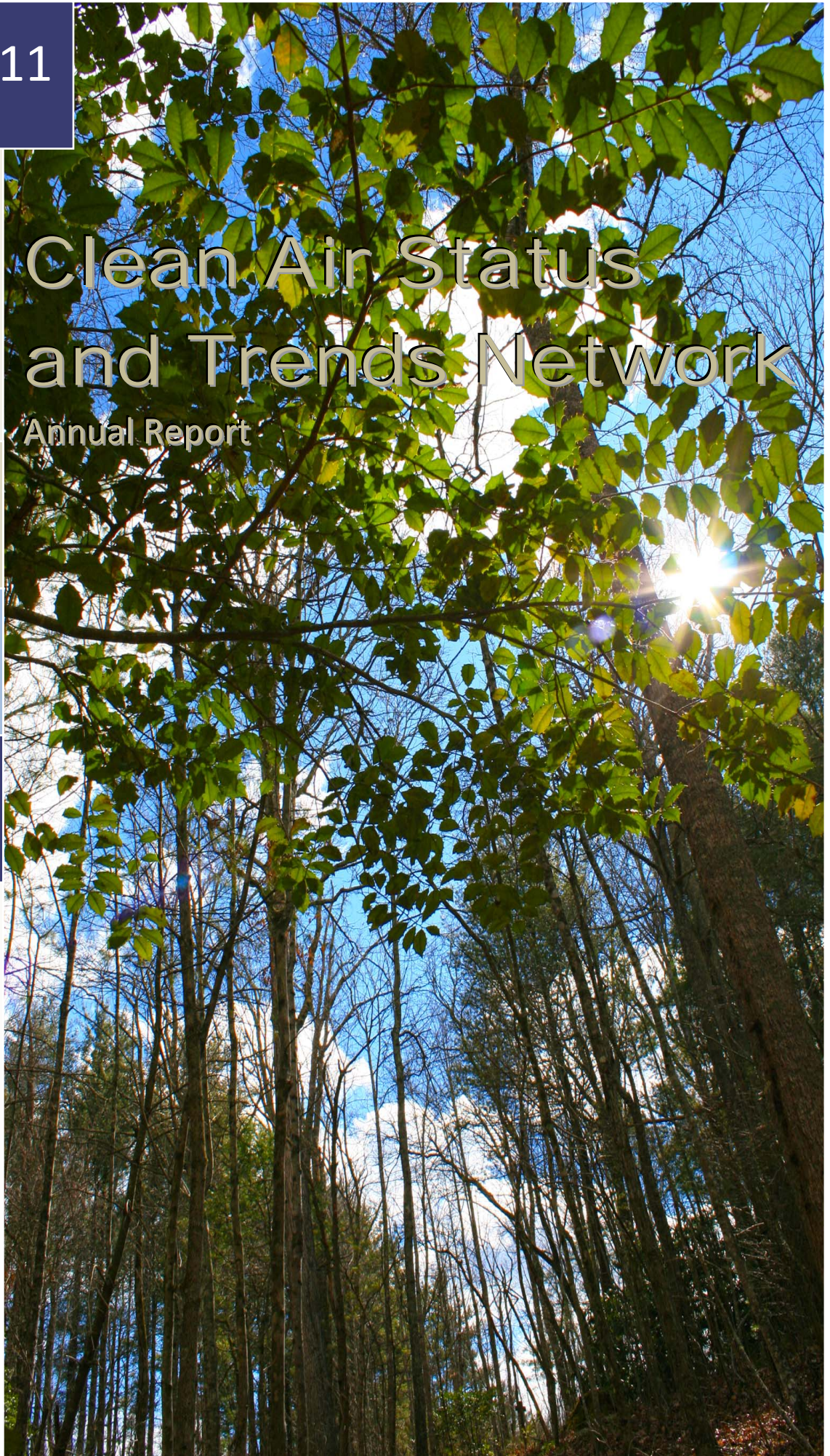2011

Clean Air Status and Trends Network

Annual Report

Clean Air Status and Trends Network (CASTNET)

2011 Annual Report

Prepared by:

AMEC Environment & Infrastructure, Inc.

Prepared for:

U.S. Environmental Protection Agency

Office of Air and Radiation

Clean Air Markets Division

Washington, DC

EPA Contract No. EP-W-09-028

February 2013

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Executive Summary

The EPA Clean Air Status and Trends Network (CASTNET) measures atmospheric pollution concentrations in order to evaluate the effectiveness of national and regional air pollution control programs. This report presents 2011 maps of the geographic distribution of sulfur and nitrogen pollutant concentrations, ozone (O_3) levels, and deposition fluxes and examines trends in air quality since 1990. CASTNET measured rural, regionally representative concentrations of sulfur and nitrogen species and O_3 at 83 sites in the United States and Canada during 2011.

