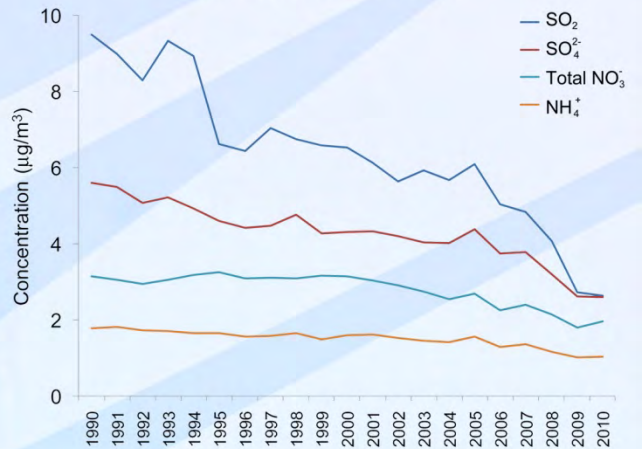# Clean Air Status and Trends Network

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Trend in Annual Mean Pollutant Concentrations (µg/m³)
Eastern Reference Sites

- SO₂
- SO₄²⁻
- Total NO₃⁻
- NH₄⁺

2010 Annual Report

Clean Air Status and Trends Network (CASTNET)

2010 Annual Report

Prepared by:

AMEC Environment & Infrastructure, Inc.

formerly known as
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Prepared for:

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

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Executive Summary

The EPA Clean Air Status and Trends Network (CASTNET) provides measured atmospheric pollution concentration data in order to evaluate the effectiveness of national and regional air pollution control programs. This report presents maps of the geographic distribution of sulfur and nitrogen pollutant concentrations, ozone levels, and deposition fluxes measured in 2010 and examines trends in air quality since 1990. CASTNET measured rural, regionally representative concentrations of sulfur and nitrogen species and ozone at 84 sites in the United States and Canada during 2010.

Key Results through 2010

- Mean annual sulfur dioxide and particulate sulfate concentrations declined significantly over the 21-year period 1990 through 2010 and showed a substantive decline since 2005. Three-year average sulfur dioxide (SO_2) levels declined 65 percent while sulfate concentrations declined 48 percent at eastern reference sites from 1990 through 2010. SO_2 concentrations measured at western reference sites were reduced by 49 percent over the 15-year period (1996–1999 through 2008–2010). Western sulfate levels dropped by 40 percent over the same time period.

- Total (dry + wet) sulfur deposition measured in the East declined by 55 percent from 1990 through 2010. Total sulfur deposition aggregated over western reference sites fell by 28 percent over the 15 years 1996 through 2010. The 2010 total sulfur flux at western sites was higher than the 2009 flux.

- Three-year mean annual concentrations of total nitrate (nitric acid plus particulate nitrate) declined 35 percent at eastern sites over the 21-year period. The 2010 concentration was about 8 percent higher than the 2009 level. Total nitrate levels measured at western reference sites dropped by 35 percent over the 15 years.

- Total nitrogen deposition fell by 26 percent from 1990 through 2010 at eastern reference sites. Total nitrogen deposition estimated for western reference sites was reduced by 20 percent over the 15 years. The 2010 total nitrogen flux at western sites was higher than the 2009 flux.

- The mean fourth highest daily maximum 8-hour average ozone concentration for 2010 (69 ppb) was higher than the 2009 value of 64 ppb, which was the lowest in the history of the network. Only three eastern and five California sites recorded exceedances of the 8-hour standard of 0.075 ppm during the most recent 3-year period (2008–2010).

- Measurements taken during 2010 and historical data collected over the period 1990-2009 were analyzed relative to data quality objectives and their numerical measures. These analyses demonstrate that CASTNET data can be used with confidence and that CASTNET continues to produce information of the highest quality.

Chapter 1: CASTNET Overview

CASTNET is a national, long-term environmental monitoring program designed to provide data for assessing trends in air quality, atmospheric deposition, and ecological effects that result from air pollutant emission reductions. The Environmental Protection Agency and the National Park Service operate the network. CASTNET was established under the 1990 Clean Air Act Amendments and continued and expanded the National Dry Deposition Network, which began in 1987. During 2010, the network operated 84 monitoring stations throughout the contiguous United States, Alaska, and Canada. Measurements collected in 2010 show the continuing decline in sulfur pollutants and a slight increase in nitrogen pollutants and ozone concentrations relative to 2009. All pollutants have declined significantly over the last 21 years.

Background

The Acid Rain Program (ARP), which was established under Title IV of the 1990 Clean Air Act Amendments (CAAA), was promulgated to reduce emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) from electric generating units (EGUs). The U.S. Environmental Protection Agency (EPA) established the Clean Air Status and Trends Network (CASTNET) under Title IX in the CAAA to assess the effectiveness of the ARP and to assess and track real-world environmental results as the ARP was implemented and emission reductions became effective. The U.S. Congress mandated that CASTNET provide consistent, long-term measurements for determining relationships between changes in emissions and subsequent changes in air quality, atmospheric deposition, and ecological effects.

The ARP has produced significant reductions in SO_2 and NO_x emissions from EGUs since 1995. The SO_2 program set a permanent cap on the total amount of SO_2 emissions allowed annually from EGUs and included provisions for trading and banking emission allowances. The program has been phased in with the final 2010 SO_2 emissions cap set at 8.95 million tons, a level about one-half of the total SO_2 emissions from the power sector in 1980. Actual SO_2 emissions from EGUs in 2010 were about 5.1 million tons.

NO_x reductions under the ARP are achieved through a program that applies to a subset of coal-fired EGUs by limiting the NO_x emission rate based on a unit's boiler type. Actual NO_x emissions from ARP EGUs in 2010 were about 2.1 million tons. Although the ARP was responsible for a large portion of these annual NO_x reductions, other emission control programs have also produced substantive declines in NO_x emissions in the eastern United States. These programs include the Ozone Transport Commission (OTC) NO_x Budget (1999–2002) and the NO_x State Implementation Plan (SIP) Call/NO_x Budget Trading Program (NBP), which operated from 2003 through 2008. The NBP placed a cap on total NO_x emissions from EGUs in the eastern United States during the ozone (O_3) season (May 1 through September 30) when the potential for O_3 formation is high.

The Clean Air Interstate Rule (CAIR) was promulgated in March 2005 to permanently lower SO_2 and NO_x emissions in the eastern United States. The rule was designed to continue the progress achieved under the ARP and NBP. CAIR established three compliance programs: an annual NO_x program, an O_3 season NO_x program, and an annual SO_2 program. Although CAIR was remanded back to EPA in 2008, these programs remained in effect through 2011. The first phase of the CAIR annual and O_3 season NO_x requirements began in 2009. The requirement to hold allowances in the SO_2 program began on January 1, 2010. On July 6, 2011, EPA promulgated the Cross-State Air Pollution Rule (CSAPR) to replace CAIR. The CSAPR requires 28 states to produce additional reductions in power plant SO_2 and/or NO_x emissions. See the box on page 4 for a summary of the CSAPR (also known as the Transport Rule).

CASTNET was developed from the National Dry Deposition Network (NDDN), which began operation in 1987. The 50 NDDN sites were transferred to CASTNET in 1991. During 2010, the network included 84 monitoring stations at 82 site locations throughout the contiguous United States, Alaska, and Canada. CASTNET is sponsored by EPA and the National Park Service (NPS). NPS began its participation in CASTNET in 1994 under an agreement with EPA. With the participation of NPS, the network became a national, rather than a primarily eastern, network. NPS is responsible for the protection and enhancement of air quality and related values in national parks and wilderness areas. Twenty-five CASTNET sites were sponsored by NPS during 2010. Additional information on the NPS Air Monitoring program can be found on the Web site: http://www.nature.nps.gov/air/monitoring/.

CASTNET stations measure rural, regionally representative concentrations of sulfur and nitrogen pollutants and O_3 in order to detect and quantify trends, define the geographic distribution of rural pollutants, and estimate dry deposition of pollutants. Dry deposition is calculated from CASTNET concentration measurements and modeled deposition velocities using the Multi-Layer Model (MLM) or from historical deposition velocity measurements. The model requires several meteorological parameters and information on vegetation and land use specific to each site. CASTNET data are also used for atmospheric model evaluation, e.g., the Community Multiscale Air Quality (CMAQ) modeling system, and to provide input to ecological models, such as the Model of Acidification of Groundwater in Catchments (MAGIC).

As of October 2010, EPA decided to discontinue meteorological measurements at all but four EPA-sponsored CASTNET sites. Meteorological measurements were phased out over the fourth quarter as sites were calibrated. NPS sites are continuing meteorological data collection. For this report, missing meteorological data were replaced using the standard procedure used in previous years of "near site" data replacement. Data were replaced only for those EPA sites with designated "near sites." However, the discontinuance of the

meteorological measurements requires a long-term method to obtain missing deposition velocity/flux data in order to estimate quarterly and annual dry deposition rates. EPA and AMEC selected a method based on the results in Bowker *et al.* (2011). Bowker's method substitutes hour-specific historical averages of deposition velocity (V_d) for missing V_d values at specific sites. The substitution procedure was shown to result in long-term, unbiased estimates of the annual mean V_d. A variation of Bowker's method will be applied to all sites with discontinued/missing meteorological data for the period October through December 2010 and also for sites missing historical deposition velocities. The results of the updated estimates of dry deposition will be presented in a report that supplements this 2010 Annual Report. The current MLM modeling approach that was used to estimate dry deposition fluxes in this report will continue to be used for the four EPA sites with continued meteorological measurements and all NPS-sponsored sites.

In order to improve estimates of wet deposition, EPA decided to use the Parameter-elevation Regressions on Independent Slopes Model (PRISM) to develop a continuous grid of precipitation data instead of using cubic inverse distance weighting (IDW). PRISM uses terrain elevation, slope, and aspect and climatic measurements to estimate precipitation on a 4-kilometer (km) resolution grid. Pollutant concentrations in precipitation were estimated for the PRISM grid. These two grids were merged in order to estimate pollutant wet deposition rates. Wet deposition rates for CASTNET sites were estimated from four nearby gridded values. Chapter 3 summarizes the new methods used to estimate wet deposition for CASTNET.

This report summarizes CASTNET monitoring activities and the resulting concentration and deposition data collected over the 21-year period from 1990 through 2010. 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 "Download Data" link on EPA's CASTNET Web page. The Web site provides a complete archive of concentration and deposition data for all EPA- and NPS-sponsored CASTNET sites. Fully validated data are available approximately 10 months following collection. NPS data collected during 2010 from the NPS-sponsored CASTNET sites and the NPS Gaseous Pollutant Monitoring Program are available in the NPS Annual Data Summary 2010 (Ray, 2011) and the 2010 Data Quality Assurance NPS Gaseous Pollutant Monitoring Program (NPS, 2011).

Cross-State Air Pollution Rule

The Cross-State Air Pollution Rule (CSAPR), also known as the Transport Rule, was promulgated on July 6, 2011 to improve air quality by reducing power plant emissions that contribute to pollution in downwind states. CSAPR replaces CAIR, which was issued in March 2005 and remanded back to EPA in December 2008. CSAPR was finalized under the good neighbor provision of the Clean Air Act and represents a continuation of the EPA emission reduction strategies that began with the 1990 CAAA via the ARP and continued under the NBP and CAIR. The rule requires significant reductions of SO_2 and NO_x emissions that contribute to O_3 and fine particulate matter ($PM_{2.5}$) pollution in downwind states (EPA, 2011a; 2011b).

In a related action, EPA finalized a supplemental rulemaking on December 15, 2011 to require five states (Iowa, Michigan, Missouri, Oklahoma, and Wisconsin) to institute summer NO_x reductions under the CSAPR ozone season program. The CSAPR requires 28 states (Figure 1a) in the eastern United States to reduce annual power plant SO_2 and NO_x emissions and/or ozone season NO_x emissions that cross state lines and contribute to O_3 and $PM_{2.5}$ pollution. EPA expects that by 2014, the CSAPR and other state and EPA actions will reduce power plant SO_2 emissions by 73 percent and NO_x emissions by 54 percent from 2005 levels.

Figure 1a CSAPR Covered States

States controlled for both fine particles (annual SO_2 and NO_x) and ozone (ozone season NO_x) (20 States)

States controlled for fine particles only (annual SO_2 and NO_x) (3 States)

States controlled for ozone only (ozone season NO_x) (5 States)

States not covered by the Cross-State Air Pollution Rule
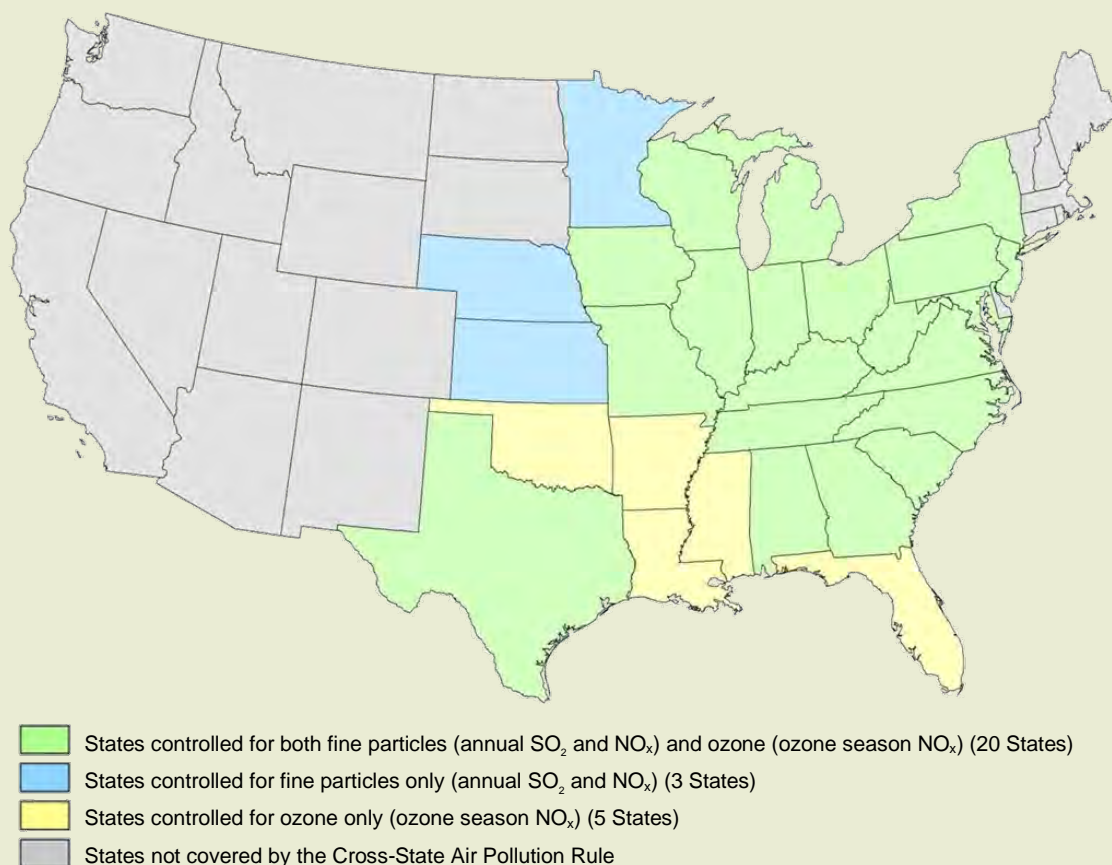
Source: EPA (2011b)

On December 30, 2011 the United States Court of Appeals for the District of Columbia Circuit issued its ruling to stay the CSAPR pending judicial review. This decision is not a ruling on the merits of the CSAPR. EPA will continue to administer CAIR pending the Court's resolution of the petitions for review.

Cooperating Networks

CASTNET monitors air quality and deposition in cooperation with other national networks.

🌱 **National Atmospheric Deposition Program (NADP)** operates:

National Trends Network (NTN), which includes 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.

Mercury Deposition Network (MDN), which operates samplers to measure mercury in precipitation. MDN samplers are operated at several CASTNET sites.

Ammonia Monitoring Network (AMoN), which operates triplicate passive ammonia (NH_3) samplers at about 46 NTN locations. AMoN, in operation for three years, provides information on 2-week average NH_3 concentrations.

Atmospheric Mercury Network (AMNet), which measures atmospheric concentrations of gaseous oxidized, particulate-bound, and elemental mercury at about 25 locations in the continental United States, Canada, Hawaii, and Taiwan in order to estimate dry and total mercury deposition. See the discussion on page 11. See NADP's Web site for more information on the complementary networks: http://nadp.isws.illinois.edu/.

🌱 **Canadian Air and Precipitation Monitoring Network (CAPMoN)** operates 33 measurement sites throughout Canada and one in the United States. CASTNET and CAPMoN both operate filter pack samplers in Ontario, Canada. CAPMoN operates a wet deposition sampler at Pennsylvania State University. Visit CAPMoN's Web site at http://www.ec.gc.ca/rs-mn/default.asp?lang=En&n=752ce271-1.

🌱 **Interagency Monitoring of Protected Visual Environments (IMPROVE)** measures aerosol pollutants near more than 20 CASTNET sites. IMPROVE measures particulate air pollutants that affect visibility. For more information on IMPROVE, see http://vista.cira.colostate.edu/IMPROVE/.

EPA relies on CASTNET and these other long-term national networks to generate the data needed to assess the effectiveness of promulgated 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 Canada – United States Air Quality Agreement.

Although EPA and NPS are the primary sponsors of CASTNET, other organizations, Native American tribes, universities, and government agencies play a role in sponsoring individual CASTNET sites. These co-sponsors provide in-kind services that support the overall operation of a site, including site operation, land use, or both. All of the sites added during recent expansion of the network (since 2001) have an associated co-sponsor. Three CASTNET monitoring sites are located on tribal lands: Cherokee Nation in eastern

Oklahoma (CHE185), Alabama-Coushatta in eastern Texas (ALC188), and Santee Sioux in northern Nebraska (SAN189). State agencies also operate special purpose air pollutant measurement devices at some CASTNET sites.

Locations of Monitoring Sites

Figure 1-1 shows the locations of CASTNET monitoring sites during 2010. Eighty-four sites were operational at 82 distinct locations. Two CASTNET sites ceased sampling activities. Lykens, OH (LYK123) closed during October. Filter pack sampling at Converse Station, CA (CON186) ended with the last sampling week of 2010. Most CASTNET sites are located in rural or remote locations away from pollutant emission sources and heavily populated areas. Appendix A provides the location of each site by state and includes information on start date, latitude, longitude, elevation, and the parameters measured. 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 the lower pollutant concentrations generally found in the western United States.

Abington, CT (ABT147)

Figure 1-1 CASTNET Sites Operational during 2010

Figure 1-1 CASTNET Sites Operational during 2010
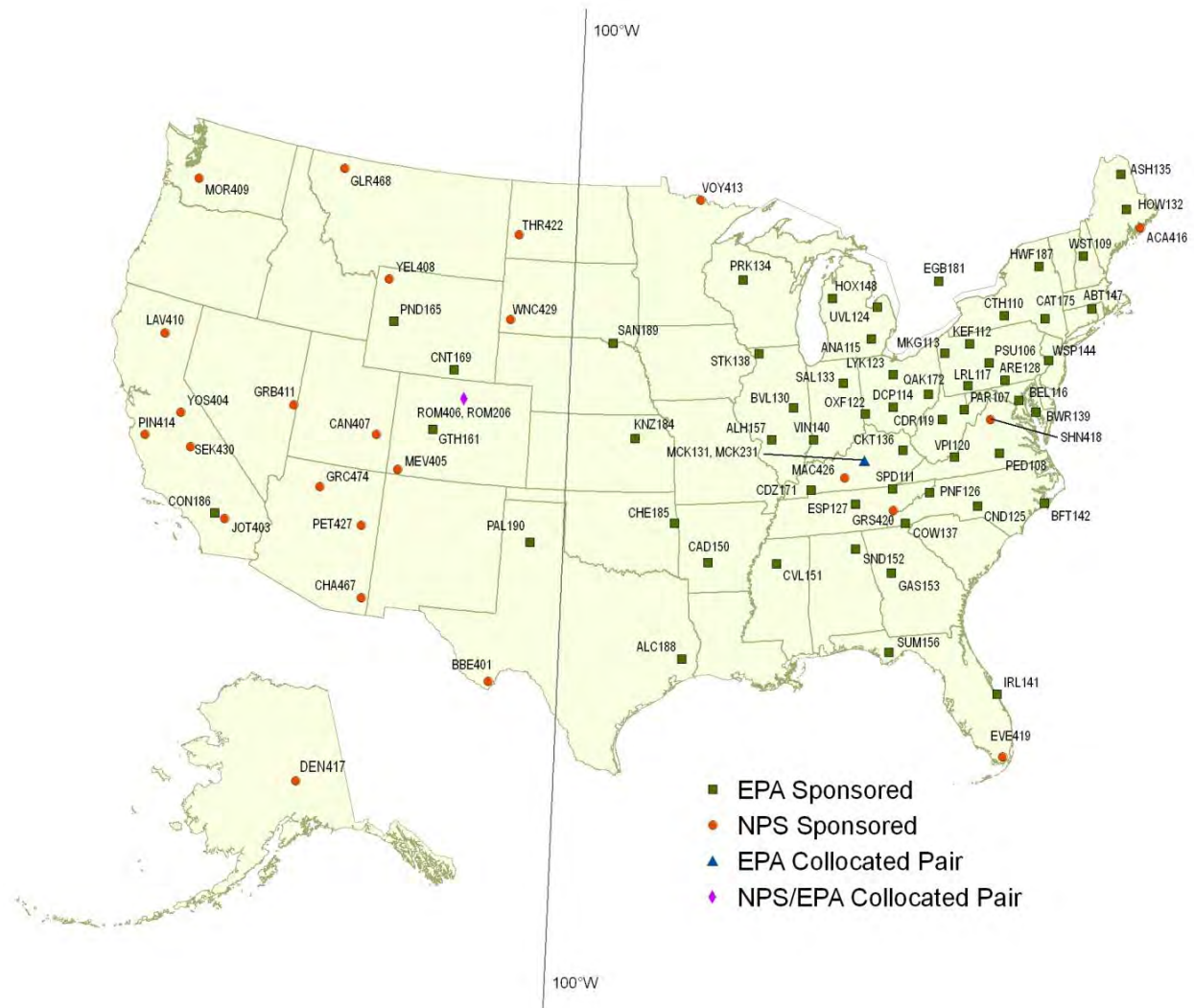
CASTNET Reference Sites

Chapters 2, 3, and 4 show maps of pollutant concentrations and deposition fluxes across the United States. In addition, measurements from 34 CASTNET eastern reference sites (Figure 1-2) were analyzed for each pollutant in order to determine trends in concentrations and rates of dry, wet, and total deposition. These 34 sites have been reporting CASTNET measurements since at least 1990. 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. Because of the closing of the site at LYK123, OH in October 2010, the site at Ann Arbor, MI (ANA115) was selected to replace LYK123 as an eastern reference site. ANA115 has been operating since June 1988. Trends in pollutant concentrations measured at CASTNET western reference

sites (Figure 1-3) are also presented. The 17 western reference sites have been operating since at least 1996.

The data from the 34 eastern reference sites were aggregated and then presented using box plots for the 21-year period 1990 through 2010. Data from the 17 western reference sites were aggregated and then presented using box plots for the period 1996 through 2010.

Sand Mountain, AL (SND152)

Figure 1-2 CASTNET Eastern Reference Sites

Eastern Reference Sites

Figure 1-3 CASTNET Western Reference Sites

Western Reference Sites

Measurements Recorded at CASTNET Sites

CASTNET was designed primarily to measure trends in seasonal and annual average concentrations and to model deposition fluxes over many years. Consequently, measurement of weekly (Tuesday to Tuesday) average concentrations was selected as the basic sampling strategy. Over the course of the seven days, air is drawn at a controlled flow rate through an open-face 3-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.

Figure 1-4 Three-Stage Filter Pack


```
Cellulose  =  Gaseous: sulfur dioxide
Nylon      =  Gaseous: nitric acid, sulfur dioxide
Teflon     =  Particulate: sulfate, nitrate, ammonium, sodium,
                calcium, magnesium, potassium, and chloride
```

CASTNET Ambient Measurements
- Sulfur species:
  - Sulfur dioxide
  - Particulate sulfate
- Nitrogen species:
  - Particulate nitrate
  - Nitric acid
  - Particulate ammonium
- Metal cations:
  - Particulate calcium
  - Particulate sodium
  - Particulate magnesium
  - Particulate potassium
- Particulate chloride
- Ozone
- Meteorological variables
- Information on land use and vegetation
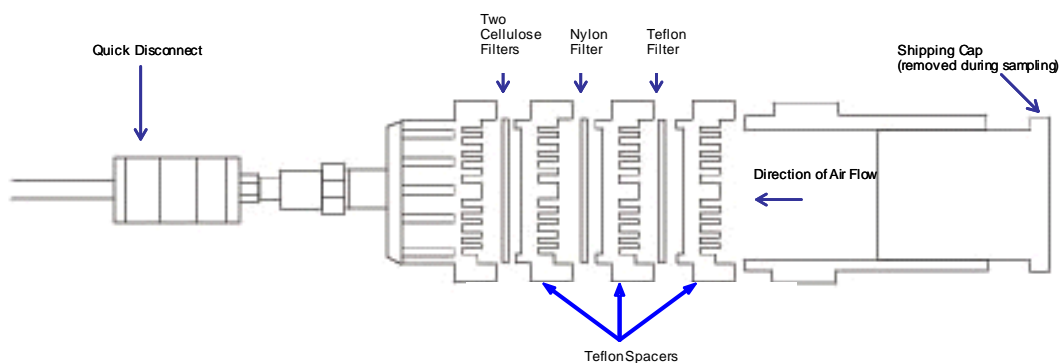
The filter packs are prepared, loaded, shipped, received, extracted, and analyzed at the AMEC Gainesville, FL laboratory. Following receipt from the field, exposed Teflon filters and blanks are extracted and then analyzed for sulfate (SO_4^{2-}), nitrate (NO_3^-), and concentrations of chloride (Cl^-) by micromembrane-suppressed ion chromatography (IC) and also for ammonium (NH_4^+) by the automated indophenol method with the Bran+Luebbe AutoAnalyzer 3. Additionally, Teflon filter extracts are analyzed for calcium (Ca^{2+}), sodium (Na^+), magnesium (Mg^{2+}), and potassium (K^+) by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a Perkin Elmer Optima 7300 Dual View spectrometer. The cellulose filter extracts are analyzed for SO_2 as sulfate using IC. The nylon filter extracts are analyzed via IC for nitric acid (HNO_3) as nitrogen and for SO_2 as sulfate. The SO_2 concentrations from the cellulose and nylon filters are summed to obtain total SO_2.

CASTNET also measures hourly O_3 concentrations, one of the major components of smog. Ozone measurements are recorded continually and archived as hourly averages. In addition to the air pollutant concentrations, CASTNET sites collected hourly meteorological measurements, which are used as input to the MLM, a numerical model used for estimating dry deposition to ecosystems in the atmospheric boundary layer. As of October 2010, EPA decided to discontinue meteorological measurements at all but four EPA-sponsored sites. The four sites continuing meteorological measurements are Beltsville, MD (BEL116); Bondville, IL (BVL130); Palo Duro State Park, TX (PAL190); and CHE185, OK. Meteorological measurements are continuing at all NPS sites. For the discontinued sites, measurements were phased out by the end of 2010 as sites were calibrated. The meteorological measurements are recorded continuously and archived as hourly averages.

CASTNET Meteorological Measurements
- Temperature:
  - Temperature (at 2 and 9 meters)
  - Delta temperature (difference between 2 and 9 meters)
- Relative Humidity
- Solar Radiation
- Winds:
  - Speed
  - Direction
  - Sigma theta (standard deviation of direction)
- Precipitation
- Surface Wetness

Atmospheric Mercury Network

Figure 1b shows 22 of the 25 AMNet sites that are currently operating in the continental United States, Canada, Hawaii, and Taiwan. Most sites are collocated with MDN sites and include meteorological measurements. Table 1a lists the AMNet sites, their locations, and sponsoring organizations. Information about AMNet can be found on the NADP Web site (http://nadp.isws.illinois.edu/amn).

