations began utilizing portable relative humidity chambers instead of aqueous saturated salts to verify the accuracy of the relative humidity sensors.

Statistical analyses were completed to support acceptance testing of the nylon filters.

October

Sponsorship of the CASTNET site at Indian River Lagoon, FL (IRL141) passed from the St. Johns River Water Management District to EPA.

The draft of the CASTNET QAPP, Revision 4.0 was submitted to EPA.

November

Version 2.5 of the Multi-Layer Model (MLM) was received from EPA.

Chapter 2:

Georgia Station, GA (GAS153)

Atmospheric Concentrations

Three-stage filter packs are used to measure concentrations of sulfur dioxide (SO_2), sulfate (SO_4^{2-}), nitric acid (HNO_3), nitrate (NO_3^-), ammonium (NH_4^+), chloride (Cl^-), and several earth metals. Since 1990, measured concentrations of sulfur species have decreased significantly. Concentrations of nitrogen species remained relatively steady from 1990 until 2000 when they began to show a slight decline. Trends in mean annual SO_2, SO_4^{2-}, total nitrate, and NH_4^+ concentrations are discussed in this chapter.

The geographic distribution and magnitude of annual mean concentrations across the United States are presented for sulfur dioxide (SO_2), sulfate (SO_4^{2-}), total nitrate ($HNO_3 + NO_3^-$), and ammonium (NH_4^+) concentrations. A map is provided for each pollutant. Maps of other filter pack measurements are provided in CASTNET quarterly reports (MACTEC, 2006b; 2006d; 2007a; 2007c). The concentration shading in the figures in this chapter was prepared using an algorithm based on inverse distance cubed weighting with a radius of influence of 500 kilometers (km). In addition, trends in concentration data from the 34 CASTNET reference sites (Figure 1-6) are presented using box plots for each year of the 17-year period from 1990 through 2006.

Sulfur Dioxide

Figure 2-1 presents annual mean sulfur dioxide (SO_2) concentrations for 2006. The map shows a large region in the eastern United States with concentrations greater than or equal to 5.0 micrograms per cubic meter ($\mu g/m^3$). The region extends from western Kentucky northeastward along the Ohio River Valley to Pennsylvania and to New Jersey, Maryland, and Virginia. The Ohio River Valley is the major SO_2 emission source region (see Figure 1-7) in the United States. A concentration of 5.5 $\mu g/m^3$ was observed at Georgia Station, GA (GAS153). Two sites in West Virginia – Parsons (PAR107) and Cedar Creek State Park (CDR119) – recorded concentrations slightly less than 5.0 $\mu g/m^3$. The single highest SO_2 concentration (13.1 $\mu g/m^3$) was measured in eastern Ohio at Quaker City (QAK172). Only two western sites (i.e., sites west of 100 degrees west longitude) measured an annual mean SO_2 concentration greater than 1.0 $\mu g/m^3$. These sites were Theodore Roosevelt National Park, ND (THR422) and Petrified Forest National Park, AZ (PET427).

Figure 2-2 provides box plots that show the 1990-2006 trend in annual mean SO_2 concentrations aggregated over the 34 reference sites. The diagram shows a significant downward trend with small interannual changes. Three-year means for 1990-1992 and 2004-2006 were 9.0 $\mu g/m^3$ and 5.6 $\mu g/m^3$, respectively. This change demonstrates a significant reduction of 37 percent in 3-year mean SO_2 concentrations for the two time periods. Annual mean SO_2 concentrations measured in 2006 were the lowest measured by CASTNET reference sites.

Figure 2-1 Annual Mean SO_2 Concentrations ($\mu g/m^3$) for 2006

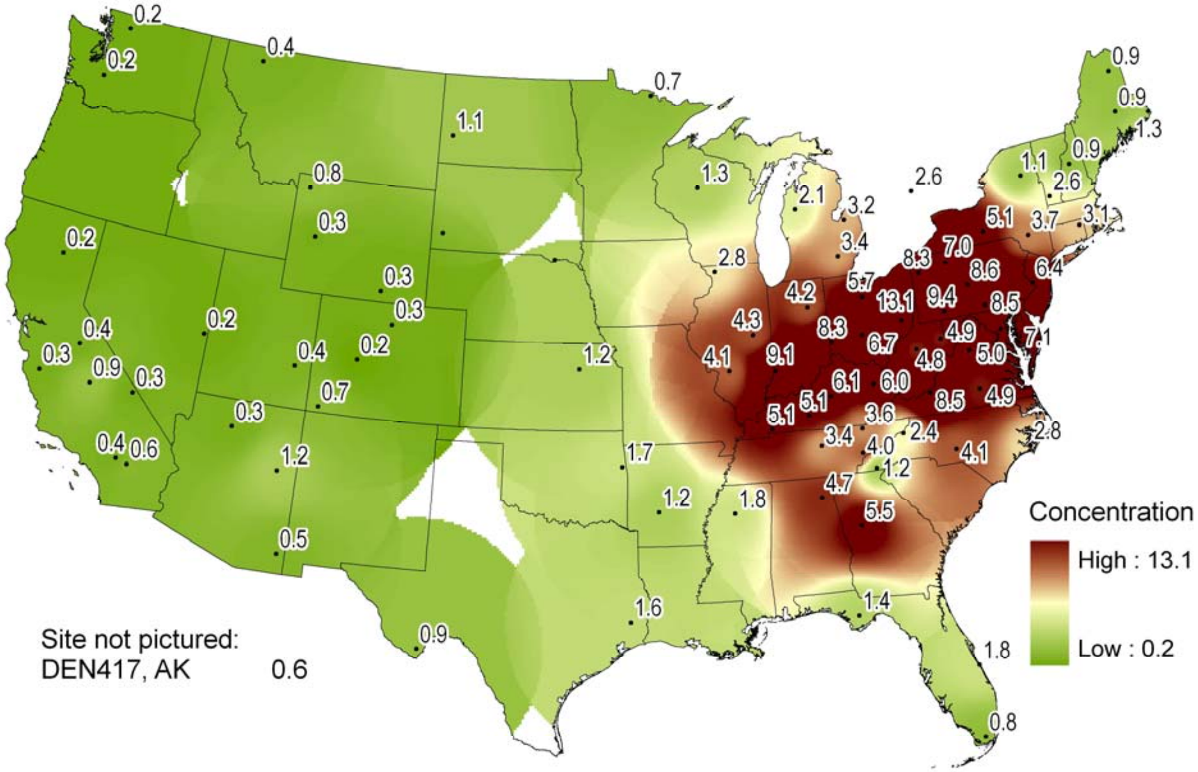
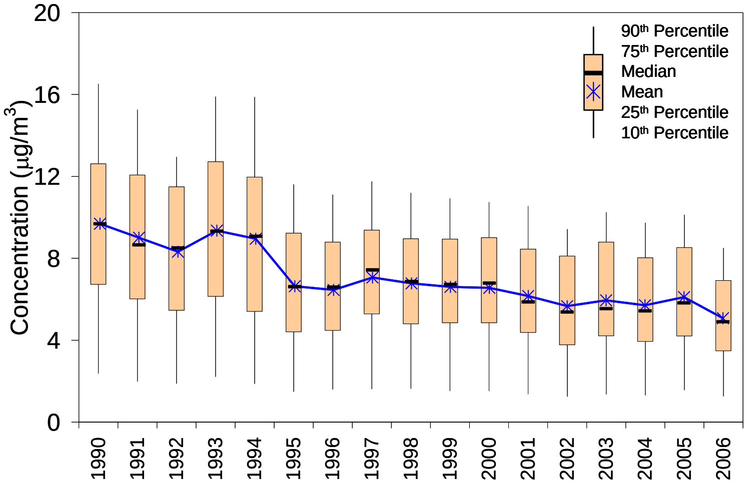


Figure 2-2 Trend in Annual Mean SO_2 Concentrations ($\mu g/m^3$)



Note: All trend diagrams are based on data collected at 34 reference sites.

Particulate Sulfate

Sulfate is formed in the atmosphere through the transformation of SO_2, which is emitted directly from sources burning fossil fuels. Sulfate is formed via both gas and aqueous (cloud) phase reactions. Since SO_2 can be transported by the winds away from the emission source, meteorological conditions and atmospheric chemical constituents determine the path by which sulfate is formed. Sulfur dioxide gas can have a lifetime of up to a week in the atmosphere before it is subsequently oxidized by hydroxyl (OH) radicals to form sulfur trioxide. In the presence of water vapor, sulfur trioxide quickly forms sulfuric acid (H_2SO_4). In turn, H_2SO_4 reacts with particles to form particulate sulfate. These gas phase reactions are relatively slow, approximately equivalent to a SO_2 conversion rate of 1.0 percent per hour.

On the other hand, SO_2 is a soluble gas and can dissolve in cloud droplets during transport if they are present. These droplets act as cloud condensation nuclei for sulfate formation. As SO_2 is dissolved in cloud droplets, it is oxidized by hydrogen peroxide to form sulfate. Dissipating clouds produce ambient particulate SO_4^{2-}.

Sulfate can also be formed directly in stack gases before release to the atmosphere. This type of production results in a direct emission of SO_4^{2-}. However, a typical emission rate of SO_4^{2-} is significantly smaller than an emission rate of SO_2.

Sulfate concentrations were generally lower in 2006 than in 2005. A map of annual mean sulfate (SO_4^{2-}) concentrations for 2006 is presented in Figure 2-3. The map shows a complex region of concentrations greater than or equal to 4.0 $\mu g/m^3$. The region extends from Georgia northward to Kentucky and along the Ohio River Valley to Pennsylvania, Maryland, Virginia, and central North Carolina. In 2006, the Quaker City, OH (QAK172) site recorded the highest concentration of 4.7 $\mu g/m^3$. Sulfate concentrations greater than or equal to 1.0 $\mu g/m^3$ were measured at three sites in California – Pinnacles National Monument (PIN414), Sequoia National Park (SEK430), and Joshua Tree National Monument (JOT403) – and along the southern tier to Chiricahua National Monument, AZ (CHA467) and Big Bend National Park, TX (BBE401). The CASTNET site in North Dakota (THR422) measured a SO_4^{2-} level of 1.1 $\mu g/m^3$.

Figure 2-4 provides box plots of annual mean SO_4^{2-} data from 1990 through 2006 for the 34 CASTNET eastern reference sites. Overall, the figure depicts a significant reduction in SO_4^{2-} over the last 17 years with some interannual changes. The 2006 mean level was lower than the 2005 value. The difference between 3-year means from 1990-1992 to 2004-2006 is 25 percent, a change from 5.4 $\mu g/m^3$ to 4.1 $\mu g/m^3$, respectively. Over the 2005 to 2006 time period CASTNET recorded the largest single year drop in sulfate concentrations.

Figure 2-3 Annual Mean SO_4^{2-} Concentrations (μg/m^3) for 2006

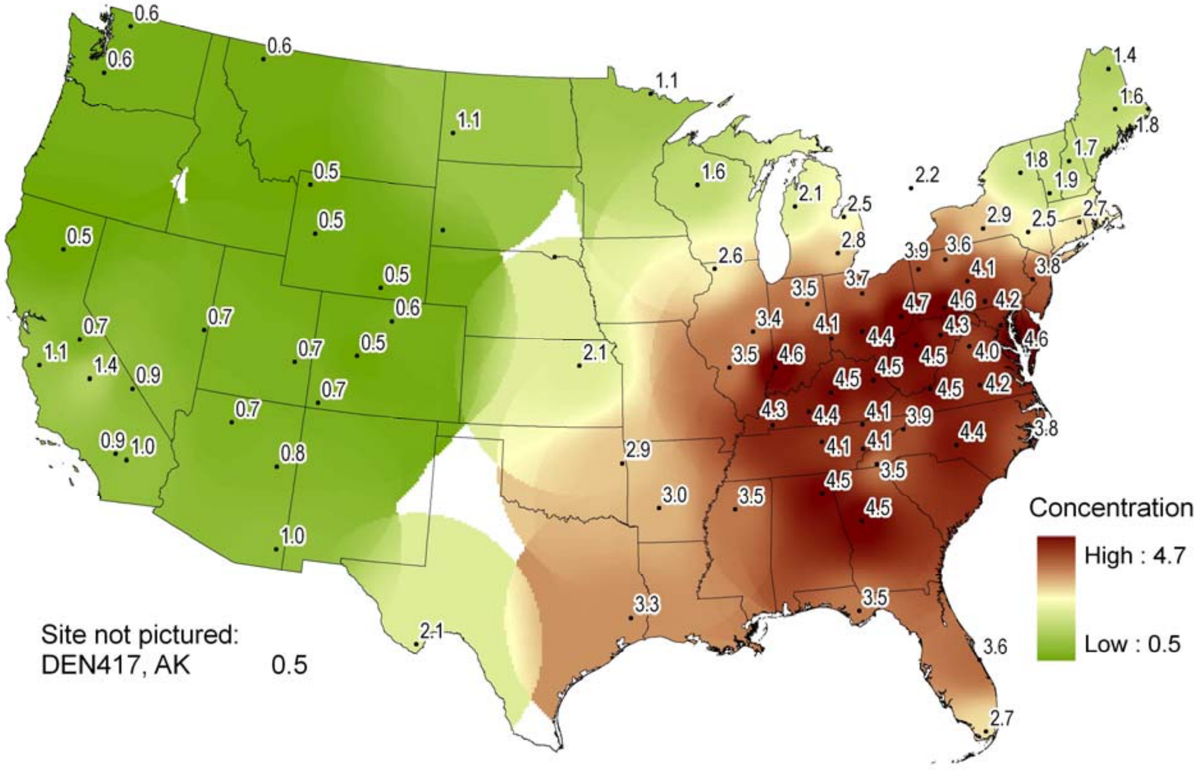
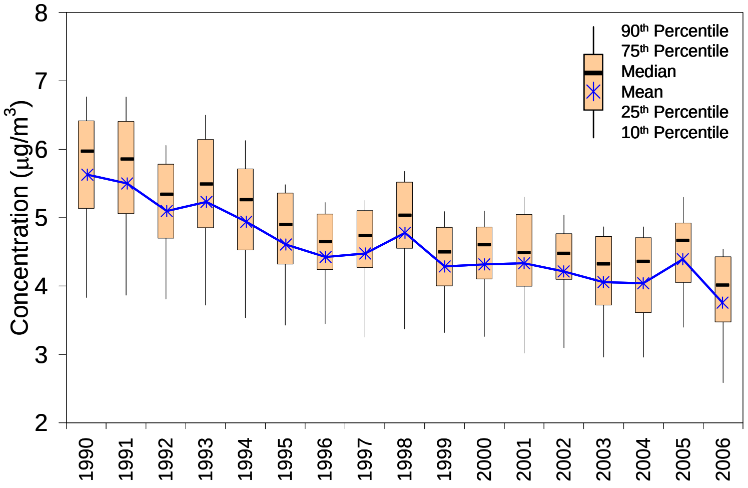


Figure 2-4 Trend in Annual Mean SO_4^{2-} Concentrations (μg/m^3)



Total Nitrate

A map of annual mean total nitrate concentrations for 2006 is given in Figure 2-5. Total nitrate is defined as the sum of gaseous nitric acid (HNO_3) and particulate nitrate (NO_3^-). Measurement of total nitrate concentrations measures the response to changes in nitrogen oxides (NO_x) emissions more accurately than measurement of either of its constituents alone. Also, measurements of the individual constituents are thought to include measurement uncertainties. See the call out box in Chapter 3 (page 28) for a discussion of the uncertainties in CASTNET HNO_3 and NO_3^- measurements.

The map in Figure 2-5 shows a complex pattern of total nitrate concentrations in the eastern United States. Most CASTNET monitors recorded values greater than 2.0 $\mu g/m^3$. The geographic variability in concentrations is caused by changes in the elevation and location of the monitoring stations and the associated differences in deposition velocities, inversion heights, and exposure to fresh NO_x emissions. The highest annual mean total nitrate values were recorded in Illinois, Indiana, and Ohio. Three CASTNET sites in California measured total nitrate concentrations above 3.0 $\mu g/m^3$. Two sites – Converse Station (CON186) and JOT403 – are located downwind of the Los Angeles Basin. The third California site, SEK430, is located in the Sierra Nevada Mountains adjacent to the agricultural region known as the Central Valley.

Box plots of annual total nitrate values from the 34 CASTNET reference sites are provided in Figure 2-6. The data show a decline in total nitrate from 2000 to 2006. The 2006 mean concentration was the lowest in the history of the network. The overall trend depicts an 18 percent reduction in total nitrate from 1990 to 2006.