Key Results and Highlights through 2011

- Mean annual sulfur dioxide (SO_2) and particulate sulfate (SO_4^{2-}) concentrations declined significantly over the 22-year period 1990 through 2011 and showed a substantive decline since 2005. Three-year mean annual SO_2 levels declined 72 percent while SO_4^{2-} concentrations declined 52 percent at eastern reference sites from 1990 through 2011. SO_2 concentrations measured at western reference sites were reduced by 54 percent, and SO_4^{2-} levels dropped by 21 percent over the 16-year period (1996 through 2011).
- Total (dry + wet) sulfur deposition estimated in the eastern United States declined by 59 percent from 1990 through 2011. Total sulfur deposition aggregated over western reference sites fell by 35 percent over the 16 years 1996 through 2011.
- Three-year mean annual concentrations of total nitrate (NO_3), which is comprised of nitric acid (HNO_3) plus particulate NO_3^- declined 37 percent at eastern sites over the 22-year period. Total NO_3^- levels measured at western reference sites dropped by 29 percent over the 16 years.
- Total nitrogen deposition [particulate NO_3^- (dry + wet) and HNO_3] fell by 26 percent from 1990 through 2011 at eastern reference sites. Total nitrogen deposition estimated for western reference sites was reduced by 22 percent over the 16 years. However, total nitrogen deposition increased significantly at eastern reference sites from 2010 to 2011 because of increased nitrogen concentration in precipitation. The network recorded the highest annual average precipitation over the 22 years.
- The mean fourth highest daily maximum 8-hour average O_3 concentration for 2011 was 68 parts per billion (ppb), which was lower than the 2010 value of 69 ppb and higher than the 2009 concentration of 64 ppb, the lowest in the history of the network. Four eastern and three California sites recorded exceedances of the 8-hour standard of 0.075 parts per million during the most recent 3-year period (2009 through 2011).
- Measurements taken during 2011 and historical data collected over the period 1990 through 2010 were analyzed relative to data quality indicators 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.
- In 2011, EPA-sponsored CASTNET sites became compliant with the requirements of 40 CFR Part 58, and O_3 data from EPA sites were delivered to the EPA Air Quality System.

- EPA discontinued meteorological measurements at all but five EPA-sponsored CASTNET sites by December 31, 2010. NPS sites are continuing meteorological data collection. Consequently, missing deposition velocity (V_d) values resulting from missing meteorological data were replaced based on the results in Bowker *et al.* (2011), which substitutes hour-specific historical averages of 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.

- In 2010, in order to improve estimates of wet deposition, EPA used the Parameter-elevation Regressions on Independent Slopes Model (PRISM) to develop a continuous grid of precipitation data. PRISM uses terrain elevation, slope, and aspect and climatic measurements to estimate precipitation on a 4-kilometer resolution grid.

- The V_d substitution procedure and the use of PRISM resulted in more complete, improved estimates of dry, wet, and total deposition for 2011.

Prince Edward, VA (PED108)

Chapter 1: CASTNET Overview
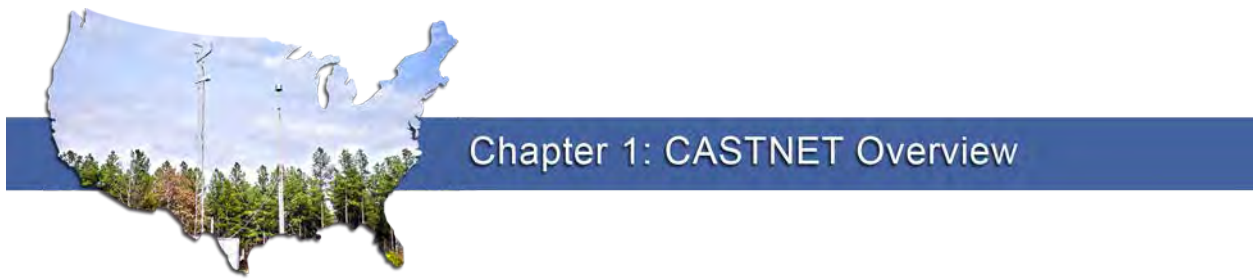
The Clean Air Status and Trends Network (CASTNET) began operation in 1991 to provide long-term monitoring of air quality in rural areas and to determine trends in regional atmospheric sulfur, nitrogen, and ozone concentrations and in deposition fluxes of sulfur and nitrogen pollutants. CASTNET was designed to provide data for use in assessing trends in air quality, atmospheric deposition, and ecological effects that result from air pollutant emission reductions by electric generating units. 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 2011, the network operated 83 monitoring stations throughout the contiguous United States, Alaska, and Canada. Measurements collected in 2011 show the continuing decline in sulfur and nitrogen pollutant concentrations and ozone concentrations in the eastern United States relative to 2010. All pollutants have declined significantly over the last 22 years.

Background

The U.S. Congress established the Acid Rain Program (ARP) under Title IV of the 1990 Clean Air Act Amendments (CAAA). The ARP was promulgated to reduce emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) from electric generating units (EGUs). Congress further directed the U.S. Environmental Protection Agency (EPA) to institute CASTNET under Title IX of the CAAA in order 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. 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 the groundwork for trading and banking emission allowances. One allowance provides a regulated EGU limited authorization to emit one ton of SO_2. The program was 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 2011 were about 4.5 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 2011 were about 2.0 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 Program, the NO_x State Implementation Plan (SIP) Call/NO_x Budget Trading Program (NBP), and the Clean Air Interstate Rule (CAIR).