Figure 1b Atmospheric Mercury Network Sites as of December 2011
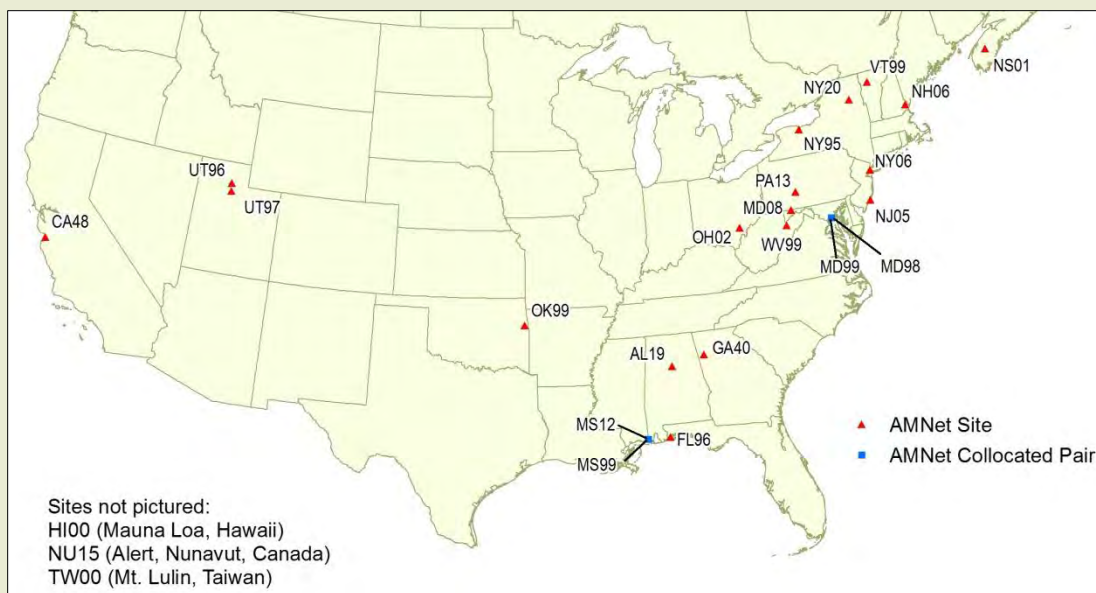
Table 1a Atmospheric Mercury Network Site Locations and Sponsors

Site ID	Name	Location	Latitude	Longitude	Organization
AL19	Birmingham	Alabama	33.55303	-86.8148	SEARCH
CA48	Elkhorn Slough	California	36.81000	-121.780	UC Santa Cruz
FL96	Pensacola	Florida	30.43671	-87.2571	SEARCH
GA40	Yorkville	Georgia	33.92833	-85.0456	SEARCH
HI00	Mauna Loa	Hawaii	19.5400	-155.5800	NOAA/EPA
MD08	Piney Reservoir	Maryland	39.7053	-79.0122	State MD
MD99	Beltsville				
MD98	Beltsville Collocated	Maryland	39.0284	-76.8172	NOAA/EPA
MS12	Grand Bay NERR				
MS99	Grand Bay NERR Collocated	Mississippi	30.4294	-88.4277	NOAA
NH06	Thompson Farm	New Hampshire	43.1100	-70.9500	U New Hampshire
NJ05	Brigantine	New Jersey	39.4020	-74.3790	State NJ
NS01	Kejimkujik	Nova Scotia	44.4300	-65.2100	Env. Canada
NU15	Alert	Nunavut	54.0000	-90.0000	Env. Canada
NY06	NYC	New York	40.7146	-74.0058	State NY
NY20	Huntington Wildlife Forest	New York	43.9731	-74.2232	Clarkson U.
NY95	Rochester	New York	43.1544	-77.6160	State NY
OH02	Athens	Ohio	39.3000	-82.1167	Ohio U.
OK99	Stilwell	Oklahoma	35.7514	-94.6717	Cherokee Nation
PA13	Allegheny Portage Railroad National Historic Site	Pennsylvania	40.45971	-78.5618	NOAA, PDEP & NPS
TW00	Mt. Lulin	Taiwan	25.4700	120.8730	National Central U & EPA (Taiwan)
UT96	Antelope Island	Utah	41.0467	-112.0248	U Utah
UT97	Salt Lake City	Utah	40.7118	-111.9609	State Utah
VT99	Underhill	Vermont	44.5283	-72.8689	Ecosystems Res. Gr.
WV99	Canaan Valley Institute	West Virginia	39.0636	-79.4222	NOAA

Note: Collocated CASTNET sites are highlighted in yellow.   **Source:** NADP/AMNet, 2010

Modeling 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 V_d. The equation to estimate flux is shown in Figure 1-5. 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 V_d, is influenced by meteorological conditions, vegetation, and atmospheric and plant chemistry. The deposition velocity values for each site are calculated for each hour of each year using the MLM. The MLM is summarized 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. The deposition velocities and fluxes presented in Chapter 3 were calculated using the MLM. The decision to discontinue meteorological measurements at all but four EPA CASTNET sites, plus the need to improve V_d data completeness, resulted in the development of a method by EPA (Bowker *et al.*, 2011) to substitute historical average hourly V_d values for missing MLM simulations. The substitution method will be applied to the CASTNET database and reported in a supplemental report.

Arendtsville, PA (ARE128)

Figure 1-5 Multi-Layer Model

$$\text{Flux} \quad = \quad \overline{C} \; x \; \overline{V_d}$$

$$1/V_d \quad = \quad \cfrac{1}{\cfrac{1}{r_s + r_b} + \cfrac{1}{r_{cut} + r_b} + \cfrac{1}{r_{a,\,soil} + r_{soil}}} \quad + \quad r_a$$

Resistances

r_a = aerodynamic

$r_{a,\,soil}$ = aerodynamic near soil

r_b = boundary layer in thin layer at surface

r_{cut} = cuticular

r_s = stomatal

r_{soil} = soil
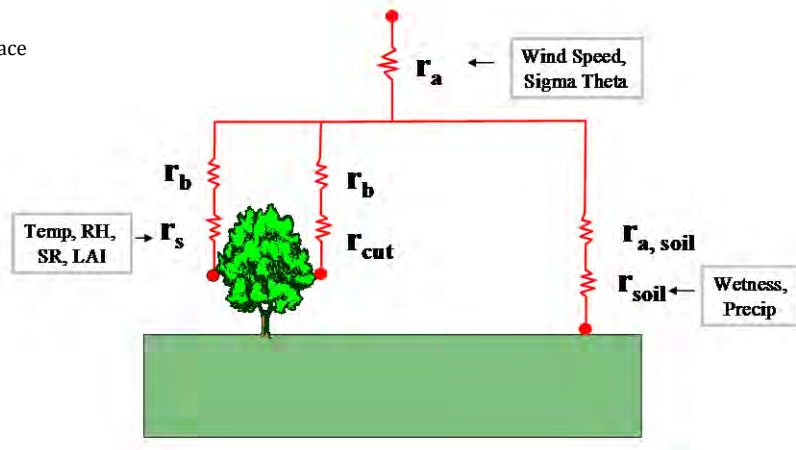
Prince Edward, VA (PED108)

Canada Reduces SO$_2$ Emissions by 46 Percent since 1990

The Canada – United States Air Quality Agreement (AQA) and its Acid Rain Annex, which was negotiated in 1991, committed both countries to reduce emissions of SO$_2$ and NO$_x$. These pollutants are precursors to acid rain. The Ozone Annex was added in 2000 to address transboundary levels of ozone. This annex committed both countries to reduce emissions of NO$_x$ and volatile organic compounds (VOCs) in a defined region known at the Pollutant Emission Management Area (PEMA), which includes central and southern Ontario, southern Quebec, 18 U.S. states (Connecticut, Delaware, Illinois, Indiana, Kentucky, Maine, Maryland, Massachusetts, Michigan, New Hampshire, New York, New Jersey, Ohio, Pennsylvania, Rhode Island, Vermont, West Virginia, and Wisconsin) and the District of Columbia. The AQA and related national emission reduction programs have resulted in substantive declines in emissions of SO$_2$, NO$_x$, and VOCs. The results are summarized in the Canada – United States Air Quality Agreement Progress Report 2010 (International Joint Commission, 2011).

Canada's total SO$_2$ emissions in 2008 were 1.7 million tonnes (1 tonne = 1.1 tons), which represent a 46 percent decrease from the 1990 emission level and a 63 percent reduction from 1980 (Figure 1c). Canada has also met its commitment to reduce NO$_x$ emissions from metal smelting operations, power plants, and major combustion sources by 100,000 tonnes. Total NO$_x$ emissions declined from 2.5 million tonnes in 1990 to 2.1 million tonnes in 2008. Canada is continuing to develop programs to further reduce NO$_x$ emissions nationwide. The United States' emission reductions are discussed elsewhere in this report.

Figure 1c Total Canadian Emissions of SO$_2$ (1980–2008)
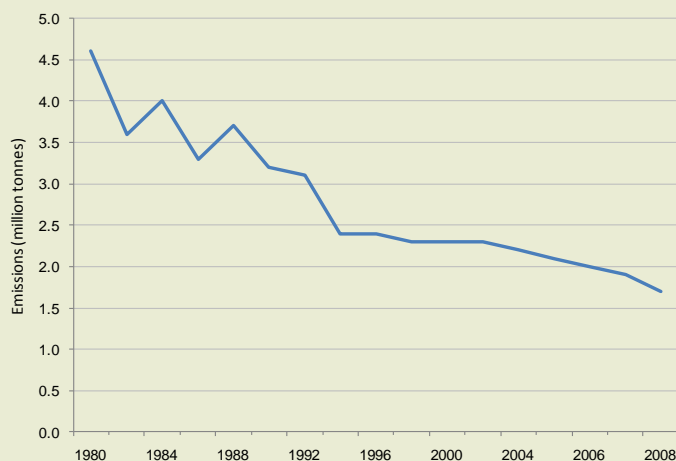
Source: International Joint Commission (2011)

The Ozone Annex was developed to reduce concentrations of ozone pollution in the PEMA around the Canadian – United States border. Strategies for reducing emissions of NO$_x$ and VOCs discussed in the Annex indicate that Canadian emissions of NO$_x$ and VOCs in the PEMA will have been reduced by 34 percent and 29 percent, respectively, by 2010 from 1990 levels. Figure 1d shows Canadian NO$_x$ and VOCs emissions for 1990 and approximate emissions for 2010. Figure 1e illustrates emissions of U.S. NO$_x$ and VOCs for PEMA states for 1990 and 2010. NO$_x$ emissions declined by 53 percent and VOCs emissions by 41 percent (International Joint Commission, 2011).

Canada and the United States developed procedures for providing notification when potential new sources of transboundary air pollution are identified and when existing sources are modified. The purpose is to mitigate any significant transboundary pollution before the new or modified sources

begin operation. Since this agreement was initiated, Canada has issued 55 notifications to the United States and the United States issued 61 to Canada.

The AQA also includes consultation, cooperation, and research on other matters:

- Reporting emissions
- Reporting air quality measurements taken within 500 km of the border
- Studying health and exposure
- Tracking public health

The CASTNET site at Egbert, ON (EGB181) is located within the PEMA. Canadian and United States emission reductions have resulted in improved air quality at this site. Figure 1f provides trends in annual mean SO_2 and total nitrate concentrations from 1995 through 2010. Annual mean SO_2 concentrations have been reduced by 59 percent based on 3-year average concentrations from 1995–1997 to 2008–2010. Total nitrate concentrations declined by 39 percent.

Figure 1d Canadian NO_x and VOCs PEMA Emissions and Projections
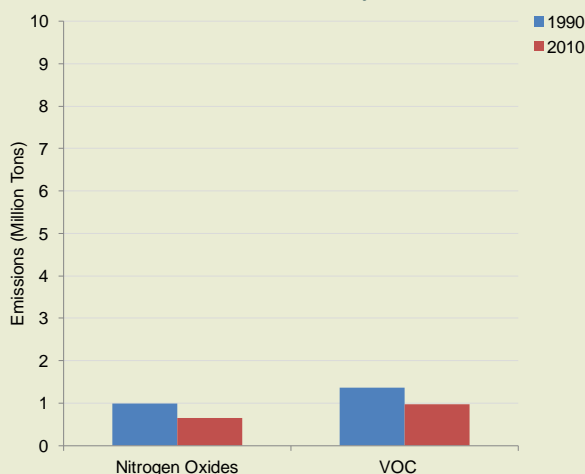
Source: International Joint Commission (2011)

Figure 1e U.S. NO_x and VOCs PEMA Emissions
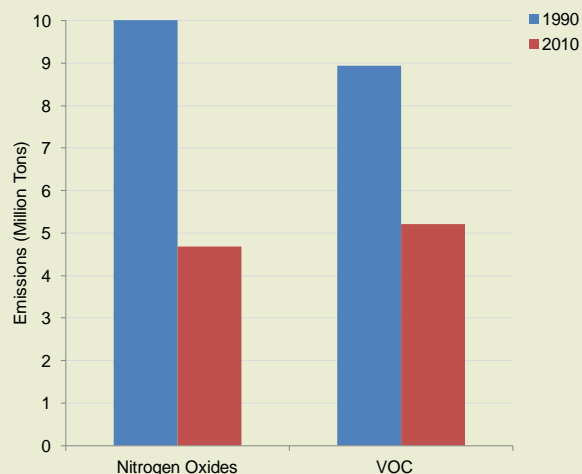
Source: International Joint Commission (2011)

Figure 1f Trends in Annual SO_2 and Total Nitrate Concentrations for Egbert, ON
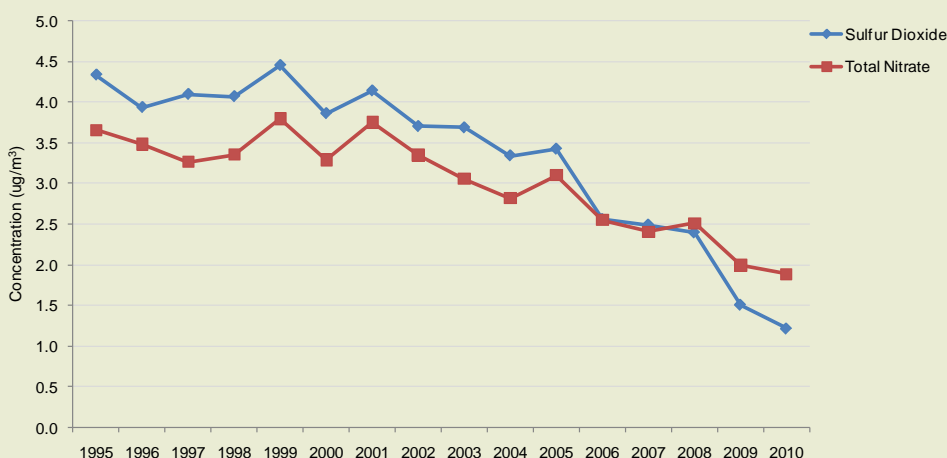
Sulfur Dioxide and Nitrogen Oxides Emissions

The ARP was designed to reduce the effects of acid deposition by requiring major reductions of SO_2 and NO_x emissions from the electric power industry. EPA issues annual progress reports (e.g., EPA, 2011a) on the effects of the ARP and related programs. The 2010 EPA report summarizes 2010 emission and compliance data, market analyses, and environmental and human health results.

Under the ARP, 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 annually by all regulated EGUs in the contiguous United States. The program, which began in 1995, has required incremental reductions in SO_2 emissions yearly with the final 2010 SO_2 emissions cap set at 8.95 million tons, a level equal to about one-half of the emissions from the power sector in 1980. Use of 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 CAAA allocated 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 NO_x limits apply to most of the coal-fired electric utility boilers subject to the SO_2 emission reductions, and 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. Two prominent control programs are the OTC NO_x Budget (1999–2002) and the NO_x SIP Call/NBP, which began in 2003 and continued through 2008. The NBP placed a cap on total NO_x emissions from EGUs during the ozone season (May 1 through September 30) when the potential for ozone formation is high. The CAIR NO_x programs include annual and ozone season control programs. CAIR was designed to further SO_2 and NO_x emission reductions. The CAIR NO_x ozone season trading program replaced the NBP in 2009. Although CAIR was remanded back to EPA in 2008, the CAIR programs remain in effect until the CSAPR becomes effective. The CSAPR requires significant reductions in SO_2 and NO_x emissions that contribute to ozone and $PM_{2.5}$ pollution in downwind states. EPA has set emission budgets for each state. See the summary of CSAPR on page 4.

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 EGUs from 1995 through 1999 for SO_2 emissions and from 1996 through 1999 for NO_x emissions. Phase II for both pollutants began in 2000. In 2010, the Phase II ARP SO_2 requirements affected 3,613 operating units. The Phase II ARP NO_x requirements applied to 956 of those operating units that exceed 25 megawatts and

burned coal between 1990 and 1995 (EPA, 2011a). The CAIR NO_x ozone season program affected 3,309 units in 2010, and the NO_x and SO_2 annual programs affected 3,349 units. Under the ARP's and CAIR's emission reduction requirements, total SO_2 emissions from affected sources were 5.1 million tons in 2010; total NO_x emissions from NBP and CAIR sources were 599,000 tons.

Figure 1-6 presents state-by-state total annual SO_2 emissions for CAIR and ARP electric utility plants for five years (1990, 1995, 2000, 2005, and 2010). The most significant reduction in SO_2 emissions occurred in and near the Ohio River Valley where many coal-fired power plants are located. Many of the states east of the Mississippi River realized reduced SO_2 emissions by more than 50 percent over the 21 years; the larger emitting states (Illinois, Indiana, Kentucky, Ohio, Pennsylvania, and West Virginia) reduced SO_2 emissions by more than 65 percent. Annual NO_x emissions by state are depicted in Figure 1-7 for the same five years. States with the highest NO_x emissions also produced the most significant declines. Every state east of the Mississippi River experienced a significant decline in annual NO_x emissions from 2000 to 2010. For example, NO_x emissions from Indiana EGUs declined by 67 percent from 2000 to 2010.

Horton Station, VA (VPI120)

Figure 1-6 Annual SO₂ Emissions (for CAIR and ARP Sources)

Annual Emissions of Sulfur Dioxide

■ 1990
■ 1995
■ 2000
■ 2005
■ 2010

Scale: Largest bar equals
2,212 thousand short
tons (Ohio, 1990).
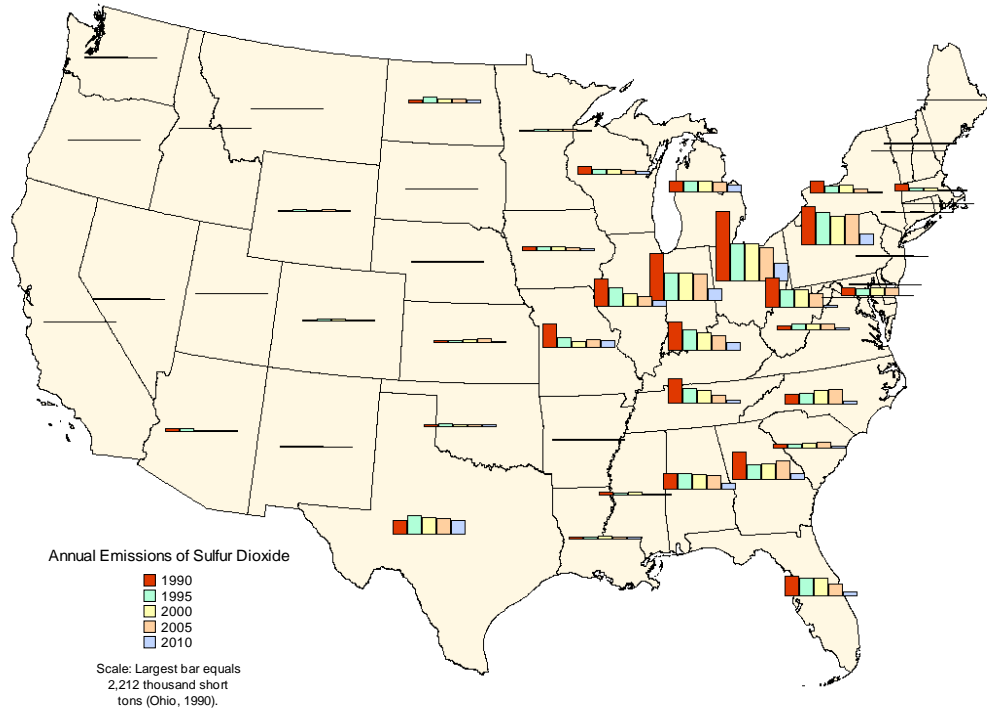
Figure 1-7 Annual NOₓ Emissions (for CAIR and ARP Sources)

Annual Emissions of Nitrogen Oxides

■ 1990
■ 1995
■ 2000
■ 2005
■ 2010

Scale: Largest bar equals
534 thousand short
tons (Ohio, 1990).
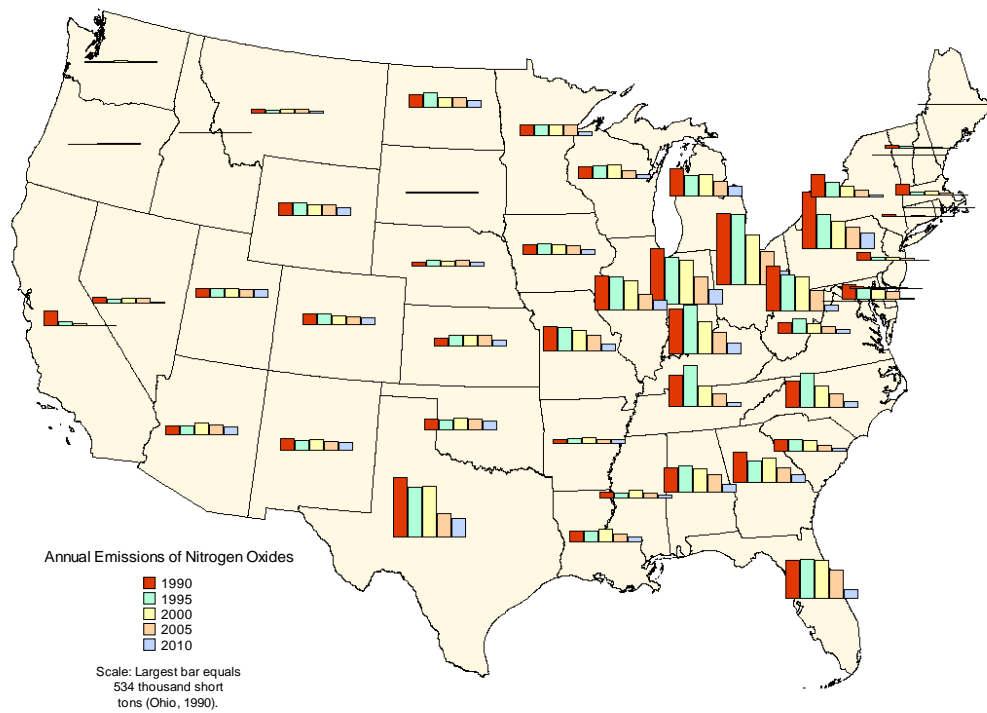
Chapter 2: Atmospheric Concentrations

Three-stage filter packs were used to measure weekly average concentrations of SO_2, SO_4^{2-}, HNO_3, NO_3^-, NH_4^+, Cl^-, and 4 earth metals at 84 CASTNET monitoring stations. Trends in mean annual SO_2, SO_4^{2-}, total NO_3^-, and NH_4^+ concentrations aggregated over the 34 eastern reference sites are shown over the period 1990 through 2010 and for 17 western reference sites for the period 1996 through 2010 using box plots for each year. All four parameters measured at the eastern sites declined over the 21-year period although total nitrate and NH_4^+ concentrations increased slightly in 2010 relative to 2009. Measured annual mean concentrations of SO_2 and SO_4^{2-} have decreased steadily with a significant reduction since 2005. Concentrations of total nitrate showed little change from 1990 until 2000 when they began to drop in response to NO_x emission reduction programs. SO_2, total nitrate, and NH_4^+ concentrations measured at the 17 western reference sites declined over the 15 years.

This chapter presents maps of 2010 annual mean concentrations of SO_2, SO_4^{2-}, total nitrate $(HNO_3 + NO_3^-)$, and NH_4^+. Additional maps are provided in CASTNET quarterly reports (MACTEC, 2010a; 2010d; 2011a; 2011c). Trends in annual mean concentrations over the 21-year period (1990 through 2010) are presented using box plots derived from measurements from the 34 CASTNET eastern reference sites (Figure 1-2). Trends in annual mean concentrations were also estimated from data from 17 CASTNET western reference sites (Figure 1-3) for the period 1996 through 2010. This chapter also includes information on ambient mercury concentrations measured at CHE185, OK, and it compares cloud chemistry measurements collected at Clingmans Dome, TN and Whiteface Mountain, NY.

Sulfur Dioxide

Sulfur dioxide is a major air pollutant that affects human health and plant communities. It is a reactive, gaseous pollutant emitted during the combustion of coal, oil, and other fossil fuels that contain sulfur. EGUs constitute the largest source of SO_2 in the United States. Some industrial facilities also emit SO_2. To be compliant under the SO_2 National Ambient Air Quality Standard (NAAQS), the 3-year average of the 99th percentile of the yearly distribution of daily maximum 1-hour SO_2 concentrations must be at or below 75 parts per billion (ppb) [215 micrograms per cubic meter ($\mu g/m^3$) of air]. SO_2 gas reacts in the atmosphere to form various acidic compounds including sulfuric acid (H_2SO_4), a significant contributor to acid rain, and ammonium sulfate [$(NH_4)_2SO_4$], a major component of $PM_{2.5}$. Fine particles are also regulated by the NAAQS since $PM_{2.5}$ adversely affects health and contributes to degradation of atmospheric visibility.

Figure 2-1 shows annual mean SO_2 concentrations measured in 2010. Three sites in the eastern United States measured mean concentrations greater than 5.0 $\mu g/m^3$ of air. The highest concentration (7.3 $\mu g/m^3$) was measured at Quaker City, OH (QAK172). The other two sites with levels above 5.0 $\mu g/m^3$ were Horton Station, VA (VPI120) and

Oxford,OH (OXF122). SO_2 concentrations recorded in 2010 were somewhat lower than SO_2 levels measured in previous years. For comparison, the 3-state geographic average of mean SO_2 concentrations measured in 2010 at 11 monitoring stations in Indiana, Ohio, and Pennsylvania was 4.3 $\mu g/m^3$ versus a 3-state average of 4.7 $\mu g/m^3$ in 2009. Only two western sites (Figure 1-1) measured a 2010 annual mean SO_2 concentration equal to 1.0 $\mu g/m^3$. The western sites are PAL190, TX and Theodore Roosevelt National Park, ND (THR422).

Figure 2-1 Annual Mean SO_2 Concentrations ($\mu g/m^3$) for 2010
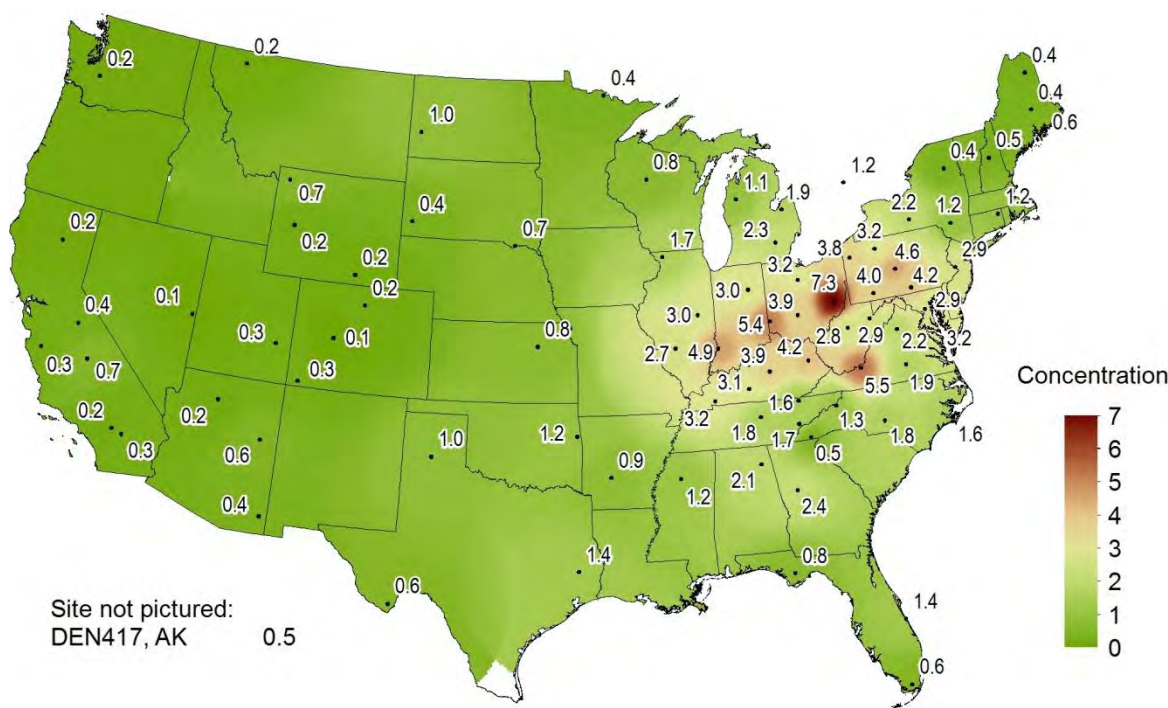
Figure 2-2 shows box plots of annual mean SO_2 concentrations aggregated over the 34 eastern reference sites from 1990 through 2010 (right side) and the 17 western reference sites from 1996 through 2010 (left side). Because concentrations measured at the western CASTNET sites were much lower than concentrations measured at the eastern sites, the y-axes on the western and eastern plots have different scales.

The box plots for the eastern sites show a downward trend. A significant reduction in ambient SO_2 was recorded in 1995 at the beginning of the ARP. A sharp decline was also recorded from 2005 through 2010, although the rate of decline was lower in 2010 relative to the previous four years. Three-year mean concentrations for the eastern reference sites for 1990–1992 and 2008–2010 were 8.9 $\mu g/m^3$ and 3.2 $\mu g/m^3$, respectively. This change constitutes a 65 percent reduction in 3-year mean SO_2 concentrations between the two periods. The 2010 mean level of 2.6 $\mu g/m^3$ was the lowest mean value measured by the

eastern reference sites in the history of the network and represents a significant decline over the past five years from the 2005 concentration of 6.1 μg/m^3.

The box plots for the western reference sites indicate a decline in annual mean SO_2 concentrations aggregated over the 17 sites. Three-year mean SO_2 concentrations for 1996–1998 and 2008–2010 were 0.61 μg/m^3 and 0.31 μg/m^3, respectively. This change constitutes a 49 percent reduction in 3-year mean SO_2 concentrations over the 15 years. The aggregated mean SO_2 concentrations from the western reference sites were typically more than 10 times lower than mean concentrations measured at the eastern reference sites.

Figure 2-2 Trend in Annual Mean SO_2 Concentrations (μg/m^3)
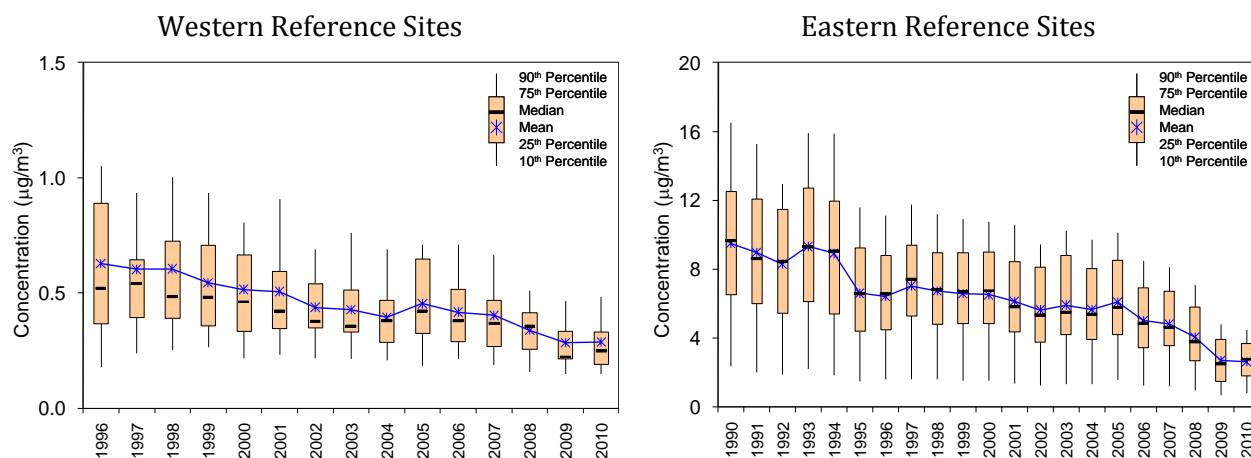
Particulate Sulfate

Particulate SO_4^{2-} is formed in the atmosphere through the transformation of SO_2 via both gas and aqueous (cloud) phase reactions. SO_4^{2-} exists in the atmosphere typically as $(NH_4)_2SO_4$, a major component of PM2.5. Figure 2-3 depicts a map of annual mean particulate SO_4^{2-} concentrations measured during 2010. The map shows a fairly uniform distribution of SO_4^{2-} concentrations greater than or equal to 3.0 μg/m^3 centered on the major SO_2 source region in the vicinity of the Ohio River Valley. CASTNET monitors in five contiguous states (Kentucky, Indiana, Ohio, Pennsylvania, and West Virginia) plus the monitor at Sand Mountain, AL (SND152) measured sulfate concentrations greater than or equal to 3.0 μg/m^3. Sulfate concentrations greater than or equal to 1.0 μg/m^3 in the western region were measured at Big Bend National Park, TX (BBE401); PAL190, TX; THR422, ND; and Sequoia National Park, CA (SEK430).