Figure 2-5 Annual Mean Total Nitrate (NO_3^- + HNO_3) Concentrations (µg/m^3) for 2006

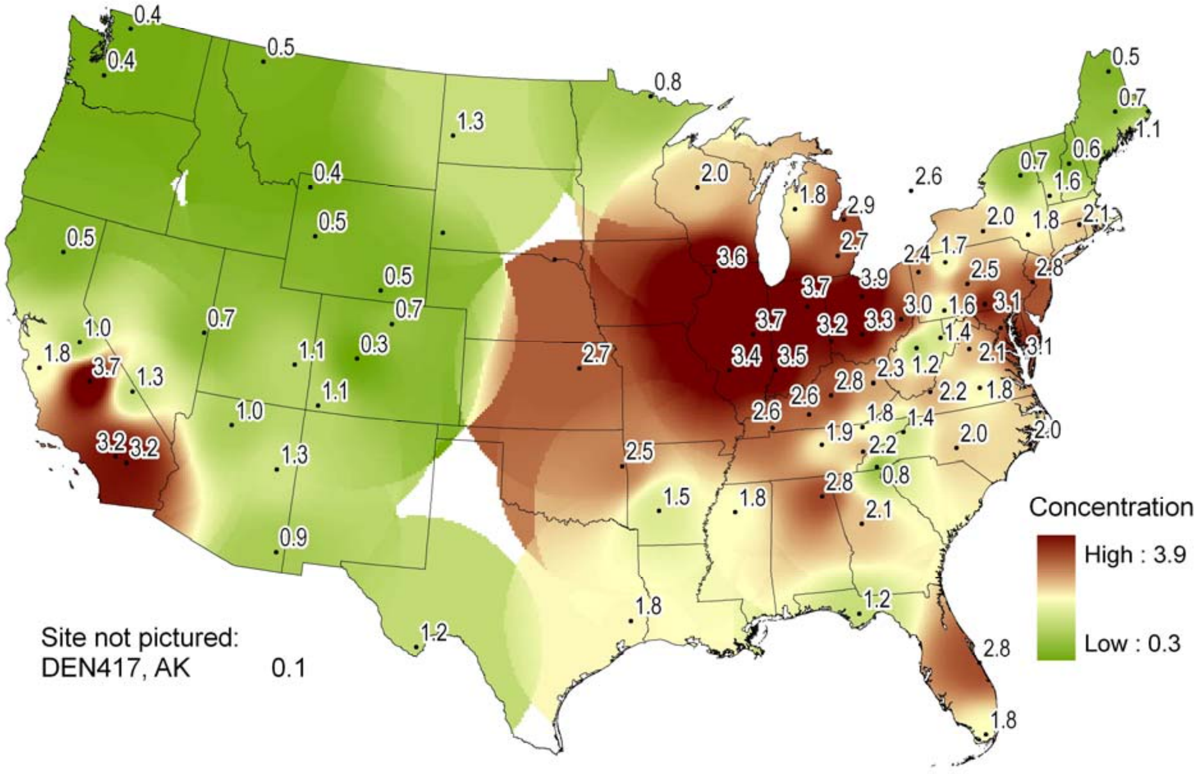
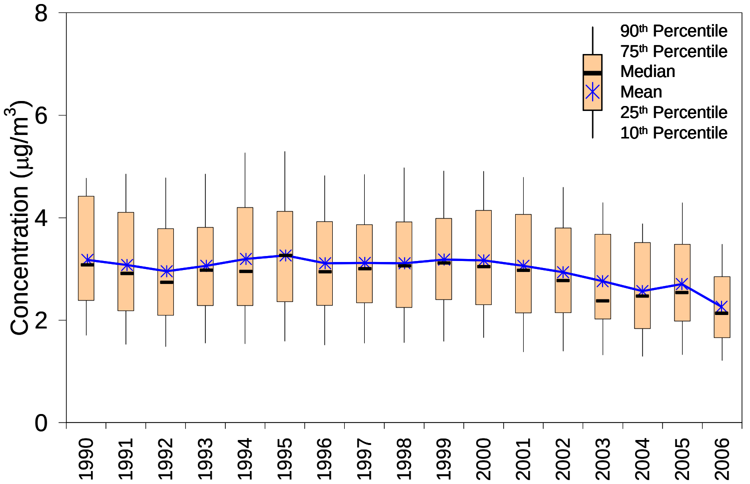


Figure 2-6 Trend in Annual Total Nitrate (NO_3^- + HNO_3) Concentrations (µg/m^3)



Air Quality Concerns in the Four Corners Region

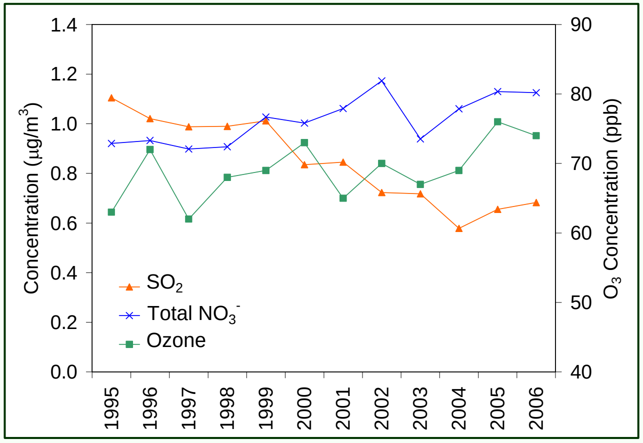
The Four Corners region of Colorado, New Mexico, Arizona, and Utah is experiencing significant energy development including new oil and gas wells, more power plants, and an increasing population. The Bureau of Land Management has expressed concern that Class I areas in the region may experience a deterioration in visibility and air quality in addition to an increase in ozone (O_3) concentrations as a result of the growth in energy development. This led to the formation of a multi-stakeholder task force to focus on air quality in the region (NM Environment Dept., 2007).

Mesa Verde National Park, CO (MEV405)

The states of Colorado and New Mexico convened the task force in 2005. The efforts of this task force are shared by federal, tribal, state, and local air quality management agencies in the Four Corners region. The public is also participating, and NPS has been actively involved since 2005. The task force is assessing existing conditions and developing options for improving air quality in the area. The goal is to create options that will consider accommodating energy growth and the associated economic development without compromising air quality (NM Environment Dept., 2007). For more information on the task force, visit http://www.nmenv.state.nm.us/aqb/4C/index.html.

Data from the CASTNET site at Mesa Verde National Park, CO (MEV405), which is located in the Four Corners region, provide information on changes in sulfur and nitrogen pollutants and ozone over the period 1995 through 2006. The figure shows annual mean concentrations of sulfur dioxide (SO_2) and total nitrate (NO_3^-) and fourth highest daily maximum 8-hour average ozone (O_3) concentrations for the 12 years. The data suggest increases in total nitrate concentrations and an overall decline in SO_2. However, SO_2 values have increased over the last two years. Three-year average fourth highest daily maximum 8-hour average O_3 concentrations increased by about 10 percent from 1995 to 2006.

Trend in Pollutant Concentrations at MEV405, CO



Particulate Ammonium

A map of annual mean ammonium (NH_4^+) concentrations is presented in Figure 2-7. The map shows no annual concentrations greater than 2.0 μg/m^3. The NH_4^+ concentrations measured at western sites were low with all sites measuring concentrations below 1.0 μg/m^3. The trend diagram for annual mean NH_4^+ values is provided in Figure 2-8. The box plots show a 20 percent decline in 3-year mean NH_4^+ concentrations from 1990 to 2006 (1.79 μg/m^3 to 1.43 μg/m^3). The 2006 mean was the lowest in CASTNET history. It is important to note that these mean values were based only on data from the 34 CASTNET reference sites (Figure 1-6), which include only one site west of the Mississippi River. Additional studies using wet deposition data from NADP/NTN have shown an increase in NH_4^+ concentrations in the Great Plains where the geographic coverage of CASTNET sites is less in extent (i.e., fewer sites) than the coverage provided by NTN (NADP, 2003).

Figure 2-7 Annual Mean NH_4^+ Concentrations (μg/m^3) for 2006

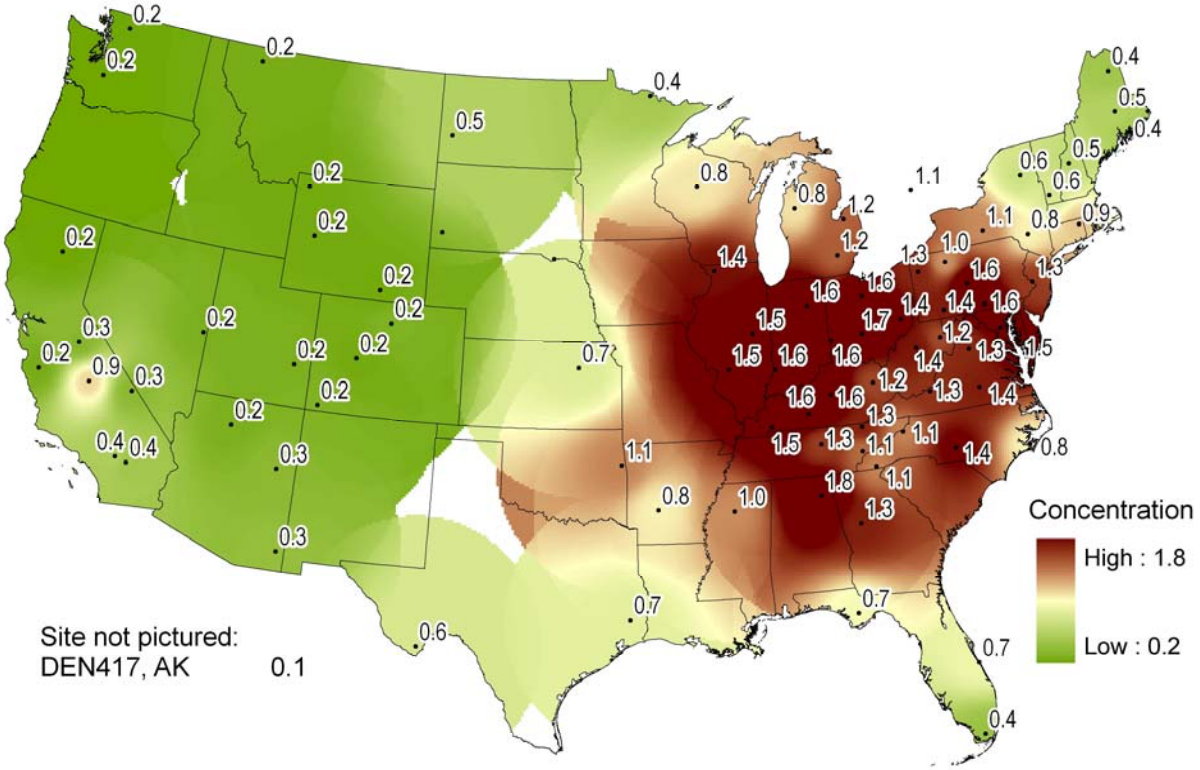
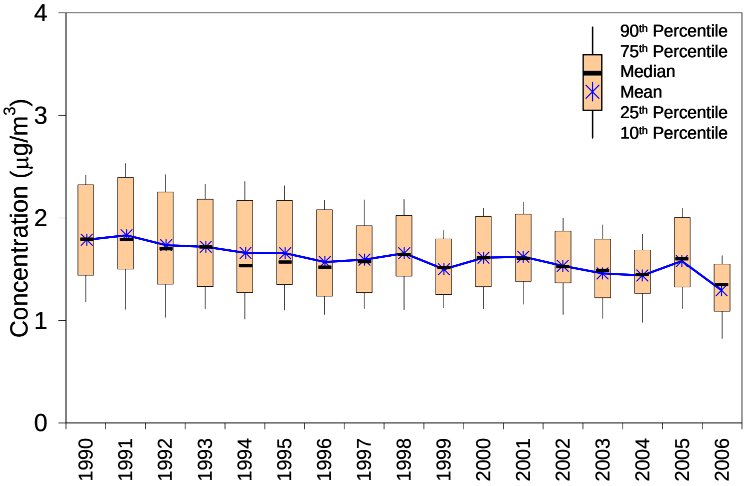


Figure 2-8 Trend in Annual Mean NH_4^+ Concentrations (µg/m^3)



Petrified Forest National Park (PET427), AZ

Chapter 3:

Denali National Park, AK (DEN417)

Atmospheric Deposition

One of the principal objectives of CASTNET is to provide estimates of the dry deposition of sulfur and nitrogen pollutants across the United States. CASTNET uses a hybrid approach to estimating dry deposition by combining measured pollutant concentrations and modeled deposition velocities. The Multi-Layer Model (MLM) is the computer model used to calculate site-by-site deposition velocities based on meteorological measurements and information on the surrounding vegetation. Total deposition is the sum of estimated dry deposition and measured wet deposition. Since 1990, total sulfur deposition has declined significantly. The data show a 28 percent reduction in 3-year mean sulfur fluxes over the period from 1990-1992 to 2004-2006. Total nitrate deposition declined by 12 percent over the same period. Dry deposition is responsible for approximately 20 to 80 percent of total deposition depending on location and climate. The percentage is higher in major source regions.

Gaseous and aerosol sulfur and nitrogen pollutants are deposited into ecosystems through dry and wet atmospheric processes. One of the most critical objectives of CASTNET is to estimate the rate, or flux, of dry deposition from measured meteorological and other environmental conditions. Flux values are estimated as the product of measured concentration data and MLM-modeled dry deposition velocities. For this report, wet deposition measurements were obtained from NADP/NTN and combined with CASTNET dry deposition data to estimate total deposition. Dry sulfur and nitrogen deposition rates decreased slightly during 2006 while total deposition stayed about the same. Precipitation-weighted mean concentrations in precipitation of total atmospheric sulfur have declined over the past 17 years. Nitrogen concentrations in precipitation have declined slowly since 1996.

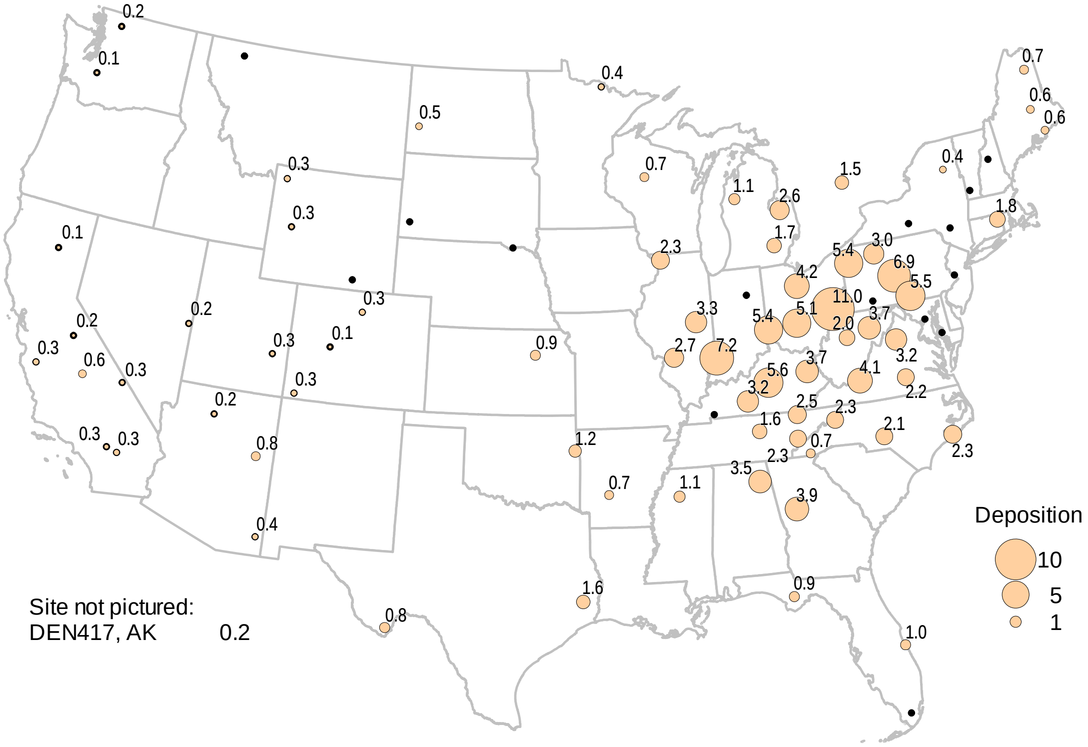
Dry deposition processes were simulated using the MLM (Figure 1-5) as described by Meyers *et al.* (1998) and Finkelstein *et al*. (2000). An improved version of the MLM (Schwede, 2006) was provided to MACTEC in 2006. For this report, the MLM was run using CASTNET filter pack concentrations and meteorological measurements with information on land use, vegetation, and surface conditions to calculate deposition velocities for sulfur dioxide

(SO_2), nitric acid (HNO_3), ozone (O_3), and the particles sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+). The deposition velocities were assumed to be identical for all particle species. Deposition velocity values were calculated for each pollutant species for each hour with valid meteorological data for each CASTNET site for the entire period 1990 through 2006. For a deposition velocity to be estimated, temperature, solar radiation, relative humidity, wind speed, and standard deviation of the wind direction (sigma theta) must all be valid for the hour. Aggregation rules for CASTNET require three valid quarters for the calculation of an annual value. If an annual value is not available for a specific site, the results are not included on maps presented in this chapter. For trends analyses, missing values are replaced by interpolation or extrapolation using valid annual estimates.

Sulfur Deposition

MLM simulations were run separately for sulfur dioxide (SO_2) and sulfate (SO_4^{2-}). The model calculations were summed to obtain estimates of dry sulfur deposition [as sulfur (S)]. Figure 3-1 provides a map of estimates of dry sulfur deposition for 2006. The magnitude of a deposition rate is illustrated by the size of the circle. The map shows a narrow region with fluxes greater than 5.0 kilograms per hectare per year (kg/ha/yr) centered around and downwind of the Ohio River Valley from southern Indiana and central Kentucky to eastern Pennsylvania. Locations on the map with no value had insufficient data to calculate fluxes. The highest deposition rate was estimated for Quaker City, OH (QAK172) with a flux of 11.0 kg/ha/yr. The highest dry sulfur deposition rates were coincidental to the major SO_2 source region (Figure 1-7) and declined sharply with distance. The dry deposition rates for the western sites were all less than 1.0 kg/ha/yr with the majority of sites less than 0.5 kg/ha/yr.

Figure 3-1 Dry Sulfur ($SO_2 + SO_4^{2-}$) Deposition (as S) (kg/ha/yr) for 2006



Wet deposition values used to estimate total deposition represent a combination of historical CASTNET wet deposition data with NADP/NTN wet deposition data. For CASTNET sites where wet concentrations were measured prior to January 1999 (when responsibility for wet deposition monitoring activities at CASTNET sites was transferred to NADP/NTN), those values were used in the data set. For sites where no wet concentrations were measured and for all sites after January 1999, values were obtained from a grid of concentration estimates derived from available NADP/NTN sites by using an inverse distance weighting function. Estimated concentrations were multiplied by the precipitation measured at the CASTNET sites to obtain estimates of wet deposition.

Figure 3-2 provides a map of estimates of total sulfur deposition. The map was constructed by adding dry and wet deposition. The circles in the figure illustrate the magnitude of total sulfur deposition and also the relative contributions from wet and dry deposition. The dark shading (blue) signifies the percent wet deposition and the light shading (tan) shows the percent dry deposition. A region with total (dry + wet) sulfur deposition (kg/ha/yr) greater than 10.0 kg/ha/yr extended from southwestern Indiana and central Kentucky along the Ohio River Valley and into Ontario, Canada. Sites in Virginia, Tennessee, and Alabama also had total sulfur fluxes greater than or equal to 10.0 kg/ha/yr. Sulfur deposition at western sites was less than 2.0 kg/ha/yr. The contribution of dry deposition was much more significant in and near major source regions. For example, the contribution of dry sulfur deposition ranged from about half of total sulfur deposition at Oxford, OH (OXF122) to less than 25 percent at sites in New England.