Other Programs Contributing to Nitrogen Oxides Emission Reductions

Ozone Transport Commission (OTC) *– Established under the 1990 CAAA, this commission consists of states primarily located in the Northeast and Mid-Atlantic regions. The OTC developed the OTC NO_x Budget Program, which operated from 1999 to 2002. As part of this program, 11 states and the District of Columbia entered into a memorandum of understanding to achieve regional emission reductions of NO_x through the use of control technologies and an ozone (O_3) season cap and trade program.*

NO_x State Implementation Plan (SIP) Call *– Issued in 1998 to reduce the regional transport of ground-level O_3, the NO_x SIP Call required states to reduce O_3 season NO_x emissions by meeting emission budgets.*

NO_x Budget Trading Program (NBP) *– This market-based cap and trade program was developed under the NO_x SIP Call and replaced the OTC NO_x Budget Program in 2003. The NBP was created to reduce NO_x emissions from power plants and other large combustion sources in 20 eastern states and the District of Columbia and operated from 2003 to 2008.*

Clear Air Interstate Rule (CAIR) *– Promulgated in 2005, CAIR was designed to reduce emissions of SO_2 and NO_x in 27 eastern states and the District of Columbia and replaced the NBP in 2009. This rule created three separate trading programs: an annual NO_x program, an O_3 season NO_x program, and an annual SO_2 program. In December 2008, CAIR was remanded, but remained in place while EPA developed a replacement rule (EPA, 2012b).*

Cross-State Air Pollution Rule (CSAPR) *– On July 6, 2011, CSAPR was promulgated to require 28 states in the eastern half of the United States to significantly improve air quality by reducing power plant emissions that cross state lines and contribute to ground-level O_3 and fine particle pollution in other states. The rule was scheduled to replace CAIR starting in 2012 and would have reduced annual SO_2, annual NO_x, and O_3 season NO_x emissions, while providing sources with flexibility in how to comply with the program. On December 30, 2011, the court stayed CSAPR pending judicial review, and on August 21, 2012, the court decided to vacate the rule. On October 5, 2012, the U.S. Government filed a petition for rehearing en banc, asking the full court to reconsider that decision. The court denied the U.S. Government's petition for an en banc rehearing on January 24, 2013. In the meantime, as the court stated in its opinion, CAIR remains in place, and states and affected sources are expected to comply with the 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. In 2011, the

network included 83 monitoring stations at 81 site locations throughout the contiguous United States, Alaska, and Canada. In September 2011, a new CASTNET site was installed in Howland, ME (HOW191) at the AmeriFlux Network site. This site represents the first collaboration between the two long-standing national networks. AmeriFlux's purpose is to measure ecosystem level exchanges of carbon dioxide, water, energy, and momentum. AmeriFlux sites utilize a 30-meter (m) tower to enable measurements in the lower boundary layer (AmeriFlux, 2012). CASTNET is interested in similar processes for O_3 and sulfur and nitrogen species. At the HOW191 site, hourly O_3 concentrations are collected at eight elevations within and above the forest canopy on a scaffold tower. Filter pack sampling systems are operated at two elevations.

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 protecting air quality and resources sensitive to air quality in national parks and wilderness areas. Twenty-five CASTNET sites were sponsored by NPS during 2011. 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. During 2011, O_3 measurements at EPA-sponsored CASTNET sites became compliant with the requirements of Title 40 Code of Federal Regulations (CFR) Part 58, and O_3 data from EPA sites were delivered to the EPA Air Quality System (AQS).

Dry deposition is calculated from CASTNET concentration measurements and modeled deposition velocities (V_d) using the Multi-Layer Model (MLM) or from historical V_d measurements. The MLM requires several meteorological parameters and information on vegetation and land use specific to each site. CASTNET data are also used for atmospheric model evaluation and as input to ecological models.

EPA discontinued meteorological measurements at all but five EPA-sponsored CASTNET sites by December 31, 2010. NPS sites are continuing meteorological data collection. For this report, missing V_d values resulting from missing meteorological data were replaced using the method described in Bowker *et al*. (2011). Bowker's method substitutes hour-specific historical averages of 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 was applied to all sites with discontinued/missing meteorological data for the period October through December 2010 and for 2011 and also for sites missing historical V_d values. Sulfur and nitrogen

dry deposition fluxes based on updated values of V_d through 2011 are reported herein. The current MLM modeling approach that is used to estimate dry deposition fluxes will continue to be used for the five EPA-sponsored sites with continuing meteorological measurements and all NPS-sponsored sites.

In order to improve estimates of wet deposition, EPA used 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 that were estimated for the PRISM grid were provided by National Atmospheric Deposition Program (NADP)/National Trends Network (NTN). 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 for this report.