Figure 2-3 Annual Mean SO$_4^{2-}$ Concentrations (μg/m^3) for 2010
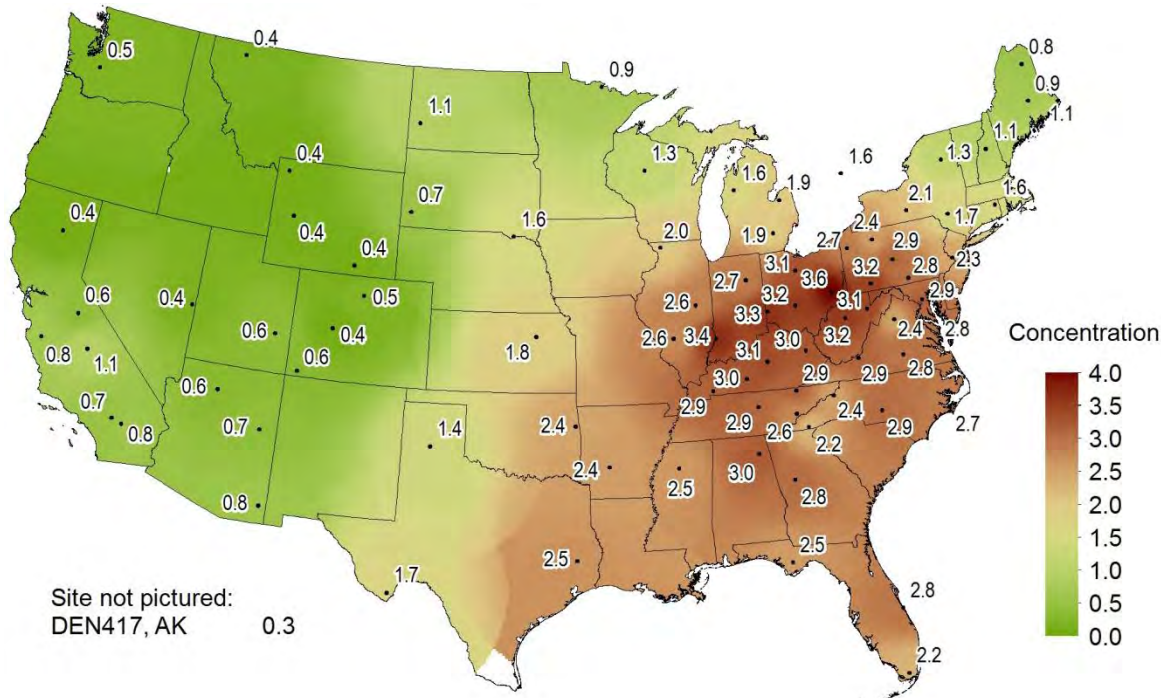
The right side of Figure 2-4 provides 1990–2010 box plots of annual mean SO$_4^{2-}$ concentrations from the 34 eastern reference sites. The figure shows a substantial decline in SO$_4^{2-}$. Like SO$_2$, sulfate concentrations declined significantly from 2005 through 2010. The difference between 3-year means from 1990–1992 to 2008–2010 represents a 48 percent reduction in SO$_4^{2-}$ from 5.4 μg/m^3 to 2.8 μg/m^3, respectively. The mean SO$_4^{2-}$ level of 2.6 μg/m^3, which was measured for both 2009 and 2010, was the lowest in the history of the network.

The box plots for the western reference sites are provided on the left side of Figure 2-4. The boxes show a 40 percent reduction in annual mean SO$_4^{2-}$ concentrations aggregated over the 17 sites, with 1996–1998 and 2008–2010 concentrations of 0.80 μg/m^3 and 0.48 μg/m^3, respectively. The 2010 aggregated mean concentration (0.6 μg/m^3) was the lowest recorded.

Figure 2-4 Trend in Annual Mean SO_4^{2-} Concentrations ($\mu g/m^3$)

Western Reference Sites

Eastern Reference Sites
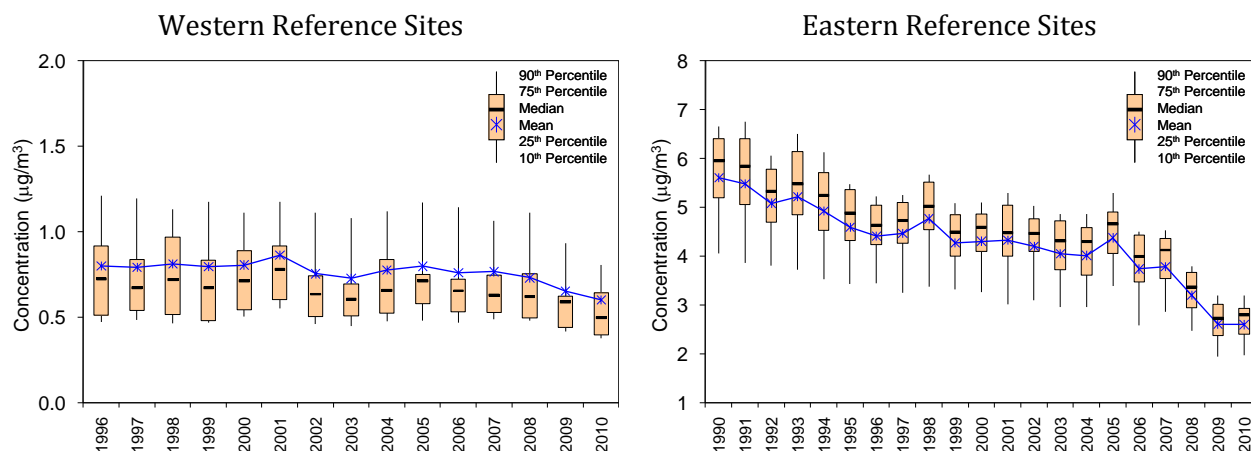
Ambient Mercury Concentrations Measured at Cherokee Nation, OK

The Cherokee Nation operates AMNet and MDN monitoring systems at its CASTNET site (CHE185) in Oklahoma. Ambient air concentrations of gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate-bound mercury (PBM$_{2.5}$) with a mean aerodynamic diameter of less than 2.5 micrometers (μm) are measured with a Tekran 2537A, 1130, and 1135 speciation measurement system using AMNet protocols (NADP, 2011a). The system operates on a 3-hour cycle (NADP, 2011b). GEM concentrations are measured every five minutes during the first two hours of the cycle. Integrated 2-hour concentrations of GOM and PBM$_{2.5}$ are also collected during the first two hours. During the third hour, the PBM$_{2.5}$ and GOM samples are analyzed sequentially. No air sampling occurs during the third hour. Additionally, CHE185 incorporates a MDN sampler to collect Hg in precipitation in order to measure wet deposition of Hg (NADP/MDN, 2012).

GEM, GOM, and PBM$_{2.5}$ concentration data were assembled from the AMNet database for the year 2010. Concentration data were obtained as 2-hour values every three hours. Table 2a summarizes the 2010 measurements. Note the different reporting units. The mean GEM value of 1.40 nanograms per cubic meter of air (ng/m^3) was 300 to 600 times higher than the respective means for GOM with 2.18 picograms per cubic meter of air (pg/m^3) and PBM$_{2.5}$ with 4.22 pg/m^3. GEM values showed a relatively small range and little variability. GOM in the air is reactive and can be removed from the atmosphere quickly by dry and wet deposition. GEM and PBM$_{2.5}$ are relatively inert and have a low propensity for deposition.

Table 2a 2010 Annual Atmospheric Mercury Species Concentrations

	GEM (ng/m^3)	GOM (pg/m^3)	PBM$_{2.5}$ (pg/m^3)
Minimum	0.64	0.00	0.00
Mean	1.40	2.18	4.22
Median	1.42	0.74	3.33
Maximum	2.13	52.52	30.64
Standard Deviation	0.18	4.00	3.47
Count	2468	2325	2251

Time series of weekly average concentrations are shown in Figure 2a. The lowest GOM concentrations were measured in May through July and the highest in early spring. This was unexpected given the reactivity of this species and its hypothesized production through the oxidation of ozone. Figure 2b shows the average diurnal cycle of GOM for 2010. The figure shows

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a distinct diurnal cycle with minimum values during the night and early morning and a peak in the afternoon. The figure suggests the production of GOM is related to daytime meteorological conditions (mixing after sunrise, temperature, and sunlight intensity) and perhaps atmospheric photochemistry, although the data in Figure 2a indicate GOM concentrations are lowest during the time of year with most active photochemical conditions.

Annual average GEM, GOM, and $PBM_{2.5}$ concentration values were used to estimate the annual dry deposition flux of total ambient Hg for CHE185. Dry fluxes of the individual Hg constituents were approximated based on annual V_d of 0.1, 2.0, and 0.1 centimeters per second (cm/sec) for the respective species. The deposition velocity values were selected from the scientific literature (e.g., Castro *et al.*, 2011; Lindberg and Stratton, 1998). Annual fluxes were calculated as the product (Figure 1-5) of annual concentrations and deposition velocity values. Total Hg flux, 45.60 micrograms per square meter per year ($\mu g/m^2/yr$) was estimated as the sum of the fluxes for the three species. Even though the V_d for GOM is roughly 20 times higher than V_d values for the other two species, the dry flux of GEM contributed the largest fraction of total dry deposition because the GEM concentration was greater than 300 to 600 times higher than the other two species concentrations. However, given the bi-directional deposition/evasion of GEM, the GEM deposition velocity is likely a high estimate at 0.1 cm/s. While 44.10 $\mu g/m^2/yr$ is a good estimate of the total GEM deposition, net GEM deposition would likely be less due to evasion back into the atmosphere.

Table 2b Estimates of 2010 Dry and Total Deposition of Atmospheric Mercury Species

Species	Annual Average Concentration (pg/m^3)	V_d (cm/sec)	Flux ($\mu g/m^2/yr$)
GEM	1,400.00	0.1	44.10
GOM	2.18	2.0	1.37
$PBM_{2.5}$	4.22	0.1	0.13
Total			45.60
Hg in Precipitation			12.30
Total Dry + Wet			57.89

The annual wet flux of 12.30 $\mu g/m^2/yr$ of Hg for the CHE185 site was obtained from the NADP/MDN (NADP/MDN, 2012b) Web site. The total Hg deposition for 2010 was 57.89 $\mu g/m^2/yr$. The dry flux was about four times higher than the wet flux at the eastern Oklahoma site.

Figure 2a Time Series of Weekly $PBM_{2.5}$, GOM, and GEM Concentrations for 2010
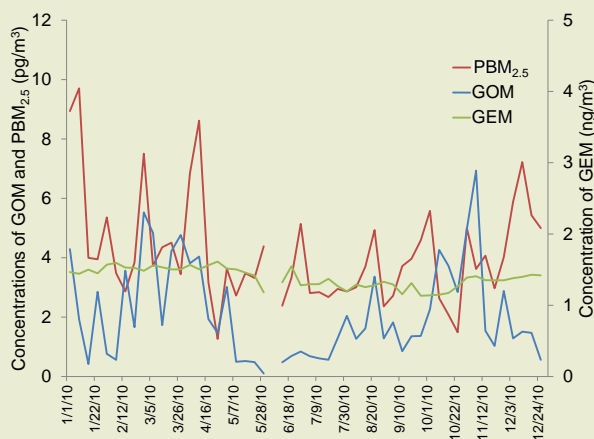
Figure 2b Average Diurnal Cycle of GOM for 2010
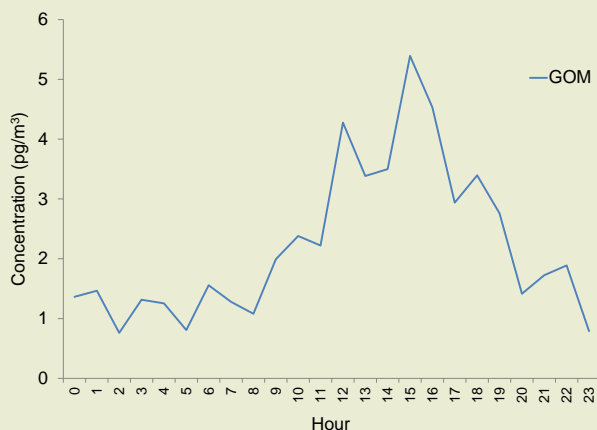
Total Nitrate

Total nitrate is the sum of HNO_3 and NO_3^-, which are formed in the atmosphere from the NO_x emitted when fossil fuels combust at high temperatures. Transportation sources (e.g., automobiles and trucks) are the largest contributors of NO_x emissions in the United States and produce more than 50 percent of nationwide NO_x emissions. NO_x is also emitted from EGUs and industrial processes. A natural source of NO_x is lightning in the atmosphere. Nitric acid exists as a gas and contributes to acid deposition. Nitrate is a component of $PM_{2.5}$ in the form of ammonium nitrate (NH_4NO_3) and as larger particles such as sodium nitrate or calcium nitrate. This chapter discusses data on total nitrate rather than HNO_3 and NO_3^- individually because of the uncertainty in individual species measurements and because total nitrate is more representative of a response to changes in NO_x emissions than either of its constituents alone. A map of annual mean total nitrate concentrations for 2010 is given in Figure 2-5. The map shows a 3-state region with mean concentrations greater than or equal to 3.0 μg/m^3. The region includes the states of Illinois, Indiana, and Ohio. Three sites, SEK430, CON186, and Joshua Tree National Park (JOT403) in California measured annual mean total nitrate concentrations greater than 2.0 μg/m^3. Salamonie Reservoir, IN (SAL133) measured the highest concentration (4.0 μg/m^3) in the network.

Box plots of total nitrate levels for eastern sites for the years 1990 through 2010 are given in Figure 2-6. The data shown on the right side of the figure were aggregated from the 34 eastern reference sites. The data show no trend in mean concentrations until 2000 when nitrate levels began to decline in response to NO_x emission control programs. Three-year mean levels declined from 3.1 μg/m^3 to 2.0 μg/m^3 from 1990–1992 to 2008–2010, producing a 35 percent reduction in total nitrate. Total nitrate levels measured at the eastern reference sites declined from a mean value of 3.2 μg/m^3 in 2000 to a mean value of 2.0 μg/m^3 in 2010.

Salamonie Reservoir, IN (SAL133)

Figure 2-5 Annual Mean Total Nitrate (NO_3^- + HNO_3) Concentrations ($\mu g/m^3$) for 2010
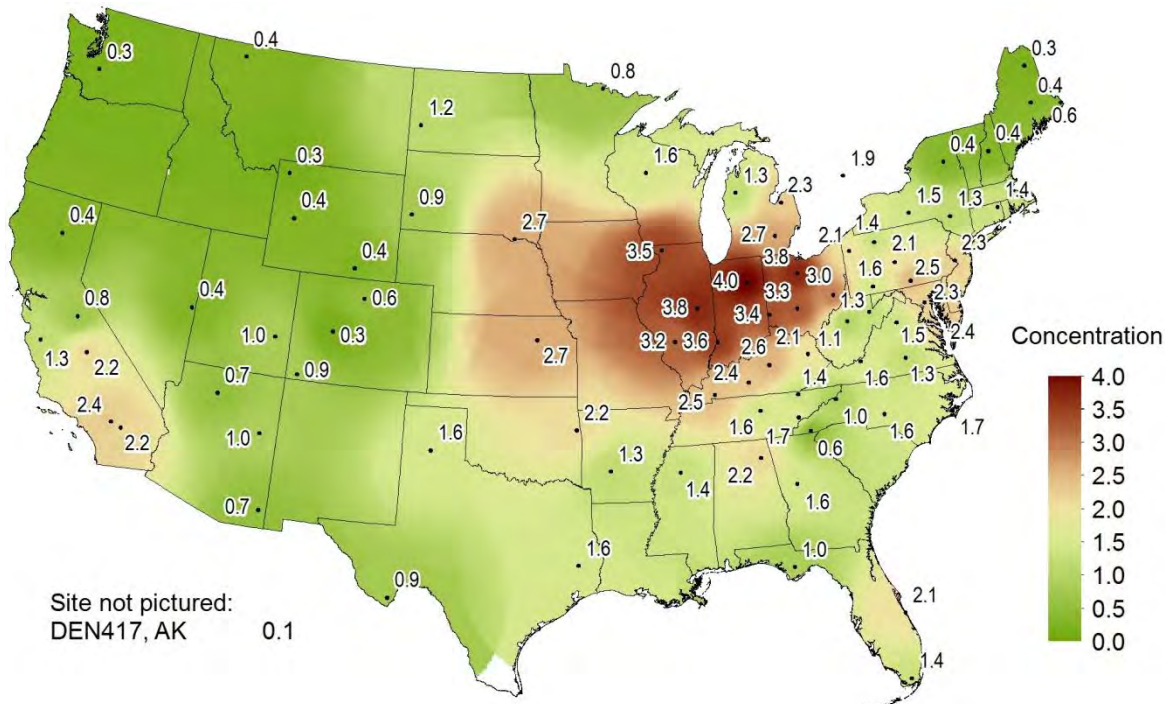
Data aggregated from the 17 western sites are shown on the left side of Figure 2-6. The 3-year mean total nitrate concentration for 2008–2010 was 35 percent lower than the corresponding 1996–1998 level with 3-year mean concentrations of 0.7 $\mu g/m^3$ and 1.0 $\mu g/m^3$, respectively. The two mean concentrations for 2009 and 2010 were the lowest over the 15-year period.

Figure 2-6 Trend in Annual Total Nitrate (NO_3^- + HNO_3) Concentrations ($\mu g/m^3$)
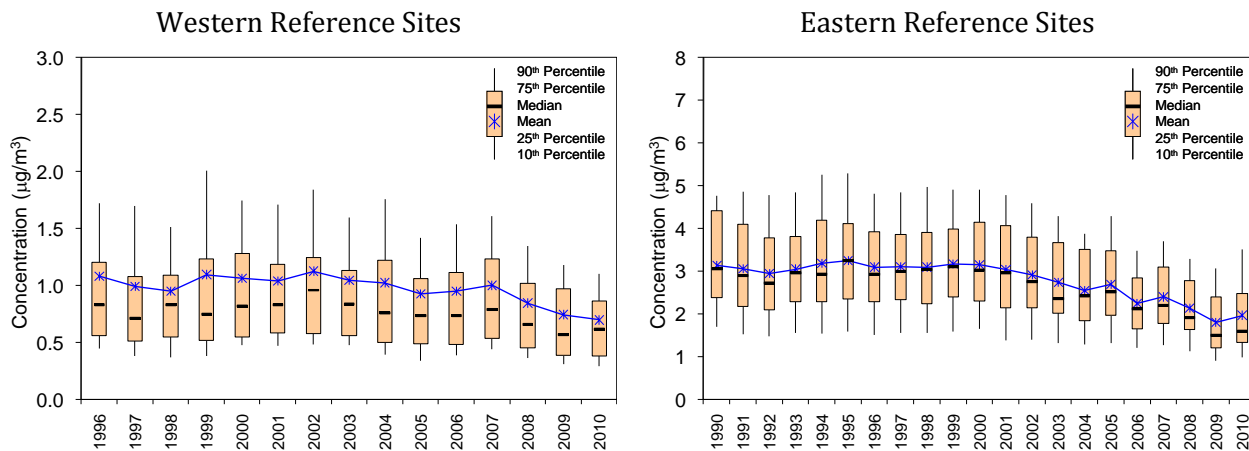
Particulate Ammonium

Particulate ammonium is formed when gaseous NH_3 reacts with other gases and particles in the atmosphere including HNO_3, particulate SO_4^{2-}, and particulate NO_3^-. Particulate ammonium exists in the atmosphere typically as $(NH_4)_2SO_4$ and NH_4NO_3. A map of annual mean NH_4^+ concentrations for 2010 is depicted in Figure 2-7. No monitors measured concentrations above 2.0 μg/m^3. The data show a flat geographic distribution across the central and eastern United States with more than half the sites reporting values less than or equal to 1.0 μg/m^3. Higher concentrations were measured in Illinois, Indiana, Ohio, Kentucky, and northern Alabama. The NH_4^+ concentrations measured at western sites were low with all sites measuring concentrations less than 1.0 μg/m^3.

Figure 2-7 Annual Mean NH_4^+ Concentrations (μg/m^3) for 2010
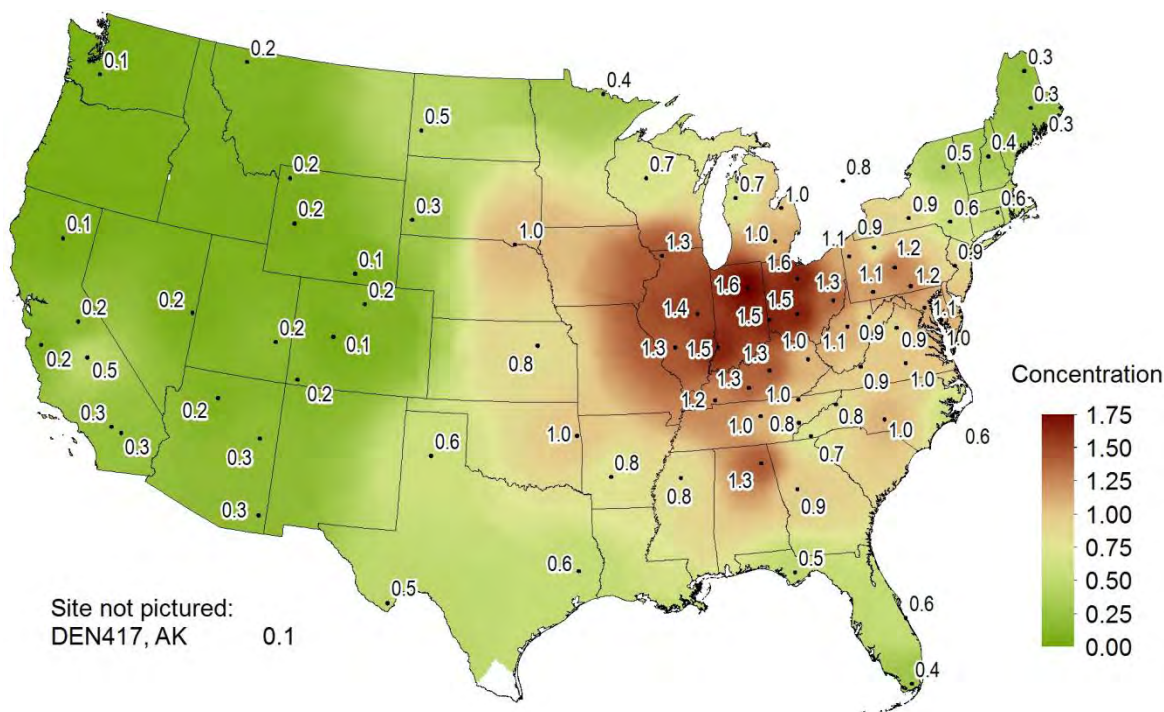
Box plots of NH_4^+ concentrations are provided in Figure 2-8. The trend diagram for the eastern sites shows a reduction in mean NH_4^+ levels from 1990–1992 to 2008–2010. The 1990–1992 mean concentration was 1.8 μg/m^3, and the 2008–2010 value was 1.1 μg/m^3, a 39 percent decline. The box plots characterizing the western sites show no significant change.

Figure 2-8 Trend in Annual Mean NH_4^+ Concentrations ($\mu g/m^3$)
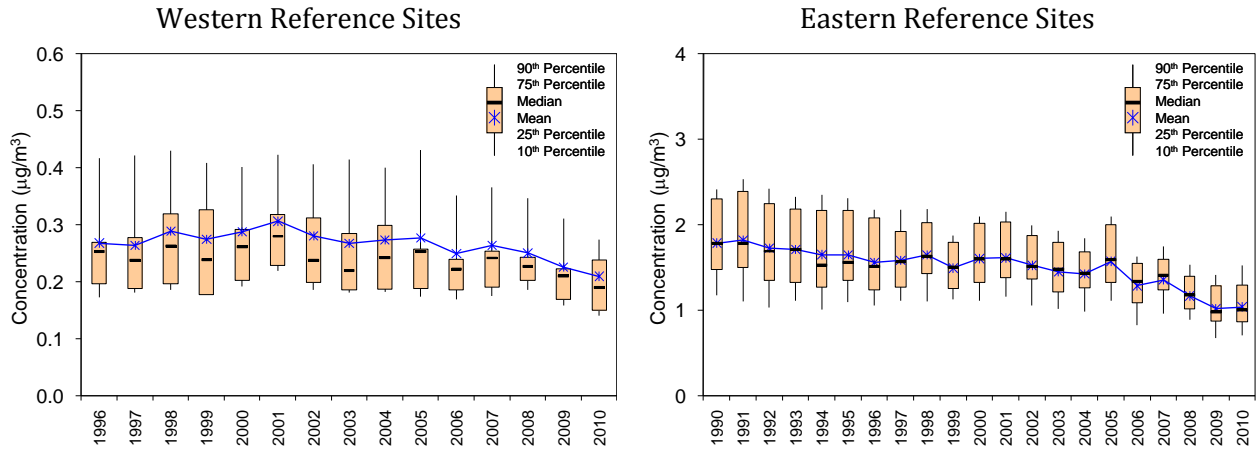
Speedwell, TN (SPD111)

Cloud Chemistry Measurements at Clingmans Dome, TN and Whiteface Mountain, NY

The Mountain Acid Deposition Program (MADPro) was initiated in 1993 to measure cloud water and its chemical constituents and their trends at mountaintop sites in the eastern United States. MADPro's main objective is to update the cloud water concentration and deposition data collected in the Appalachian Mountains during the National Acid Precipitation Assessment Program in the 1980s. MADPro measurements were conducted from 1994 through 1999 during the warm season (May through October) at three mountaintop sampling stations located at Whiteface Mountain, NY (WFM300); Clingmans Dome, TN (CLD303); and Whitetop Mountain, VA. A mobile manual sampling station also was operated at two locations in the Catskill Mountains in New York during 1995, 1997, and 1998. Measurements during the 2000 and 2001 sampling seasons were collected from WFM300 and CLD303. Beginning with the 2002 sampling season, cloud water measurements have been collected under CASTNET solely from the site at CLD303. The CLD303 site did not operate in 2008 because funding was unavailable. For the 2009 and 2010 sampling seasons, CLD303 was operated under the direction and funding of EPA and the Tennessee Valley Authority with infrastructure support provided by NPS. Since 2001, the WFM300 site has been operated by New York State Department of Environmental Conservation.

Data from CLD303 and WFM300 are available for the years 2000 through 2009 and are presented herein. Data from CLD303 for 2010 are presented also. Cloud liquid water content (LWC) and sulfate and nitrate concentrations for both sites are shown in Figures 2c through 2e, respectively.

LWC is the measure of the mass of water in a cloud and is typically expressed as grams per cubic meter (g/m^3) of air. LWC varies significantly with the cloud type. Figure 2c shows that seasonal LWC values at WFM300 were consistently higher than the seasonal LWC values at CLD303. The 10-year average (2000–2009) value of 0.528 g/m^3 at WFM300 was 46 percent higher than the 10-year average value of 0.285 g/m^3 at CLD303. Higher LWC values usually result in greater water deposition to surrounding ecosystems. Cloud pollutant deposition depends on pollutant concentrations in cloud water, LWC, and several other parameters.

Figure 2c Seasonal Cloud Liquid Water Content (g/m^3) Measured at CLD303 and WFM300
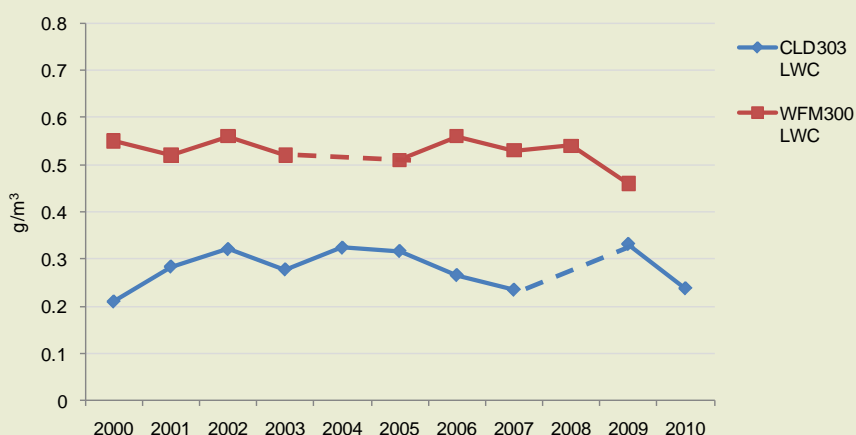
Cloud deposition estimates for CLD303 were provided by MACTEC (2011d). Sulfate and nitrate deposition estimates calculated using the CLOUD model declined by 82 percent and 78 percent, respectively. Cloud water deposition estimates are not currently available for WFM300.

However, Aleskic *et al.* (2009) presents data for 1994 through 2006. They estimated sulfate and nitrate depositions declined by 10 percent and 17 percent, respectively, at WFM300 over that time period.

Seasonal sulfate concentrations from 2000 through 2010 are presented in Figure 2d. Yearly variations in concentrations at both sites were considerable. Sulfate concentrations were consistently higher at CLD303 with a 10-year average seasonal concentration of 359.46 microequivalents per liter (µeq/L) compared to 208.85 µeq/L at WFM300. Sulfate concentrations were 42.9 percent higher at CLD303. Both sites experienced an overall downward trend from 2000 through 2009. The 2000–2009 decrease in sulfate concentrations was 60.8 percent at CLD303 and 38.1 percent at WFM300.