Figure 3-2 Total (Dry + Wet) Sulfur Deposition (as S) (kg/ha/yr) for 2006

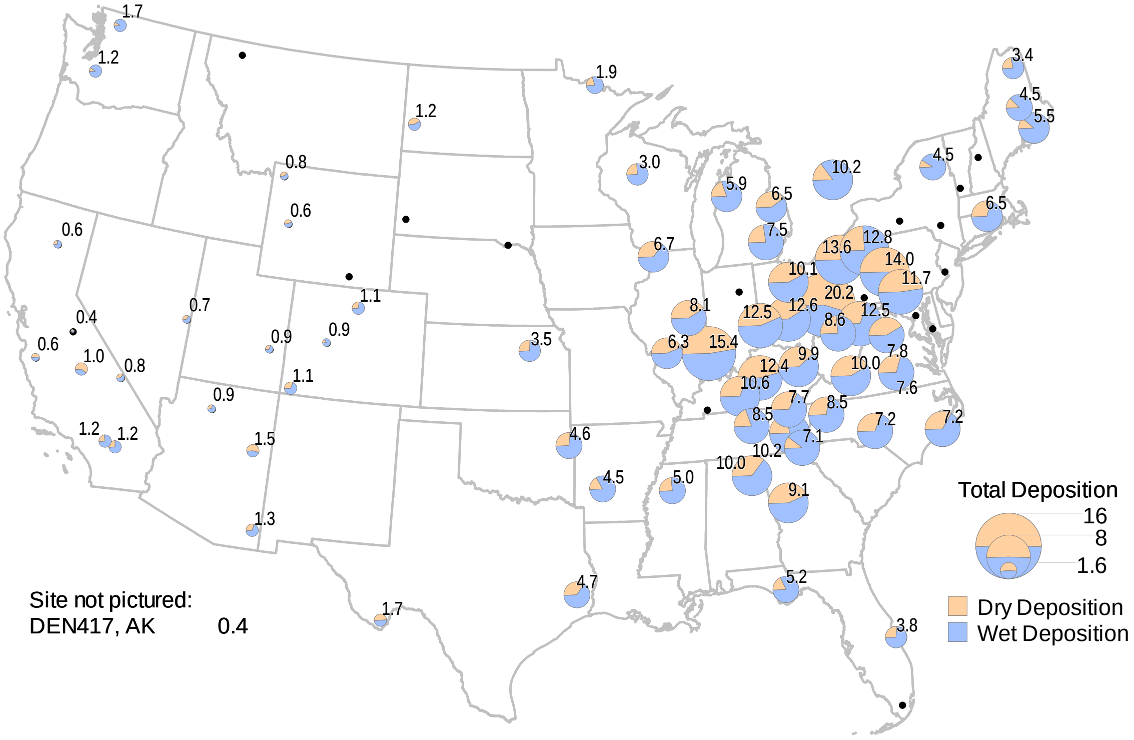


Figure 3-3 presents box plots that show the trend in dry sulfur deposition (as S), and Figure 3-4 shows the trend in annual total (dry + wet) sulfur deposition (as S) over the 17 years, 1990 through 2006. The box plots were based on data obtained from the 34 eastern CASTNET reference sites (Figure 1-6). Sulfur deposition at these sites declined significantly over the 17 years. Figure 3-5 presents estimates of trends in dry, wet, and total deposition of sulfur (as S) on the same diagram. The trend line for precipitation-weighted mean sulfur concentrations in precipitation shows a continuing decrease over the last several years with small increases in 2005 and 2006.

The influence of precipitation on total sulfur deposition is illustrated by comparing the solid (top) line to the dotted blue line in Figure 3-5. The solid line shows total deposition, which depends on sulfur concentrations in precipitation and precipitation amounts. The dotted line shows concentrations in precipitation, which reflect changes in SO_2 emissions. The year 2003 experienced relatively high total sulfur deposition even though the sulfur concentration in precipitation was relatively low. Above average precipitation produced the relatively high total flux of sulfur. Nonetheless, total sulfur deposition declined from a 1990-1992 mean of 13.2 kg/ha/yr to a 2004-2006 mean of 9.5, a 28 percent reduction.

Figure 3-3 Trend in Dry Sulfur Deposition (kg/ha/yr)

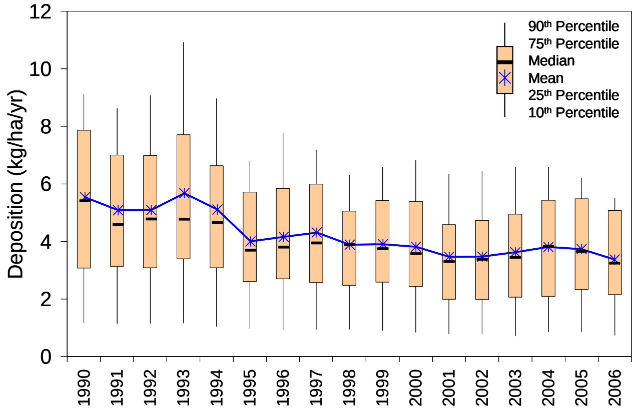


Figure 3-4 Trend in Total Sulfur Deposition (kg/ha/yr)

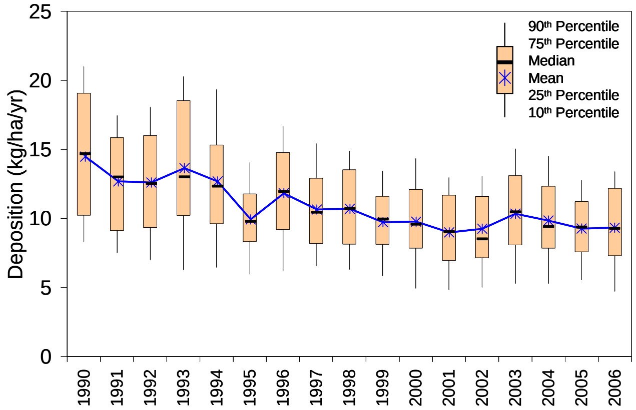
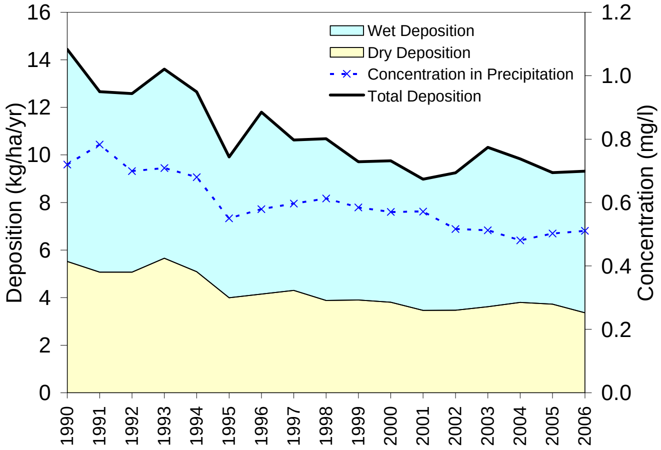


Figure 3-5 Trend in Sulfur Deposition (kg/ha/yr) with Concentrations in Precipitation (mg/l)



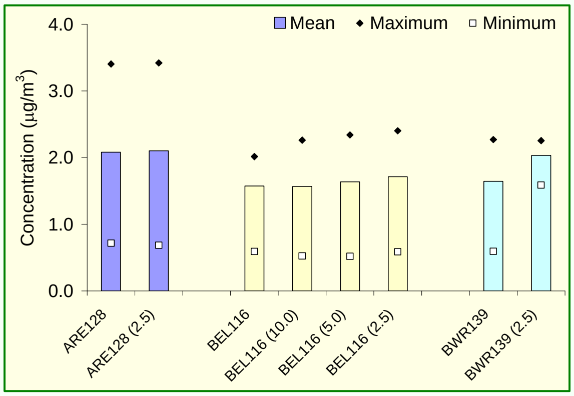
Note: All trend diagrams are based on data collected at 34 reference sites.

Uncertainties in Estimates of Dry Nitrogen Deposition

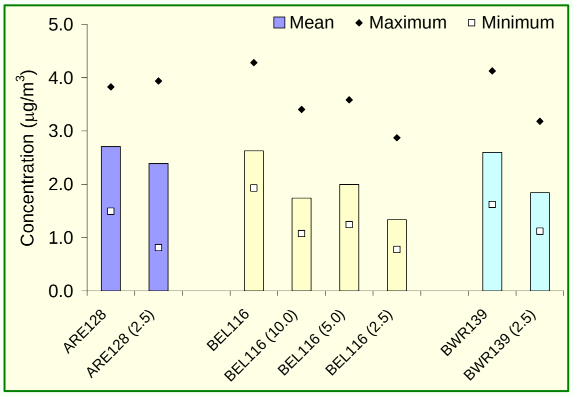
EPA's National Exposure Research Laboratory (NERL), which is part of the Office of Research and Development (ORD), recently sponsored a short, warm-season study to investigate the measurement uncertainties for CASTNET nitrogen species. The study examined the size distribution of CASTNET particle measurements through additional sampling in 2006 at three Mid-Atlantic CASTNET sites: Beltsville, MD (BEL116), Arendtsville, PA (ARE128), and Blackwater Wildlife Refuge, MD (BWR139). Weekly concentrations were measured with and without cyclone particle size separators for six measurement cycles over the period March 28, 2006 through August 22, 2006. BEL116 utilized cyclones with three different size cut off points: 10.0, 5.0, and 2.5 micrometers (µm). The other two sites operated cyclones with a 2.5 µm cut off.

The results are summarized in the three bar charts shown to the right. Mean, maximum, and minimum concentrations from the six samples are provided for ammonium (NH_4^+), nitric acid (HNO_3), and nitrate (NO_3^-) for each sampling configuration. The measurements show that the NH_4^+ concentrations at the three sites were not affected by the cyclones and existed as small (< 2.5 µm) particles. NH_4^+ results were very similar to those of SO_4^{2-} (not shown) because during the warm season (i.e., the time of the study) most NH_4^+ exists as ammonium sulfate $[(NH_4)_2SO_4^{2-}]$. However, HNO_3 and particulate NO_3^- concentrations were affected by the presence of cyclones. Higher HNO_3 concentrations were measured

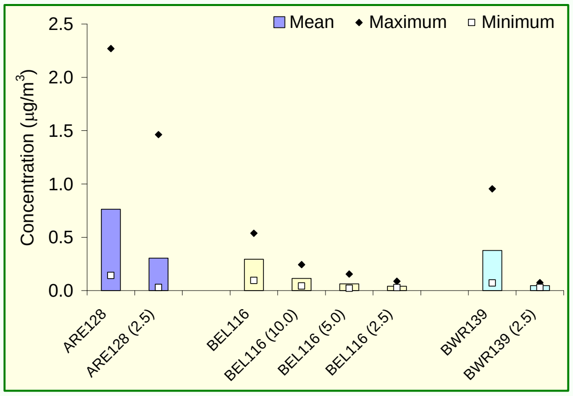
Ammonium Special Study Results



Nitric Acid Special Study Results



Nitrate Special Study Results



with the standard CASTNET open-face filter packs. Considerably higher particulate NO_3^- concentrations were measured with the open face configurations, and the concentrations decreased substantially as the cyclone cut-off points decreased (Lavery *et al.,* 2007).

Although limited in both temporal and spatial coverage, analysis of the study results provides new information on the measurement of nitrogen species using the standard CASTNET sampling protocol. The CASTNET open-face filter pack measures particles with a range of sizes from more than 10.0 µm to less than 2.5 µm. The larger particles are comprised of salts and trace metals, which are produced by sea spray and soil dust. Sodium nitrate ($NaNO_3$) and calcium nitrate [$Ca(NO_3)_2$] constitute a significant fraction of the coarse particles. These nitrate particles are produced by the reaction of HNO_3 with sodium chloride (NaCl) and calcium carbonate ($CaCO_3$) in ambient air, on the Teflon® filter, or both. The fine particles are comprised of ammonium nitrate (NH_4NO_3), which is produced by the reaction of ammonia (NH_3) with HNO_3.

A comparison of CASTNET measurements with data from other studies suggests that the right combination of atmospheric conditions (e.g., temperature, relative humidity, and solar radiation) causes the volatilization and conversion of NH_4NO_3 to HNO_3 and NH_3 during the CASTNET weekly sampling period. These reactions result in a decrease in NO_3^- and an increase in HNO_3 on the filters. These $NO_3^- \rightarrow HNO_3$ concentration changes were corroborated by Teflon® and nylon filter measurements that were part of the Midwest Ammonia Monitoring Project (Sweet *et al.,* 2005). The relative loss of NO_3^- and gain of HNO_3 are unknown and vary significantly based on the geographic location of the monitoring site and on the season (Ames and Malm, 2001).

One of the goals of CASTNET is to estimate dry deposition of particles and gases. The collection of coarse nitrate particles complicates the calculation of deposition velocities. The coarse particles are affected by the meteorological and biochemical processes that are simulated by the MLM. However, these particles are also subject to gravitational settling, which is not simulated. The net effect is likely an underestimation of the dry deposition of nitrate particles. Since dry deposition is directly proportional to the concentration of the pollutant, an uncertainty in the concentration measurement produces an uncertainty in the flux estimate. In the case of nitrogen species, an overestimation of HNO_3 or NO_3^- affects the modeled dry nitrogen deposition. Since HNO_3 deposition velocities are significantly higher than that of NO_3^-, bias in the HNO_3 concentration is amplified in the total nitrogen deposition reported.

Nitrogen Deposition

Figure 3-6 presents a map of dry fluxes of nitrogen [as nitrogen (N)] for 2006. Nitrogen fluxes are comprised of nitric acid (HNO_3) + nitrate (NO_3^-) + ammonium (NH_4^+). This map was constructed by summing the individual MLM simulations for the three species. Almost all of the CASTNET sites in the eastern United States had estimated dry nitrogen deposition rates greater than 1.0 kg/ha/yr. Other than the relatively low deposition rates at Cedar Creek State Park, WV (CDR119) and Coweeta, NC (COW137), the nitrogen fluxes were fairly uniform geographically, reflecting a wide distribution of nitrogen oxides (NO_x) sources (such as motor vehicles). The flux values ranged from 0.4 kg/ha/yr in upstate New York to 3.1 kg/ha/yr in eastern Ohio. The values at the western sites ranged from 0.2 kg/ha/yr at Mount Rainier National Park, WA (MOR409) to 3.0 kg/ha/yr at Sequoia National Park, CA (SEK430). Locations on the map with no value had insufficient data to calculate fluxes.

Figure 3-6 Dry Nitrogen (HNO_3 + NO_3^- + NH_4^+) Deposition (as N) (kg/ha/yr) for 2006

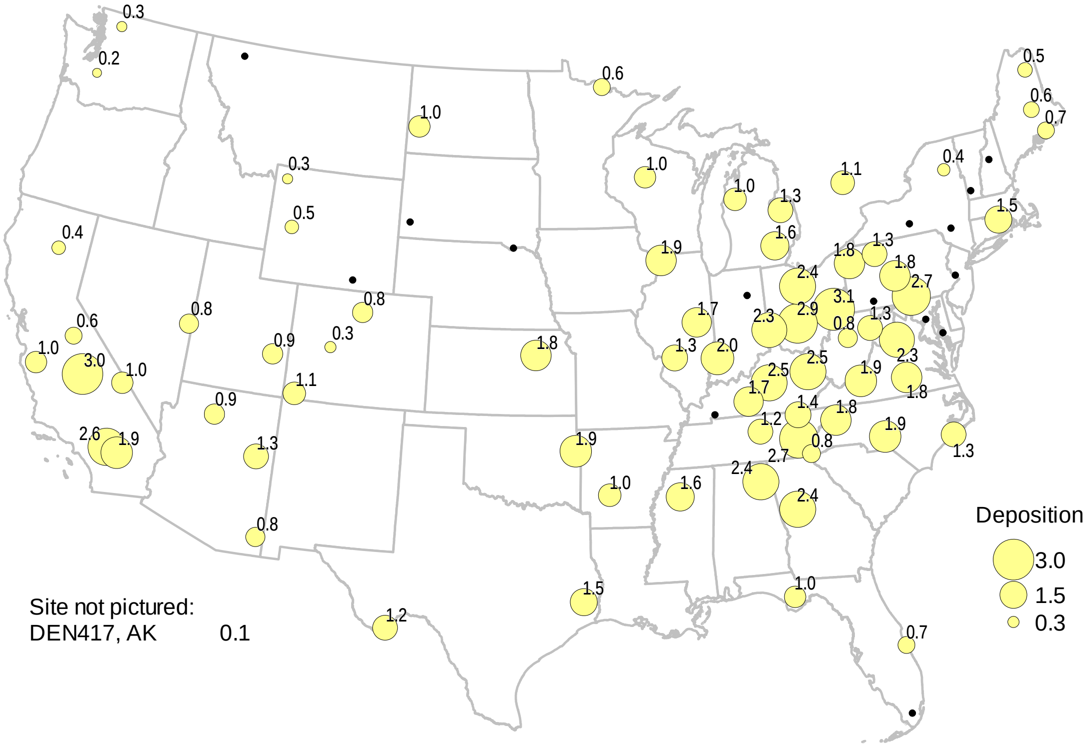


Figure 3-7 presents a map of total nitrogen deposition (as N) for 2006. The map was constructed by summing the estimates of dry (light shading) and wet (dark shading) deposition. The figure shows that a large majority of the eastern sites recorded deposition rates greater than 5.0 kg/ha/yr. No values above 10.0 kg/ha/yr were observed in 2006. The highest total nitrogen flux (9.2 kg/ha/yr) was estimated for Vincennes, IN (VIN140) and Quaker City, OH (QAK172). Fluxes with values less than 5.0 kg/ha/yr in the eastern United States were estimated for New England, upstate New York, Minnesota, Florida, and Texas. The values at the western sites ranged from 1.2 kg/ha/yr at Yosemite National Park, CA (YOS404), Pinedale, WY (PND165), and MOR409, WA to 5.1 kg/ha/yr in southern California at Converse Station (CON186). The contributions of dry nitrogen deposition to total nitrogen were lower than the corresponding contributions of dry sulfur deposition. Dry nitrogen deposition typically contributed less than 50 percent of total deposition in the East. Interestingly, dry nitrogen deposition contributed more than half of total nitrogen deposition at sites in California, a region with elevated concentrations of nitrogen species and limited rainfall. The CASTNET site at QAK172, OH had the distinction of measuring both the highest total sulfur and total nitrogen deposition rates.