This report summarizes CASTNET monitoring activities and the resulting concentration and deposition data collected over the 22-year period from 1990 through 2011. 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 2011 from the NPS-sponsored CASTNET sites and the NPS Gaseous Pollutant Monitoring Program are available in the NPS Annual Data Summary 2011 (Ray, 2013) and the Data Quality Assurance Report 2011, Gaseous Pollutant Monitoring Program (NPS, 2012).

Pinedale, WY (PND165)

Cooperating Networks

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

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

  o *National Trends Network (NTN), which includes about 250 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.*

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

  o *Ammonia Monitoring Network (AMoN), which operates passive ammonia (NH_3) samplers at about 57 NTN and 40 CASTNET locations. AMoN, in operation for three years, provides information on 2-week average NH_3 concentrations.*

  o *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 NADP's Web site for more information on these 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 National Acid Precipitation Assessment Program (NAPAP), Title IX of the CAAA, the Canada – United States Air Quality Agreement, and the Government Performance and Results Act.

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. In all, CASTNET has more than 50 partners. 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 to 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

The locations of CASTNET monitoring sites that were operational during 2011 are depicted in Figure 1-1. Eighty-three sites were operated at 81 distinct locations. To estimate precision across the network, collocated sites were operated at Mackville, KY (MCK131/231) and Rocky Mountain National Park, CO (ROM406/ROM206) during 2011. The ROM406/206 monitors ensure consistency between the two sponsoring agencies, EPA and NPS, since EPA operates ROM206 and NPS operates ROM406. ROM406 is considered the regulatory monitoring site for O_3. 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.

Figure 1-1 CASTNET Sites Operational During 2011
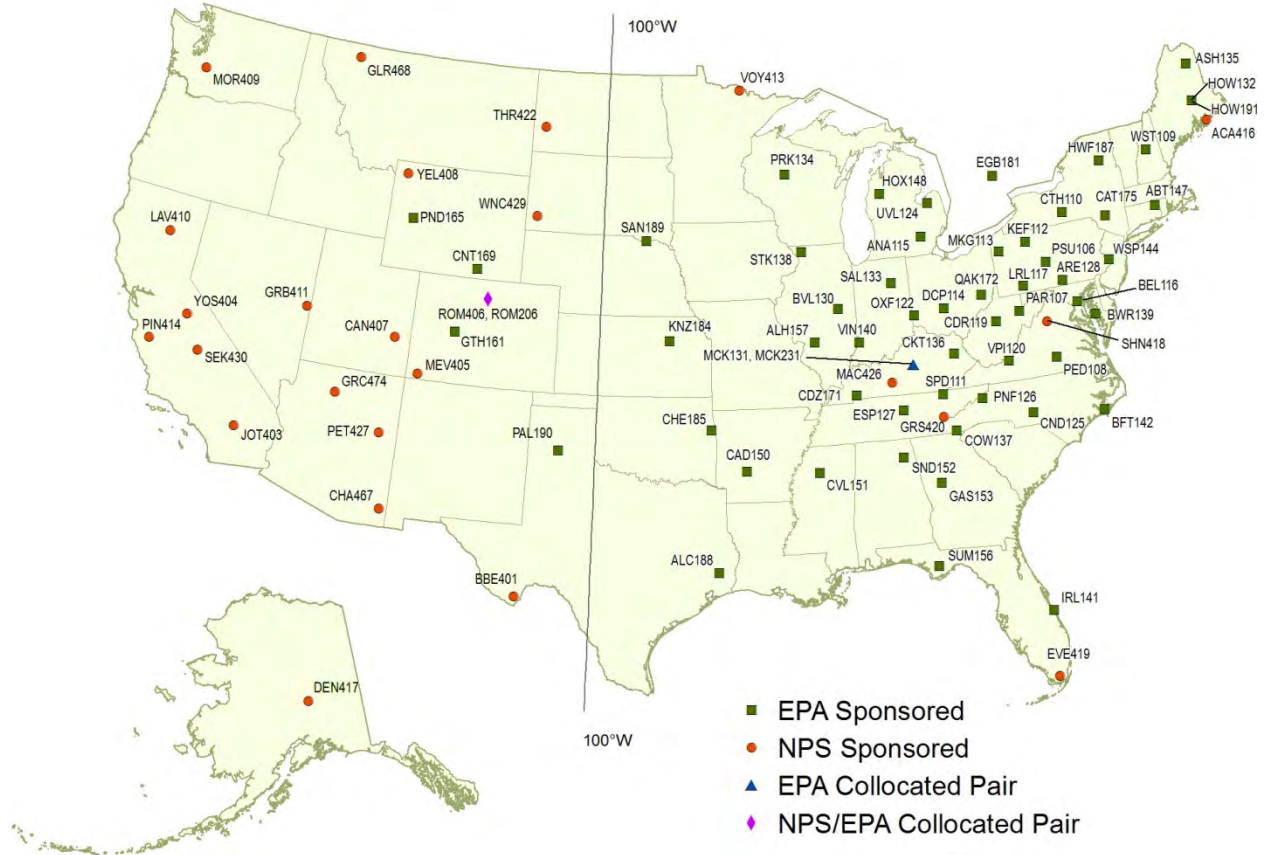
CASTNET Reference Sites

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 such as site longevity and data completeness, which were used by EPA in its National Air Quality and Emissions Trends Report (2000). Trends in pollutant concentrations measured at CASTNET western reference sites (Figure 1-2) are also presented. The 17 western reference sites have been operating since at least 1996.