Figure 2d Seasonal Sulfate Concentrations (µeq/L) Measured at CLD303 and WFM300
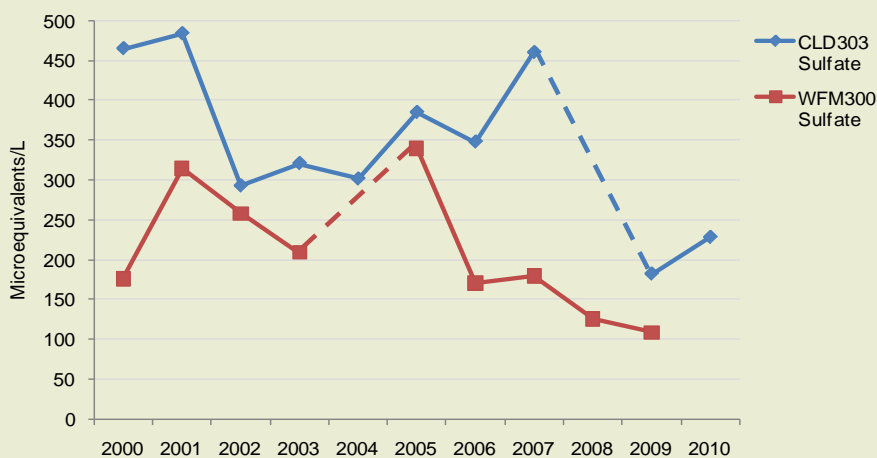
Seasonal nitrate concentrations for 2000 through 2010 are presented in Figure 2e. Nitrate concentrations were consistently higher at CLD303 with a 10-year average seasonal concentration of 139.71 µeq/L at CLD303 versus 83.76 µeq/L at WFM300. The CLD303 average was 40 percent higher than the WFM300 level. Overall downward trends were observed at both sites from 2000 through 2009. The decrease in nitrate concentrations from 2000–2009 was 58.4 percent at CLD303 and 34.0 percent at WFM300.

Figure 2e Seasonal Nitrate Concentrations (µeq/L) Measured at CLD303 and WFM300
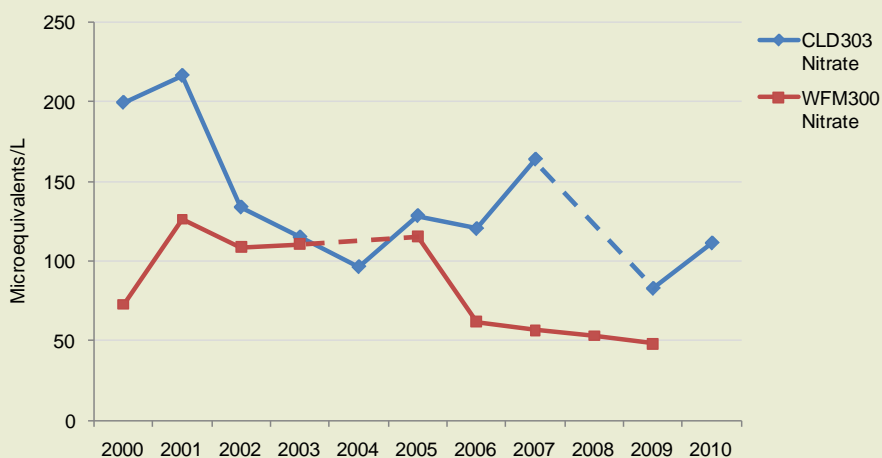
Chapter 3: Atmospheric Deposition

CASTNET was designed to provide estimates of the dry deposition of sulfur and nitrogen pollutants across the United States. CASTNET primarily uses a hybrid measurement-modeling approach to estimate dry deposition. The hybrid approach combines measured pollutant concentrations and modeled deposition velocities. The MLM is used to calculate hourly deposition velocities for each monitoring site based on meteorological measurements and information on the vegetative cover within 1 km of each site. Dry deposition is calculated as the product of the modeled deposition velocity and measured pollutant concentration. In order to improve estimates of wet deposition, the Parameter-elevation Regressions on Independent Slopes Model (PRISM) was selected to develop grids of precipitation based on data collected at NADP/NTN sites and on other related climate and terrain data. Total deposition is the sum of estimated dry and wet deposition. Three-year mean total sulfur fluxes aggregated over the eastern reference sites declined by 55 percent over the period from 1990–1992 to 2008–2010. Three-year mean total sulfur deposition estimated for 17 western sites declined by 28 percent over the period 1996–1998 to 2008–2010. Total nitrogen deposition estimates declined 32 percent for the eastern reference sites and 20 percent at the western reference sites. Dry deposition is responsible for a significant percentage of total deposition, especially in major emission source regions.

Gaseous and particulate sulfur and nitrogen pollutants are deposited to the environment through dry and wet atmospheric processes. A principal objective of CASTNET is to estimate the rate, or flux, of dry deposition from the atmosphere to sensitive ecosystems. Flux values are estimated as the product of measured concentration data and modeled dry deposition velocities. Wet deposition measurements were obtained from NADP/NTN. Wet deposition values used to estimate total deposition were based on a grid of PRISM-modeled precipitation amounts and gridded values of pollutant concentrations in precipitation. The concentrations were multiplied by precipitation rates to estimate wet fluxes. Wet flux data were interpolated to CASTNET sites and combined with CASTNET dry deposition data to estimate total deposition. Dry sulfur, total sulfur, and total nitrogen deposition decreased during 2010 at the eastern reference sites. Dry nitrogen deposition increased slightly in 2010 relative to 2009. The four deposition rates remained constant or increased slightly in 2010 at the western reference sites. Precipitation-weighted mean concentrations of atmospheric sulfur declined over the past 21 years at the eastern sites, and mean concentrations of atmospheric nitrogen in precipitation have declined slowly since 1998 at the same sites. However, nitrogen in precipitation increased slightly in 2010.

The MLM (Figure 1-5) simulates dry deposition processes. The MLM was summarized by Meyers *et al.* (1998) and Finkelstein *et al.* (2000). For this report, the MLM was run using CASTNET filter pack concentrations and meteorological measurements together with information on percent leaf-out of nearby vegetation, LAI, and surface conditions to

calculate deposition velocities for SO_2, HNO_3, O_3, and the particles, SO_4^{2-}, NO_3^-, and NH_4^+. The deposition velocities were assumed to be identical for all particle species. Deposition velocity values were calculated for each of the pollutant species for each hour with valid meteorological data for each CASTNET site for the entire period 1990 through 2010. Valid measurements of temperature, solar radiation, relative humidity, wind speed, and standard deviation of the wind direction (sigma theta) must all be available for the hour in order to estimate deposition velocity. Currently, the CASTNET measurement criteria for calculation of hourly fluxes and weekly concentrations/fluxes are approximately 70 percent completeness. In future reports, a substitution method developed by Bowker *et al.* (2011) will be used to complete missing V_d data by substituting long-term averages. This will result in nearly 100 percent data completeness. Updated dry and total deposition estimates will be presented in a separate report that supplements this 2010 Annual Report.

Using PRISM to Estimate Wet Deposition for CASTNET Sites

NADP/NTN operates wet deposition samplers to measure concentrations of pollutants in precipitation and to estimate the deposition rate of air pollutants removed by precipitation. NADP/NTN operates more than 200 monitoring sites across the United States, including monitoring stations at or near virtually every CASTNET site. Historically, wet deposition values were obtained from a grid of concentration and precipitation estimates derived from available NADP/NTN sites by using an inverse distance weighting (IDW) algorithm. Estimated concentrations were multiplied by the precipitation rates to obtain gridded estimates of wet deposition. Gridded wet deposition values were then interpolated to CASTNET sites. Utilization of this method resulted in precipitation and wet deposition rates equivalent to measured NADP/NTN values. Despite the equivalent precipitation and wet deposition values at NADP/NTN sites, the historical IDW approach produces interpolation errors, especially in regions with variable terrain and low geographic site density. The IDW approach is based simply on distances between measurements and does not include important data such as terrain elevation and slope and meteorological measurements.

PRISM was selected to produce grids of precipitation because the model provides more accurate estimates of annual precipitation values in areas with complex terrain. PRISM uses point precipitation measurements, a digital elevation model (DEM), and other geographic data to estimate annual, monthly, and event-based precipitation data. PRISM incorporates elevation, slope, and aspect ratio in the DEM with measurements of precipitation and temperature from several data sources to estimate precipitation on a 4-km grid resolution. Point precipitation measurement data used for PRISM are obtained from the National Weather Service Cooperative stations across the United States, Natural Resources Conservation Service snow telemetry (SNOTEL) sites in western states, and other local networks.

Unlike statistical models such as IDW and kriging, PRISM is not a system of equations but a coordinated set of rules, decisions, and calculations designed to emulate the decision-making process a climatologist uses when creating a map of climatic data. The model was developed and is operated by the PRISM Climate Group at Oregon State University. The Climate Group obtains, screens, and validates the model input data and produces the gridded precipitation values. In order to utilize the NADP/NTN measurements, the PRISM gridded data are adjusted to the point measurements from NADP. The first step in the adjustment process is to create a weighting factor (WF) grid where the center point is the relative difference between NADP/NTN and PRISM, and the influence of a point is inverse distance weighted up to 20 km. Each precipitation grid cell is adjusted by:

≤ 20 km from NADP/NTN site: PRISM value + (WF*NADP value)
> 20 km from NADP/NTN site: PRISM value

The adjustment process results in CASTNET estimates equal to NADP/NTN measurements at collocated sites (EPA, 2011e). The second step is to produce concentration in precipitation values for the PRISM grid. The concentration values are multiplied by the precipitation rates to obtain gridded wet deposition fluxes. The final step is to interpolate the gridded wet deposition fluxes to CASTNET monitoring locations.

The PRISM results indicate a significant improvement over the IDW estimates. Figure 3-1 presents scatter plots that show NADP/NTN measured precipitation rates compared to estimated IDW values in the left plot and measured NADP/NTN rates compared to estimated PRISM values in the right diagram. In Figure 3-1 the mean absolute relative percent difference (MARPD) calculated using a bootstrapping method for PRISM and NADP/NTN precipitation data is 2.5 percent (right panel) versus a MARPD of 39 percent between IDW-derived grid and NADP/NTN precipitation values. Figure 3-2 shows the PRISM precipitation grid for 2009, and Figure 3-3 depicts the relative percent difference (RPD) between grids creating using PRISM and NADP/NTN precipitation for 2007–2009.

Figure 3-1 Comparison to NADP Measurements

Measured NADP vs. Estimated IDW 1999–2009   Measured NADP vs. Estimated PRISM 1999–2009
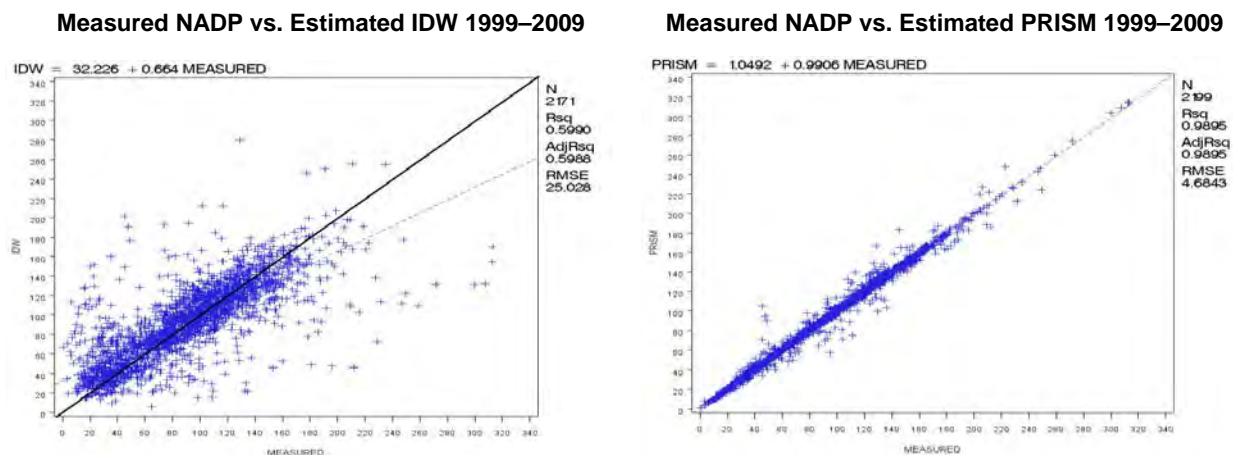
Figure 3-2 Resulting PRISM Precipitation Grid for 2009
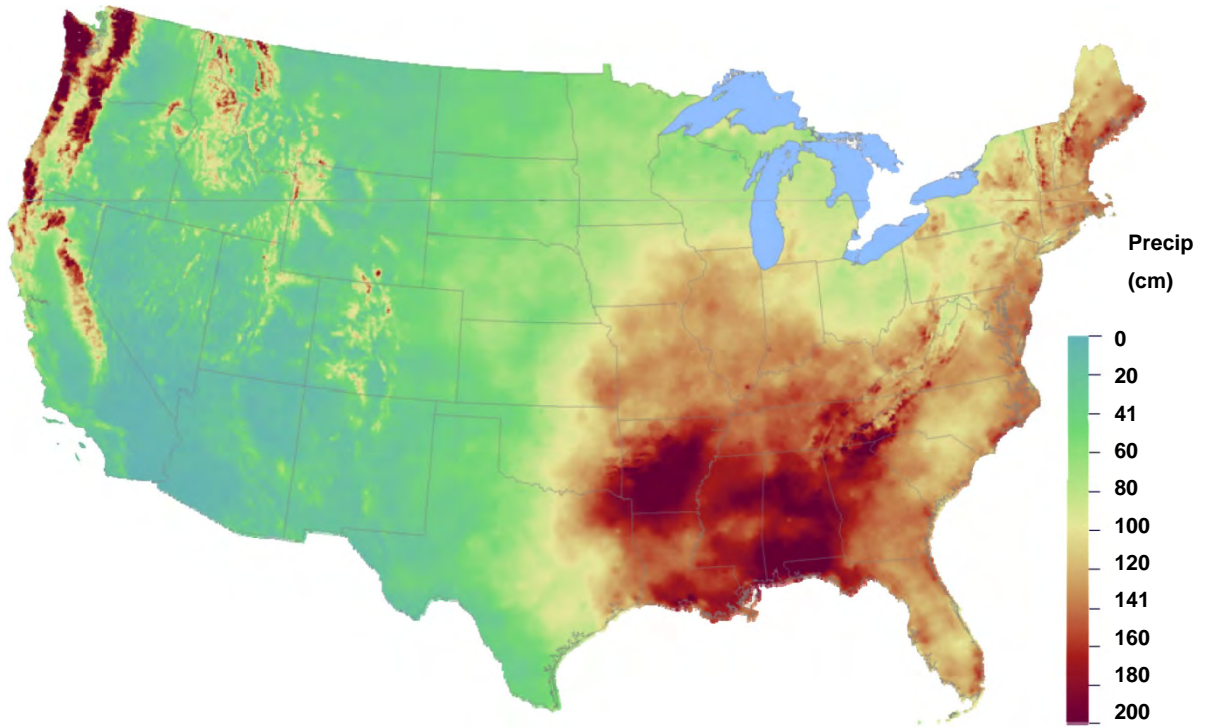
Source: EPA Clean Air Markets Division (2011e)

Figure 3-3 Relative Percent Difference in PRISM and NADP Precipitation Grids
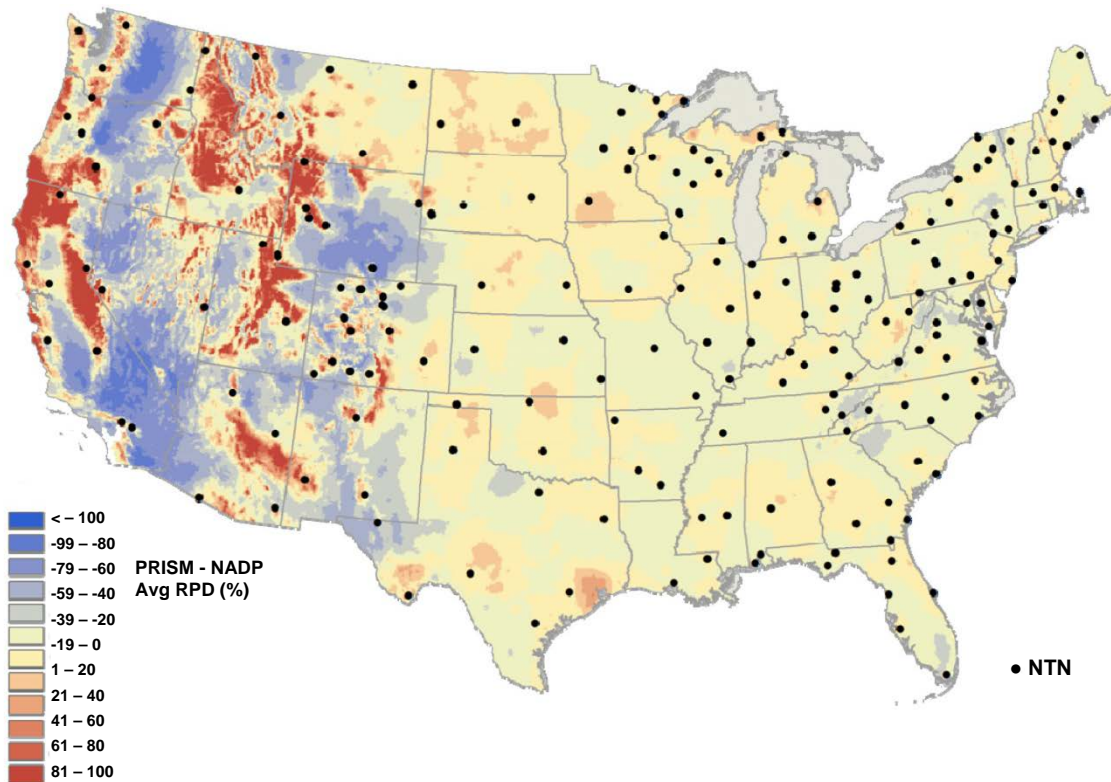
Source: EPA Clean Air Markets Division (2011e)

Sulfur Deposition

The MLM was run separately for SO_2 and SO_4^{2-}. The model calculations were summed to obtain the 2010 estimates of dry sulfur deposition (as S) shown on the map in Figure 3-4. The magnitude of a deposition rate is illustrated by the size of the circle. The map shows only seven CASTNET sites in five states with estimated fluxes greater than or equal to 3.0 kilograms per hectare per year (kg/ha/yr). These sites are located in Indiana, Kentucky, Ohio, Pennsylvania, and Virginia. The geographic extent of elevated deposition rates was about the same as 2009. The 3-state geographic average dry S deposition rate for Indiana, Ohio, and Pennsylvania was 2.9 kg/ha/yr compared to an average flux of 3.4 kg/ha/yr in 2009. The highest 2010 deposition rate was estimated for QAK172, OH with a flux of 5.5 kg/ha/yr compared to a flux of 5.4 kg/ha/yr in 2009. The highest estimated dry sulfur deposition rates coincided with the major SO_2 source region (Figures 1-6 and 2-1) and declined with distance. The dry deposition rates estimated for the western sites were all less than 1.0 kg/ha/yr with all but two sites with fluxes less than 0.5 kg/ha/yr.

Figure 3-4 Dry Sulfur ($SO_2 + SO_4^{2-}$) Deposition (kg/ha/yr) for 2010
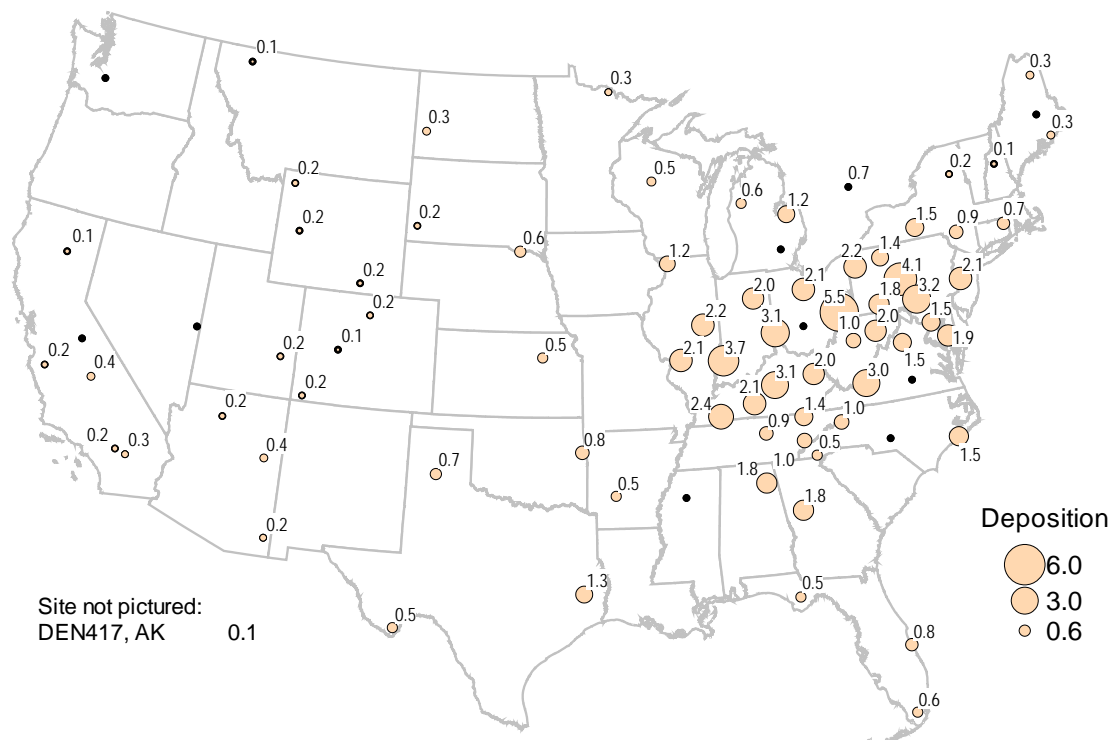
Wet deposition values used to estimate total deposition were based on a grid of PRISM-modeled precipitation amounts and gridded values of pollutant concentrations in precipitation. The concentrations were multiplied by precipitation rates to estimate wet fluxes. Wet flux data were interpolated to CASTNET sites.

A map of estimates of total sulfur deposition is given in Figure 3-5. The map was constructed by adding dry and wet deposition. The diameters of 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. Only three CASTNET sites in the states of Indiana, Ohio, and Pennsylvania had total (dry + wet) sulfur deposition fluxes greater than 7.0 kg/ha/yr in 2010. The highest total sulfur deposition rate was estimated for QAK172, OH with a value of 9.8 kg/ha/yr. The total sulfur deposition value for this site was 9.7 kg/ha/yr in 2009 and 17.2 kg/ha/yr in 2008. Total sulfur deposition at western sites was less than or equal to 2.0 kg/ha/yr, which was the estimate for PAL190, TX. 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 Mackville, KY (MCK131) to approximately a third at Beaufort, NC (BFT142).

Figure 3-5 Total (Dry + Wet) Sulfur Deposition (kg/ha/yr) for 2010
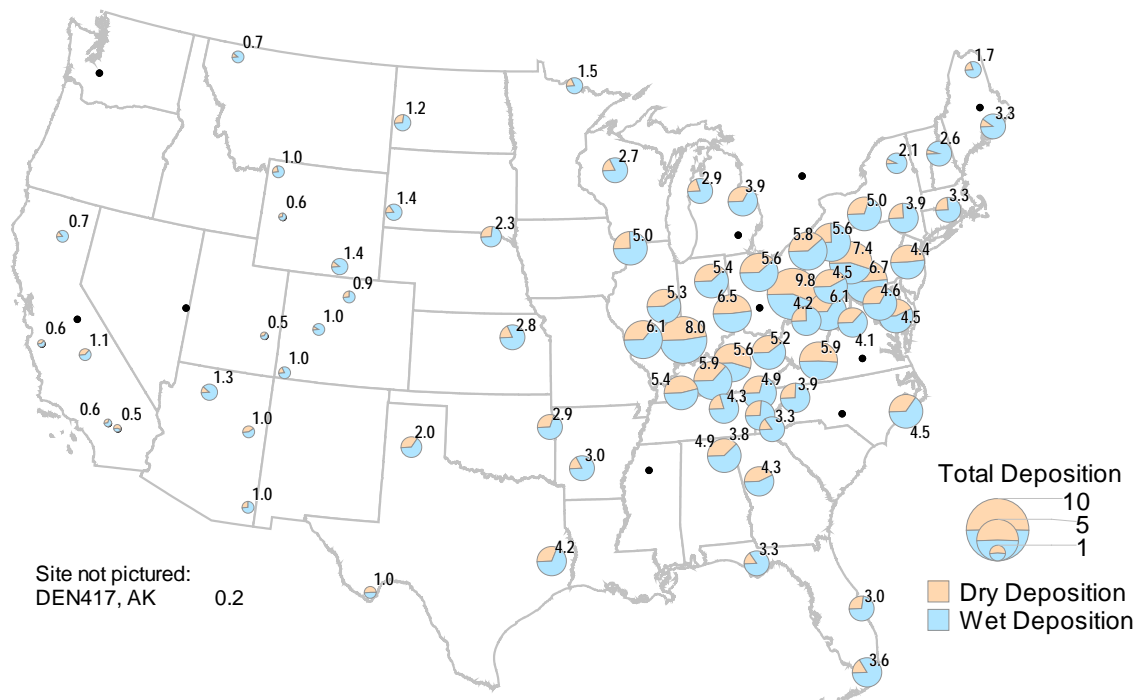
Figure 3-6 presents box plots that show the trend in dry sulfur deposition (as S) for the eastern (right side) and western (left side) reference sites. Figure 3-7 shows the trend in annual total (dry + wet) sulfur deposition (as S). The box plots were based on data obtained from the 34 CASTNET eastern reference sites (Figure 1-2) for the period 1990 through 2010 and from the 17 western reference sites (Figure 1-3) for 1996 through 2010. The y-axes on the two figures have different scales. Aggregated sulfur deposition declined considerably at the eastern and western reference sites over their respective periods. Overall, total sulfur deposition declined at the eastern reference sites from a 1990–1992 mean of 13.2 kg/ha/yr to a 2008–2010 mean of 6.0 kg/ha/yr, a 55 percent reduction. Total sulfur deposition declined at the western reference sites from a 1996–1998 mean of 1.2 kg/ha/yr to a 2008–2010 mean of 0.8 kg/ha/yr, a 28 percent reduction. The total sulfur flux for the western reference sites was somewhat higher in 2010 than in 2009.

Figure 3-6 Trend in Dry Sulfur Deposition (kg/ha/yr)
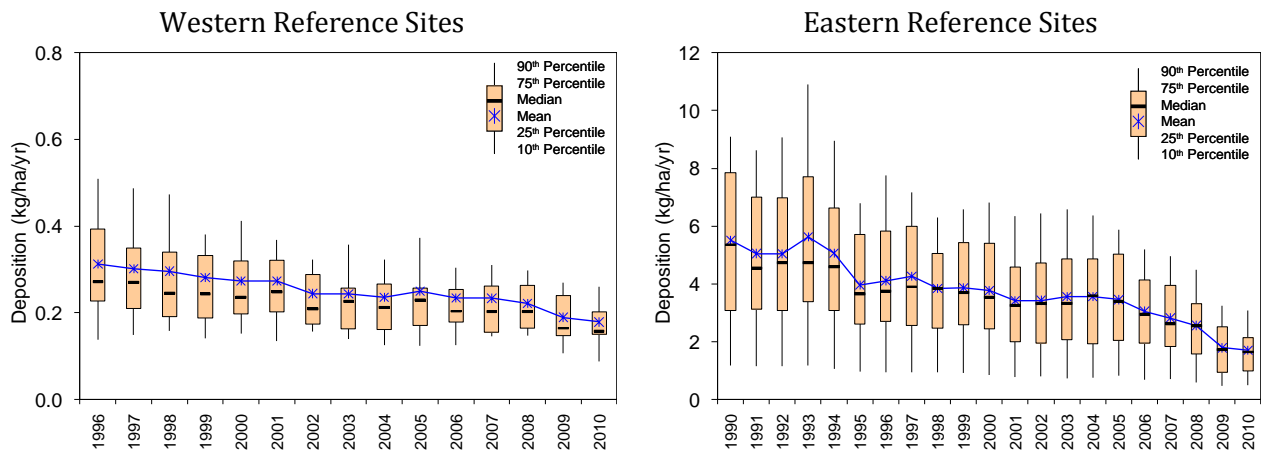
Figure 3-7 Trend in Total Sulfur Deposition (kg/ha/yr)
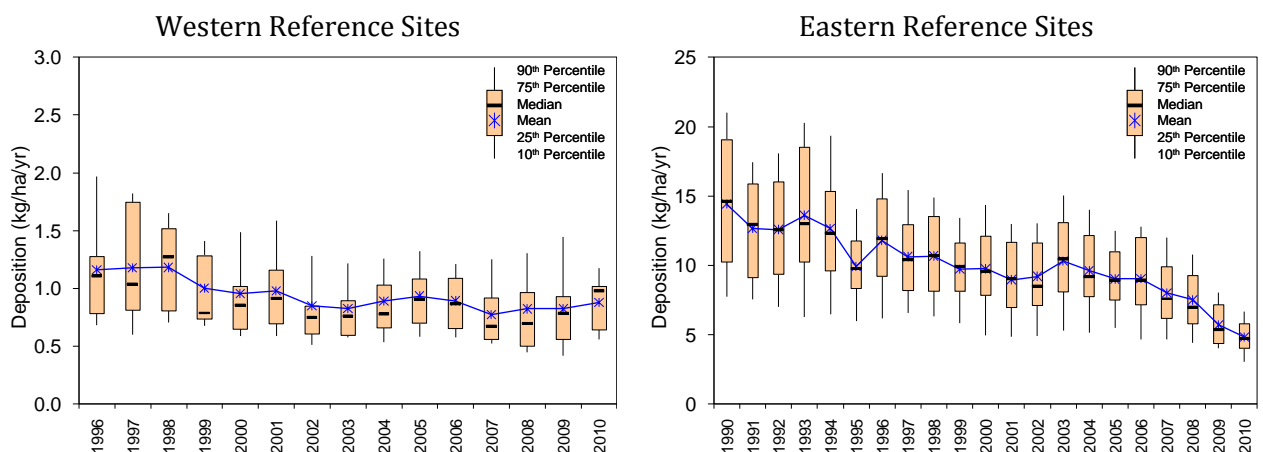
Figure 3-8 presents estimates of trends in dry, wet, and total deposition of sulfur (as S) for the eastern reference sites. The influence of precipitation on total sulfur deposition is illustrated by comparing the solid (top) line to the dotted blue line in Figure 3-8. The solid line shows total deposition, which depends on sulfur concentrations in precipitation and precipitation amounts. The dotted line shows concentrations in precipitation, which are independent of precipitation amount. The figure shows wet, dry, and total sulfur deposition have all declined significantly.