Figure 3-7 Total (Dry + Wet) Nitrogen Deposition (as N) (kg/ha/yr) for 2006

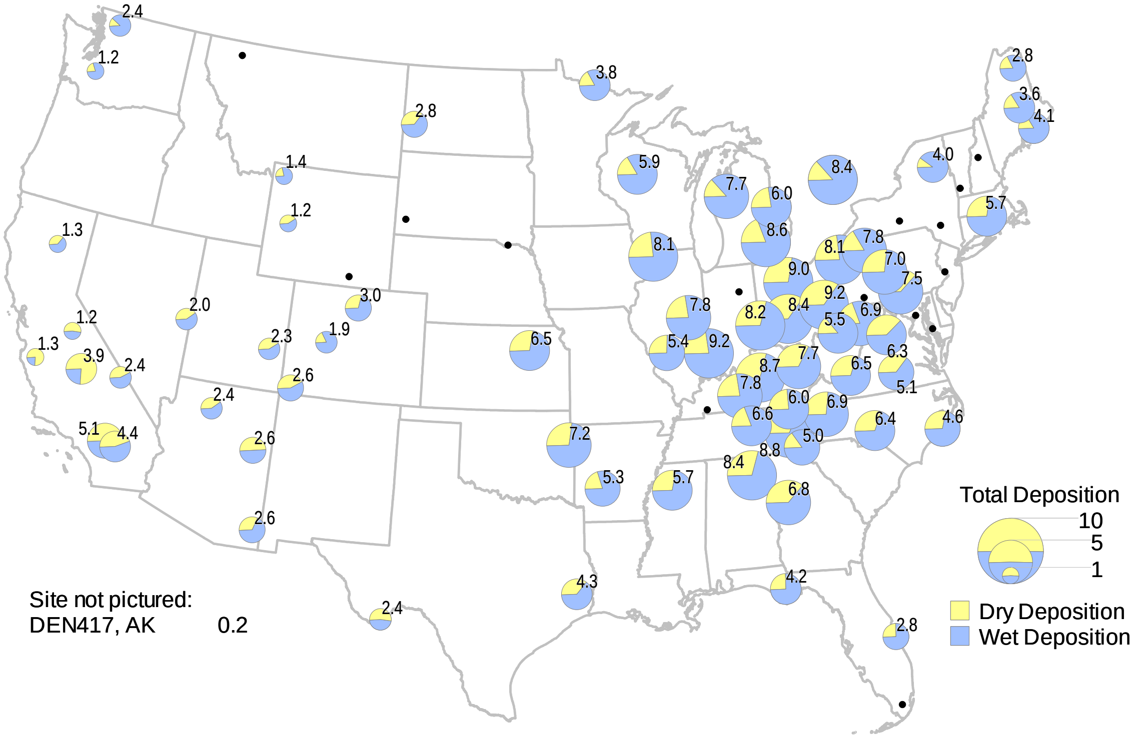


Figure 3-8 presents box plots that show the 17-year trend in dry nitrogen deposition (as N), and Figure 3-9 shows the trend in annual total (dry + wet) nitrogen deposition over the 17 years, 1990 through 2006. The box plots in Figure 3-8 show little overall trend although the data suggest a decline in dry nitrogen deposition since 1999. Total nitrogen deposition (Figure 3-9) is more variable because the annual wet and total fluxes depend on the amount of precipitation. The figure suggests that total flux has decreased since perhaps 1996. Again, the total flux in 2003 was relatively high because of unusually high precipitation.

Estimates of trends in wet, dry, and total deposition of atmospheric nitrogen (as N) are presented in Figure 3-10. The trend in precipitation-weighted mean nitrogen concentrations in precipitation is also provided on the same figure. The trend line for precipitation-weighted mean nitrogen concentrations in precipitation shows a slight downward trend since 1998. This trend line reflects the effect of changes in NO_x emissions. Total nitrogen deposition declined 12 percent over the 17 years.

Figure 3-8 Trend in Dry Nitrogen Deposition (kg/ha/yr)

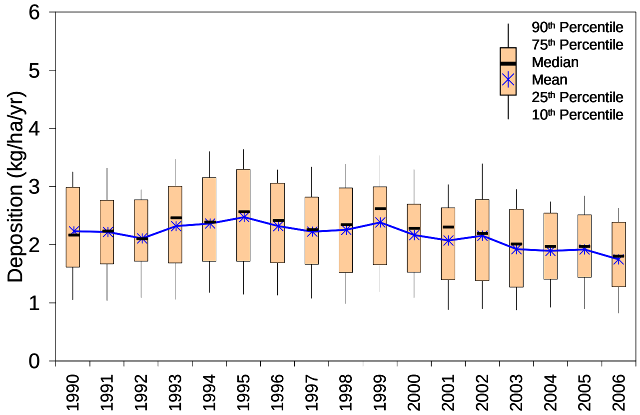


Figure 3-9 Trend in Total Nitrogen Deposition (kg/ha/yr)

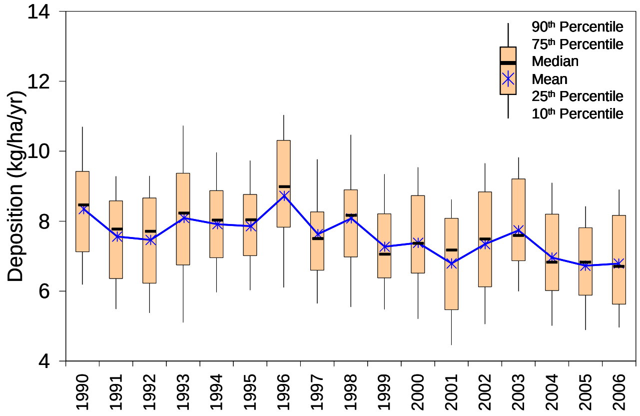
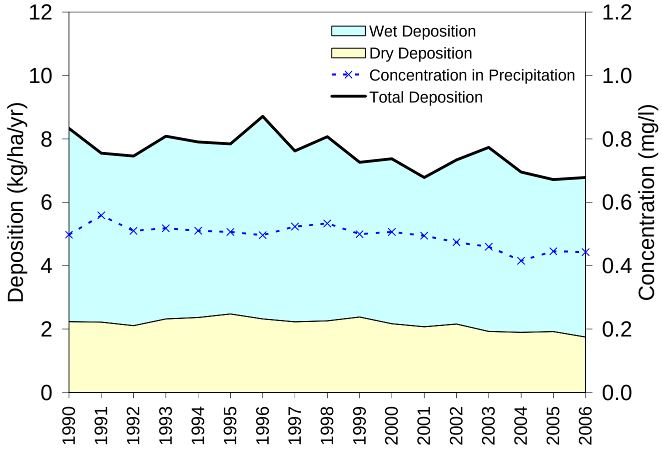


Figure 3-10 Trend in Nitrogen Deposition (kg/ha/yr) with Concentrations in Precipitation (mg/l)



Chapter 4:

Gothic, CO (GTH161)

Ozone Concentrations

CASTNET provides the primary means for monitoring rural, ground-level ozone (O_3) concentrations in the United States. Fourth highest daily maximum 8-hour average O_3 concentrations represent the critical metric for evaluating compliance with National Ambient Air Quality Standards (NAAQS). These annual fourth highest daily maximum concentrations are averaged over 3-year periods to determine potential areas of nonattainment. If the average ozone concentration for an area exceeds 0.08 ppm or reaches 85 ppb in practice, the area is designated as a "nonattainment area." For the most recent 3-year period (2004-2006), only two eastern and four California sites recorded exceedances of the 8-hour standard. This represents the fewest number of sites with exceedances over a 3-year period in the history of the network.

Most CASTNET sites operate an ozone (O_3) analyzer that provides information on ozone concentrations. Ozone data are recorded and archived as hourly averages. While CASTNET is not a compliance network, the data collected provide useful information on geographic patterns in regional O_3 and the extent to which rural areas potentially exceed concentration values mandated by the National Ambient Air Quality Standards (NAAQS). The 8-hour O_3 standard is a useful metric for assessing status and trends in rural O_3 in order to gauge the success of EPA emission reduction programs such as the NO_x Budget Program. The analyses presented in this section provide maps and examine trends in the fourth highest daily maximum 8-hour average O_3 concentrations.

Ozone is an allotrope of oxygen (made up of three oxygen atoms). At ground level, it is an air pollutant that can cause harmful effects on the human respiratory system as well as damage to vegetation and ecosystems. Ozone is formed in the troposphere when volatile organic compounds (VOC), nitrogen oxides (NO_x), and carbon monoxide (CO) react in the presence of sunlight. Ozone is a result of the photolysis of nitrogen dioxide (NO_2):

$$NO_2 + hv \rightarrow NO + O \qquad (4\text{-}1)$$

$$O + O_2 \rightarrow O_3 + M \qquad (4\text{-}2)$$

Where *hv* represents incoming solar radiation and M represents any body [e.g., nitrogen (N_2) or oxygen (O_2) molecules] present during the reaction to absorb energy. Reaction 4-2 is the only significant source of ozone in the atmosphere. Once formed, O_3 reacts with nitric oxide (NO) to regenerate NO_2:

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (4\text{-}3)$$

Measured O_3 concentrations frequently exceed those predicted by Reactions 4-1 through 4-3. Other reactions involving carbon-containing species enhance the production of O_3 by producing free radicals that oxidize NO to NO_2 and subsequently to O_3 via Reaction 4-2. In the "background" troposphere, O_3 concentrations are produced by methane and CO oxidation, transport from the stratosphere, and very long-range transport. In more polluted locations, the chemical reactions of VOC such as alkanes, alkenes, and aromatic hydrocarbons and NO_x dominate over methane and CO chemistry. Biogenic VOC emissions from trees and other vegetation contribute to O_3 formation in rural areas (EPA, 2007c). Volatile organic compound emission reduction strategies have been successful in reducing higher short-term O_3 concentrations in and downwind of urban areas. However, as discussed in this chapter, NO_x emission reductions that were mandated by the Acid Rain Program and other NO_x emission control programs were necessary to reduce O_3 concentrations, especially elevated 8-hour levels in rural areas. These reductions will continue to be required for additional declines in 8-hour O_3 levels.

During the period 2004-2006, 3-year averages of the fourth highest daily maximum 8-hour average O_3 concentrations were greater than or equal to 85 parts per billion (ppb) at four sites in California, one in New Jersey, and one in Maryland. Measurements of 8-hour concentrations during 2006 were somewhat lower than 2005 and were considerably lower than concentrations measured over the period 1990-2002. Following a peak in ozone levels in 2002, there has been a downward trend that has continued through 2006.

The concentration shading for the figures used in this chapter was prepared based on rural ozone concentration data using an algorithm inverse distance cubed weighting with a radius of influence of 500 km. Consequently, concentration estimates for areas with limited monitoring site coverage, such as much of Texas, and concentrations depicted for urban areas, such as Atlanta, are approximations. Additional maps of ozone concentrations can be viewed on the Web site for the NPS Air Atlas (http://science.nature.nps.gov/AirAtlas/AirAtlas0105/viewer.htm).

Figure 4-1 presents 3-year averages of the fourth highest daily maximum 8-hour O_3 concentrations for 2004-2006. Two eastern and four California sites measured 3-year average concentrations greater than or equal to 85 ppb. These 3-year average concentrations constitute current design values for achieving the 8-hour NAAQS for O_3. For example, the estimated value of 117 ppb at Converse Station, CA (CON186) would have to be reduced to 84 ppb to achieve the standard. Design values change as a new 3-year database becomes available.

National Ambient Air Quality Standard for Ozone

8-Hour Ozone Standard

To better protect public health, EPA (1997) revised its national air quality standards for ozone in 1997, establishing an 8-hour standard. The 8-hour standard is 0.08 parts per million (ppm). An area meets the standard if the 3-year average of the annual fourth highest daily maximum 8-hour average concentration is less than or equal to 0.08 ppm. The 3-year average reduces the influence that meteorological conditions have on the extent and magnitude of ozone formation. Recently, EPA proposed strengthening the 8-hour standard to a level within the range of 0.07 ppm to 0.075 ppm (EPA, 2007a). For more information on the 8-hour ozone standard and ozone nonattainment areas in the United States, visit http://www.epa.gov/ozonedesignations/.

What Does It Mean?

EPA collects ozone data on an hourly basis. Essentially, 8-hour average ozone concentrations at a monitor cannot exceed 0.08 ppm more than three days during the ozone season. For compliance purposes:

- Hourly ozone measurements are used to compute 8-hour average concentrations.
- The daily maximum 8-hour average is recorded for each day.
- For each year, the fourth highest daily maximum concentration is calculated.
- These annual fourth highest daily maximum concentrations are averaged over 3-year periods.
- If the fourth highest daily 8-hour average exceeds 0.084 ppm (0.085 rounds up to 0.09 thus exceeding the standard criteria) or reaches 85 ppb in practice, the area is designated as a “nonattainment area” and is held accountable for reaching the attainment status.

For comparison to current data, 3-year averages of the fourth highest daily maximum 8-hour average O_3 concentrations for 2001-2003 are presented in Figure 4-2. Sixteen eastern and the same four California sites recorded 3-year averages greater than or equal to 85 ppb. The regions with elevated concentrations were located along the East Coast from northern Virginia to Maine and in Pennsylvania, Ohio, and Michigan. A value of 92 ppb was measured at Great Smoky Mountains National Park, TN (GRS420). The period 2004-2006 represents a significant improvement in air quality. In fact, the period 2004-2006 represents the best period of air quality since the inception of CASTNET in terms of having the fewest sites with exceedances of the 8-hour O_3 NAAQS.

Figure 4-1 Fourth Highest Daily Maximum 8-Hour Ozone Concentrations (ppb) for 2004-2006

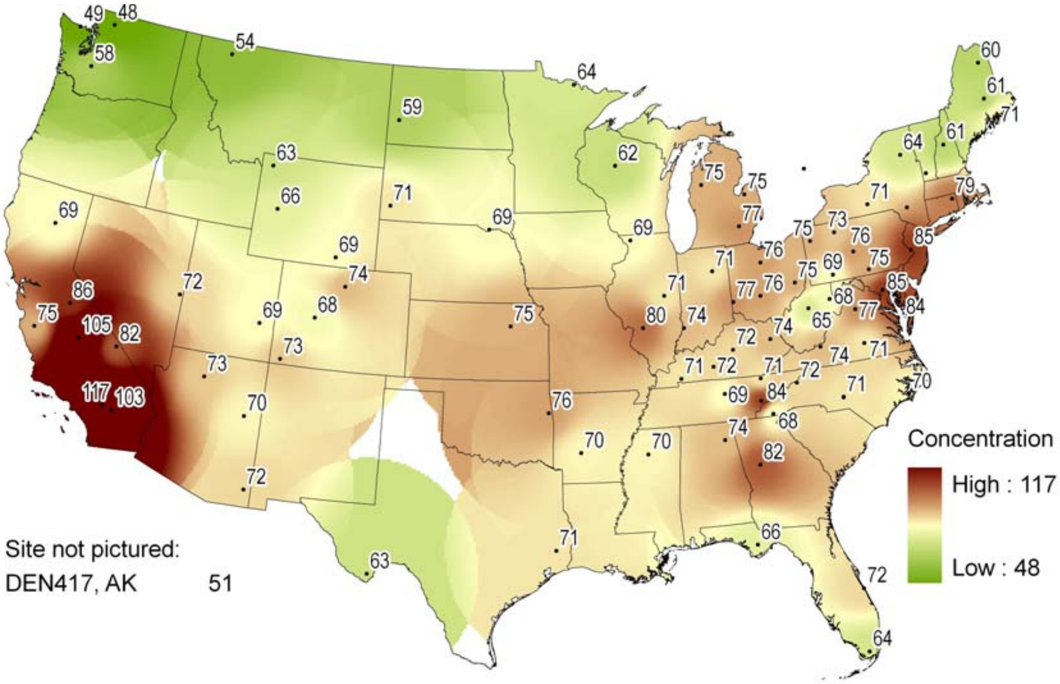
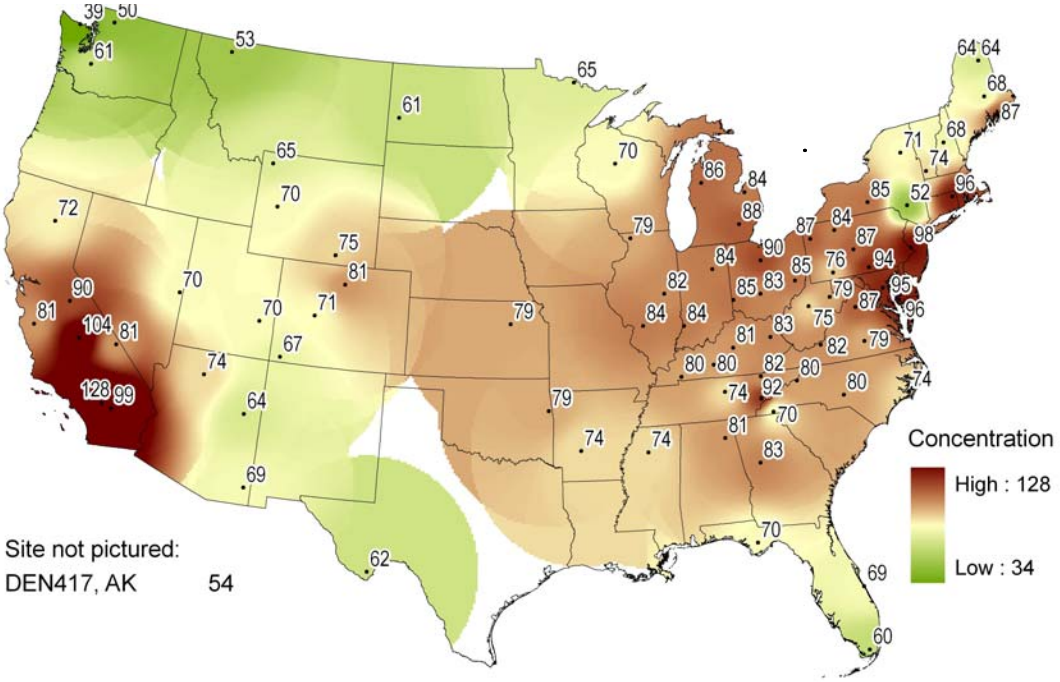
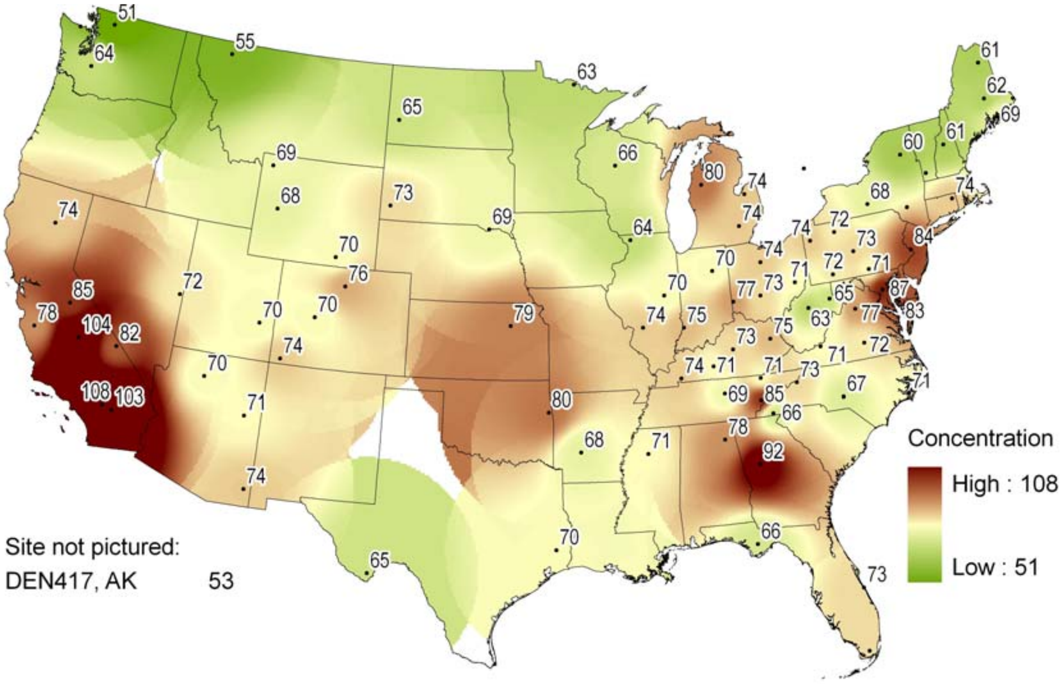


Figure 4-2 Fourth Highest Daily Maximum 8-Hour Ozone Concentrations (ppb) for 2001-2003



Fourth highest daily maximum 8-hour O_3 concentrations for 2006 are shown in Figure 4-3. Concentrations greater than or equal to 85 ppb were recorded at three sites in the East including GRS420, TN; Georgia Station, GA (GAS153); and Beltsville, MD (BEL116). In addition, four California CASTNET sites monitored exceedances of the 8-hour ozone NAAQS. The California sites include CON186, Joshua Tree National Monument (JOT403), Sequoia National Park (SEK430), and Yosemite National Park (YOS404). The 8-hour level of 108 ppb at CON186, CA was the highest value that was measured in the network during 2006.