Figure 1-2 CASTNET Western and Eastern Reference Sites
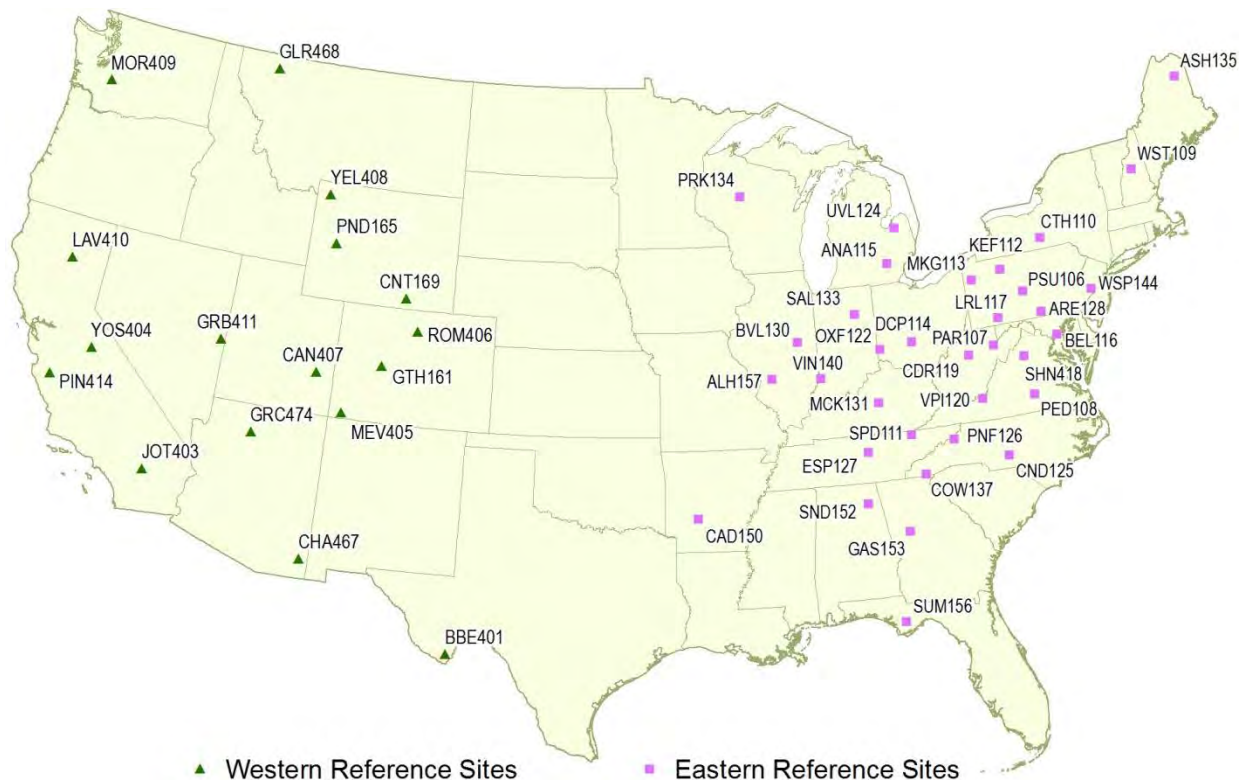
The data from the 34 eastern reference sites were aggregated and then presented using box plots for the 22-year period 1990 through 2011. Data from the 17 western reference sites were aggregated and then presented using box plots for the period 1996 through 2011.

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 7-day period, air is drawn at a controlled flow rate through an open-face 3-stage filter pack (Figure 1-3) mounted atop a 10-m tower to collect air pollutants in the form of gases and particles. The first stage of the filter pack encloses a Teflon filter, the second a nylon filter, and the third holds two potassium carbonate (K_2CO_3)-impregnated cellulose filters. The filter pack is changed out each Tuesday and shipped to the analytical chemistry laboratory for analysis.