Figure 3-8 Trend in Sulfur Deposition (kg/ha/yr) with Concentrations in Precipitation [milligrams per liter (mg/l)]
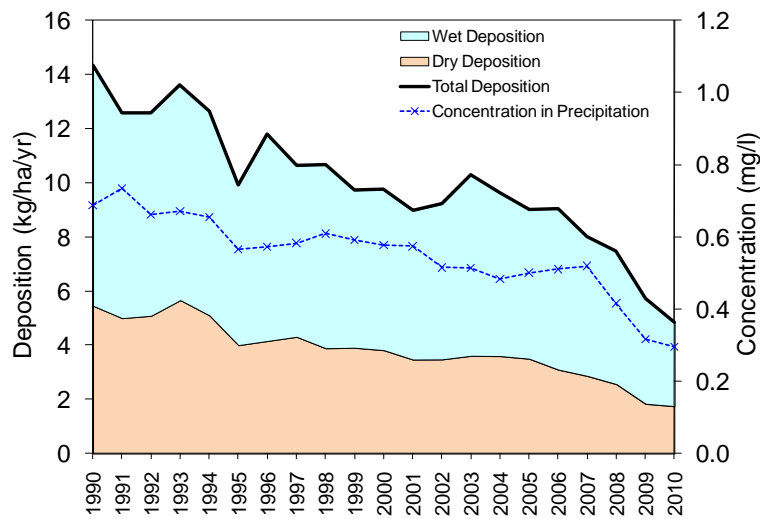
Crockett, KY (CKT136)

An Intercomparison of the CASTNET Multi-Layer Model and the CAPMoN Big-Leaf Model

CASTNET monitors air quality and deposition in cooperation with other national networks, including CAPMoN, which operates 33 monitoring sites in Canada and one in the United States. CASTNET and CAPMoN both operate filter pack samplers at Egbert, ON. Both networks combine modeled dry V_d with measured air pollutant concentrations to estimate dry deposition fluxes. CASTNET uses the MLM to simulate hourly values of V_d, and CAPMoN uses the Big-Leaf Model (BLM). The MLM uses measured meteorological conditions as model input. The BLM and other inferential models, which are used primarily as modules within regional chemical transport models, use meteorological input data produced by numerical weather prediction models. In particular, the BLM obtains meteorological input data from the Global Environmental Multiscale model. Recent studies (e.g., Flechard *et al.*, 2011) have shown that flux estimates produced by inferential models can be inconsistent because of differences in model-calculated V_d values.

Schwede and colleagues at EPA and Environment Canada (Schwede *et al.*, 2011) recently intercompared the MLM and BLM "to identify those model inputs and model algorithms that are responsible for the differences in the dry deposition velocity predictions of the gaseous trace species O_3, SO_2, and HNO_3." This section summarizes the work of Schwede and her colleagues. Their work is thoroughly described in the paper in *Atmospheric Environment* (Volume 45, Issue 6, February 2011).

Measured pollutant concentrations, modeled V_d values, and estimates of dry deposition flux from the joint CAPMoN and CASTNET site at EGB181, ON were compared for the period 2002–2007. The results, which are shown in Figure 3a, depict reasonably good agreement between SO_2 and HNO_3 concentrations measured at the two monitoring stations. The median percent differences between the two networks were -4.2 percent for SO_2 and -18.5 percent for HNO_3 (CAPMoN values are higher than CASTNET values). However, the estimated fluxes and V_d values were significantly different. The CAPMoN fluxes exceeded the CASTNET values with median percent differences of -53.6 percent for SO_2 and -46.6 percent for HNO_3. These large differences were primarily the result of differences in V_d values with higher values produced by the BLM. The median percent differences for V_d were -49.3 percent for SO_2 and -34.7 percent for HNO_3.

Estimates of deposition velocities from both the MLM and BLM were evaluated using field measurements (Meyers *et al.*, 1998; Finkelstein *et al.*, 2000), and the results showed good agreement between modeled values and field data. However, it was not possible to directly compare the MLM results with the BLM results because of averaging time and other limitations.

Both models have been used to provide estimates of the dry deposition of sulfur and nitrogen pollutants for ecological and critical loads assessments. The choice of model could have significant implications in estimating sulfur and nitrogen pollutant budgets, leading to different conclusions on the ecological assessments. For example, the use of the BLM could result in higher estimates of deposition relative to critical loads.

To identify the key model input data and model algorithms that affect V_d estimates, the BLM was inserted into the MLM framework so that measured meteorological data could be used as input to both models. The two models were run for four CASTNET sites that represent different land uses and climates. The four sites include BVL130, IL; SND152, AL; Sumatra, FL (SUM156); and EGB181, ON (see Figure 1-1 and Appendix A for site locations). After running the models for baseline conditions, the models were modified incrementally to allow the assessment of the contribution of each model algorithm to differences in modeled values of V_d. Table 3a summarizes the model runs.

Figure 3a Comparison of Weekly Values of Measured SO$_2$ and HNO$_3$ Concentrations, Estimated SO$_2$ and HNO$_3$ Fluxes, and Modeled SO$_2$ and HNO$_3$ Deposition Velocities at EGB181, ON (Schwede *et al.*, 2011)
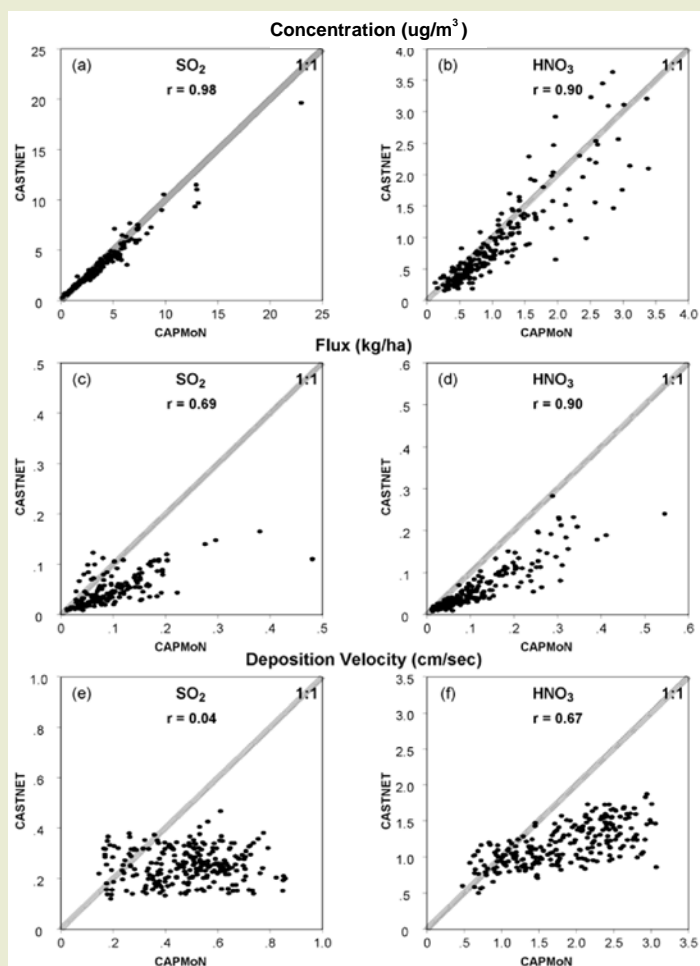
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Table 3a Model Configurations (Schwede *et al.*, 2011)

Run Name	Description
Base	Both MLM and BLM run in their native configuration using on-site meteorology from CASTNET
LAI	As with the Base run except MLM was modified to use the LAI from BLM
PP	As with the LAI run except BLM was modified to use the MLM plant parameters
Ra	As with the PP run except BLM was modified to use the MLM aerodynamic resistance
Fv	As with the Ra run except BLM was modified to use the MLM vapor pressure deficit function in the stomatal resistance calculation
Rs	As with the Fv run except BLM was modified to use the MLM water stress function in the stomatal resistance calculation
Rac	As with the Rs run except MLM was modified to use the BLM in-canopy aerodynamic resistance
Rg	As with the Rac run except MLM was modified to use the BLM ground (soil) resistance
Rcut	As with the Rg run except MLM was modified to use the BLM cuticular resistance

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Notes: PP = plant parameters   Rac = in-canopy aerodynamic resistance
        Ra = aerodynamic resistance   Rg = ground (soil) resistance
        Fv = vapor pressure deficit function   Rcut = cuticular resistance
        Rs = water stress function

Figure 3b illustrates the distributions of SO_2 V_d values for the four sites based on the model configurations listed in Table 3a. The box indicates the 25-75 percentile range, the X indicates the mean, the horizontal line indicates the median, the whiskers show the 5-95 percentile range, and the circles depict outliers. The effects of the different model configurations can be seen by comparing an individual configuration (e.g., Rcut for cuticular resistance) to the base case. For example, changing the MLM code to use the BLM value for the cuticular resistance had a significant effect in that much higher values of V_d were estimated for the MLM.

The study by Schwede *et al.*, (2011) illustrates some of the key differences in MLM and BLM. The differences in meteorological input data and the algorithm that simulates aerodynamic resistance have a strong influence on V_d for HNO_3. On the other hand, the differences in V_d estimates for SO_2 and O_3 are influenced strongly by differences in soil and cuticular resistances. Because these resistances have not been well measured or well understood, their formulation has to be considered further in both models. While some studies have compared the MLM and BLM V_d values to field data, the accuracy of the two models is not well understood. V_d values from both models will have to be compared to recent, independent, multi-year flux measurements in order to assess model accuracy.

Figure 3b Sulfur Dioxide Deposition Velocity Distributions for BVL130, EGB181, SND152, and SUM156 for Different Model Configurations (Schwede *et al.*, 2011)
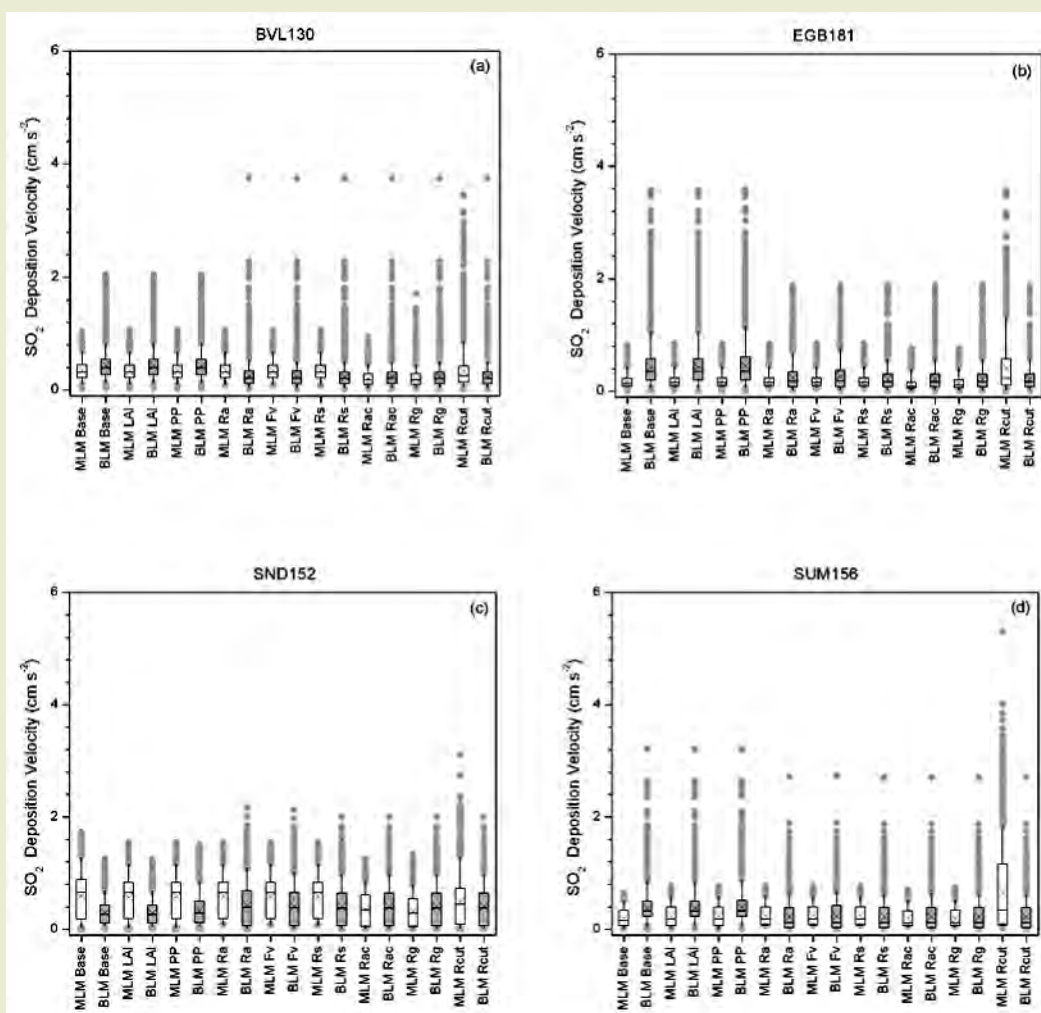
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Nitrogen Deposition

Figure 3-9 illustrates dry fluxes of nitrogen (as N) for 2010. These fluxes are the sum of fluxes of $HNO_3 + NO_3^- + NH_4^+$, based on the individual MLM simulations for the three species. A majority of CASTNET sites in the eastern United States had estimated dry nitrogen deposition rates greater than 1.0 kg/ha/yr. Five eastern and one western site had deposition rates greater than or equal to 2.0 kg/ha/yr. QAK172, OH and ARE128, PA had estimated dry nitrogen fluxes of 2.5 kg/ha/yr. The highest value for western sites was calculated for the CASTNET site in JOT403, CA with a dry nitrogen flux of 2.3 kg/ha/yr.

Figure 3-9 Dry Nitrogen ($HNO_3 + NO_3^- + NH_4^+$) Deposition (kg/ha/yr) for 2010
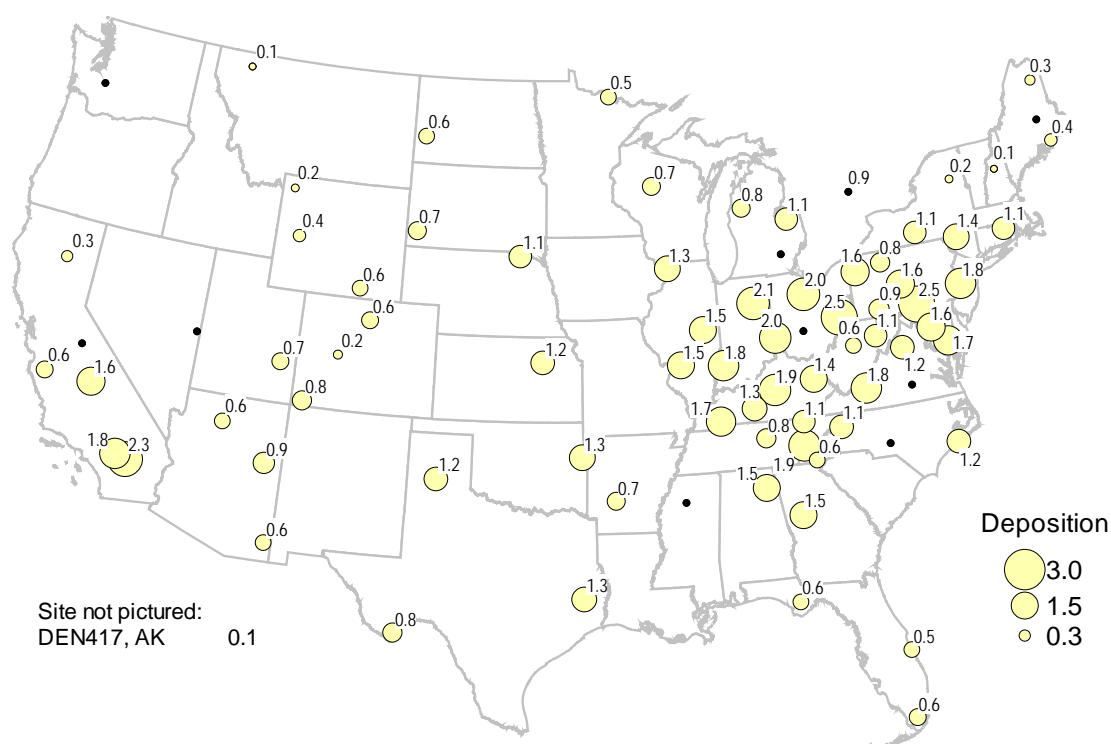
A map of total nitrogen deposition (as N) for 2010 is given in Figure 3-10. The map was constructed by summing the estimates of dry (light shading) and wet (dark shading) deposition. The figure shows that a majority of the eastern sites estimated deposition rates greater than 5.0 kg/ha/yr. Stockton, IL (STK138) recorded the highest total nitrogen flux (8.1 kg/ha/yr). Most of the western sites had estimated total nitrogen deposition rates below 3.0 kg/ha/yr. The CASTNET site at PAL190, TX had the highest total nitrogen flux for the western sites with an estimated flux of 5.1 kg/ha/yr. Six other western sites in California, Arizona, South Dakota, and North Dakota had estimated total nitrogen fluxes greater than 3.0 kg/ha/yr. The contributions of dry nitrogen deposition to total nitrogen were lower than the corresponding contributions of dry sulfur deposition. Dry nitrogen

deposition contributed less than 50 percent of total deposition in the East. On the other hand, dry nitrogen deposition contributed more than half of total nitrogen deposition at the two monitoring sites downwind of the Los Angeles in California, a region with elevated concentrations of nitrogen species and limited rainfall. Dry nitrogen deposition contributed 70 percent of the total nitrogen deposition at JOT403.

Figure 3-10 Total (Dry + Wet) Nitrogen Deposition (kg/ha/yr) for 2010
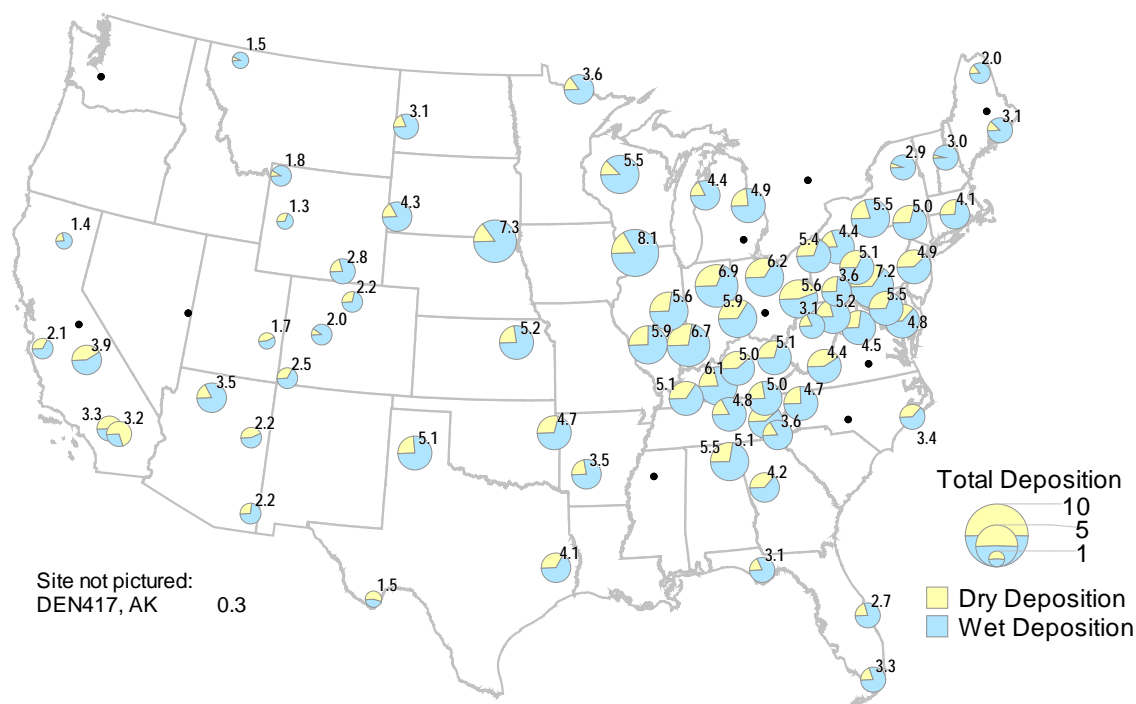
Figure 3-11 presents box plots that were constructed using data from the 34 eastern reference sites over the period 1990 through 2010 (right side) and 17 western reference sites for 1996 through 2010 (left side). The box plots show the trends in dry nitrogen deposition (as N). The box plots for the eastern sites in Figure 3-12 show a reduction in dry nitrogen deposition beginning in 1999 with a slight increase in 2010. Three-year mean fluxes declined from 2.2 kg/ha/yr for 1990–1992 to 1.3 kg/ha/yr for 2008–2010, a 41 percent reduction over the 21 years. The box plots for the western sites show a smaller 28 percent decline, a change from a mean of 0.9 kg/ha/yr for 1996–1998 to 0.6 kg/ha/yr for 2008–2010.

Figure 3-11 Trend in Dry Nitrogen Deposition (kg/ha/yr)
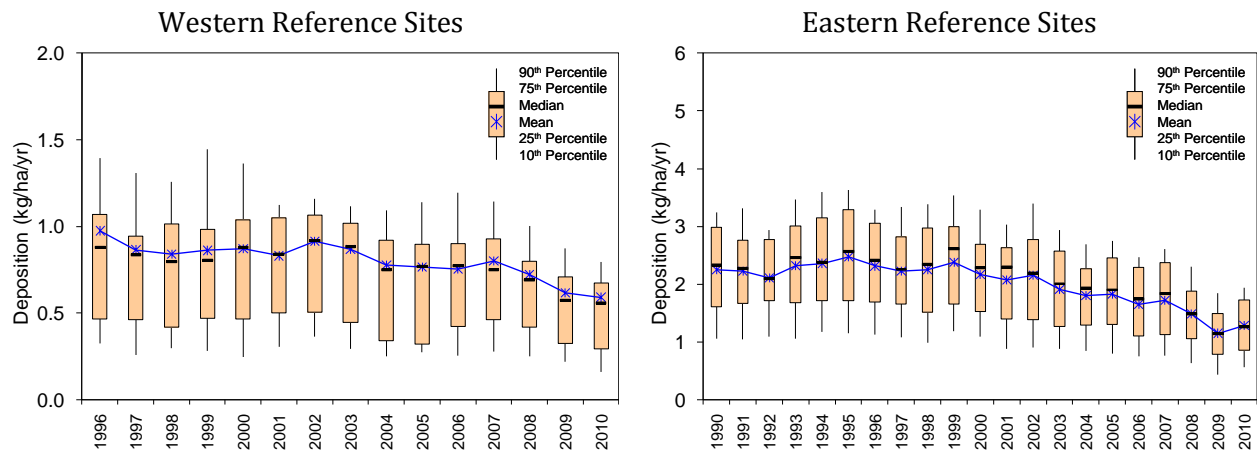
Figure 3-12 shows the trends in annual total (dry + wet) nitrogen deposition for the eastern (right side) and western (left side) reference sites. The figure suggests that total nitrogen flux in the eastern United States has decreased since 1996 with a substantial decline over the last five years. Total nitrogen flux for the western sites shows a relatively flat distribution with an increase in 2010. Estimates of trends in wet, dry, and total deposition of atmospheric nitrogen (as N) are presented in Figure 3-13 for the eastern reference sites only. The trend line (dotted) for precipitation-weighted mean nitrogen concentrations in precipitation shows an overall slow downward trend since 1998 with a slight increase in 2010. This trend line is reasonably representative of the effect of changes in NO_x emissions because it does not depend on precipitation amounts. Total nitrogen deposition declined 32 percent in the East over the 21 years and 20 percent for the aggregated western sites over the 15-year period.

Figure 3-12 Trend in Total Nitrogen Deposition (kg/ha/yr)
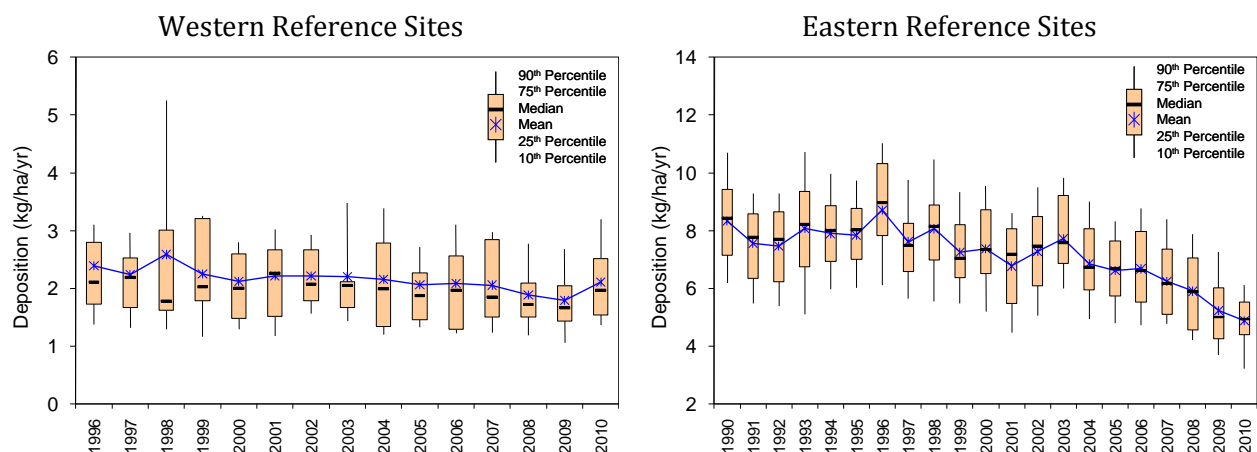
Figure 3-13 Trend in Nitrogen Deposition (kg/ha/yr) with Concentrations in Precipitation (mg/l)
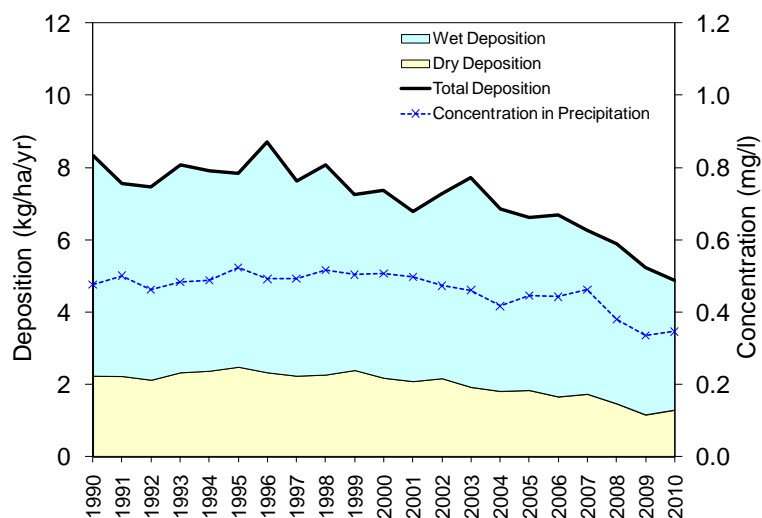
Estimates of Critical Loads in the Eastern United States

The critical load approach is an emerging assessment and regulatory tool that is used to determine the degree to which acidic deposition may be affecting the ecological health of surface waters. The recent EPA (2011d) review of the secondary NAAQS for oxides of nitrogen and oxides of sulfur explored the idea of a critical load-based approach for regulating these atmospheric oxides using an Aquatic Acidification Index (AAI). A critical load is a quantitative estimate of exposure to one or more pollutants below which significant harmful effects on specific sensitive elements of the environment do not occur according to present knowledge (Nilsson and Grennfelt, 1988). A critical load provides a benchmark against which to assess the extent to which a water body is potentially at risk due to current acidic deposition levels. If pollutant exposure is less than the critical load, adverse ecological effects (e.g., reduced reproductive success, stunted growth, or loss of biological diversity) are not anticipated, and recovery is expected over time if an ecosystem has been damaged by past exposure. A critical load exceedance is the measure of pollutant exposure above the critical load. This means pollutant exposure is higher than, or "exceeds," the critical load, and the ecosystem continues to be exposed to damaging levels of sulfur and nitrogen deposition.

This critical load assessment examined select lakes and streams within 20 km of 19 CASTNET monitoring locations in the eastern United States (Figure 3c). Critical loads were obtained for 545 lakes and streams from the National Critical Load Database (NCLD), developed in conjunction with the NADP Critical Loads of Atmospheric Deposition (CLAD) science committee. Critical loads were estimated using the Steady-State Water Chemistry (SSWC) mass-balance model, which estimates catchment weathering using the F-factor approach and surface water chemistry data (Henriksen *et al.*, 2002). The critical load in this study represents the amount of acidic deposition of S and N that a stream/lake's watershed could receive and still maintain an acid neutralizing capacity (ANC) of 50 μeq/L or higher, which supports a healthy aquatic ecosystem. Critical loads are expressed in terms of ionic charge balance as milliequivalents per square meter per year (meq/m^2/yr). Total sulfur and nitrogen deposition were determined for each lake or stream. Wet deposition for SO_4^{2-}, NO_3^-, and NH_4^+ were based on PRISM-corrected NADP estimates.

Dry deposition of SO_2, SO_4^{2-}, NO_3^-, HNO_3, and NH_4^+ were based on CASTNET modeled values for each CASTNET location. At CASTNET locations with AMoN monitors, dry NH_3 values were calculated using AMoN's air concentration and a deposition velocity from a 2002 CMAQ model run (EPA, 2011c). For CASTNET sites without AMoN monitors, dry NH_3 was determined using a dry NH_3 to wet NH_4^+ ratio (NH_3/NH_4^+) calculated for AMoN monitoring locations and applied to CASTNET locations.

Figure 3c shows critical load estimates for surface water acidification for select lakes and streams within 20 km of select CASTNET locations. Gray circles indicate CASTNET monitoring locations, and red and green symbols represent lakes or streams that exceed or do not exceed, respectively, their critical load for an ANC of 50 μeq/L. Graphs represent the 25 percentile critical load and total sulfur and nitrogen deposition for years 2008 through 2009 at CASTNET locations. On the graphs, dark and light red bars represent the maximum critical load (CLmaxS) of sulfur and the amount (CLminN) of nitrogen that is removed by the ecosystem, e.g., through immobilization and/or denitrification. Dark to light blue represents total wet and dry inorganic and organic nitrogen and sulfur deposition, respectively.