Figure 4-3 Fourth Highest Daily Maximum 8-Hour Ozone Concentrations (ppb) for 2006



Since 2002, CASTNET ozone measurements have shown a significant decline in annual fourth highest daily maximum 8-hour average concentrations throughout the 34 eastern reference sites (see Figure 1-6) used to track trends in concentrations. During 2002, 24 reference sites measured fourth highest daily maximum 8-hour O_3 concentrations greater than or equal to 85 ppb. The number of reference sites with exceedances was reduced to six in 2003, followed by a further reduction to none in 2004, and five in 2005. As shown in Figure 4-3, two eastern reference sites (BEL116, MD and GAS153, GA) recorded elevated 8-hour concentrations in 2006.

Figure 4-4 shows the 17-year trend in 8-hour O_3 concentrations aggregated over the 34 reference stations. The box plots show a significant decline from 2002 to 2004. The 2005 data show a small increase, and the 2006 data show a decrease from 2005. Median values for the aggregated measurements for the five years 2002 through 2006 were 88 ppb, 79 ppb, 70 ppb, 76 ppb, and 72 ppb, respectively.

Figure 4-4 Trend in Fourth Highest Daily Maximum 8-Hour Ozone Concentrations (ppb)

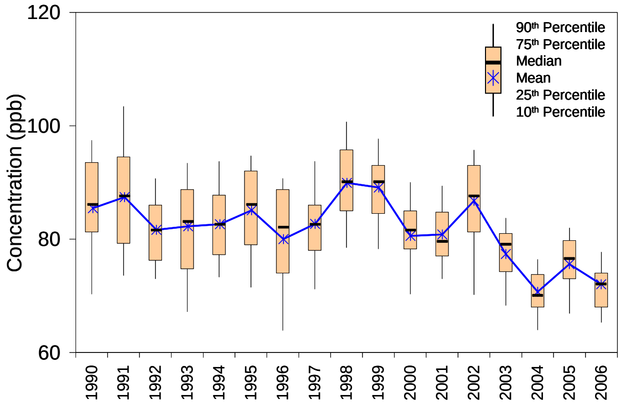
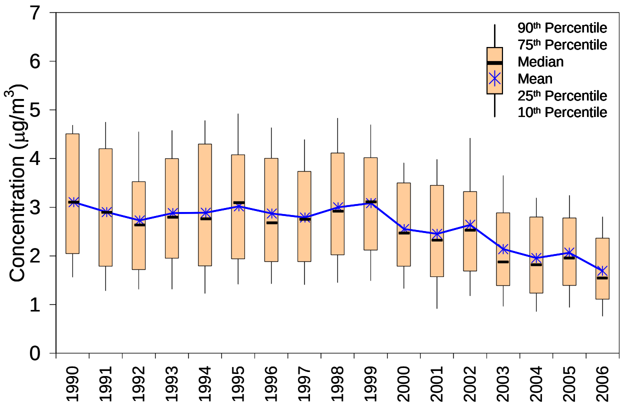


Figure 4-5 Trend in Ozone Season Mean Total Nitrate Concentrations (µg/m^3)



The median O_3 concentration for 2006 was the second lowest in the 17-year period. Additional information on ozone measurements can be found in the NPS annual reports on O_3 monitoring and O_3 trends (http://www2.nature.nps.gov/air/Monitoring/network.cfm#procedures).

The CASTNET 2005 Annual Report (MACTEC, 2006a) discussed the relationship between changes in O_3 concentrations and changes in emissions of nitrogen oxides (NO_x). EPA (2005b, 2006) attributed the decline in NO_x emissions to several effective control programs:

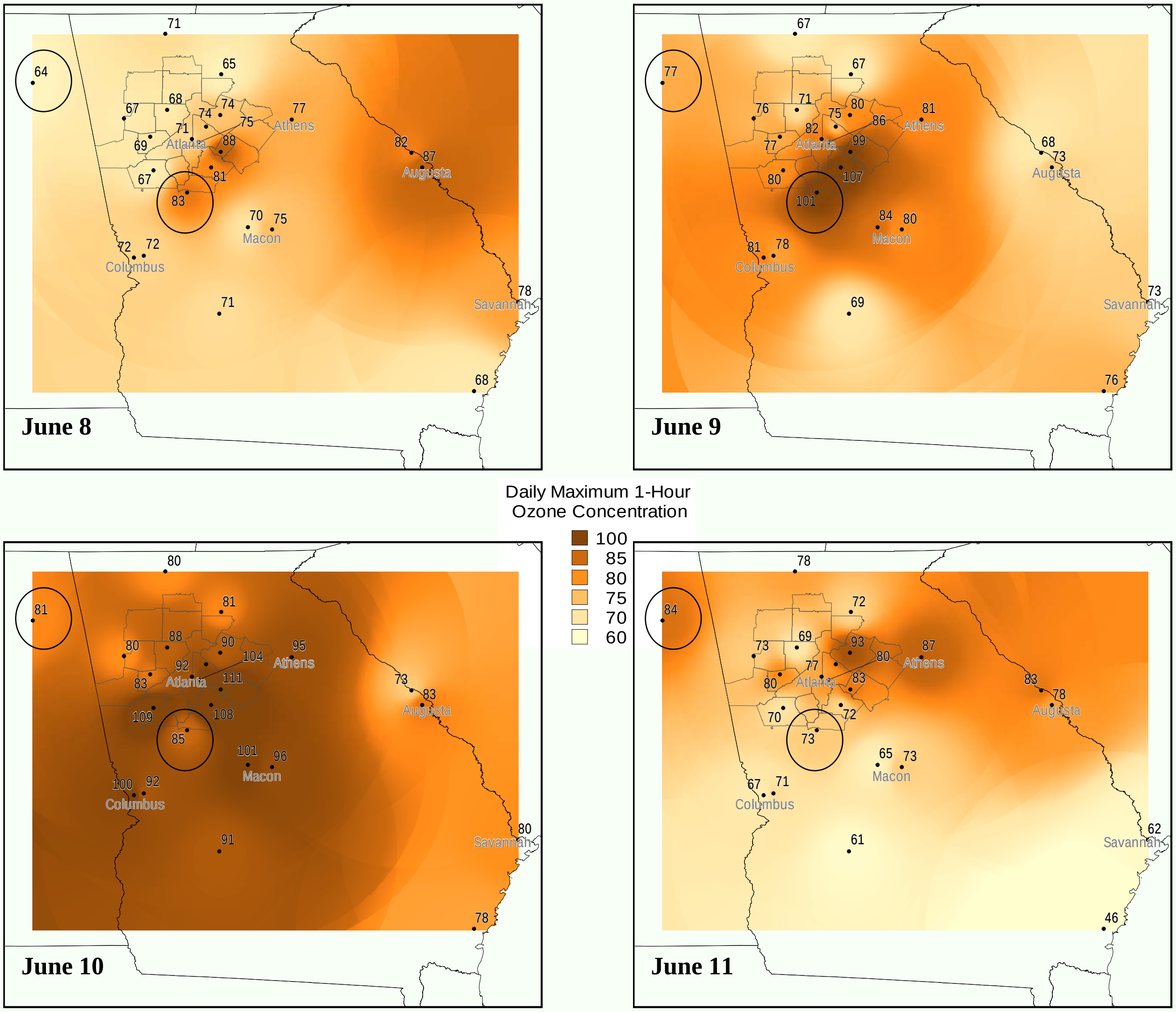
- Mobile source controls,
- Volatile Organic Compound Reasonably Available Control Technology and Maximum Available Control Technology,
- New Source Review,
- Acid Rain Program,
- Ozone Transport Commission NO_x Budget (1999-2002), and
- NO_x State Implementation Plan Call (2003-current).

These programs continue to produce reductions in NO_x emissions in the eastern United States. The trend in CASTNET measurements of total nitrate concentrations (Figure 4-5) shows a relationship between the decline in ozone and a decline in atmospheric nitrogen. The box plots show a significant reduction in total nitrate concentrations during the ozone season since 1999. The ozone season varies between states but is typically from the beginning of April through the end of September or October in the eastern United States.

Elevated Ozone Concentrations in Atlanta during 2006

The CASTNET site at Georgia Station, GA (GAS153) recorded its 2006 fourth highest daily maximum ozone (O_3) concentration of 92 ppb on June 9, 2006. This site had not recorded an exceedance since 2002. The GAS153 O_3 level was part of an ozone episode that occurred in the greater Atlanta region over the period June 8 through June 11, 2006. Daily maximum 1-hour O_3 concentrations for State and Local Ambient Monitoring Stations (SLAMS) ozone sites operated by the State of Georgia and for the GAS153 and Sand Mountain, AL (SND152) CASTNET sites are presented by four maps, one for each day from June 8 through June 11, 2006. The Atlanta Metropolitan Statistical Area, which consists of 20 counties, is shown on the four maps using gray outlines. The SLAMS data provide information on urban O_3 concentrations, which supplement the rural CASTNET measurements. The use of both SLAMS and CASTNET data provides a detailed depiction of the geographic pattern of ozone levels in the greater Atlanta area. The use of daily maximum 1-hour O_3 levels illustrates the evolution and extent of the episode over the four days. The circles on the maps designate the two CASTNET sites.

Daily Maximum 1-Hour O_3 Concentrations for CASTNET and SLAMS

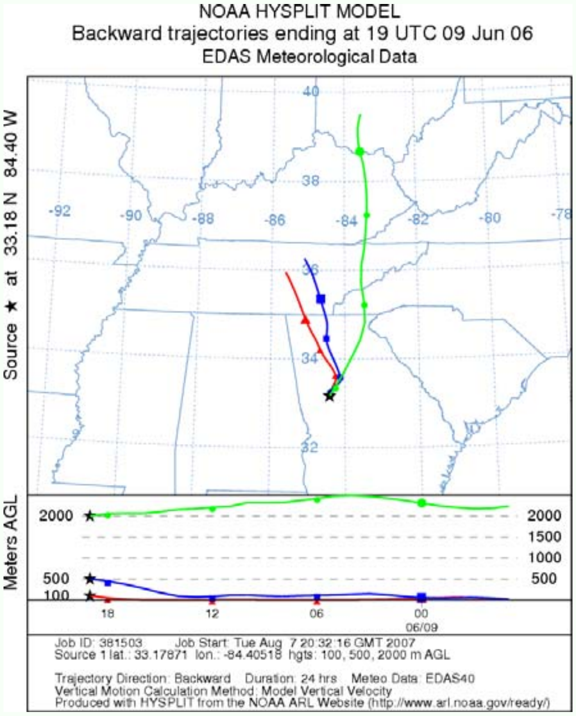


The beginning of the episode was signaled by ozone concentrations in excess of 80 ppb in southeast Atlanta on June 8. The levels increased on June 9 with concentrations as high as 107 ppb at the McDonough SLAMS site southeast of downtown Atlanta. The peak 1-hour value at GAS153 on June 9 was 101 ppb.

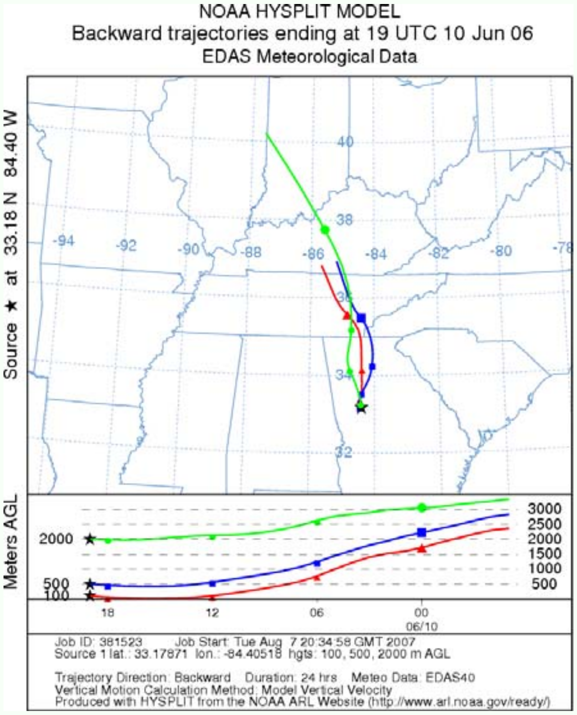
Backward trajectories from the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model for June 9, 2006 are provided. Trajectories ending at GAS153 are given for 100 meters (m), 500 m, and 2000 m above ground level (AGL). The three trajectories on June 9 indicate advection through the area of highest ozone concentrations and an area of dense, low-level precursor emissions.

Concentrations increased on June 10 with several daily maximum values in excess of 90 ppb and six stations with levels greater than or equal to 100 ppb. Backward trajectories are also provided for this day. High ozone values were widespread on June 10 because of air mass subsidence and higher temperatures. The 100 m trajectory ending at GAS153 originated at an elevation of almost 2000 m 24 hours earlier. Evidently, a localized high ozone event was observed on June 9, and the episode became more widespread on June 10 with prevalent high pressure and warm temperatures favorable to production of high ozone concentrations. Daily maximum hourly O_3 concentrations were significantly lower on June 11 with only two values above 85 ppb.

Trajectory June 9, 2006



Trajectory June 10, 2006



Chapter 5:

Claryville, NY (CAT175)

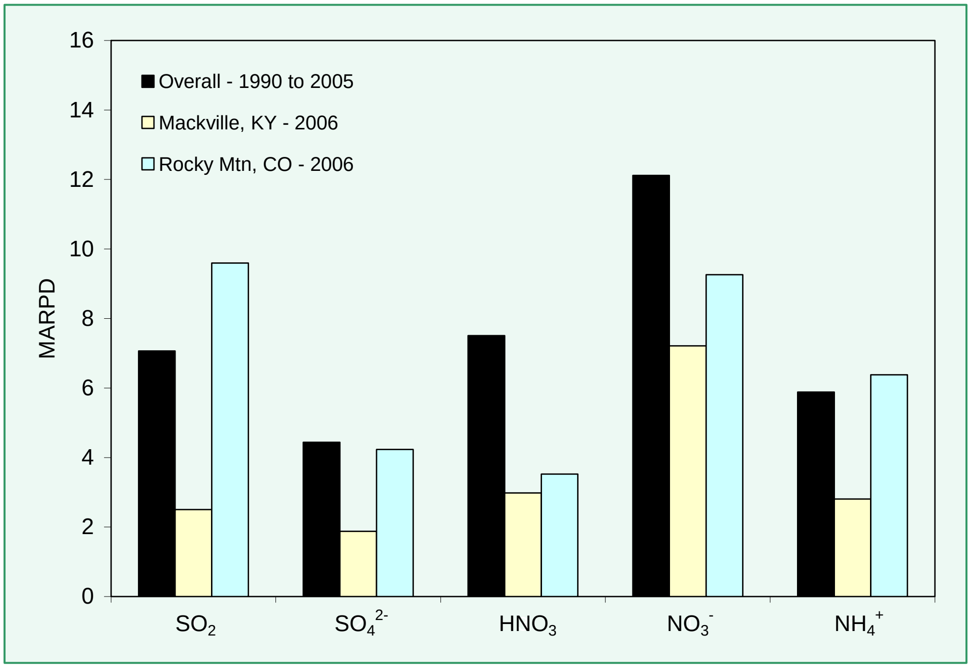
Data Quality

CASTNET measurements are assessed routinely in terms of providing high-quality information to meet CASTNET objectives. The CASTNET quality assurance program is based on specified data quality objectives, which are evaluated using data quality indicators (DQI). Measurements taken during 2006 and historical data collected over the period 1990-2005 were analyzed relative to DQI and their numerical measures. These analyses demonstrate that CASTNET data can be used with confidence and that CASTNET continues to produce data of the highest quality.