CASTNET Ambient Measurements

- Sulfur 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

Figure 1-3 Three-Stage Filter Pack

Shipping Cap (removed during sampling)

Teflon Filter

Nylon Filter

Two Cellulose Filters

Quick Disconnect

Direction of Air Flow

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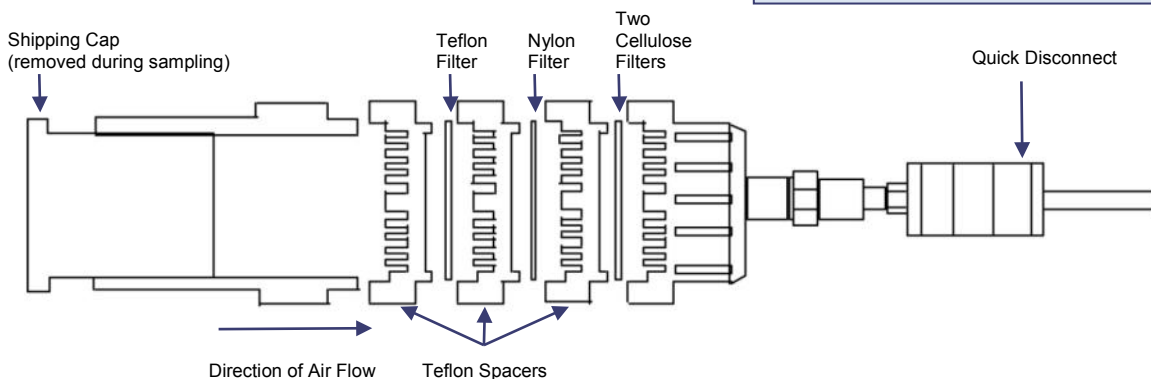
Note:
Cellulose = Gaseous: sulfur dioxide
Nylon = Gaseous: nitric acid, sulfur dioxide
Teflon = Particulate: sulfate, nitrate, ammonium, sodium, calcium, magnesium, potassium, and chloride

The filter packs are prepared, loaded, shipped, received, extracted, and analyzed at AMEC's Gainesville, FL laboratory. Following receipt from the field, exposed Teflon filters and blanks are extracted and then analyzed for concentrations of sulfate (SO_4^{2-}), nitrate (NO_3^-), and 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 SO_4^{2-} using IC. The nylon filter extracts are analyzed via IC for nitric acid (HNO_3) as nitrogen and for SO_2 as SO_4^{2-}. 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. O_3 measurements are recorded continually and archived as hourly averages. CASTNET O_3 measurements meet 40 CFR Part 58 compliance regulations, and the hourly O_3 concentrations are delivered to the EPA AQS. In addition to the air pollutant concentrations, five EPA-sponsored and all NPS-sponsored CASTNET sites collect 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. The five sites continuing all meteorological measurements are Beltsville, MD (BEL116); Bondville, IL (BVL130); Palo Duro Canyon State Park, TX (PAL190); CHE185, OK; and Beaufort, NC (BFT142). Temperature will continue to be measured at all sites in the network. While meteorological data collection is continuing at all NPS sites, NPS discontinued measurements of 2-m temperature and surface wetness at most sites. During 2011, delta temperature was measured at the five EPA sites plus the NPS sites at Acadia National Park, ME (ACA416); Great Smoky Mountains National Park, TN (GRS420); and ROM406, CO. Surface wetness was measured at the five EPA sites plus GRS420. The meteorological measurements are recorded continuously and archived as hourly averages.

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

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 1-4. 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 V_d values for each site are calculated for each hour of each year using the MLM. The MLM was 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 1-4 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 or were estimated from historical data. The decision to discontinue meteorological measurements at all but five 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 was applied to the CASTNET database and used for the dry deposition estimates reported herein.
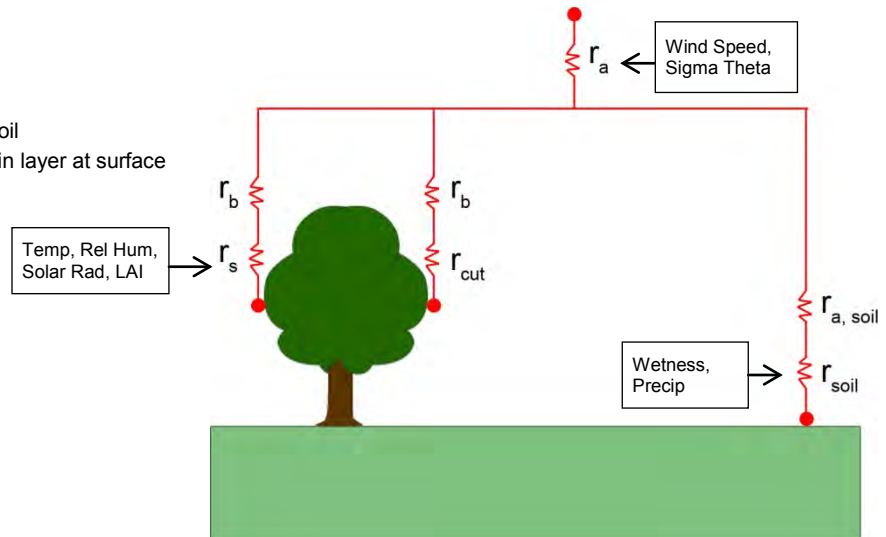
Figure 1-4 Multi-Layer Model