For the period from 2008 through 2009, 29 percent of the 545 modeled lakes and streams received levels of S and N deposition that exceeded the critical load (Figure 3c). Figure 3c also shows a comparison between the 25 percentile critical load for lakes and streams within 20 km of a CASTNET location and total average N and S deposition. For the 19 selected CASTNET locations, 8 received total S and N deposition greater than the 25 percentile critical load, indicating that at least a quarter of the modeled lakes or streams 20 km from the CASTNET locations exceeds total S and N deposition. Many of the eight locations, such as Laurel Hill State Park, PA (LRL117); Cranberry, NC (PNF126); SND152, AL; Cowetta, NC (COW137); Shenandoah National Park, VA (SHN418); OXF122, OH; BEL116, MD; and Pennsylvania State University, PA (PSU106), with exceedances are located in the central and southern Appalachian Mountains where many streams are still at risk of acidification despite significant reductions of emissions of sulfur and nitrogen oxides.

Springtime view of Bluestone River in West Virginia

Figure 3c Critical Load Estimates for Select Lakes and Streams
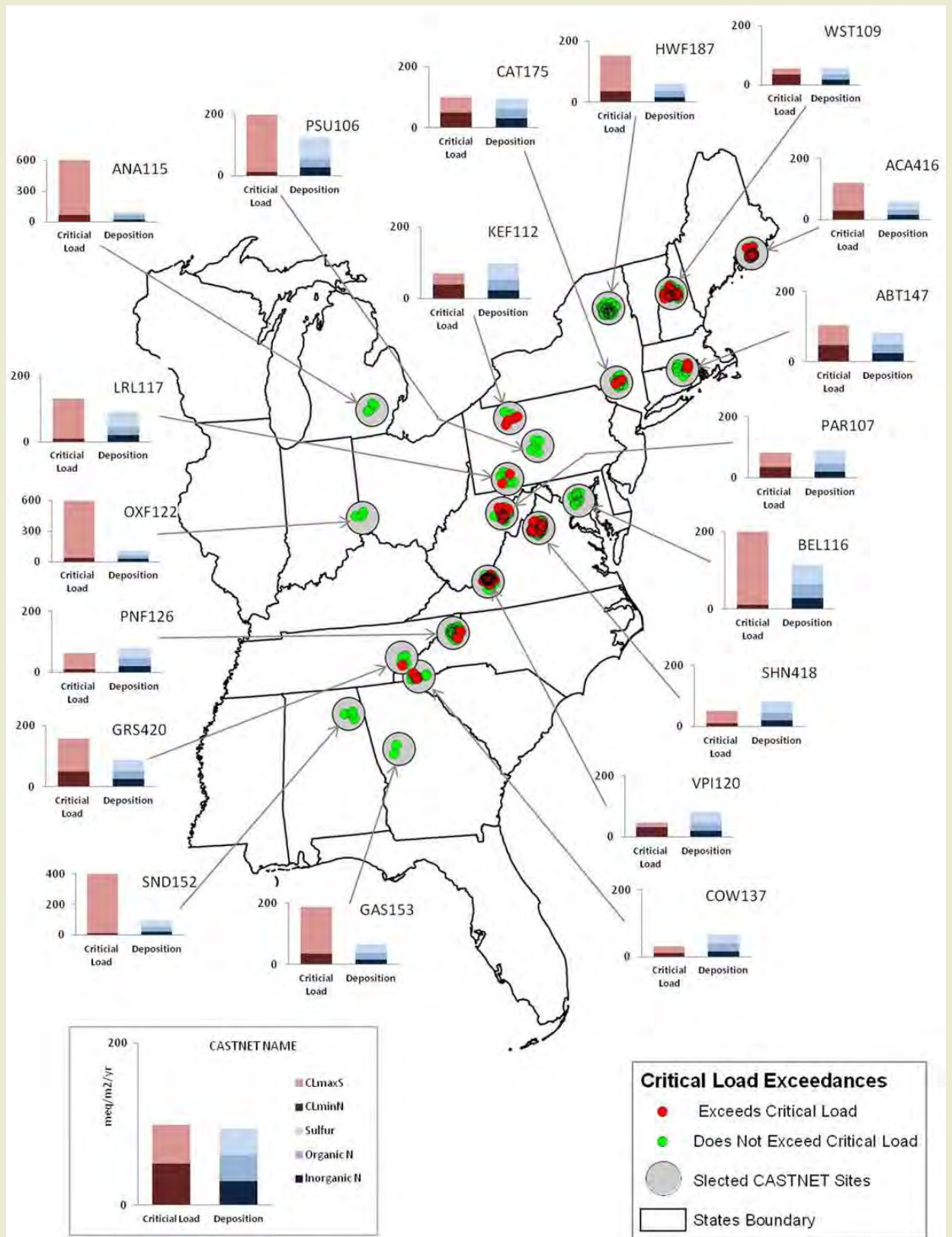
Source: J. Lynch

Chapter 4: Ozone Concentrations

CASTNET provides the primary platform for monitoring rural, ground-level O_3 concentrations in the United States and for providing information on geographic patterns in rural O_3 levels. CASTNET was not originally designed to operate as a regulatory network. However, as of May 2011, CASTNET O_3 monitoring systems comply with regulatory monitoring requirements, and data collected during the 2011 ozone season were submitted to the EPA Air Quality System. In this report, O_3 measurements collected during 2008–2010 were evaluated with respect to both the 1997 O_3 standard (EPA, 1997) of 0.08 parts per million (ppm) and the 2008 standard (EPA, 2008a) of 0.075 ppm. For the 2008–2010 period, only three eastern and four California sites recorded exceedances of the 0.075 ppm standard.

All but 3 of CASTNET's 84 sites operate an O_3 analyzer that measures hourly concentrations. CASTNET's geographic coverage of the United States provides data that are useful in terms of presenting information on geographic patterns in regional O_3 and for evaluating rural O_3 concentrations in the context of the O_3 NAAQS. The analyses presented in this chapter provide maps and examine trends in the annual fourth highest daily maximum 8-hour average (DM8A) O_3 concentrations measured at CASTNET sites. A map of 2010 W126 values is also presented. The concentration shading for the figures used in this chapter was prepared using the scales shown on each map. The NPS Air Atlas incorporates all O_3 monitoring reported to the EPA Air Quality System (AQS) plus the CASTNET O_3 measurements. Additional maps of O_3 concentrations can be viewed at http://science.nature.nps.gov/AirAtlas/AirAtlas0105/viewer.htm.

Ground-level O_3 is an air pollutant that can cause a number of human respiratory effects and damage to vegetation and ecosystems. It is formed in the lower atmosphere when VOCs and NO_x react in the presence of sunlight. Ozone is the main component of smog. Emissions from motor vehicle exhaust, industrial facilities, chemical solvents, gasoline vapors, and power plants are the major anthropogenic sources of NO_x and VOCs. Also, biogenic VOC emissions from trees and other vegetation contribute to O_3 formation in rural areas. Meteorological conditions play a significant role in O_3 formation. O_3 concentrations are generally higher in the warmer months because sunlight and hot weather accelerate its formation, but episodes of high O_3 concentrations can vary by region of country. For example, the highest O_3 concentrations measured in Maryland occur during summer and early fall while the highest O_3 concentrations measured in Wyoming occur during late winter and early spring. See the discussion on page 57 about Wyoming ozone data.

The DM8A O_3 standard can be used to assess the status and trends in rural O_3 levels in order to gauge the success of EPA emission reduction programs such as the NO_x SIP Call/NBP, CAIR, and now CSAPR. On May 1, 2009, the CAIR NO_x ozone season trading program began, replacing the NBP in states covered by the new program and requiring

further NO_x emission reductions from the power sector. Implementation of the NO_x emission reductions that were mandated by the ARP and other NO_x emission control programs have contributed to reductions in O_3 concentrations, especially in rural areas with elevated DM8A levels, because regional transport of pollutants contributes to O_3 formation. VOCs emission reduction strategies also have been successful in reducing higher, short-term O_3 concentrations in and downwind of urban areas.

The O_3 NAAQS are summarized in the following table. The primary standard is designed to protect public health, including the health of at-risk populations. The secondary standard is designed to protect public welfare and the environment, including sensitive vegetation and ecosystems. Both the primary and secondary O_3 NAAQS are given in terms of an O_3 concentration of 0.075 ppm and an 8-hour averaging time. O_3 concentrations collected in 2010 were also analyzed in terms of W126, a cumulative metric that sums weighted hourly O_3 concentrations during the O_3 season. For this report, W126 was calculated for the months of May through September. The highest of the rolling 3-month sums during the five months is the W126 value.

National Ambient Air Quality Standards for Ozone

	Primary Standard		Secondary Standard	
	Level	Averaging Time	Level	Averaging Time
Ozone[1]	0.075 ppm	8-hour[1]	0.075 ppm	8-hour[1]

Note: [1] To attain this standard, the 3-year average of the fourth-highest DM8A O_3 concentrations measured at each monitor within a specified area must not exceed 0.075 ppm or 75 ppb in practice (effective May 27, 2008; EPA, 2008a).

Rocky Mountain National Park, CO (ROM406/ROM206)

CASTNET's Transition to AQS Monitoring

Background

CASTNET was originally designed to provide information on geographic patterns in regional, rural O_3 levels. However, because of interest in rural O_3 concentrations by the regulatory and scientific communities, EPA directed MACTEC, now known as AMEC, to prepare the EPA-sponsored sites that measure O_3 concentrations to meet 40 CFR Part 58 monitoring requirements and to ultimately deliver CASTNET O_3 measurements to AQS for demonstration of compliance with NAAQS.

AMEC began this effort in July 2010, and installed the initial 19 sites prior to October 1, 2010. Data from these sites were evaluated, and protocols were refined prior to installing Part 58-compliant systems at the remaining sites. The remaining sites were upgraded in 2011. As of May 26, 2011, the effort was complete with compliant systems installed at 55 EPA-sponsored sites. In addition, NPS operates 24 AQS-compliant sites for a total of 79 AQS-compliant CASTNET sites.

Instrument upgrades were performed to support conversion to regulatory-compliant operating and reporting procedures. CASTNET monitoring equipment was upgraded to include new ozone analyzers, data loggers with improved data communication, and internal shelter temperature sensors. The new data loggers also provide system monitoring data that enable remote troubleshooting and optimization of operations. The data logger is programmed to control daily zero/span/precision checks for the O_3 analyzer. Zero air is used for the daily zero checks and as the dilution medium for the precision and span checks. The O_3 concentrations needed for the precision (90 ppb) and span (400 ppb) checks are produced by a separate on-site transfer standard.

Traceability of Standards

The on-site transfer standards initially carried Level 4 authority, which is three generations removed from a standard reference photometer (SRP) – see Figure 4a, which was taken from the EPA (2010c) Technical Assistance Document, *Transfer Standards for the Calibration of Air Monitoring Analyzers for Ozone*. In order to maintain the highest level of authority practical for the on-site transfer standards, AMEC subsequently opted to have all of its traveling transfer standards verified by a National Institute of Standards and Technology (NIST) SRP. Therefore, the traveling transfer standards now carry Level 2 authority. This facilitates the maintenance of Level 3 authority for all EPA-sponsored CASTNET on-site standards.

Figure 4a Ambient Air Ozone Traceability Scheme

Source: EPA (2010c)

Eight-Hour Ozone Concentrations

Figure 4-1 presents 3-year averages of the fourth highest DM8A O_3 concentrations for 2008–2010. During this period, 3-year averages of the fourth highest DM8A O_3 concentrations were greater than 75 ppb at three eastern sites and five sites in California. The eastern sites include Washington's Crossing, NJ (WSP144); BEL116, MD; and Great Smoky Mountains National Park, TN (GRS420). The five California sites include Yosemite National Park (YOS404), SEK430, Pinnacles National Monument (PIN414), CON186, and JOT403. Three California CASTNET sites measured concentrations greater than or equal to the 1997 NAAQS of 85 ppb. The California sites include SEK430, CON186, and JOT403. Three-year average concentrations were generally lower in 2008–2010 than in 2007–2009.

The 2008–2010 3-year average of fourth highest DM8A O_3 concentrations constitutes the current design value for achieving the DM8A O_3 NAAQS. A design value is a statistic that describes the air quality status of a given area relative to the level of the NAAQS. Design values change as each new 3-year database of monitored O_3 concentrations becomes available. Design values are typically used to classify nonattainment areas, assess progress towards meeting the NAAQS, and develop control strategies to achieve the NAAQS. For example, the value of 106 ppb at CON186 that was measured during 2008–2010 would have to be reduced to 84 ppb to achieve the level of the 1997 standard and to 75 ppb to achieve the level of the 2008 standard. Similarly, the concentration of 78 ppb at WSP144 would have to be reduced to 75 ppb to meet the 2008 NAAQS.

Figure 4-1 Three-year Average of Fourth Highest DM8A Ozone Concentrations (ppb) for 2008–2010
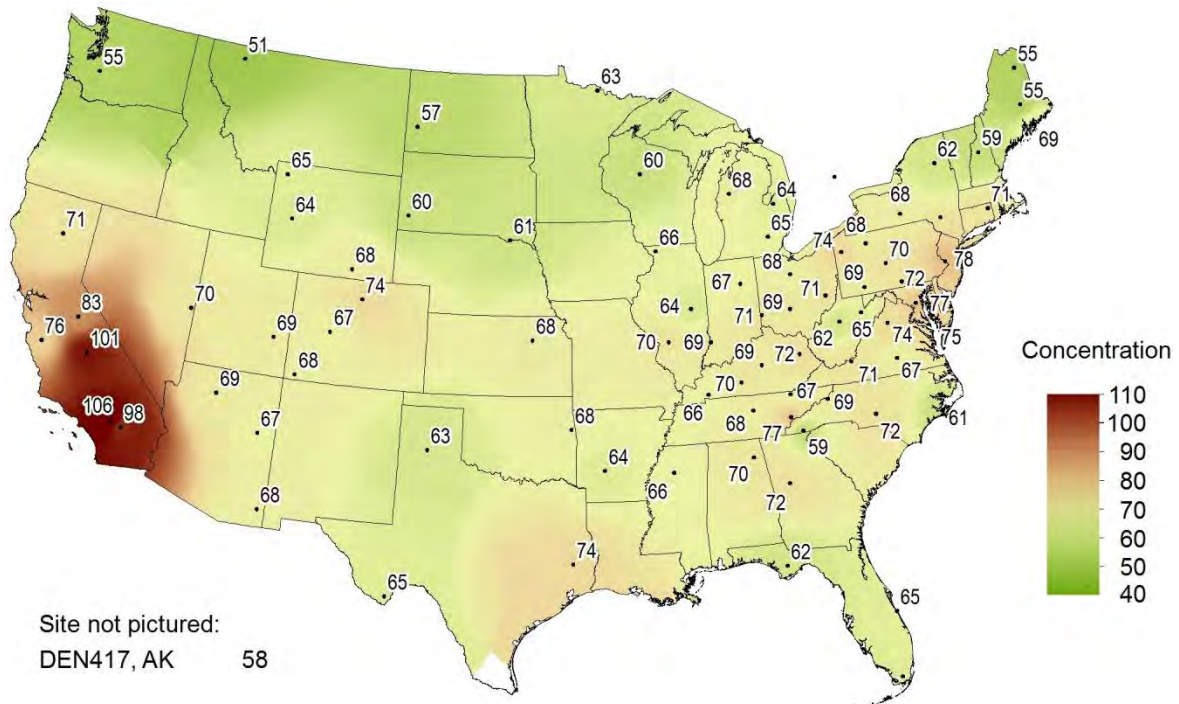
Figure 4-2 Three-year Average of Fourth Highest DM8A Ozone Concentrations (ppb) for 2000–2002
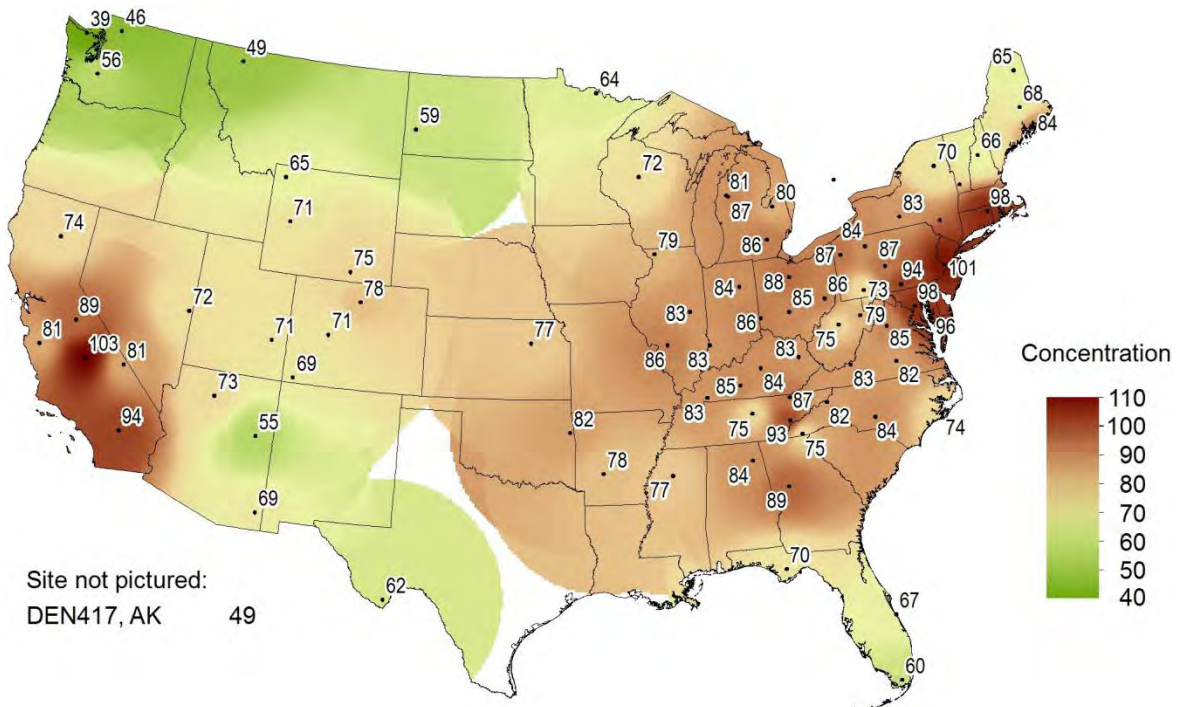
Three-year averages of the fourth highest DM8A O_3 concentrations for 2000–2002 are presented in Figure 4-2 for comparison with the 2008–2010 design values shown in Figure 4-1. The period 2000–2002 was selected because the NO_x SIP Call/NBP began in 2003 for the eastern United States. The changes in O_3 concentrations from 2000–2002 to 2008–2010 illustrate the effectiveness of the emission reduction programs. Based on the 84 ppb NAAQS level, 19 eastern and 3 California sites recorded 3-year averages greater than or equal to 85 ppb during 2000–2002. The regions with elevated DM8A O_3 concentrations were located along the East Coast from northern Virginia to Connecticut, extending almost to Maine, and in the central states of Pennsylvania, Ohio, Michigan, Indiana, and Illinois. Exceedances were also recorded in Kentucky, Tennessee, and the greater Atlanta area. The map in Figure 4-2 shows that most of the eastern sites measured O_3 concentrations greater than 75 ppb, the current standard. Five monitors in California and the site at Rocky Mountain National Park (ROM406) also recorded concentrations greater than 75 ppb. The period 2008–2010 represents a significant improvement in air quality.

Measurements of fourth highest DM8A O_3 concentrations during 2010 (Figure 4-3) were somewhat higher than 2009 but considerably lower than concentrations measured during the period 2000–2002. Seven eastern CASTNET sites measured concentrations above 75 ppb. These include WSP144; BEL116; GRS420; MK Goddard State Park, PA (MKG113); Quaker City, OH; OXF122, OH; and Crockett, KY (CKT136). Four sites in California plus ROM406, the primary of the collocated site at Rocky Mountain National Park, measured fourth highest DM8A O_3 concentrations greater than 75 ppb. The four California sites include YOS404, SEK430, CON186, and JOT403. Three of the four sites measured concentrations above 84 ppb. The monitor at CON186 measured the highest value (101 ppb) in the network during 2010.

Washington's Crossing, NJ (WSP144)

MK Goddard State Park, PA (MKG113)

Beltsville, MD (BEL116)

Figure 4-3 Fourth Highest DM8A Ozone Concentrations (ppb) for 2010
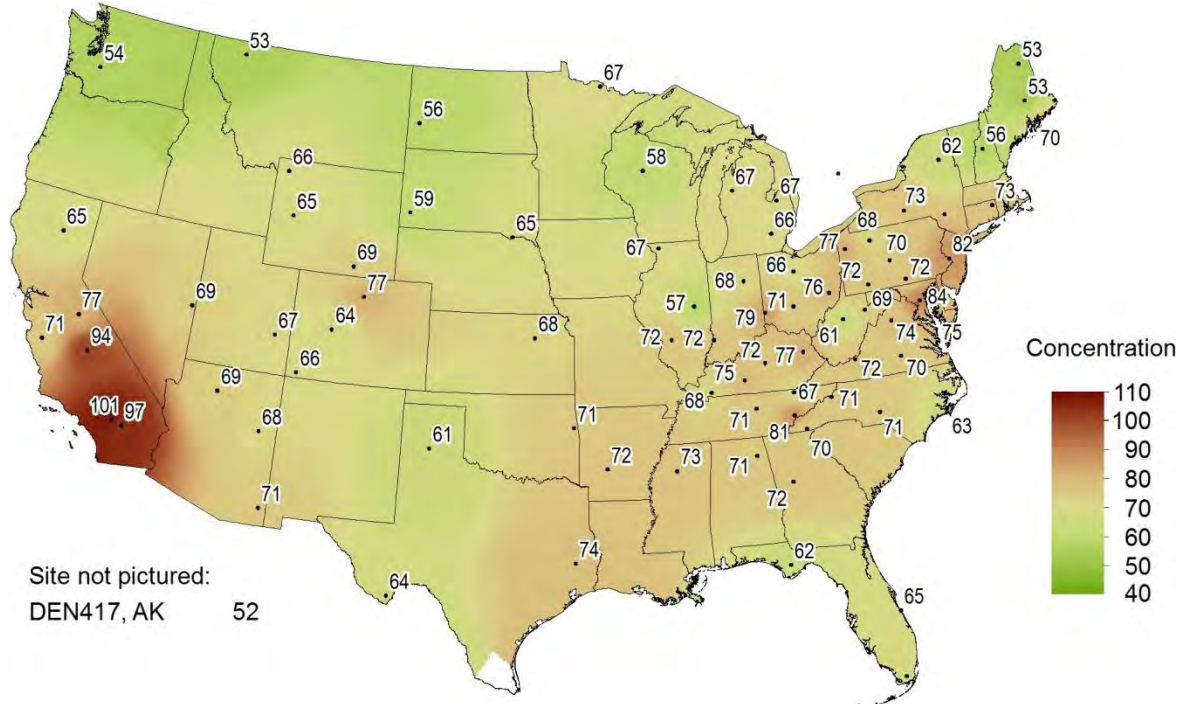
Figure 4-4 provides box plots depicting trends in fourth highest DM8A O_3 concentrations from the 34 CASTNET eastern reference sites (right side) and 17 western reference sites (left side). The eastern O_3 data show an overall reduction since 2002. However, the figure shows an increase in 2010. The mean aggregated value (69 ppb) for the eastern reference sites for 2010 was higher than the 2009 value of 64 ppb, which was the lowest in the history of the network. The concentrations in 2009 and 2010 represent a substantive improvement over the mean value of 90 ppb measured in 1998. The box plots constructed from the aggregated western O_3 sites show no trend. The 2008–2010 average of the fourth highest DM8A O_3 concentrations for the western reference sites was 69 ppb.

Converse Station, CA (CON186)

Figure 4-4 Trend in Fourth Highest DM8A Ozone Concentrations (ppb)
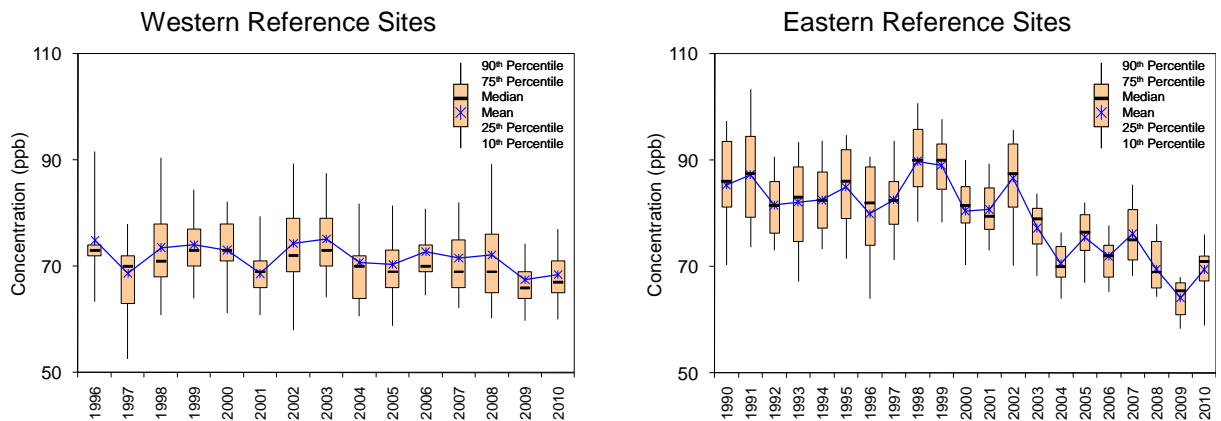
W126 Values for 2010

The W126 O_3 exposure index is a biologically-based, cumulative exposure index (Lefohn and Runeckles, 1987; EPA, 1996; 2006) for characterizing O_3 trends and relating vegetation yield reduction losses with O_3 exposure. Many researchers (e.g., Musselman *et al.*, 2006) concluded that both peak concentrations and cumulative effects are important in relating atmospheric O_3 to vegetation damage. Consequently, W126 was developed as a seasonal metric from the sum of weighted hourly values measured during the 12-hour daylight period during the O_3 season, with the higher hourly concentrations being weighted more heavily than lower concentrations (EPA, 2010b). In this report, W126 was used to characterize high concentrations over a seasonal, 3-month exposure period.

The W126 index is represented as the sum of all hourly O_3 concentrations, where each measured concentration is weighted by a function, w_i, to assign greater emphasis to the higher measured concentrations. This weighting function provides a weighting value that is unique for each hourly O_3 concentration. The weighting function, as described by Lefohn *et al.* (1988) is:

$$\text{Hourly Weighting} \; = \; w_i = \frac{1}{1 + 4403\exp(-0.126c_i)} \qquad \text{Equation 4-1}$$

Where:

w_i = weighting value for hourly concentration i, and

c_i = hourly concentration i in ppb.

Each hourly weighting value is multiplied by its corresponding hourly concentration. This product is summed over all valid hours to calculate the W126 exposure. Thus, the W126 exposure is:

$$\text{W126} = \sum_{i=1}^{n} w_i c_i \qquad \text{Equation 4-2}$$

Where:

        n = number of hours with valid O$_3$ concentrations.

The exposure unit is ppm-hours. For CASTNET W126 exposures are calculated using O$_3$ values measured during the 12 hours (n = 12) from 8:00 a.m. to 8:00 p.m. in the months of May through September of each year.

CASTNET hourly O$_3$ concentrations were used to calculate W126 values for 2010. First, the daily value for each site was calculated. The daily values were then used to calculate the monthly values for the months of May through September. The highest of the rolling 3-month sums for a consecutive 3-month period was the W126 value for each site.

W126 levels for 2010 are presented in Figure 4-5. The higher W126 values were measured in California and at western sites in high terrain. The highest W126 value (54.1 ppm-hour) was measured at SEK430, CA. Ozone concentrations measured at high elevation sites (MACTEC, 2003) typically show low variability from hour to hour because dry deposition and scavenging of O$_3$ by nitric oxide are low at night, resulting in the persistence of daytime values throughout the night. Nighttime dry deposition is low because shallow boundary layers typically do not form at elevated sites, and scavenging is low because little fresh nitric oxide is available to react with the existing O$_3$. The persistence of moderate O$_3$ concentrations at night produces steady exposure and high W126 levels.

Figure 4-5 W126 Values (ppm-hour) for 2010
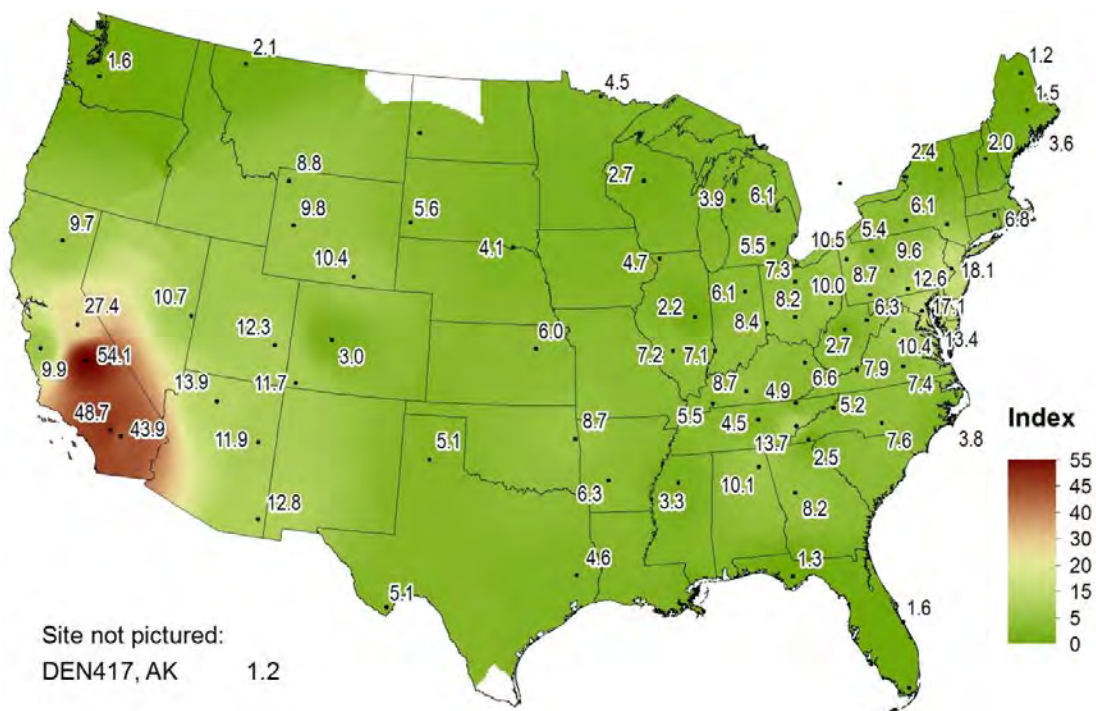
Air Quality Concerns in the Upper Green River Basin, WY

The Upper Green River Basin (UGRB) of southwest Wyoming has experienced substantive growth in gas and oil exploration, drilling, and production. Thousands of wells operate in the region of the Pinedale Anticline, located near the town of Pinedale, south to the Jonah field. These wells and related activities produce emissions of VOCs and NO_x to the atmosphere. Consequently, state and local government officials and the general population have expressed concern about O_3 levels, regional haze, and sulfur and nitrogen deposition. While this discussion focuses primarily on data collected through 2010, some data were available for 2011 and are included to provide current context.