The CASTNET Quality Assurance (QA) program was designed to ensure that all reported data are of known and documented quality in order to meet CASTNET objectives and to be reproducible and comparable with data from other monitoring networks and laboratories. The QA program elements are documented in the Quality Assurance Project Plan (QAPP), Revision 3.0 (MACTEC, 2005). The QAPP is comprehensive and includes standards and policies for all components of project operation from site selection through final data reporting. It includes major sections on field measurements, chemical analysis of field samples, data management, and assessments and response actions. Standard operating procedures are included as appendices.

Data quality indicators (DQI) are quantitative statistics and qualitative descriptors used in interpreting the degree of acceptability and utility of the data collected. The DQI for CASTNET are precision, accuracy, completeness, bias, representativeness, and comparability. Precision, accuracy, and completeness for CASTNET 2006 data were analyzed and compared with historical data collected during the period 1990-2005. The information in this report is supplemented by analyses that are discussed in quarterly CASTNET Quality Assurance Reports (e.g., MACTEC, 2007b). These QA reports are produced four times per year with the fourth quarter report including an annual summary.

Figure 5-1 Historical and 2006 Precision Data for Atmospheric Concentrations



Precision

Exposed Filter Concentrations

Figure 5-1 provides a bar chart in which the bars represent precision estimates for five CASTNET analytes. Precision is defined as the mean absolute relative percent difference (MARPD) for both the historical (1990–2005) data for all collocated site pairs and the 2006 data for the current collocated sites at Mackville, KY (MCK131/231) and Rocky Mountain National Park, CO (ROM406/206). Trace cations and chloride are excluded from this figure but are shown later in Figure 5-2. The historical results vary from about 4 percent for particulate sulfate (SO_4^{2-}) to about 12 percent for particulate nitrate (NO_3^-). The historical MARPD for SO_4^{2-} met the criterion for the CASTNET filter pack measurements shown in Table 5-1. The historical results for sulfur dioxide (SO_2) and nitric acid (HNO_3) were above the 5 percent criterion but are considered reasonable. The results for ammonium (NH_4^+) met the goal of 10 percent. The results for NO_3^- were significantly above the 5 percent goal. Historically, the precision of NO_3^- measurements has been consistently worse than for the other analytes, possibly because NO_3^- concentrations are the lowest of all the pollutants and nitrate species include sampling artifacts (Lavery *et al.*, 2007).

The 2006 precision results shown in Figure 5-1 indicate that the MARPD data for MCK131/231 were lower than (i.e., more precise than) the historical results for all five parameters. Four parameters (SO_2, SO_4^{2-}, HNO_3, and NH_4^+) met precision criteria. The 2006 results for ROM406/206 showed greater precision than historical results for SO_4^{2-}, HNO_3, and NO_3^-; the results for SO_4^{2-}, HNO_3, and NH_4^+ met the DQI criteria. Overall, the filter pack precision results for 2006 showed some improvement over 2005.

Table 5-1 Data Quality Indicator Criteria for CASTNET Laboratory Measurements

Analyte	Method	Precision[1] (MARPD)	Accuracy[2] (%)	Nominal Reporting Limits
Ammonium (NH_4^+)	Automated colorimetry	10	90 - 110	0.020 mg-N/L
Sodium (Na^+)	ICP-AES	5	95 - 105	0.005 mg/L
Potassium (K^+)	ICP-AES	5	95 - 105	0.005 mg/L
Magnesium (Mg^{2+})	ICP-AES	5	95 - 105	0.003 mg/L
Calcium (Ca^{2+})	ICP-AES	5	95 - 105	0.003 mg/L
Chloride (Cl^-)	Ion chromatography	5	95 - 105	0.020 mg/L
Nitrate (NO_3^-)	Ion chromatography	5	95 - 105	0.008 mg-N/L
Sulfate (SO_4^{2-})	Ion chromatography	5	95 - 105	0.040 mg/L

Note: [1] This column lists precision goals for both network precision calculated from collocated filter samples and laboratory precision based on replicate samples. The goal for the ICP-AES precision RPD criterion changed from 10 percent to 5 percent at the onset of the current contract beginning on July 30, 2003. The precision criterion is applied as described below:

QC conditions: (v1 = initial response; v2 = replicate response; RL = nominal reporting limit)
Condition 1: if (v1 or v2 < RL and the absolute value of (v1 – v2) < RL) = OK
Condition 2: if (v1-v2) < RL and v1 < 5 x RL) = OK
Condition 3: if (v1 > 5*RL and RPD < 5%) = OK
Status: one of the conditions is OK = Precision QC Passes

[2] This column lists laboratory accuracy goals based on reference standards and continuing calibration verification spikes. The goal for the ICP-AES accuracy criterion changed from 90 – 110 percent to 95 – 105 percent for continuing calibration verification spikes at the onset of the current contract beginning on July 30, 2003. The criterion remains 90 – 110 percent for ICP-AES reference standards.

ICP-AES = inductively coupled plasma-atomic emission spectrometry
MARPD = mean absolute relative percent difference
N = as nitrogen

For more information on analytical methods and associated precision and accuracy criteria, see the CASTNET QAPP – Revision 3.0 (MACTEC, 2005).

Precision statistics for 2006 for four cations and chloride (Cl^-) are summarized in Figure 5-2. The historical MARPD statistics for both MCK131/231 and ROM406/206 did not meet the DQI criterion of 5 percent, except for Cl^-, which had a MARPD of approximately 5 percent. As discussed in earlier CASTNET reports (e.g., MACTEC, 2004 and MACTEC, 2003), the very high historical MARPD for sodium (Na^+) was the result of sample bottle contamination. These bottles are no longer purchased. Also, acceptance testing of the Teflon® filters was instituted for the trace cations and Cl^- in 2003. The 2006 precision results show that Na^+ and Cl^- met the precision criterion at MCK131/231. The MARPD for Cl^- calculated for ROM406/206 met the criterion for 2006. The 2006 results are similar to the precision data for 2005.

Table 5-2 summarizes 2005 precision results by quarter for the two sets of collocated sites. See the 2006 Quarterly Data Reports (MACTEC, 2006b; 2006d; 2007c; 2007a;) and QA Quarterly Reports (MACTEC, 2006c; 2006e; 2006f; 2007b;) for discussions of quarterly precision data.

Figure 5-2 Historical and 2006 Precision Data for Cation and Cl^- Concentrations

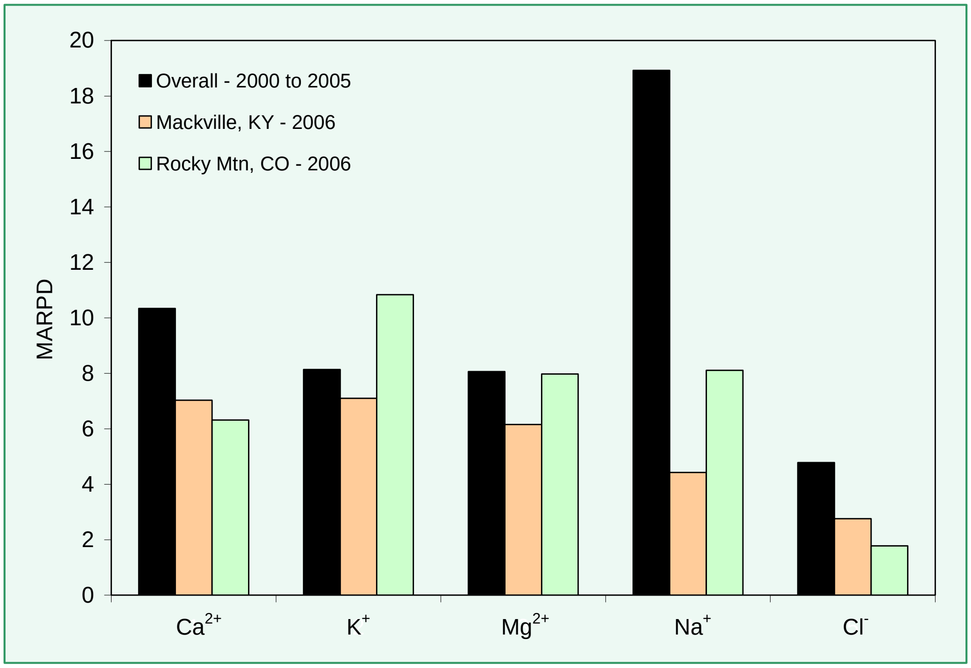


Table 5-2 Collocated Precision Results for 2006 Filter Pack Data by Quarter (MARPD)

Site Pairs	SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	HNO_3	SO_2	Total NO_3^-	Cl^-
MCK 131/231, KY											
Quarter 1	3.22	8.71	3.86	12.17	10.49	6.40	10.30	2.90	2.98	4.74	3.46
Quarter 2	0.96	7.49	1.70	4.79	5.20	4.28	11.16	3.90	1.81	3.82	2.06
Quarter 3	1.35	6.36	1.62	2.86	2.33	3.03	1.85	2.37	2.35	2.26	0.46
Quarter 4	1.96	6.30	4.03	8.33	6.61	4.00	5.09	2.74	2.86	2.89	5.05
2006	1.87	7.21	2.80	7.03	6.16	4.43	7.10	2.98	2.50	3.43	2.76
ROM 406/206, CO											
Quarter 1	4.68	3.64	2.43	7.52	8.07	6.38	9.21	4.55	8.64	2.63	1.32
Quarter 2	5.66	8.03	4.84	5.86	11.10	6.17	14.89	2.36	4.97	3.56	1.14
Quarter 3	3.70	12.13	3.09	5.89	5.28	10.74	7.56	2.54	13.00	1.65	1.76
Quarter 4	2.89	13.26	15.16	5.99	7.44	9.15	11.69	4.63	11.78	2.11	2.89
2006	4.23	9.26	6.38	6.31	7.97	8.11	10.84	3.52	9.60	2.49	1.78

Note: Shaded values exceed DQI criterion

The 2006 analytical precision results for five analytes and the three filter types are presented in Figure 5-3. The results were based on analysis of 5 percent of the samples that were randomly selected for replication in each batch. The results of in-run replicate analyses were compared to the results of the original concentrations. The laboratory precision data met the 5 percent measurement criterion listed in Table 5-1.

Figure 5-3 Precision Results for Laboratory Replicate Samples (2006)

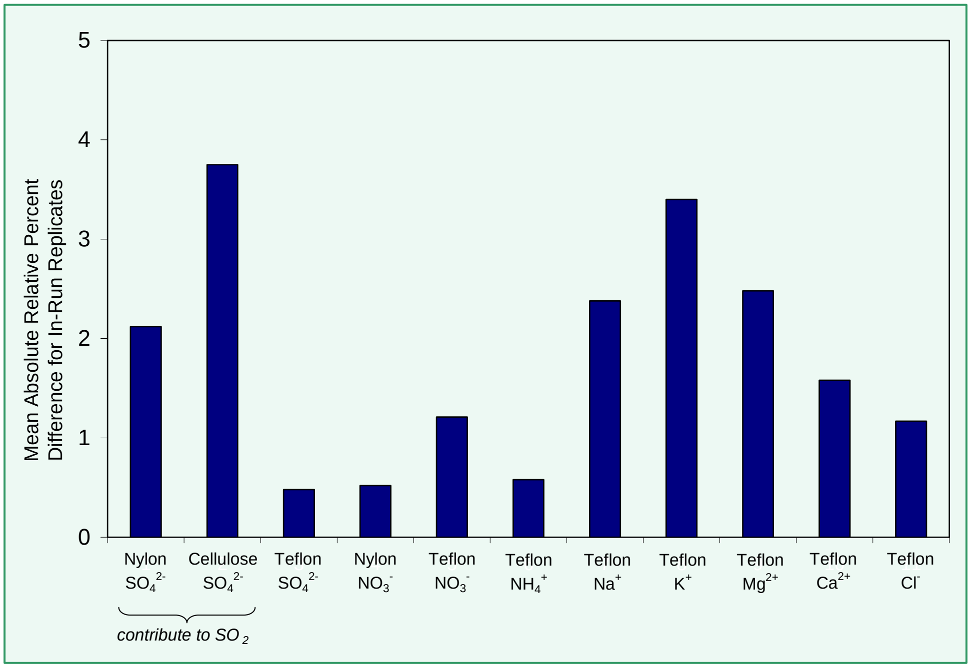


Table 5-3 Data Quality Indicator Criteria for CASTNET Field Measurements

Measurement		**Criteria***	
Parameter	**Method**	**Precision**	**Accuracy**
Wind Speed	Anemometer	± 0.5 m/s	The greater of ± 0.5 m/s for winds < 5 m/s or ± 5% for winds ≥ 5 m/s
Wind Direction	Wind Vane	± 5°	± 5°
Sigma Theta	Wind Vane	Undefined	Undefined
Relative Humidity	Thin Film Capacitor	± 10% (of full scale)	± 5%, relative humidity > 85% ± 20%, relative humidity ≤ 85%
Solar Radiation	Pyranometer	± 10% (of reading taken at local noon)	± 10%
Precipitation	Tipping Bucket Rain Gauge	± 10% (of reading)	± 0.05 inch†
Ambient Temperature	Platinum RTD	± 1.0°C	± 0.5°C
Delta Temperature	Platinum RTD	± 0.5°C	± 0.5°C
Surface Wetness	Conductivity Bridge	Undefined	Undefined
Ozone	UV Absorbance	± 10% (of reading)	± 10%
Filter Pack Flow	Mass Flow Controller	± 10%	± 5%

Note:

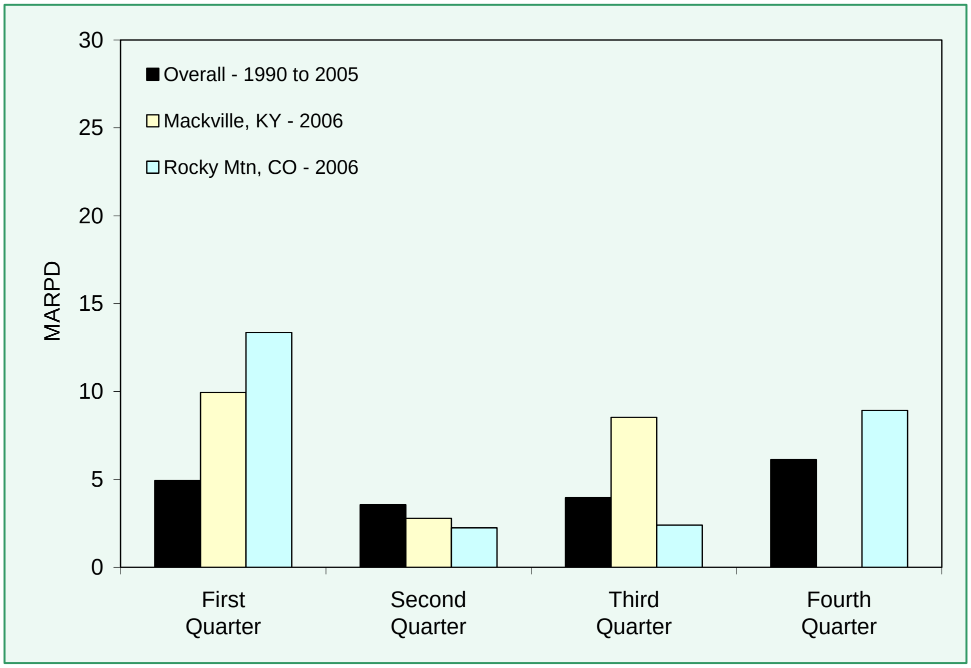
°C = degrees Celsius
m/s = meters per second
RTD = resistance-temperature device
UV = ultraviolet
* Precision criteria apply to collocated instruments, and accuracy criteria apply to calibration of instruments.
† For target value of 0.50 inch.

Ozone Concentrations

CASTNET QA procedures for the EPA-sponsored ozone (O_3) analyzers are different from the EPA QA requirements for SLAMS monitoring (EPA, 1998). The QA procedures for the O_3 analyzers at the NPS-sponsored sites also do not meet the SLAMS requirements. While NPS utilizes the appropriate procedures and equipment, the NPS sites are calibrated twice per year versus the SLAMS requirements of four times per year. In any event, the operation of the collocated O_3 analyzers at ROM406/206, CO provides an opportunity to evaluate the precision of the independent systems. Table 5-3 provides the DQI criteria for the CASTNET continuous measurements including O_3. The precision criterion for the collocated O_3 data is 10 percent.

MARPD statistics were calculated from hourly O_3 measurements obtained from the collocated sites MCK131/231, KY and ROM406/206, CO during 2006. In addition, quarterly historical precision statistics were compiled for all collocated sites. Quarterly precision results are summarized in Figure 5-4. The data show the historical results met the 10 percent criterion. The 2006 precision data also met the 10 percent criterion for the second and third quarters for both MCK131/231 and ROM406/206. The results for ROM406/206 did not meet the criterion during the first quarter. The high MARPD was caused by unusually low O_3 concentrations. Many hourly levels were less than 10 ppb. MARPD was not calculated for MCK131/231 fourth quarter O_3 data. The MCK131 analyzer exhibited significant drift that began near the end of October, and the data are considered suspect and are undergoing additional review.

Figure 5-4 Historical and 2006 Precision Data by Quarter for Ozone Concentrations



Accuracy

Laboratory Filter Concentrations

Accuracy of laboratory measurements is assessed through the analysis of reference samples and continuing calibration verification (CCV) samples. Reference samples and CCV are procured from independent suppliers and are National Institute of Standards and Technology (NIST) traceable. Reference samples are analyzed at the beginning and end of each analytical batch to verify the accuracy and stability of the calibration curve. The target value of the CCV solution is set to the midrange of the calibration curve. In 2006, the CCV were analyzed every tenth sample to verify that instrument calibration had not drifted beyond established limits. Table 5-4 presents the percent recoveries and standard deviations for reference samples and CCV relative to target concentrations. The table shows that the DQI goals (see Table 5-1) were met in 2006. Table 5-4 also lists the precision results that were shown in Figure 5-3.