$$\text{Flux} = \overline{C} \times \overline{V_d}$$

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

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

2011 NAPAP Report to Congress

The National Acid Precipitation Assessment Program (NAPAP) was reauthorized in 1991 under Title IX of the 1990 CAAA and was tasked "to periodically assess and report to Congress on (1) the implementation of the ARP, (2) the most recent scientific information related to acid deposition and its effects, and (3) additional decreases in acid deposition necessary to prevent adverse ecological effects." Title IX of the CAAA requested that NAPAP conduct acid rain research and monitoring and periodically assess the costs, benefits, and effectiveness of Title IV. The NAPAP member agencies are the EPA, the U.S. Department of Energy, the U.S. Department of Agriculture, the U.S. Department of Interior, the National Aeronautics and Space Administration, and the National Oceanic and Atmospheric Administration. The 2011 NAPAP report is the fourth published since 1990. It focuses on EGU emission reductions, summarizes changes in atmospheric deposition rates, and projects the ecological effects of additional decreases in emissions of SO_2 and NO_x. A copy of the report is available at http://ny.water.usgs.gov/projects/NAPAP/.

CASTNET data support the NAPAP report, which concludes that Title IV has successfully reduced emissions of SO_2 and NO_x from the power sector. CASTNET data depicted in the figures in Chapters 2, 3, and 4 of this report show significant reductions in ambient concentrations of sulfur and nitrogen pollutants, in total atmospheric deposition rates of sulfur and nitrogen species, and in fourth highest daily maximum O_3 concentrations. These figures support the findings of the NAPAP report, which concludes that Title IV has successfully reduced power sector emissions of SO_2 and NO_x. EPA emissions data show SO_2 emissions from EGUs (Figure 1a) were reduced to 4.5 million tons in 2011, 64 percent lower than 1990 emissions and below the 2010 statutory cap of 8.95 million tons. NO_x emissions from EGUs (Figure 1b) were reduced to 2.0 million tons in 2011, 67 percent lower than 1995 emissions and substantially exceeding the Title IV goal.

Figure 1a *SO_2 Emissions from CAIR SO_2 Annual Program and ARP Sources, 1980 through 2011 (EPA, 2012b)*
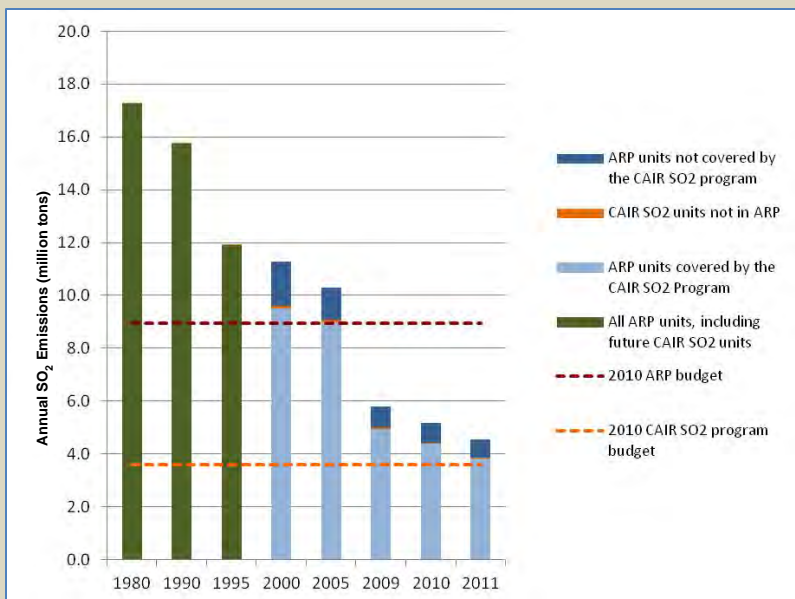
The success of the SO_2 emission-reduction program is due to the combined use of an overall emission cap for SO_2 with a trading system that encourages cost-effective emission reductions. The inherent flexibility for sources to choose how to control the SO_2 emissions in the cap and trade approach for SO_2 has been successful at reducing compliance costs to a fraction of the cost estimated in 1990. Several factors are responsible for the relatively low costs of SO_2 reductions realized under Title IV, including the widespread availability of low sulfur coal and technical innovations that facilitated use of that coal; lower than anticipated scrubber costs; the opportunity to bank allowances; and development of an efficient, high-volume market for allowances.