Figure 4b Upper Green River Winter Ozone Study 2010 Monitoring Site Locations

Note: YEL408 and CNT169 locations are shown in Figure 1-1.

Elevated O_3 concentrations have been recorded at air quality monitoring stations (Figure 4b) in UGRB during late winter and early spring since 2005. DM8A O_3 concentrations above the 75 ppb NAAQS were measured in 2005, 2006, 2008, and 2011, typically during episodes of from one to six days. For example, during 2008, DM8A O_3 concentrations exceeded 75 ppb during six episodes. The higher DM8A concentrations exceeded 100 ppb. The fourth highest DM8A concentration during the principal period (2005–2010) was 101 ppb during 2008 at the Boulder, WY monitor. Table 4a was prepared by Meteorological Solutions, Inc. (MSI, 2010). The table lists average and maximum 8-hour O_3 concentrations for the six years 2005 through 2010 at monitors operated by the Wyoming Department of Environmental Quality (WDEQ) plus the CASTNET site at Pinedale, WY (PND165).

The PND165 CASTNET site is located northeast of the Town of Pinedale on a ridge with an elevation about 700 feet higher than the town's elevation in the UGRB. Although the O_3 concentrations recorded at PND165 were generally not as high as those measured in the UGRB, hourly concentrations have exceeded 80 ppb, and DM8A concentrations have exceeded 70 ppb. O_3 levels measured at the PND165 ridge site were higher during ozone episodes experienced simultaneously in the basin. Figure 4c shows trends in fourth highest DM8A O_3 concentrations and first quarter DM8A O_3 concentrations measured at the PND165 site from 1990–2010.

Table 4a Eight-Hour Monthly Average and Maximum Ozone by Year (2005–2010) at Selected WDEQ and CASTNET Sites

January	Average Ozone (ppb)				Maximum Ozone (ppb)			
Year	Jonah	Boulder	Daniel	PND165	Jonah	Boulder	Daniel	PND165
2005	35	NA	NA	45	78	NA	NA	60
2006	33	41	43	42	49	67	53	56
2007	27	43	40	41	57	71	53	52
2008	29	39	42	44	47	58	56	59
2009	24	34	37	41	52	55	48	51
2010	34	38	39	44	57	69	49	64
February								
2005	42	51	NA	50	98	89	NA	79
2006	39	48	49	47	93	71	82	65
2007	29	42	40	43	46	59	57	56
2008	40	54	50	49	102	122	76	82
2009	33	42	43	48	69	67	64	62
2010	44	51	46	46	54	62	52	59
March								
2005	40	48	NA	50	58	71	NA	68
2006	44	48	50	51	68	67	71	70
2007	32	44	40	46	44	65	55	60
2008	39	53	50	53	98	102	75	89
2009	39	46	43	49	63	70	67	82
2010	48	53	48	49	55	66	54	63

Note: NA = not available

Source: MSI (2010)

The time series (Figure 4c) of fourth highest DM8A O_3 concentrations shows no trend over the 21 years. However, despite the significant variability, the first quarter daily maxima increased over the period. The 2008–2010 average of the DM8A O_3 concentrations was 66 ppb compared to a 1990–1992 average of 57 ppb. The most recent years (2005, 2006, and 2008) with elevated O_3 concentrations at PND165 correspond to years with elevated first quarter DM8A O_3 concentrations in the UGRB. In short, although O_3 concentrations measured at PND165 were generally not as high as those observed in the basin, O_3 levels at PND165 increased when pollution accumulated in the UGRB.

Figure 4c Trends in Fourth Highest DM8A O_3 Concentrations and First Quarter DM8A O_3 Levels at PND165, WY
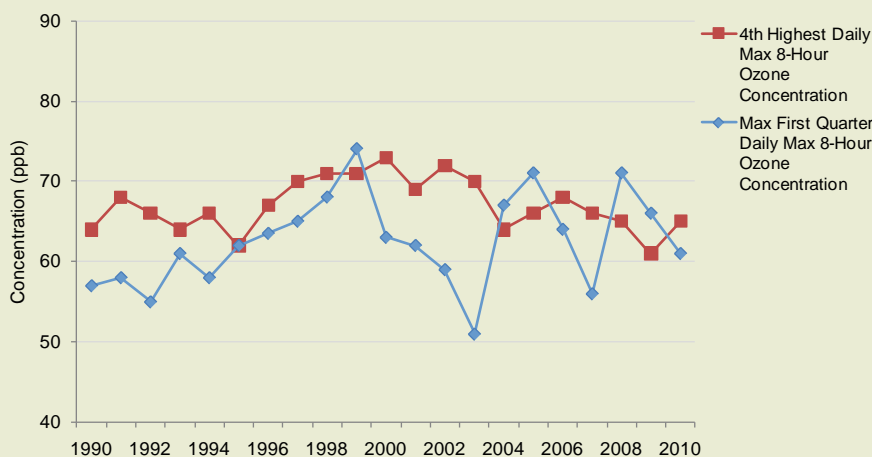
During the winters of 2007 through 2010, WDEQ sponsored a study (MSI, 2010; Environ, 2010) of ozone formation and corresponding meteorological conditions in the UGRB called the Upper Green River Winter Ozone Study (UGWOS).

Data from the 2007 through 2010 field studies can be obtained from the WDEQ Air Quality Division's monitoring information page: http://deq.state.wy.us/aqd/Monitoring%20Data.asp. The field campaigns measured 14 DM8A O_3 concentrations above the 75 ppb NAAQS in 2008. Thirteen exceedances were measured in 2011. The highest hourly concentrations exceeded 150 ppb, and the highest DM8A levels exceeded 120 ppb. Natural gas operators on the Anticline have effected significant emission reductions since 2008. VOCs emissions were reduced 50 percent and NO_x emissions 75 percent. VOCs emissions have declined by 20 percent and NO_x emissions by 25 percent throughout Sublette County, WY since 2008. The shale gas deposits in the UGRB are located in concentrated areas, which makes it possible to consolidate facilities and employ additional emission control technologies. However, elevated O_3 concentrations were measured in 2011 despite the emission reductions.

The occurrence of elevated O_3 concentrations in the late winter and early spring is unusual relative to the understanding that ozone is produced during sunny, hot, summertime weather. Data from the 2008 UGWOS were analyzed by Environ (2010) to understand the key characteristics of winter ozone episodes in the UGRB. Environ scientists (2010) analyzed air quality and meteorological measurements and developed a conceptual model of these episodes. The features (Environ, 2010) of the winter ozone episodes include:

♦ Presence of a strong, shallow ground-based inversion with warm temperatures aloft associated with a 700 millibar ridge. Extensive snow cover reduces daytime heating and maintains the inversion, which is typically less than 150 meters deep. The shallow mixed layer traps and concentrates pollutants near the surface.

♦ Northwest surface winds during the night and morning hours and southeast winds during afternoon, which result in recirculation of pollutants within the basin.

♦ Extensive snow cover that reflects incoming solar radiation and increases flux of ultraviolet (UV) radiation to levels comparable to those in midsummer. The increased UV radiation drives the photochemical reactions that produce ozone.

♦ High concentrations of precursor emissions produced by well pads and drill rigs in the basin.

♦ No significant transport of precursor emissions or ozone from upwind urban areas or other source regions.

O_3 concentrations measured at PND165 are lower than those measured in basin because the CASTNET site elevation is typically above the top of the ground-based inversion. However, O_3 levels at PND165 are higher than normal during the episodes that occur in the UGRB.

The unusual adverse weather conditions that produce elevated O_3 concentrations can occur at any time in the months of January through March in the UGRB, albeit infrequently. Twenty-seven days in the last four years experienced high daily DM8A O_3 concentrations.

Data from PND165 also provides information on changes in sulfur and nitrogen pollutant concentrations over the period 1990 through 2010 (Figures 4d and e). The figures show annual and first quarter mean SO_2 and total nitrate concentrations. SO_2 concentrations have declined over the 21 years, and total nitrate concentrations show an overall increase with interannual variability.

Figure 4d Trend in Annual Mean Atmospheric Concentrations of SO_2 and Total NO_3^- at PND165, WY
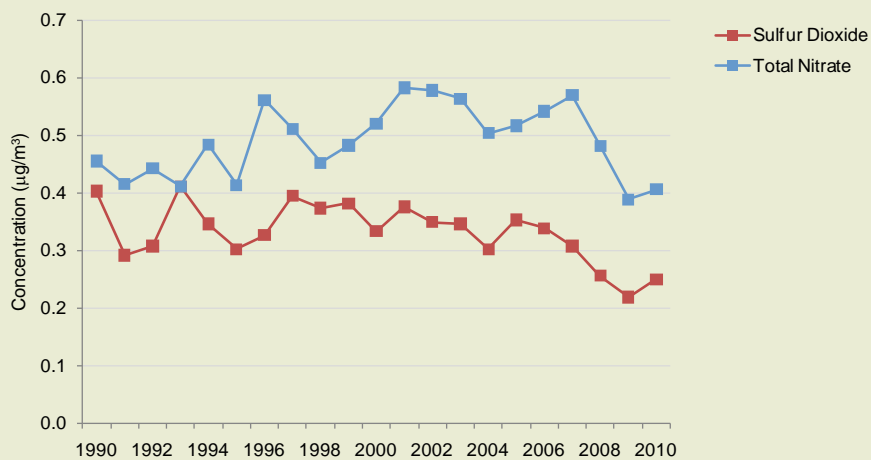
Figure 4e Trend in First Quarter Mean Atmospheric Concentrations of SO_2 and Total NO_3^- at PND165, WY
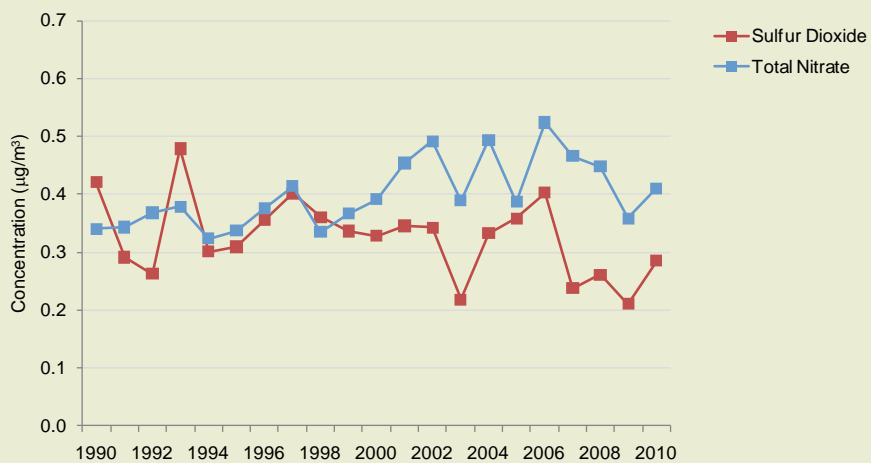
Chapter 5: Data Quality

CASTNET measurements and supporting activities are assessed routinely in order to provide high-quality information to meet data quality objectives (DQO). DQO are evaluated using data quality indicators (DQI) such as precision, accuracy, and completeness. Measurements taken during 2010 and historical data collected over the period 1990–2009 were analyzed relative to DQI and their associated metrics. These analyses demonstrate that CASTNET data can be used with confidence and that CASTNET continues to produce information of the highest quality.

The CASTNET 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 2010 QA program elements are documented in the CASTNET Quality Assurance Project Plan (QAPP), Revision 6.0 (MACTEC, 2010c). The QAPP is comprehensive and includes standards and policies for all components of project operation from site selection through final data reporting. Sections on field measurements, chemical analysis of field samples, data management, and assessments and response actions are included. Standard operating procedures (SOPs) for all aspects of CASTNET operations are provided in the appendices.

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 2010 data were analyzed and compared with historical data collected during the period 1990 through 2009. The information in this report is supplemented by analyses that are discussed in quarterly CASTNET Quality Assurance Reports (MACTEC, 2010b; 2010e; 2010f; 2011b). These QA reports are produced four times per year with the fourth quarter report including an annual summary.

Precision

Exposed Filter Concentrations

Figure 5-1 provides a bar chart in which the bars represent precision estimates for five CASTNET filter pack pollutants. Precision is expressed as MARPD. Table 5-1 lists the precision and accuracy criteria for laboratory filter pack measurements.

Figure 5-1 Historical and 2010 Precision Data for Atmospheric Concentrations
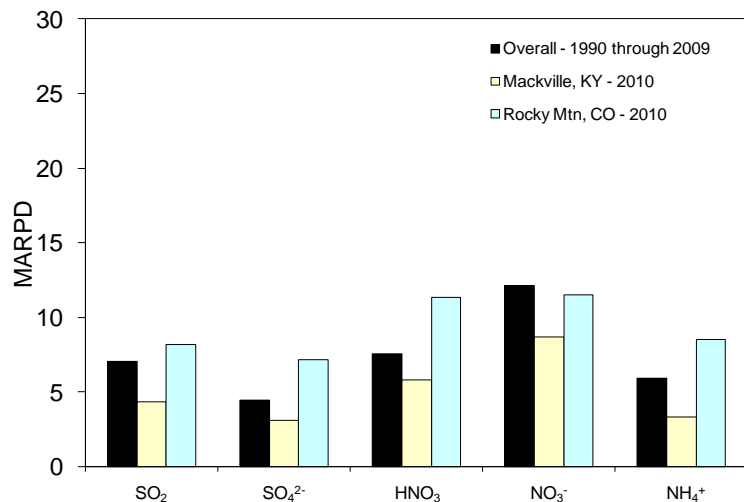
Table 5-1 Data Quality Indicator Criteria for CASTNET Laboratory Measurements

Analyte	Method	Precision[1] (MARPD)	Accuracy[2] (%)	Nominal Reporting Limits mg/l	Nominal Reporting Limits µg/Filter
Ammonium (NH_4^+)	AC	20	90 – 110	0.020*	0.5
Sodium (Na^+)	ICP-AES	20	95 – 105	0.005	0.125
Potassium (K^+)	ICP-AES	20	95 – 105	0.006	0.15
Magnesium (Mg^{2+})	ICP-AES	20	95 – 105	0.003	0.075
Calcium (Ca^{2+})	ICP-AES	20	95 – 105	0.006	0.15
Chloride (Cl^-)	IC	20	95 – 105	0.020	0.5
Nitrate (NO_3^-)	IC	20	95 – 105	0.008*	0.2
Sulfate (SO_4^{2-})	IC	20	95 – 105	0.040	1.0

Note: [1] This column lists precision goals for both network precision calculated from collocated filter samples and laboratory precision based on replicate samples.

[2] This column lists laboratory accuracy goals based on reference standards and continuing calibration verification spikes. The criterion is 90-110 percent for ICP-AES reference standards.

AC = automated colorimetry
µg/Filter = micrograms per filter
* = as nitrogen

Historical (1990 through 2009) data for all 11 collocated site pairs operated over the history of the network and the 2010 data for the current collocated sites at Mackville, KY (MCK131/231) and Rocky Mountain National Park, CO (ROM406/206) are provided in Figure 5-1. The two sites at Rocky Mountain National Park are operated independently. ROM206 is operated on behalf of EPA and ROM406 on behalf of NPS. Trace cations and Cl^- are excluded from Figure 5-1 but are shown later in Figure 5-2. The historical results vary from just over 4 percent for particulate SO_4^{2-} to more than 12 percent for particulate NO_3^-. The historical MARPD results and the MARPD values for 2010 met the 20 percent criterion for the CASTNET filter pack measurements shown in Table 5-1. The precision of NO_3^-

measurements was consistently worse than for the other analytes, possibly because NO_3^- concentrations include sampling artifacts.

The 2010 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 parameters and met the criterion of 20 percent. The 2010 results for ROM406/206 showed better precision than historical results for NO_3^-. All the parameters met the 20 percent criterion. The MARPD results were higher for ROM406/206 because of lower concentrations measured at this site. Overall, the filter pack precision estimates for 2010 were somewhat higher than the 2009 results.

Historical and 2010 precision statistics for four metal cations and Cl^- are summarized in Figure 5-2. The historical MARPD statistics for both MCK131/231 and ROM406/206 met the DQI criterion of 20 percent. The 2010 precision results for four of five ions were reasonable, and met the criterion. The MARPD values for K^+ exceeded the DQI criterion at ROM406/206. The 2010 precision results were about the same as for 2009.

Possible sources for the suspected intermittent K^+ contamination of filters used for filter packs and filter blanks were investigated during 2010. Audits of all stages of handling procedures (e.g., filter pack packing and unpacking, extraction and analysis, and impregnation of the potassium carbonate filters) indicated that SOPs are followed, and contamination is not likely to be introduced by current handling methods. Additionally, the reagents used were checked and verified to be stored properly. Recent investigations have included verifying that adequate time is allowed for drying freshly impregnated cellulose filters and reviewing sample intake coding. Review of the intake coding procedures resulted in clarification of the defining rule for coding filters as being excessively wet. A filter with visible wetness is to be coded as showing "excessive wetness." The room where filters are handled is now isolated during handling procedures. Only filter packs and filter blanks have showed evidence of contamination. Method blanks, filter acceptance test results, and all other quality control (QC) samples remained within established limits. The next investigation involved the potential for volatization and migration of the cellulose filter impregnation solution (K_2CO_3) during shipping in periods of hot weather. The contamination correlates with high temperatures in the shipping tube and primarily occurs during the warmest months and in warmer regions. AMEC has evaluated other carbonates for impregnation of the cellulose filters. Carbonate salts completely free of target analytes are cost-prohibitive.

Table 5-2 summarizes 2010 precision results by quarter for the two sets of collocated sites. See the 2010 Quarterly Data Reports (MACTEC, 2010a; 2010d; 2011a; 2011c) and QA Quarterly Reports (MACTEC, 2010b; 2010e; 2010f; 2011b) for discussions of quarterly precision data.

Figure 5-2 Historical and 2010 Precision Data for Cation and Cl⁻ Concentrations
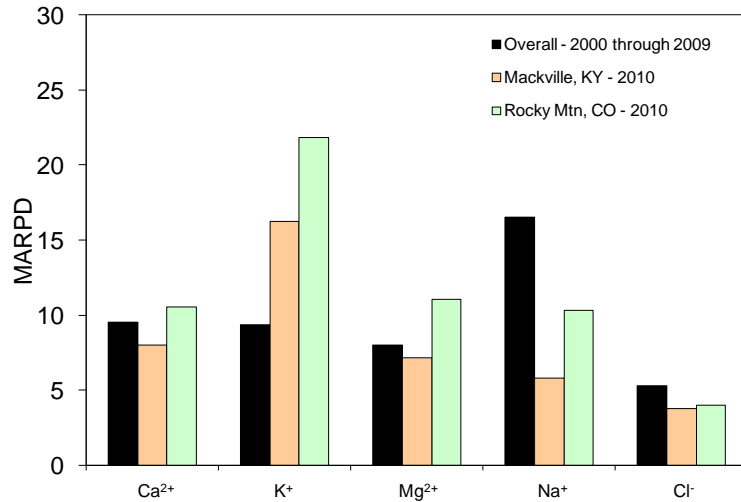
Table 5-2 Collocated Precision Results (MARPD) for 2010 Filter Pack Data by Quarter

Site Pairs	SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	HNO_3	SO_2	Total NO_3^-
MCK131/231, KY											
Quarter 1	3.62	7.23	4.65	9.32	9.18	6.06	18.43	9.38	6.08	3.80	5.99
Quarter 2	2.52	13.57	2.54	6.38	4.91	4.82	15.96	0.90	4.15	4.42	4.78
Quarter 3	2.80	6.68	2.77	6.19	5.61	5.39	21.87	0.00	7.80	6.36	5.65
Quarter 4	3.49	7.21	3.31	10.01	8.87	6.98	8.77	4.81	5.12	2.74	5.16
2010	3.11	8.67	3.32	7.97	7.14	5.81	16.26	3.77	5.79	4.33	5.40
ROM406/ROM206, CO											
Quarter 1	14.15	12.93	16.92	16.49	16.76	15.36	27.85	3.09	12.01	10.12	12.83
Quarter 2	5.69	8.03	6.40	10.91	12.11	9.65	20.43	6.61	7.83	8.58	5.12
Quarter 3	4.80	9.06	3.83	5.47	7.76	6.72	19.33	3.18	14.25	7.72	11.33
Quarter 4	4.11	16.07	6.88	9.32	7.50	9.57	19.79	3.08	11.29	6.37	11.59
2010	7.19	11.52	8.51	10.55	11.03	10.32	21.85	3.99	11.34	8.20	10.22

The 2010 analytical precision results for eight 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 original concentration results. The laboratory precision data met the measurement criterion listed in Table 5-1.

Figure 5-3 Precision Results for Laboratory Replicate Samples (2010)
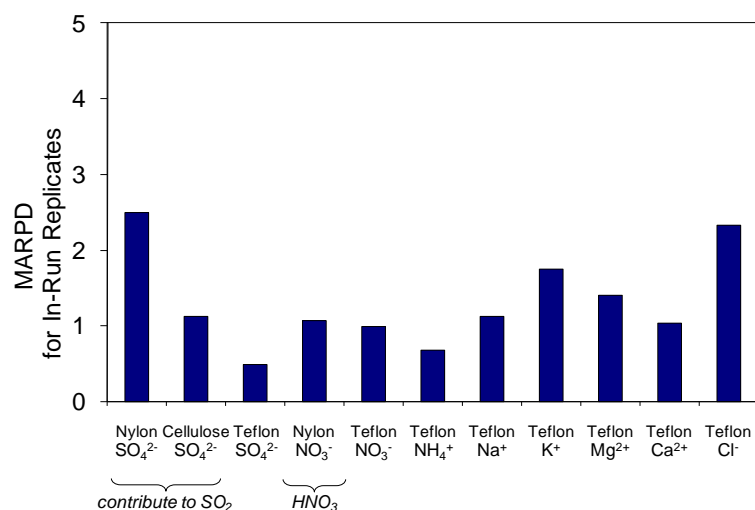
Ozone Concentrations

CASTNET was originally designed to report on regional, rural O_3 levels. The QA procedures for the EPA-sponsored O_3 analyzers at CASTNET sites have differed from the EPA QA requirements for State and Local Monitoring Stations (SLAMS) monitoring (EPA, 2010a; 2008a), including ozone monitoring in 2010. EPA directed MACTEC, now known as AMEC, to prepare EPA-sponsored ozone monitoring to meet 40 CFR Part 58 monitoring requirements. This effort was completed in 2011. In any event, despite differences in QA procedures, operation of the collocated EPA and NPS O_3 analyzers at ROM406/206 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 and ROM406/206 during 2010. In addition, quarterly historical precision statistics were compiled for all collocated sites. Quarterly precision results are summarized in Figure 5-4. Table 5-4 provides precision results for O_3 concentrations by quarter for 2010. The data show the historical and 2010 results met the 10 percent criterion. However, the 2010 results (MACTEC, 2011b) show a consistent bias between ROM406 and ROM206 O_3 measurements with ROM406 measuring higher concentrations by about 4 ppb. The historical data are based on the operation of 11 collocated site pairs over the history of the network.

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

| Measurement | | MARPD/MAD | Criteria* | |
Parameter	Method		Precision	Accuracy
Filter Pack Flow	Mass Flow Controller	MARPD	± 10%	± 5%
Ozone	UV Absorbance	MARPD	± 10% (of reading)	± 10%
Ambient Temperature	Platinum RTD	MAD	± 1.0°C	± 0.5°C
Wind Speed	Anemometer	MAD	± 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	MAD	± 5°	± 5°
Sigma Theta	Wind Vane	MAD	Undefined	Undefined
Delta Temperature	Platinum RTD	MAD	± 0.5°C	± 0.5°C
Relative Humidity	Thin Film Capacitor	MARPD	± 10% (of full scale)	± 10 percent
Solar Radiation	Pyranometer	MARPD	± 10% (of reading taken at local noon)	± 10%
Precipitation	Tipping Bucket Rain Gauge	MARPD	± 10% (of reading)	± 0.05 inch[†]
Surface Wetness	Conductivity Bridge	MAD	Undefined	Undefined

Note: MARPD is the precision measure for percentage criteria such as relative humidity.
Mean absolute difference (MAD) is the precision measure for difference criteria such as wind speed.

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

Figure 5-4 Historical and 2010 Precision Data by Quarter for Ozone Concentrations
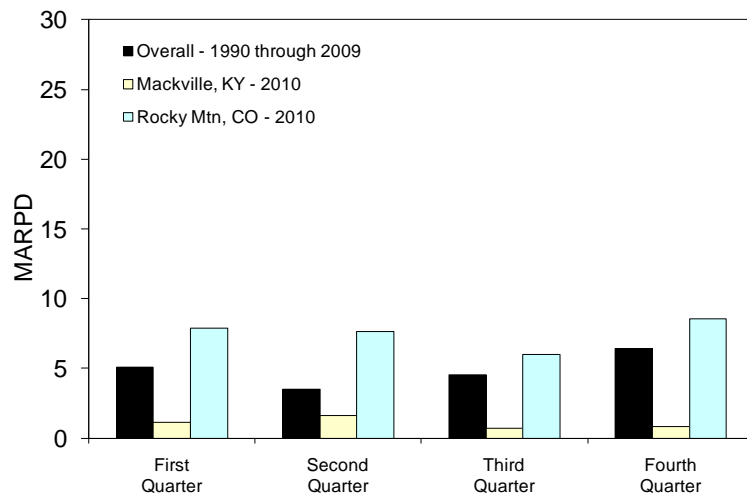
Table 5-4 Collocated Precision Results (MARPD) for 2010 Ozone Concentrations by Quarter

Sampling Period	MCK131/231, KY	ROM406/206, CO
Quarter 1	1.13	7.87
Quarter 2	1.60	7.63
Quarter 3	0.69	6.03
Quarter 4	0.82	8.57
2010	1.06	7.53

Continuous Measurements

Precision criteria for the continuous measurements are listed in Table 5-3. Figure 5-5 provides precision results for historical data (1990 through 2009) at all collocated site pairs and 2010 precision statistics for the two current collocated site pairs. Precision was calculated in terms of the MARPD or mean absolute difference (MAD) of hourly measurements. All historical precision results met the DQI criteria. However, relative humidity and solar radiation measurements taken at ROM406/206 and wind direction data from MCK131/231 did not meet the precision goals during 2010. Table 5-5 gives precision data by quarter for 2010 for the two collocated sites. The results show overall good instrument precision. All but 11 (of 110) 2010 annual and quarterly precision results met the DQI criteria. The first, second, and fourth quarter and annual MARPD values for relative humidity and the first two quarters and annual MARPD values for solar radiation at ROM406/206 did not meet the 10 percent criterion. All four quarters plus the annual MAD values for wind direction at MCK131/231 did not meet the 5-degree goal.

Figure 5-5 Historical and 2010 Precision Data for Continuous Measurements
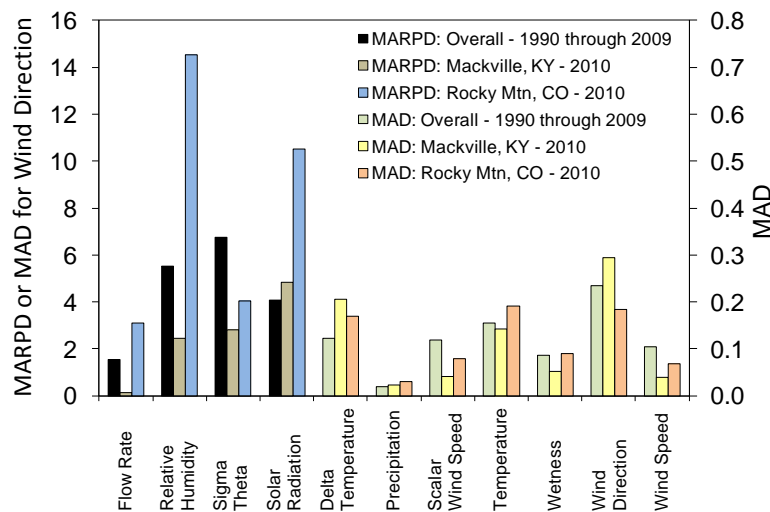
Note: The left y-axis indicates MARPD for these parameters with percentage criteria (Table 5-3) and MAD for wind direction only.

Table 5-5 Collocated Precision Results for 2010 Continuous Measurements by Quarter

Site Pairs	MARPD				MAD						
	Flow Rate	Relative Humidity	Sigma Theta	Solar Radiation	Delta Temperature	Precipitation	Scalar Wind Speed	Temperature	Wetness	Wind Direction	Wind Speed
MCK131/231, KY											
Quarter 1	0.01	4.14	1.95	6.00	0.29	0.02	0.05	0.16	0.05	5.53	0.05
Quarter 2	0.00	1.02	2.69	1.38	0.25	0.02	0.04	0.21	0.07	6.17	0.04
Quarter 3	0.00	1.05	4.16	4.49	0.15	0.02	0.03	0.11	0.03	6.14	0.03
Quarter 4	0.47	3.65	2.47	7.48	0.13	0.03	0.04	0.10	0.06	5.77	0.04
2010	0.12	2.46	2.82	4.84	0.21	0.02	0.04	0.14	0.05	5.90	0.04
ROM406/206, CO											
Quarter 1	1.51	13.89	4.06	12.07	0.15	0.02	0.09	0.18	NC	3.66	0.08
Quarter 2	0.72	16.89	3.25	12.22	0.19	0.05	0.07	0.12	0.06	4.84	0.05
Quarter 3	1.79	NC	4.36	8.89	NC	0.01	0.07	0.22	NC	3.51	0.06
Quarter 4	8.39	12.84	4.55	8.85	NC	0.04	0.08	0.24	0.12	2.72	0.07
2010	3.10	14.54	4.06	10.51	0.17	0.03	0.08	0.19	0.09	3.68	0.07

Note: NC = not calculated

Accuracy

Laboratory Filter Concentrations

Accuracy of laboratory measurements is assessed through the analysis of reference and continuing calibration verification (CCV) samples. Reference samples and CCV are procured from independent suppliers and are traceable to NIST. 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. The CCV were analyzed every tenth sample to verify that instrument calibration had not drifted beyond established limits. Table 5-6 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 2010.