Table 5-4 Filter Pack QC Summary for 2006

Filter Type	Parameter	Reference Sample[1] Recovery (%R)			Continuing Calibration Verification Samples (%R)			In-Run Replicate[2] (RPD)		
		Mean	Std. Dev.	Count[3]	Mean	Std. Dev.	Count[3]	Mean	Std. Dev.	Count[3]
Teflon®	SO_4^{2-}	98.50	1.67	155	99.74	1.21	781	0.48	0.57	322
	NO_3^-	101.81	1.07	155	99.10	1.21	781	1.21	1.48	322
	NH_4^+	100.71	1.73	153	99.48	1.73	751	0.58	0.63	266
	Ca^{2+}	103.02	2.73	194	100.72	1.10	797	1.58	2.34	324
	Mg^{2+}	101.61	1.85	194	99.96	0.74	797	2.48	2.95	324
	Na^+	94.43	1.69	194	100.23	1.00	797	2.38	4.51	324
	K^+	100.79	2.44	194	100.50	0.98	797	3.40	3.29	324
	Cl^-	100.97	1.39	155	99.25	2.41	781	1.17	1.48	322
Nylon	SO_4^{2-}	101.01	1.45	144	99.90	1.99	730	2.12	2.82	305
	NO_3^-	99.95	1.46	144	99.53	1.96	730	0.52	0.88	306
Cellulose	SO_4^{2-}	101.46	0.59	182	99.16	0.80	740	3.75	5.87	257

Note: % R = percent recovery
RPD = relative percent difference

[1] Results of reference sample analyses provide accuracy estimates
[2] Results of replicate analyses provide precision estimates
[3] Number of QC Samples

Continuous Measurements

Table 5-5 presents field accuracy results for 2006 based on instrument challenges performed using independent reference standards during site calibration visits. CASTNET sites were calibrated every six months with NIST-traceable standards. The calibration results were evaluated using the accuracy criteria listed in Table 5-3. Each parameter was within its criterion with at least 90 percent frequency with the exception of high (> 85 percent) relative humidity at 72.8 percent, solar radiation at 88.1 percent, wind direction north at 88.0 percent, and wind direction south at 88.9 percent. However, these results did not adversely affect data collection because data are not considered invalid unless criteria are exceeded by more than their own magnitude. Using the two times standard, the four parameters ranged from 92.6 percent to 98.0 percent frequency.

Table 5-5 Accuracy Results for 2006 Field Measurements

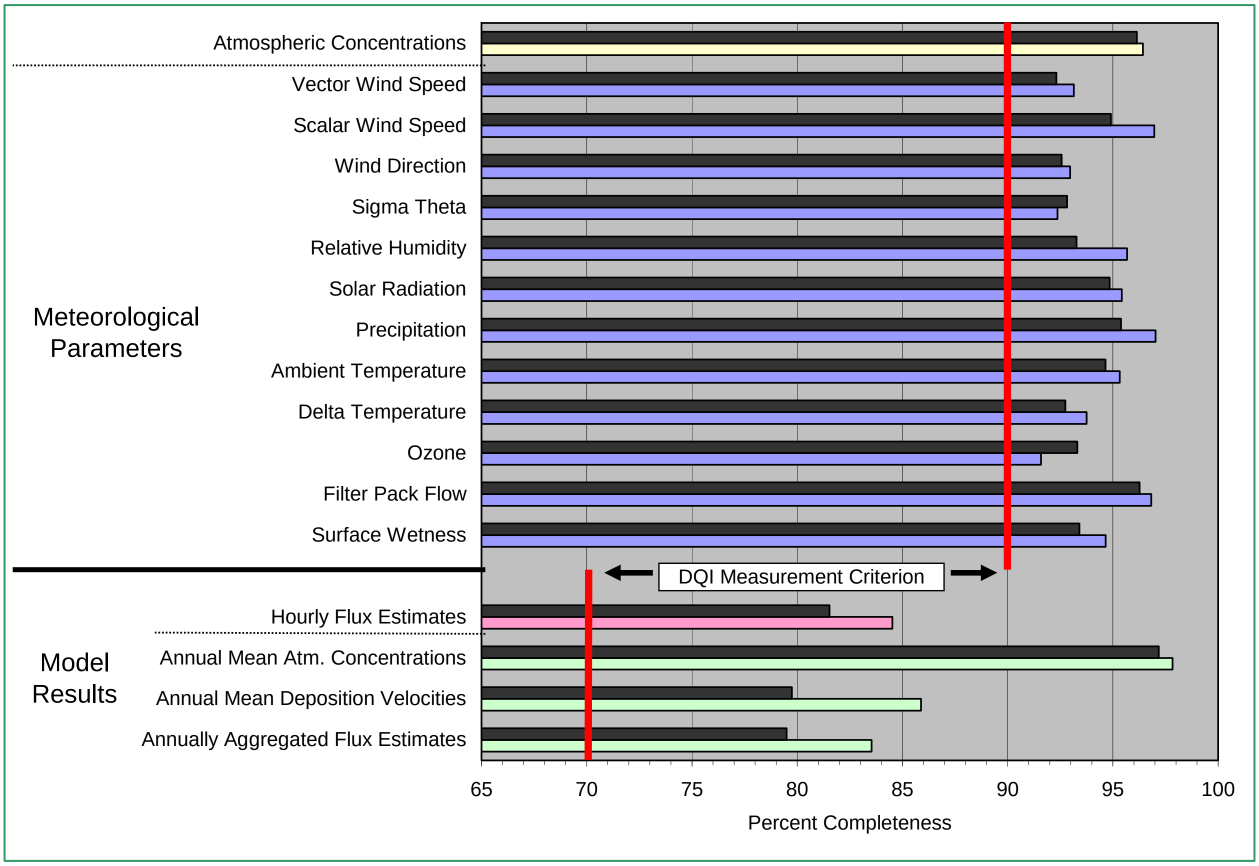
Parameter	Percent Within Criterion
Temperature (0°C)	99.0 percent
Temperature (ambient)	98.1 percent
Delta Temperature (0°C)	100.0 percent
Delta Temperature (ambient)	97.1 percent
*Relative Humidity > 85%	72.8 percent
Relative Humidity ≤ 50%	94.3 percent
*Solar Radiation	88.1 percent
*Wind Direction North	88.0 percent
*Wind Direction South	88.9 percent
Wind Speed < 5 m/s	100.0 percent
Wind Speed ≥ 5 m/s	95.3 percent
Precipitation	99.1 percent
Wetness (w/in 0.5 volts)	100.0 percent
Ozone Slope	96.8 percent
Ozone Intercept	100.0 percent
Flow Rate	97.1 percent

Note: °C = degrees Celsius.
m/s = meters per second.
* Per CASTNET project protocols, data are flagged as "suspect" (S) but still considered valid if the calibration criterion is not exceeded by more than its magnitude (i.e., if within 2x the criterion). The percent within 2x criterion for these parameters ranged from 92.6 percent to 98 percent.

Completeness

Completeness is defined as the percentage of valid data points obtained from a measurement system relative to total possible data points. The CASTNET measurement criterion for completeness requires a minimum completeness of 90 percent for every measurement for each quarter. In addition, data aggregation procedures require approximately 70 percent completeness for hourly fluxes and weekly concentrations/fluxes. Figure 5-5 presents historical and 2006 completeness data for all sites for measured filter concentrations, continuous measurements, and calculated parameters. The figure shows that the 2006 direct measurements met the 90 percent goal. The 2006 results show that data completeness exceeded 95 percent for six continuous measurements, including filter pack flow. The four parameters derived from model results exceeded 83 percent completeness for 2006. Completeness results for 2006 are better than historical results for all parameters except sigma theta and ozone.

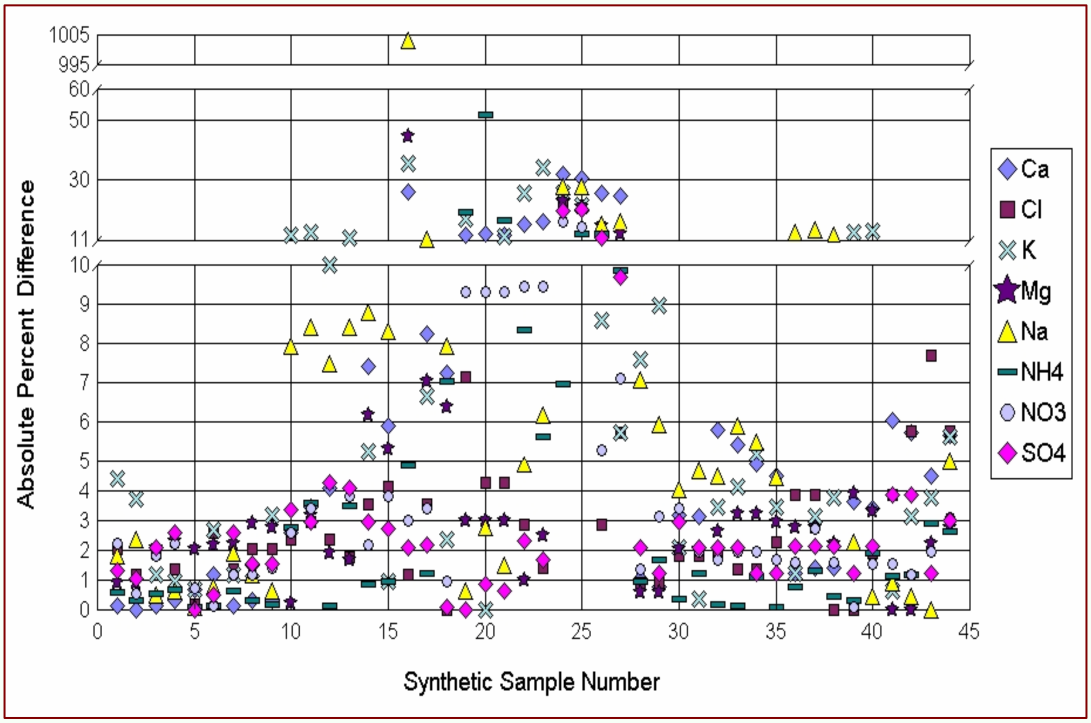
Figure 5-5 Historical and 2006 Percent Completeness of Measurements and Modeled Estimates (black bars are 1990-2005)



Laboratory Intercomparison Studies

The MACTEC laboratory is one of eight laboratories that participate in the U.S. Geological Survey (USGS) interlaboratory comparison program. The laboratory receives four samples for chemical analysis from USGS every two weeks. The samples are a mix of 44 synthetically prepared samples, 8 deionized water samples, and 52 natural wet deposition samples. MACTEC reported the eight CASTNET parameters for 104 samples during 2006. Results for only the 44 synthetically prepared samples are depicted in the figure below as the absolute percent difference of the MACTEC value from the median value for all laboratories.

Results from Intercomparison of 44 Synthetic Samples



As shown above, a single sodium result was very high. Internal investigation led to the conclusion that this sample had been contaminated. The probable timing and mechanism for the contamination event are indeterminate. The results for the eight ultra-pure deionized water samples analyzed during the year were all below the laboratory reporting limits for every parameter.

Additionally, precision results for the 52 natural wet deposition samples were reported as absolute percent differences for replicate analyses. By parameter, less than 4 percent of approximately 208 paired natural wet deposition sample data points exceeded 10 percent difference. These results are presented in the USGS report (USGS, 2006).

MACTEC generally participates in two to three studies by the National Water Research Institute (NWRI) of Canada’s Proficiency Testing QA Program each year in addition to interlaboratory comparison studies for the USGS. MACTEC’s laboratory was rated free of systemic bias for all eight parameters for the three NWRI 2006 studies. MACTEC was ranked number six out of 37 participating laboratories at the end of 2006 (Environment Canada, 2006).

Conclusion

DQI results demonstrate that field and laboratory processes were adequately monitored through QA/QC procedures and were generally free of systemic bias during 2006. Accuracy data met the established criteria for field and laboratory parameters with the exception of relative humidity > 85 percent, solar radiation, wind direction north, and wind direction south. However, since the criterion was exceeded by a value less than its own magnitude, the associated continuous data collected are considered valid.

Precision data for sulfur constituents, HNO_3, and ammonium are considered acceptable. Precision data for nitrate analyses of collocated field samples have not met the established criterion due, most likely, to the low concentrations generally measured and the unpredictable nature of the gas-particle equilibrium of the nitrate species.

Precision data for ozone concentrations measured at ROM406/206 did not meet the 10 percent goal during the first quarter because of unusually low levels. MARPD was not calculated for MCK131/231 fourth quarter ozone data because the analyzer at MCK131 exhibited significant drift that began near the end of October. Results for other quarters are considered acceptable.

Completeness criteria were met for all parameters in 2006. Completeness results for 2006 were generally better than historical results.

Rocky Mountain National Park, CO (ROM406/206)

References

Ames, R.B. and Malm, W.C. 2001. Comparison of Sulfate and Nitrate Particle Mass Concentrations Measured by IMPROVE and the CDN. *Atmospheric Environment*. Vol. 35(5) 905-916.

Environment Canada. 2006. Water Science and Technology Directorate. Proficiency Testing Program. Rain and Soft Waters PT Studies 0087, 0088, and 0089. http://www.nwri.ca/nlet-lnee/ptp-pec/prof-e.html (accessed November 1, 2007).

Finkelstein, P.L., Ellestad, T.G., Clarke, J.F., Meyers, T.P., Schwede, D.B., Hebert, E.O., and Neal, J.A. 2000. Ozone and Sulfur Dioxide Dry Deposition to Forests: Observations and Model Evaluation. *J. Geophys. Res*. 105:D12:15,365-15,377.

Lavery, T.F., Rogers, C.M., Baumgardner, R., and Mishoe, K.P. 2007 (in press). Intercomparison of CASTNET NO_3^- and HNO_3 Measurements with Data from Other Monitoring Programs. *Journal of Air & Waste Management Association (JAWMA)*.

Long Term Ecological Research (LTER) Program. 2004a. Coweeta LTER – CWT. http://www.lternet.edu/sites/cwt/ (accessed June 5, 2007).

Long Term Ecological Research (LTER) Program. 2004b. Hubbard Brook LTER – HBR. http://www.lternet.edu/sites/cwt/ (accessed June 5, 2007).

Long Term Ecological Research (LTER) Program. 2004c. Konza Prairie LTER – KNZ. http://www.lternet.edu/sites/knz/ (access June 5, 2007).

MACTEC Engineering and Consulting, Inc. (MACTEC). 2007a. *Clean Air Status and Trends Network (CASTNET) Fourth Quarter 2006 Data Report.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, D.C. Contract No. 68-D-03-052. Gainesville, FL.

MACTEC Engineering and Consulting, Inc. (MACTEC). 2007b. *Clean Air Status and Trends Network (CASTNET): Fourth Quarter 2006 Quality Assurance Report with 2006 Annual Summary*. Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, D.C. Contract No. 68-D-03-052., Gainesville, FL.

References (continued)

MACTEC Engineering and Consulting, Inc. (MACTEC). 2007c. *Clean Air Status and Trends Network (CASTNET) Third Quarter 2006 Data Report.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, D.C. Contract No. 68-D-03-052., Gainesville, FL.

MACTEC Engineering and Consulting, Inc. (MACTEC). 2006a. *Clean Air Status and Trends Network (CASTNET) 2005 Annual Report.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, D.C. Contract No. 68-D-03-052. Gainesville, FL.

MACTEC Engineering and Consulting, Inc. (MACTEC). 2006b. *Clean Air Status and Trends Network (CASTNET) First Quarter 2006 Data Report.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, D.C. Contract No. 68-D-03-052. Gainesville, FL.

MACTEC Engineering and Consulting, Inc. (MACTEC). 2006c. *Clean Air Status and Trends Network (CASTNET) First Quarter 2006 Quality Assurance Report.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, D.C. Contract No. 68-D-03-052. Gainesville, FL.

MACTEC Engineering and Consulting, Inc. (MACTEC). 2006d. *Clean Air Status and Trends Network (CASTNET) Second Quarter 2006 Data Report.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, D.C. Contract No. 68-D-03-052. Gainesville, FL.

MACTEC Engineering and Consulting, Inc. (MACTEC). 2006e. *Clean Air Status and Trends Network (CASTNET) Second Quarter 2006 Quality Assurance Report.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, D.C. Contract No. 68-D-03-052. Gainesville, FL.

MACTEC Engineering and Consulting, Inc. (MACTEC). 2006f. *Clean Air Status and Trends Network (CASTNET) Third Quarter 2006 Quality Assurance Report.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, D.C. Contract No. 68-D-03-052. Gainesville, FL.

MACTEC Engineering and Consulting, Inc. (MACTEC). 2005. *Clean Air Status and Trends Network (CASTNET) Quality Assurance Project Plan (QAPP), Revision 3.0.* Prepared for U.S. Environmental Protection Agency (EPA), Research Triangle Park, NC, Contract No. 68-D-98-112. Gainesville, FL.

References (continued)

MACTEC Engineering and Consulting, Inc. (MACTEC). 2004. *Clean Air Status and Trends Network (CASTNET) 2002 Quality Assurance Report.* Prepared for U.S. Environmental Protection Agency (EPA), Research Triangle Park, NC, Contract No. 68-D-03-052. Gainesville, FL.

MACTEC Engineering and Consulting, Inc. (MACTEC). 2003. *Clean Air Status and Trends Network (CASTNET) 2002 Annual Report.* Prepared for U.S. Environmental Protection Agency (EPA), Research Triangle Park, NC, Contract No. 68-D-03-052. Gainesville, FL.

Meyers, T. P., Finkelstein, P., Clarke, J., Ellestad, T.G., and Sims, P.F. 1998. A Multilayer Model for Inferring Dry Deposition Using Standard Meteorological Measurements. *J. Geophys. Res.* 103D17:22,645-22,661.

National Atmospheric Deposition Program, 2003. National Atmospheric Deposition Program 2002 Annual Summary. NADP Data Report 2003-01. Illinois State Water Survey, Champaign, IL.

National Park Service (NPS). 2007. Air Quality Monitoring & Access to Data. NPS Air Quality Monitoring. http://www2.nature.nps.gov/air/Monitoring/ (accessed June 5, 2007).

National Science Foundation (NSF). 2005. Translating Science for Society: Broader Impacts of NSF’s Long-Term Ecological Research Program. http://intranet.lternet.edu/archives/ documents/ Publications/brochures/nsf0533.pdf (accessed June 5, 2007).

New Mexico Environment Department. 2007. Four Corners Air Quality Task Force. http://www.nmenv.state.nm.us/aqb/4C/ (accessed June 1, 2007).

Schwede, D.B. 2006. *A Comparison of the Deposition Velocity Estimates from the CASTNET and CAPMoN Networks.* (Working paper). Research Triangle Park, NC.

Sweet, C., Caughey, M., and Gay, D. 2005. Midwest Ammonia Monitoring Project, Summary for October 2003 through November 2004. http://www.ladco.org/reports/rpo/ MWRPOprojects/Monitoring/YearOneReport(Final).pdf (accessed November 5, 2007).

U.S. Environmental Protection Agency (EPA). 2007a. 8-Hour Ground–level Ozone Designations. http://www.epa.gov/ozonedesignations/ (accessed March 1, 2007).

References (continued)

U.S. Environmental Protection Agency (EPA). 2007b. Clean Air Interstate Rule. http://www.epa.gov/cair/index.html (accessed March 1, 2007).

U.S. Environmental Protection Agency (EPA). 2007c. Vegetation and Air Quality. http://www.epa.gov/heatisland/strategies/level3_vegairquality.html (accessed December 6, 2007).

U.S. Environmental Protection Agency (EPA). 2006. NO_x Budget Trading Program. *2005 Program Compliance and Environmental Results.* EPA 430-R-06-013. September 2006.

U.S. Environmental Protection Agency (EPA). 2005a. *Acid Rain Program 2004 Progress Report.* EPA 430-R-05-012. October 2005.

U.S. Environmental Protection Agency (EPA). 2005b. *Evaluating Ozone Control Programs in the Eastern United States.* EPA 454-K-05-001. August 2005.

U.S. Environmental Protection Agency (EPA). 2000. *National Air Quality and Emissions Trends Report, 1998.* EPA-454-R-00-003. OAQPS, RTP, NC 27711.

U.S. Environmental Protection Agency (EPA). 1998. *Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS).* 40 CFR 50, Appendix L.

U.S. Environmental Protection Agency (EPA). 1997. *National Ambient Air Quality Standards for Ozone.* 40 CFR 50.

U.S. Geological Survey (USGS). 2006. Office of Water Quality. Branch of Quality Systems. Interlaboratory Comparison Program http://bqs.usgs.gov/precip/new/frontpage_home.htm (accessed November 1, 2007).

Appendix A

Locational and Operational Characteristics of CASTNET Sites

Table A-1. Locational and Operational Characteristics of CASTNET Sites

Site ID	Site Name	Start date	Latitude (°N)	Longitude (°W)	Elevation (m)	Deposition Filter Pack[1]	Ozone and Meteorology[2]	Wet Deposition	Primary Land Use	Terrain	Representative to the MLM[3]	Sponsor
Alabama												
SND152	Sand Mountain	12/27/88	34.2894	85.9704	352	•	•		Agri.	Rolling	Y	EPA
Alaska												
DEN417	Denali National Park	10/06/98	63.7258	148.9633	661	•	•		Forested	Complex	N	NPS
Arizona												
CHA467	Chiricahua National Monument	04/25/89	32.0092	109.3892	1570	•	•	◊	Range	Complex	N	NPS
GRC474	Grand Canyon National Park	05/16/89	36.0597	112.1822	2073	•	•		Forested	Complex	M	NPS
PET427	Petrified Forest National Park	09/24/02	34.8225	109.8919	1723	•	•		Desert	Flat	Y	NPS
Arkansas												
CAD150	Caddo Valley	10/04/88	34.1792	93.0989	71	•	•		Forested	Rolling	N	EPA
California												
CON186	Converse Station	06/17/03	34.1941	116.9130	1837	•	•		Agri./Forested	Complex	N	EPA
DEV412	Death Valley National Monument	02/21/95	36.5092	116.8481	125	•	•		Desert	Complex	Y	NPS
JOT403	Joshua Tree National Monument	02/16/95	34.0714	116.3906	1244	•	•		Desert	Complex	M	NPS
LAV410	Lassen Volcanic National Park	07/25/95	40.5403	121.5764	1756	•	•		Forested	Complex	M	NPS
PIN414	Pinnacles National Monument	05/16/95	36.4850	121.1556	335	•	•		Forested	Complex	M	NPS
SEK430	Sequoia National Park	04/07/05	36.4894	118.8269	457	•	•		Forested	Mountaintop	N	NPS
YOS404	Yosemite National Park	09/25/95	37.7133	119.7061	1605	•	•		Forested	Complex	N	NPS

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Colorado												
GTH161	Gothic	05/16/89	38.9573	106.9854	2926	•	•	◊	Range	Complex	N	EPA
MEV405	Mesa Verde National Park	01/10/95	37.1983	108.4903	2165	•	•		Forested	Complex	M	NPS
ROM206	Rocky Mountain National Park	07/03/01	40.2778	105.5453	2743	•	•		Forested	Complex	M	EPA
ROM406	Rocky Mountain National Park	12/20/94	40.2778	105.5453	2743	•	•		Forested	Complex	M	NPS
Connecticut												
ABT147	Abington	12/28/93	41.8402	72.0111	209	•	•	◊	Urban-Agri.	Rolling	M	EPA
Florida												
EVE419	Everglades National Park	10/06/98	25.3911	80.6806	2	•	•[4]		Swamp	Flat	Y	NPS
IRL141	Indian River Lagoon	07/09/01	30.1065	80.4554	2	•	•		Beach	Flat	Y	EPA
SUM156	Sumatra	12/28/88	30.1065	84.9938	14	•	•	◊	Forested	Flat	Y	EPA
Georgia												
GAS153	Georgia Station	06/28/88	33.1812	84.4100	270	•	•		Agri.	Rolling	M	EPA
Illinois												
ALH157	Alhambra	06/28/88	38.8690	89.6229	164	•	•	◊	Agri.	Flat	Y	EPA
BVL130	Bondville	02/09/88	40.0520	88.3725	212	•	•		Agri.	Flat	Y	EPA
STK138	Stockton	12/28/93	42.2872	89.9998	274	•	•		Agri.	Rolling	M	EPA

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Indiana												
SAL133	Salamonie Reservoir	06/28/88	40.8164	85.6608	250	•	•		Agri.	Flat	Y	EPA
VIN140	Vincennes	08/04/87	38.7406	87.4844	134	•	•		Agri.	Rolling	M	EPA
Kansas												
KNZ184	Konza Prairie	03/26/02	39.1021	96.6096	348	•	•		Prairie	Flat	Y	EPA
Kentucky												
CDZ171	Cadiz	10/01/93	36.7841	87.8500	189	•	•		Agri.	Rolling	M	EPA
CKT136	Crockett	08/24/93	37.9211	83.0658	455	•	•		Agri.	Rolling	Y	EPA
MAC426	Mammoth Cave National Park	07/24/02	37.1319	86.1478	243	•	•		Agri./Forested	Rolling	M	NPS
MCK131	Mackville	07/31/90	37.7044	85.0483	353	•	•		Agri.	Rolling	M	EPA
Maine												
ACA416	Acadia National Park	12/01/98	44.3769	68.2608	158	•	•		Forested	Complex	M	NPS
ASH135	Ashland	12/20/88	46.6039	68.4142	235	•	•		Agri.	Flat	Y	EPA
HOW132	Howland	11/24/92	45.2158	68.7085	69	•	•		Forested	Rolling	Y	EPA
Maryland												
BEL116	Beltsville	11/01/88	39.0283	76.8175	46	•	•		Urban-Agri.	Flat	N	EPA
BWR139	Blackwater National Wildlife Refuge	07/04/95	38.4448	76.1115	4	•	•		Forest-Marsh	Coastal	M	EPA

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Michigan												
ANA115	Ann Arbor	06/28/88	42.4164	83.9019	267	•	•	◊	Forested	Flat	M	EPA
HOX148	Hoxeyville	10/31/00	44.1809	85.7390	298	•	•		Forested	Flat	Y	EPA
UVL124	Unionville	06/28/88	43.6139	83.3597	201	•	•	◊	Agri.	Flat	Y	EPA
Minnesota												
VOY413	Voyageurs National Park	06/13/96	48.4128	92.8292	429	•	•		Forested	Rolling	M	NPS
Mississippi												
CVL151	Coffeeville	12/27/88	34.0028	89.7989	134	•	•		Forested	Rolling	M	EPA
Montana												
GLR468	Glacier National Park	12/27/88	48.5103	113.9956	976	•	•		Forested	Complex	N	NPS
Nebraska												
SAN189	Santee Sioux	07/05/06	42.8292	97.8541	429	•	•		Agri.	Rolling	N	EPA
Nevada												
GRB411	Great Basin National Park	05/16/95	39.0053	114.2158	2060	•	•		Forested	Complex	M	NPS
New Hampshire												
WST109	Woodstock	12/27/88	43.9446	71.7008	258	•	•		Forested	Complex	N	EPA
New Jersey												
WSP144	Washington’s Crossing	12/27/88	40.3133	74.8726	61	•	•		Urban-Agri.	Rolling	M	EPA

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New York												
CAT175	Claryville	05/10/94	41.9423	74.5519	765	•	•[5]		Forested	Complex	N	EPA
CTH110	Connecticut Hill	09/28/87	42.4010	76.6535	515	•	•	◊	Forested	Rolling	N	EPA
HWF187	Huntington Wildlife Forest	05/28/02	43.9732	74.2232	502	•	•		Forested	Complex	N	EPA
North Carolina												
BFT142	Beaufort	12/28/93	34.8843	76.6213	2	•	•	◊	Agri.	Flat	Y	EPA
CND125	Candor	09/25/90	35.2643	79.8382	198	•	•	◊	Forested	Rolling	M	EPA
COW137	Coweeta	11/04/87	35.0605	83.4302	686	•	•		Forested	Complex	N	EPA
PNF126	Cranberry	12/27/88	36.1040	82.0448	1250	•	•	◊	Forested	Mountaintop	M	EPA
North Dakota												
THR422	Theodore Roosevelt National Park	10/06/98	46.8947	103.3778	850	•	•		Range	Rolling	Y	NPS
Ohio												
DCP114	Deer Creek State Park	09/28/88	39.6358	83.2600	267	•	•	◊	Agri.	Rolling	Y	EPA
LYK123	Lykens	01/10/89	40.9169	82.9981	303	•	•	◊	Agri.	Flat	M	EPA
OXF122	Oxford	08/18/87	39.5314	84.7231	284	•	•		Agri.	Rolling	N	EPA
QAK172	Quaker City	09/28/93	39.9431	81.3378	372	•	•		Agri.	Rolling	M	EPA
Oklahoma												
CHE185	Cherokee Nation	04/02/02	35.7507	94.6700	299	•	•		Agri.	Rolling	Y	EPA
Ontario												
EGB181	Egbert, Ontario	12/27/94	44.2317	79.7840	251	•[6]	•[4]		Agri.	Rolling	Y	EPA

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Pennsylvania												
ARE128	Arendtsville	06/28/88	39.9231	77.3078	269	•	•	◊	Agri.	Rolling	M	EPA
KEF112	Kane Experimental Forest	01/03/89	41.5981	78.7683	622	•	•		Forested	Rolling	Y	EPA
LRL117	Laurel Hill State Park	12/15/87	39.9883	79.2522	615	•	•		Forested	Complex	N	EPA
MKG113	M.K. Goddard State Park	01/12/88	41.4250	80.1447	384	•	•		Forested	Rolling	N	EPA
PSU106	Penn. State University	01/06/87	40.7209	77.9316	376	•	•		Agri.	Rolling	M	EPA
South Dakota												
WNC429	Wind Cave National Park	11/18/03	43.5578	103.4839	1292	•	•		Prairie	Rolling	M	NPS
Tennessee												
ESP127	Edgar Evins State Park	03/22/88	36.0389	85.7330	302	•	•		Forested	Rolling	N	EPA
GRS420	Great Smoky Mountains National Park	10/06/98	35.6331	83.9422	793	•	•		Forested	Complex	N	NPS
SPD111	Speedwell	06/12/89	36.4698	83.8265	361	•	•	◊	Agri.	Rolling	Y	EPA
Texas												
ALC188	Alabama-Coushatta	04/02/04	30.4210	94.4045	101	•	•		Forested	Rolling	Y	EPA
BBE401	Big Bend National Park	07/18/95	29.3022	103.1772	1052	•	•		Forested	Complex	M	NPS
Utah												
CAN407	Canyonlands National Park	01/24/95	38.4586	109.8211	1809	•	•		Desert	Complex	M	NPS
Vermont												
LYE145	Lye Brook	03/30/94	43.0510	73.0613	730	•	•[5]	◊	Forested	Mountaintop	N	EPA

Table A-1. Locational and Operational Characteristics of CASTNET Sites

Site ID	Site Name	Start date	Latitude (°N)	Longitude (°W)	Elevation (m)	Deposition Filter Pack[1]	Ozone and Meteorology[2]	Wet Deposition	Primary Land Use	Terrain	Representative to the MLM[3]	Sponsor
Virginia												
PED108	Prince Edward	11/03/87	37.1653	78.3070	150	•	•	◊	Forested	Rolling	M	EPA
SHN418	Shenandoah National Park	06/28/88	38.5231	78.4347	1073	•	•		Forested	Mountaintop	M	NPS
VPI120	Horton Station	06/02/87	37.3300	80.5573	920	•	•		Forested	Mountaintop	N	EPA
Washington												
MOR409	Mount Rainier National Park	08/29/95	46.7583	122.1244	415	•	•		Forested	Complex	N	NPS
NCS415	North Cascades National Park	02/14/96	48.5397	121.4472	109	•	•		Forested	Complex	M	NPS
West Virginia												
CDR119	Cedar Creek State Park	11/10/87	38.8794	80.8478	234	•	•	◊	Forested	Complex	N	EPA
PAR107	Parsons	01/19/88	39.0906	79.6614	510	•	•		Forested	Complex	N	EPA
Wisconsin												
PRK134	Perkinstown	09/27/88	45.2066	90.5972	472	•	•	◊	Agri.	Rolling	M	EPA
Wyoming												
CNT169	Centennial	08/19/91	41.3722	106.2422	3178	•	•		Range	Complex	M	EPA
PND165	Pinedale	12/27/88	42.9214	109.7900	2388	•	•		Range	Rolling	M	EPA
YEL408	Yellowstone National Park	06/26/96	44.5597	110.4006	2400	•	•		Forested	Rolling	N	NPS

1. The dry deposition filters are analyzed for the following constituents:

   Teflon® = SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, K^+, Na^+, Mg^{2+}, Ca^{2+}

   Nylon = SO_4^{2-}, NO_3^- (reported as HNO_3)

   Cellulose = SO_4^{2-} (reported as SO_2)

2. Meteorological sensors: temperature, delta temperature, relative humidity, solar radiation, vector wind speed, scalar wind speed, wind direction, sigma theta, surface wetness, and precipitation via tipping bucket rain gauge.

3. N = No; Y = Yes; M = Marginal.

4. O_3 not measured.

5. Solar-powered sites.

6. Composite filter pack, day filter pack, and night filter pack.

● Indicates current monitoring.

◊ Indicates discontinued monitoring.
Measurements were discontinued at the various sites because of several reasons including:
(1) rotate limited number of instruments;
(2) redundant measurements (e.g., with IMPROVE and NADP/NTN); and
(3) funding limitations.

100 and 200 series = EPA – Operated Sites
400 series = NPS – Operated Sites

Appendix B

Acronyms and Abbreviations

List of Acronyms and Abbreviations

AGL	above ground level
ARP	Acid Rain Program
BLM	Bureau of Land Management
°C	degrees Celsius
Ca^{2+}	particulate calcium ion
CAAA	Clean Air Act Amendments
$CaCO_3$	calcium carbonate
CAIR	Clean Air Interstate Rule
$Ca(NO_3)_2$	calcium nitrate
CAPMoN	Canadian Air and Precipitation Monitoring Network
CASTNET	Clean Air Status and Trends Network
CCV	continuing calibration verification samples
Cl^-	particulate chloride ion
CLASS™	Chemical Laboratory Analysis and Scheduling System
CO	carbon monoxide
DQI	data quality indicator
EPA	U.S. Environmental Protection Agency
H_2SO_4	sulfuric acid
HNO_3	nitric acid
HYSPLIT	HYbrid Single-Particle Lagrangian Integrated Trajectory
IMPROVE	Interagency Monitoring of Protected Visual Environments
ITEC	Inter-Tribal Environmental Council
K^+	particulate potassium ion
K_2CO_3	potassium carbonate
kg/ha/yr	kilograms per hectare per year
km	kilometer
LAI	leaf area index
LCS	laboratory control sample
lpm	liters per minute
LTER	Long Term Ecological Research Program
m	meter
MACTEC	MACTEC Engineering and Consulting, Inc.
MARPD	mean absolute relative percent difference
Mg^{2+}	particulate magnesium ion
mg/l	milligrams per liter
MLM	Multi-Layer Model
mm	millimeter
MSA	Metropolitan Statistical Area
N	nitrogen
N_2	nitrogen gas in atmosphere

List of Acronyms and Abbreviations (continued)

Na^+	particulate sodium ion
NAAQS	National Ambient Air Quality Standards
NaCl	sodium chloride
NADP/NTN	National Atmospheric Deposition Program/National Trends Network
NADP/MDN	National Atmospheric Deposition Program/Mercury Deposition Network
$NaNO_3$	sodium nitrate
NAPAP	National Acid Precipitation Assessment Program
NERL	National Exposure Research Laboratory
NDDN	National Dry Deposition Network
NH_3	ammonia
NH_4^+	particulate ammonium
NH_4NO_3	ammonium nitrate
$(NH_4)_2SO_4$	ammonium sulfate
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO_2	nitrogen dioxide
NO_3^-	particulate nitrate
NO_x	nitrogen oxides [nitric oxide (NO) + nitrogen dioxide (NO_2)]
NOAA	National Oceanic and Atmospheric Administration
NPS	National Park Service
NSF	National Science Foundation
NWRI	Environment Canada's National Water Research Institute
O_2	oxygen gas in atmosphere
O_3	ozone
OH	hydroxyl
ORD	EPA's Office of Research and Development
OTC	Ozone Transport Commission
ppb	parts per billion
ppm	parts per million
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
S	sulfur
SIP	State Implementation Plan
SLAMS	State and Local Monitoring Stations
SO_2	sulfur dioxide
SO_4^{2-}	particulate sulfate
total NO_3^-	gaseous nitric acid (HNO_3) + particulate nitrate (NO_3^-)
$\mu g/m^3$	micrograms per cubic meter

List of Acronyms and Abbreviations (continued)

µm	micrometer
USGS	U.S. Geological Survey
V_d	deposition velocity
VOC	volatile organic compounds

For More Information

U.S. Environmental Protection Agency
Office of Air and Radiation
Clean Air Markets Division
Washington, D.C.

On the Web:

CASTNET Home Page:	Clean Air Markets Division Home Page:	EPA Home Page:
www.epa.gov/castnet	**www.epa.gov/airmarkets**	**www.epa.gov**