Table 5-6 Filter Pack Quality Control Summary for 2010

Filter Type	Parameter	Reference Sample[1] Recovery (%R)			Continuing Calibration Verification Samples (%R)			In-Run Replicate[2] (RPD)		
		Mean	Standard Deviation	Count[3]	Mean	Standard Deviation	Count[3]	Mean	Standard Deviation	Count[3]
Teflon	SO_4^{2-}	97.54	1.19	149	99.86	1.17	720	0.49	0.71	338
	NO_3^-	99.77	1.19	149	100.44	1.21	720	0.99	1.91	338
	NH_4^+	99.76	1.66	136	98.69	1.39	714	0.68	0.89	357
	Ca^{2+}	99.83	2.80	139	100.20	1.09	725	1.04	1.15	343
	Mg^{2+}	102.53	2.18	139	99.95	0.94	725	1.40	1.64	343
	Na^+	100.97	2.17	139	100.07	1.12	725	1.13	1.50	343
	K^+	97.83	2.87	139	100.04	0.93	725	1.75	1.93	343
	Cl^-	103.09	1.10	149	100.27	1.34	720	2.33	4.44	335
Nylon	SO_4^{2-}	98.01	1.15	156	99.74	1.10	725	2.50	2.55	345
	NO_3^-	100.37	1.13	156	100.52	1.09	725	1.07	1.47	345
Cellulose	SO_4^{2-}	99.04	1.58	176	100.32	1.49	680	1.13	1.58	337

Note: % R = percent recovery

[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 5-7 presents field accuracy results for 2010 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.

Table 5-7 Accuracy Results for 2010 Field Measurements

Parameter	Percent Within Criterion	Parameter	Percent Within Criterion
Flow Rate	98.9 percent	Temperature (ambient)	100.0 percent
Ozone Slope	97.7 percent	Delta Temperature (0°C)	100.0 percent
Ozone Intercept	100.0 percent	Delta Temperature (ambient)	100.0 percent
Wind Speed < 5 m/s	100.0 percent	*Relative Humidity	98.9 percent
Wind Speed ≥ 5 m/s	98.9 percent	Precipitation	95.5 percent
Wind Direction North	96.6 percent	*Solar Radiation	90.9 percent
Wind Direction South	96.6 percent	Wetness (w/in 0.5 volts)	100.0 percent
Temperature (0°C)	100.0 percent		

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

Precision of Collocated SLAMS and Collocated CASTNET Ozone Measurements

Precision is a DQI for CASTNET ozone measurements. Precision is calculated as the MARPD of concentration measurements from collocated sites. Collocated O_3 analyzers are operated currently at MCK131/231, KY and ROM406/206, CO. MCK131/231 has operated collocated analyzers since 1992 and ROM406/206 since 2001. Nine other CASTNET sites have run collocated O_3 analyzers over the history of the network. Thermo Scientific 49i ozone analyzers are currently operated at all four collocated monitoring stations.

The SLAMS network consists of approximately 4,000 monitoring stations across the United States whose measurement systems are largely determined by the needs of State and local air pollution control agencies to meet their respective SIP requirements. Several collocated SLAMS monitoring sites were operated from 1992 through 2009. Two of these collocated ozone monitoring sites were selected for analysis based on length of collocation and availability of recent data. These sites were collocated during the period 2006 through 2009. One Thermo Scientific 49i analyzer and one Dasibi 1008 analyzer were operated at site 36-103-0009, located in Suffolk County, NY, from 2006 through 2009. Two API 400 ozone analyzers were operated at site 29-189-0014, located in St. Louis County, MO, in 2008 and 2009.

The normal precision DQI is the MARPD of hourly O_3 data. For this analysis, the precision measure is the MARPD of DM8A concentrations from the two CASTNET and two SLAMS sites. Table 5a presents quarterly MARPD results calculated from the available data from the four sites. The site average MARPD values are also presented. The best precision was realized at the St. Louis County and Mackville collocated sites. Both sites operate identical analyzers at the respective sites and are serviced by the same operator. The Suffolk County site operates two different analyzers. The CASTNET monitors at ROM406/206 are run independently and serviced by two different operators. Precision of hourly ozone concentrations discussed elsewhere in this chapter shows a consistent bias between ROM406 and ROM206 hourly O_3 data with ROM406 sampling higher concentrations by about 4 ppb. Similarly, this analysis found a consistent 4 to 5 ppb bias between the collocated Suffolk County analyzers.

Table 5a Precision (MARPD) of DM8A O_3 Concentrations Measured at CASTNET and SLAMS Sites

Year	Quarter	MCK131/231	ROM406/206	36-103-0009 POC 1 and 2	29-189-0014 POC 1 and 2
2006	2	2.4	1.8	10.9	
2006	3	7.0	2.7	8.9	
2006	4		9.5	15.4	
2007	1	0.7	4.1	6.6	
2007	2	1.0	8.1	5.2	
2007	3	3.5	16.2	3.5	
2007	4	8.0	12.0	4.7	
2008	1	7.4	1.6		
2008	2	6.1	1.1	9.6	0.9
2008	3		2.5	12.2	0.7
2008	4	5.5	1.8	19.6	0.8
2009	1	4.7	4.5	15.2	
2009	2	1.3	4.8	13.5	1.3
2009	3	1.0	6.3	13.7	1.8
2009	4	1.2	7.7	17.4	3.0
Average		3.8	5.6	11.2	1.4

Note: Site 36-103-0009 is located in Suffolk County, NY

Site 29-189-0014 is located in St. Louis County, MO

POC 1 is primary site and POC 2 is secondary site

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. Figure 5-6 presents historical (black) and 2010 completeness data for all sites for measured filter concentrations and continuous measurements. The figure shows that the 2010 direct measurements met the 90 percent completeness goal, and nine meteorological measurements and filter pack flow exceeded 95 percent. Atmospheric concentrations also exceeded 95 percent.

Figure 5-6 Historical and 2010 Percent Completeness of Measurements (black bars are 1990–2009)
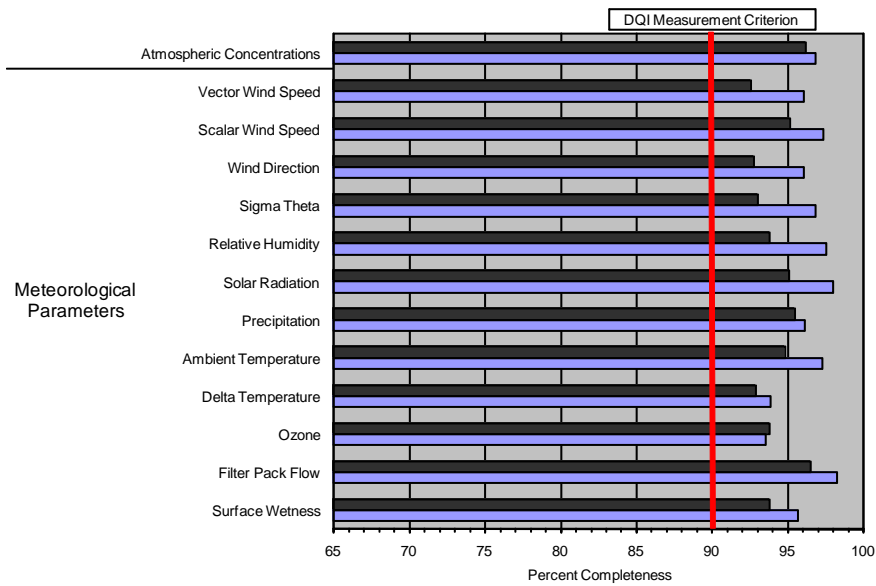
Connecticut Hill, NY (CTH110)

Results for 2010 Environment Canada Proficiency Testing

During 2010, the MACTEC (now known as AMEC) CASTNET laboratory participated in the Environment Canada (ECAN) Proficiency Testing Program for Inorganic Environmental Substances (http://www.ec.gc.ca/inre-nwri/default.asp?lang=En&n=7A20877C-1). Specifically, the laboratory is one of 41 laboratories that participated in the 2010 Rain and Soft Waters round robin studies, which consist of natural waters supplied by the National Laboratory for Environmental Testing. The CASTNET laboratory receives 10 samples of mixed rain and Canadian Shield waters for chemical analysis from ECAN every six months. The laboratory reported the eight CASTNET parameters for samples in two studies (study codes 0096 and 0097) during 2010.

The results reported by the 41 laboratories are evaluated for systematic bias and precision. Systematic bias is assessed using Youden (1969) non-parametric analysis, while precision is calculated using algorithm A from the International Organization for Standardization (ISO) standard 13528 (ISO, 2005).

Individual sample results are flagged based on the Robust Standard Deviation obtained from the ISO 13528 computation (ISO, 2005). Samples within 2 standard deviations of the assigned (median laboratory) value are not flagged; samples between 2 and 3 standard deviations are given a warning flag; and samples greater than 3 standard deviations from the assigned value are flagged as above the action limit (remedial action is required). Laboratory results are considered systematically biased when individual parameters are ranked by the Youden analysis to be consistently and significantly higher or lower than the assigned value without regard to flagged results.

The CASTNET laboratory's 2010 ECAN (2011) results for the eight CASTNET parameters are presented in Table 5b. All eight parameters received the highest possible rating of "Ideal" indicating an unbiased score with the exception of sodium in study 0096. There were no individual results flagged for study 0096, indicating that each result was within the study's acceptance limits. The score was based solely on the bias ranking. The high sodium bias found by study 0096 as compared with the ideal results for that parameter in study 0097 is illustrated in Figure 5a.

Table 5b MACTEC (AMEC) Results for Studies 0096 and 0097

Test Parameter	Analytical Method	Reference Method	Laboratory Performance Rating	
			Study 0096 Summer 2010	Study 0097 Winter 2010
Ammonia	AC	EPA Method 350.1	Ideal	Ideal
Calcium	ICP-AES	EPA Method 6010	Ideal	Ideal
Chloride	IC	EPA Method 300.0	Ideal	Ideal
Magnesium	ICP-AES	EPA Method 6010	Ideal	Ideal
Nitrate + Nitrite	IC	EPA Method 300.0	Ideal	Ideal
Potassium	ICP-AES	EPA Method 6010	Ideal	Ideal
Sodium	ICP-AES	EPA Method 6010	Biased High	Ideal
Sulfate	IC	EPA Method 300.0	Ideal	Ideal

Source: Environment Canada (2011)

Figure 5a Sodium Results Comparison – Studies 0096 and 0097
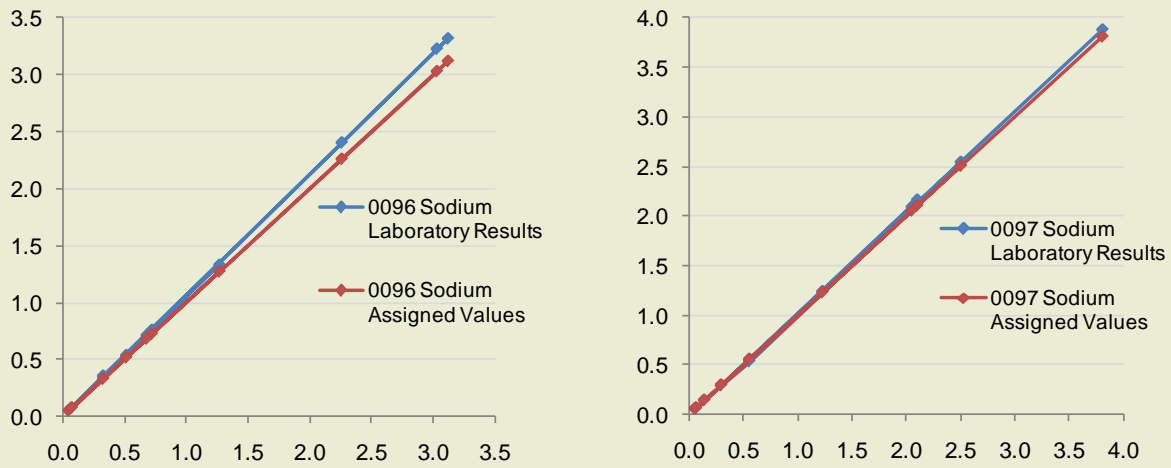
The overall laboratory performance rating was "Good" for each study conducted during 2010. This is the highest possible overall laboratory rating, indicating a percent score (the sum of parameters biased and results flagged) of 5.0 or less as described in Table 5c.

Table 5c Laboratory Performance Rating

Laboratory Performance Rating	
Rating	% Score*
Good	0 - 5
Satisfactory	> 5 - 12.5
Moderate	> 12.5 - 30
Poor	> 30
*Sum of Parameters Biased & Results Flagged	

Source: Environment Canada (2011)

The report for study 0097 included a summary of the laboratory's performance over the last five years. The laboratory achieved the highest possible rating for each of the 10 studies conducted during that period. These results are listed below in Table 5d.

Table 5d Five-Year Historical Laboratory Performance

Study No. / Date	Score*
No. 0088, Summer 2006	0.5
No. 0089, Winter 2006	1.0
No. 0090, Summer 2007	1.0
No. 0091, Winter 2007	3.0
No. 0092, Summer 2008	0.0
No. 0093, Winter 2008	0.0
No. 0094, Summer 2009	5.0
No. 0095, Winter 2009	2.0
No. 0096, Summer 2010	5.0
No. 0097, Winter 2010	0.0
5-Year Median	1.0

Note: * Percent score (sum of parameters biased and results flagged)
Source: Environment Canada (2011)

Summary of Data Quality Results

DQI results demonstrate that CASTNET field and laboratory processes were adequately monitored through QA/QC procedures and were generally free of systemic bias during 2010 with the exception of O_3 measurements at ROM406/206, CO. The O_3 concentrations measured at ROM406 were consistently higher than ROM206 by about 4 ppb. This bias is under investigation.

Historical and 2010 precision data for filter pack parameters are considered acceptable, except for K^+. The precision of K^+ filter pack measurements exceeded the established criterion at ROM406/206 during the first two quarters of the year and are not considered acceptable. The poor K^+ precision continues to be investigated.

The 2010 precision data for O_3 concentrations met the 10 percent DQI criterion. The precision of continuous measurements for 2010 was good. Ninety-nine of 110 quarterly and annual precision results for 2010 met the DQI criteria.

Accuracy data met the established criteria for field and laboratory parameters. Completeness criteria were met for all parameters in 2010. Completeness results for 2010 are considered excellent. ECAN proficiency test studies (0096 and 0097) showed that the CASTNET laboratory performed well on the interlaboratory chemical analyses with all but one parameter rated ideal.

Mackville, KY (MCK131/231)

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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]	Nearby NADP Site	Primary Land Use	Terrain	Representative to the MLM[3]	Sponsor
Alabama												
SND152	Sand Mountain	12/27/88	34.2894	85.9704	352	•	•	AL99	Agri.	Rolling	Y	EPA
Alaska												
DEN417	Denali National Park	10/06/98	63.7258	148.9633	661	•	•	AK03	Forested	Complex	N	NPS
Arizona												
CHA467	Chiricahua National Monument	04/25/89	32.0092	109.3892	1570	•	•	AZ98	Range	Complex	N	NPS
GRC474	Grand Canyon National Park	05/16/89	36.0597	112.1822	2073	•	•	AZ03	Forested	Complex	M	NPS
PET427	Petrified Forest National Park	09/24/02	34.8225	109.8919	1723	•	•	AZ97	Desert	Flat	Y	NPS
Arkansas												
CAD150	Caddo Valley	10/04/88	34.1792	93.0989	71	•	•	AR03	Forested	Rolling	N	EPA
California												
CON186	Converse Station	06/17/03	34.1941	116.9130	1837	•	•	CA94	Agri./Forested	Complex	N	EPA
JOT403	Joshua Tree National Monument	02/16/95	34.0714	116.3906	1244	•	•	CA67	Desert	Complex	M	NPS
LAV410	Lassen Volcanic National Park	07/25/95	40.5403	121.5764	1756	•	•	CA96	Forested	Complex	M	NPS
PIN414	Pinnacles National Monument	05/16/95	36.4850	121.1556	335	•	•	CA66	Forested	Complex	M	NPS
SEK430	Sequoia National Park	04/07/05	36.4894	118.8269	457	•	•	CA75	Forested	Mountaintop	N	NPS
YOS404	Yosemite National Park	09/25/95	37.7133	119.7061	1605	•	•	CA99	Forested	Complex	N	NPS
Colorado												
GTH161	Gothic	05/16/89	38.9573	106.9854	2926	•	•	CO10	Range	Complex	N	EPA
MEV405	Mesa Verde National Park	01/10/95	37.1983	108.4903	2165	•	•	CO99	Forested	Complex	M	NPS
ROM206	Rocky Mountain National Park	07/03/01	40.2778	105.5453	2743	•	•	CO98	Forested	Complex	M	EPA
ROM406	Rocky Mountain National Park	12/20/94	40.2778	105.5453	2743	•	•	CO98	Forested	Complex	M	NPS
Connecticut												
ABT147	Abington	12/28/93	41.8402	72.0111	209	•	•	CT15	Urban-Agri.	Rolling	M	EPA

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Florida												
EVE419	Everglades National Park	10/06/98	25.3911	80.6806	2	•	•[4]	FL11	Swamp	Flat	Y	NPS
IRL141	Indian River Lagoon	07/09/01	30.1065	80.4554	2	•	•	FL99	Beach	Flat	Y	EPA
SUM156	Sumatra	12/28/88	30.1065	84.9938	14	•	•	FL23	Forested	Flat	Y	EPA
Georgia												
GAS153	Georgia Station	06/28/88	33.1812	84.4100	270	•	•	GA41	Agri.	Rolling	M	EPA
Illinois												
ALH157	Alhambra	06/28/88	38.8690	89.6229	164	•	•	IL46	Agri.	Flat	Y	EPA
BVL130	Bondville	02/09/88	40.0520	88.3725	212	•	•	IL11	Agri.	Flat	Y	EPA
STK138	Stockton	12/28/93	42.2872	89.9998	274	•	•	IL18	Agri.	Rolling	M	EPA
Indiana												
SAL133	Salamonie Reservoir	06/28/88	40.8164	85.6608	250	•	•	IN20	Agri.	Flat	Y	EPA
VIN140	Vincennes	08/04/87	38.7406	87.4844	134	•	•	IN22	Agri.	Rolling	M	EPA
Kansas												
KNZ184	Konza Prairie	03/26/02	39.1021	96.6096	348	•	•	KS31	Prairie	Flat	Y	EPA
Kentucky												
CDZ171	Cadiz	10/01/93	36.7841	87.8500	189	•	•	KY99	Agri.	Rolling	M	EPA
CKT136	Crockett	08/24/93	37.9211	83.0658	455	•	•	KY35	Agri.	Rolling	Y	EPA
MAC426	Mammoth Cave National Park	07/24/02	37.1319	86.1478	243	•	•	KY10	Agri./Forested	Rolling	M	NPS
MCK131	Mackville	07/31/90	37.7044	85.0483	353	•	•	KY03	Agri.	Rolling	M	EPA
Maine												
ACA416	Acadia National Park	12/01/98	44.3769	68.2608	158	•	•	ME98	Forested	Complex	M	NPS
ASH135	Ashland	12/20/88	46.6039	68.4142	235	•	•	ME00	Agri.	Flat	Y	EPA
HOW132	Howland	11/24/92	45.2158	68.7085	69	•	•	ME09	Forested	Rolling	Y	EPA

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Maryland												
BEL116	Beltsville	11/01/88	39.0283	76.8175	46	•	•	MD99	Urban-Agri.	Flat	N	EPA
BWR139	Blackwater National Wildlife Refuge	07/04/95	38.4448	76.1115	4	•	•	MD15	Forest-Marsh	Coastal	M	EPA
Michigan												
ANA115	Ann Arbor	06/28/88	42.4164	83.9019	267	•	•	MI52	Forested	Flat	M	EPA
HOX148	Hoxeyville	10/31/00	44.1809	85.7390	298	•	•	MI53	Forested	Flat	Y	EPA
UVL124	Unionville	06/28/88	43.6139	83.3597	201	•	•	MI51	Agri.	Flat	Y	EPA
Minnesota												
VOY413	Voyageurs National Park	06/13/96	48.4128	92.8292	429	•	•	MN32	Forested	Rolling	M	NPS
Mississippi												
CVL151	Coffeeville	12/27/88	34.0028	89.7989	134	•	•	MS30	Forested	Rolling	M	EPA
Montana												
GLR468	Glacier National Park	12/27/88	48.5103	113.9956	976	•	•	MT05	Forested	Complex	N	NPS
Nebraska												
SAN189	Santee Sioux	07/05/06	42.8292	97.8541	429	•	•	SD99	Agri.	Rolling	N	EPA
Nevada												
GRB411	Great Basin National Park	05/16/95	39.0053	114.2158	2060	•	•	NV05	Forested	Complex	M	NPS
New Hampshire												
WST109	Woodstock	12/27/88	43.9446	71.7008	258	•	•	NH02	Forested	Complex	N	EPA
New Jersey												
WSP144	Washington's Crossing	12/27/88	40.3133	74.8726	61	•	•	NJ99	Urban-Agri.	Rolling	M	EPA
New York												
CAT175	Claryville	05/10/94	41.9423	74.5519	765	•	•[4, 5]	NY68	Forested	Complex	N	EPA
CTH110	Connecticut Hill	09/28/87	42.4010	76.6535	515	•	•	NY67	Forested	Rolling	N	EPA
HWF187	Huntington Wildlife Forest	05/28/02	43.9732	74.2232	502	•	•	NY20	Forested	Complex	N	EPA

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North Carolina												
BFT142	Beaufort	12/28/93	34.8843	76.6213	2	•	•	NC06	Agri.	Flat	Y	EPA
CND125	Candor	09/25/90	35.2643	79.8382	198	•	•	NC36	Forested	Rolling	M	EPA
COW137	Coweeta	11/04/87	35.0605	83.4302	686	•	•	NC25	Forested	Complex	N	EPA
PNF126	Cranberry	12/27/88	36.1040	82.0448	1250	•	•	NC45	Forested	Mountaintop	M	EPA
North Dakota												
THR422	Theodore Roosevelt National Park	10/06/98	46.8947	103.3778	850	•	•	ND00	Range	Rolling	Y	NPS
Ohio												
DCP114	Deer Creek State Park	09/28/88	39.6358	83.2600	267	•	•	OH54	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	•	•	OH09	Agri.	Rolling	N	EPA
QAK172	Quaker City	09/28/93	39.9431	81.3378	372	•	•	OH49	Agri.	Rolling	M	EPA
Oklahoma												
CHE185	Cherokee Nation	04/02/02	35.7507	94.6700	299	•	•	AR27	Agri.	Rolling	Y	EPA
Ontario												
EGB181	Egbert, Ontario	12/27/94	44.2317	79.7840	251	•	•[4]	NY10	Agri.	Rolling	Y	EPA
Pennsylvania												
ARE128	Arendtsville	06/28/88	39.9231	77.3078	269	•	•	PA00	Agri.	Rolling	M	EPA
KEF112	Kane Experimental Forest	01/03/89	41.5981	78.7683	622	•	•	PA29	Forested	Rolling	Y	EPA
LRL117	Laurel Hill State Park	12/15/87	39.9883	79.2522	615	•	•	MD08	Forested	Complex	N	EPA
MKG113	M.K. Goddard State Park	01/12/88	41.4250	80.1447	384	•	•	NY10	Forested	Rolling	N	EPA
PSU106	Penn. State University	01/06/87	40.7209	77.9316	376	•	•	PA42	Agri.	Rolling	M	EPA
South Dakota												
WNC429	Wind Cave National Park	11/18/03	43.5578	103.4839	1292	•	•	SD04	Prairie	Rolling	M	NPS

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Tennessee												
ESP127	Edgar Evins State Park	03/22/88	36.0389	85.7330	302	•	•	KY10	Forested	Rolling	N	EPA
GRS420	Great Smoky Mountains National Park	10/06/98	35.6331	83.9422	793	•	•	TN11	Forested	Complex	N	NPS
SPD111	Speedwell	06/12/89	36.4698	83.8265	361	•	•	TN04	Agri.	Rolling	Y	EPA
Texas												
ALC188	Alabama-Coushatta	04/02/04	30.4210	94.4045	101	•	•	TX10	Forested	Rolling	Y	EPA
BBE401	Big Bend National Park	07/18/95	29.3022	103.1772	1052	•	•	TX04	Forested	Complex	M	NPS
PAL190	Palo Duro Canyon State Park	04/24/07	34.8803	101.6649	1050	•	•	TX43	Prairie	Complex	M	EPA
Utah												
CAN407	Canyonlands National Park	01/24/95	38.4586	109.8211	1809	•	•	UT09	Desert	Complex	M	NPS
Virginia												
PED108	Prince Edward	11/03/87	37.1653	78.3070	150	•	•	VA24	Forested	Rolling	M	EPA
SHN418	Shenandoah National Park	06/28/88	38.5231	78.4347	1073	•	•	VA28	Forested	Mountaintop	M	NPS
VPI120	Horton Station	06/02/87	37.3300	80.5573	920	•	•	VA13	Forested	Mountaintop	N	EPA
Washington												
MOR409	Mount Rainier National Park	08/29/95	46.7583	122.1244	415	•	•	WA99	Forested	Complex	N	NPS
West Virginia												
CDR119	Cedar Creek State Park	11/10/87	38.8794	80.8478	234	•	•	WV05	Forested	Complex	N	EPA
PAR107	Parsons	01/19/88	39.0906	79.6614	510	•	•	WV18	Forested	Complex	N	EPA
Wisconsin												
PRK134	Perkinstown	09/27/88	45.2066	90.5972	472	•	•	WI35	Agri.	Rolling	M	EPA

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Site ID	Site Name	Start date	Latitude (°N)	Longitude (°W)	Elevation (m)	Deposition Filter Pack[1]	Ozone and Meteorology[2]	Nearby NADP Site	Primary Land Use	Terrain	Representative to the MLM[3]	Sponsor
Wyoming												
CNT169	Centennial	08/19/91	41.3722	106.2422	3178	•	•	WY95	Range	Complex	M	EPA
PND165	Pinedale	12/27/88	42.9214	109.7900	2388	•	•	WY06	Range	Rolling	M	EPA
YEL408	Yellowstone National Park	06/26/96	44.5597	110.4006	2400	•	•	WY08	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 site.

• Indicates current monitoring.

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

Appendix B

Acronyms and Abbreviations

List of Acronyms and Abbreviations

AAI	Aquatic Acidification Index
AMNet	Atmospheric Mercury Network
AMoN	Ammonia Monitoring Network
ANC	acid neutralizing capacity
AQA	Canada – United States Air Quality Agreement
AQS	EPA's Air Quality System
ARP	Acid Rain Program
BLM	Big-Leaf Model
C	concentration
Ca^{2+}	particulate calcium ion
CAAA	Clean Air Act Amendments
CAIR	Clean Air Interstate Rule
CAPMoN	Canadian Air and Precipitation Monitoring Network
CASTNET	Clean Air Status and Trends Network
CCV	continuing calibration verification samples
Cl^-	particulate chloride ion
CLAD	NADP Critical Loads of Atmospheric Deposition science committee
CLD303	Clingmans Dome, TN cloud sampling site
CLmaxS	maximum critical load of sulfur
CLminN	critical load of nitrogen removed by the ecosystem
cm	centimeter
cm/sec	centimeters per second
CMAQ	Community Multiscale Air Quality Modeling System
CSAPR	Cross-State Air Pollution Rule
DEM	digital elevation model
DM8A	daily maximum 8-hour average
DQI	data quality indicator
DQO	data quality objective
ECAN	Environment Canada
EGU	electric generating unit
EPA	U.S. Environmental Protection Agency
g/m^3	grams per cubic meter
GEM	gaseous elemental mercury
GOM	gaseous oxidized mercury
H_2SO_4	sulfuric acid
HNO_3	nitric acid
IC	ion chromatography
ICP-AES	inductively coupled plasma-atomic emission spectrometry
IDW	inverse distance weighting
IMPROVE	Interagency Monitoring of Protected Visual Environments

ISO	International Organization for Standardization
K^+	particulate potassium ion
K_2CO_3	potassium carbonate
kg/ha/yr	kilograms per hectare per year
km	kilometer
LAI	leaf area index
lpm	liters per minute
LWC	liquid water content
MACTEC	MACTEC Engineering and Consulting, Inc., now known as AMEC E&I, Inc.
MAD	mean absolute difference
MADPro	Mountain Acid Deposition Program
MAGIC	Model of Acidification of Groundwater in Catchments
MARPD	mean absolute relative percent difference
MDN	Mercury Deposition Network
$meq/m^2/yr$	milliequivalents per square meter per year
Mg^{2+}	particulate magnesium ion
mg/l	milligrams per liter
MLM	Multi-Layer Model
MSI	Meteorological Solutions, Inc.
N	nitrogen
Na^+	particulate sodium ion
NAAQS	National Ambient Air Quality Standards
NADP	National Atmospheric Deposition Program
NAPAP	National Acid Precipitation Assessment Program
NBP	NO_x Budget Trading Program
NCLD	National Critical Load Database
NDDN	National Dry Deposition Network
ng/m^3	nanograms per cubic meter
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_3^-	particulate nitrate
NO_x	nitrogen oxides [nitric oxide (NO) + nitrogen dioxide (NO_2)]
NPS	National Park Service
NTN	National Trends Network
O_3	ozone
OTC	Ozone Transport Commission
$PBM_{2.5}$	particulate-bound mercury with aerodynamic diameter < 2.5 μm

List of Acronyms and Abbreviations (continued)

PEMA	Pollutant Emission Management Area
pg/m^3	picograms per cubic meter
$PM_{2.5}$	fine particulate matter
PRISM	Parameter-elevation Regressions on Independent Slopes Model
ppb	parts per billion
ppm	parts per million
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
RPD	relative percent difference
S	sulfur
SIP	State Implementation Plan
SLAMS	State and Local Monitoring Stations
SNOTEL	snow telemetry (from National Resources Conservation Service)
SO_2	sulfur dioxide
SO_4^{2-}	particulate sulfate
SOP	standard operating procedure
SRP	standard reference photometer
SSWC	Steady-State Water Chemistry
total NO_3^-	gaseous nitric acid (HNO_3) + particulate nitrate (NO_3^-)
$\mu eq/L$	microequivalents per liter
μm	micrometer
$\mu g/m^3$	micrograms per cubic meter
UGRB	Upper Green River Basin, WY
UGWOS	Upper Green River Winter Ozone Study
UV	ultraviolet
V_d	deposition velocity
VOCs	volatile organic compounds
WDEQ	Wyoming Department of Environmental Quality
WF	weighting factor
WFM300	Whiteface Mountain, NY cloud sampling site

For More Information:

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

On the Web:

CASTNET Home Page:

Clean Air Markets
Division Home Page:

EPA Home Page:

www.epa.gov/castnet

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