Figure 1b *NO$_x$ Emissions from CAIR and ARP Sources, 1990 through 2011 (EPA, 2012b)*
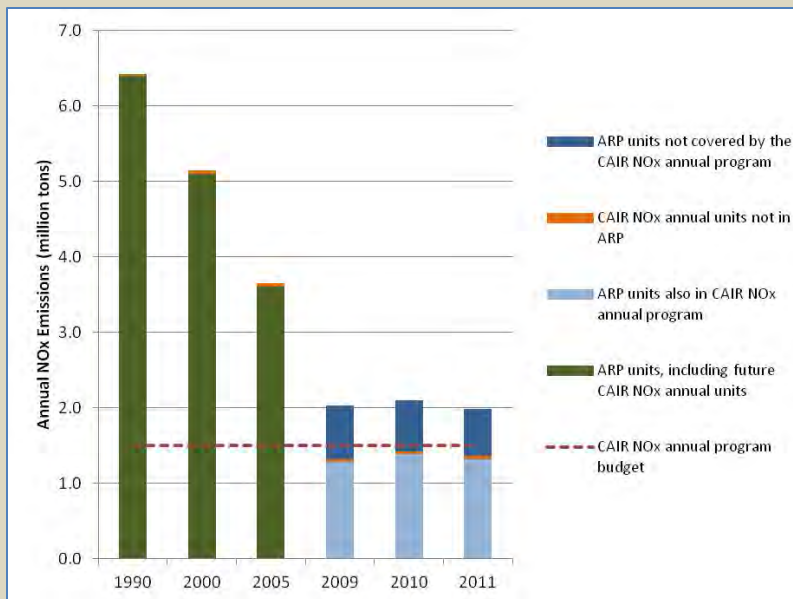
The emission reductions achieved under the ARP have contributed to measurable improvements in air quality, decreases in acid deposition, the beginnings of recovery of acid sensitive lakes and streams in some areas, and improvements in visibility. The NAPAP report also estimates the benefits and costs of complying with Title IV. Despite the environmental benefits reported by NAPAP and the declines in pollutant concentrations and deposition rates reported in this CASTNET 2011 Annual Report, recovery from the effects of acidification is not likely for many sensitive forests and aquatic ecosystems without additional decreases in emissions and acid deposition.

Source: Burns et al. (2011); EPA (2012b)

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, 2012a; 2012b) on the effects of the ARP and related programs. The 2011 EPA report (2012a) summarizes 2011 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, 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.
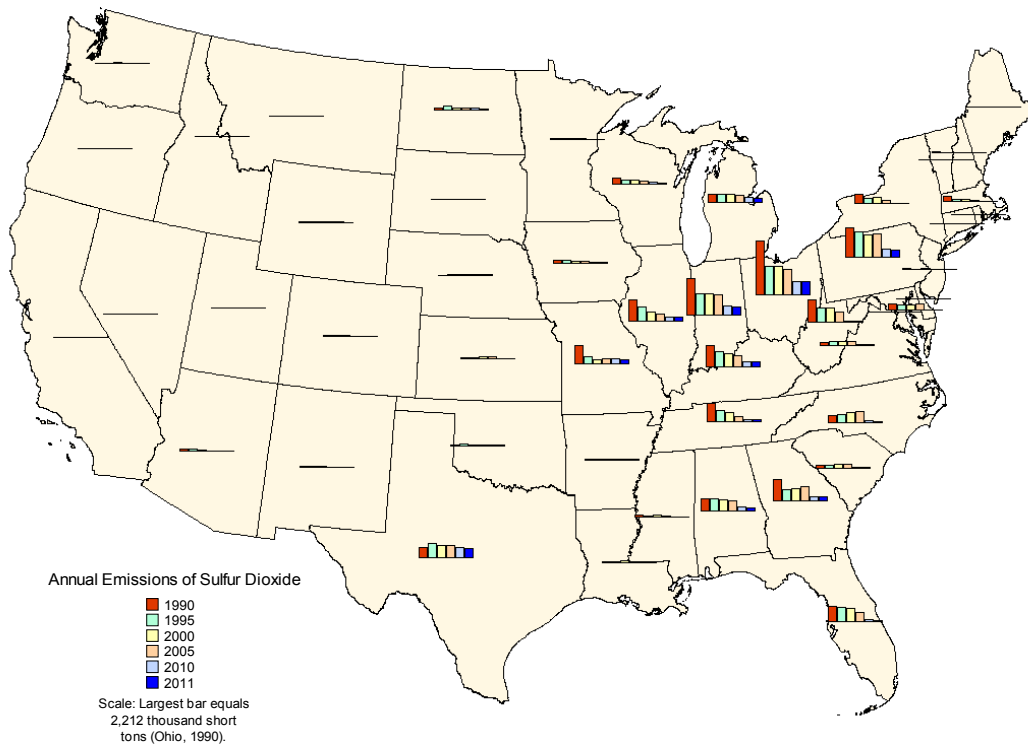
The ARP uses a more traditional approach to achieve NO_x emission reductions. Rate-based NO_x limits apply to most of the coal-fired electric utility boilers subject to the SO_2 emission reductions, and no nationwide cap has been placed on NO_x emissions. Other NO_x emission control programs have resulted in significant reductions in NO_x emissions during the O_3 season. These programs include the OTC NO_x Budget Program, the NO_x SIP Call/NBP, and the CAIR. See the discussion on page 2.

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 2011, the Phase II ARP SO_2 requirements affected 3,640 operating units. The Phase II ARP NO_x requirements applied to 930 of those operating units that exceed 25 megawatts and burned coal between 1990 and 1995 (EPA, 2012a). The CAIR NO_x O_3 season program affected 3,345 units in 2011, and the NO_x and SO_2 annual programs affected 3,307 units. Under the ARP's and CAIR's emission reduction requirements, total SO_2 emissions from affected sources were 4.5 million tons in 2011; total NO_x emissions from ARP and CAIR sources were 2.0 million tons.

Figure 1-5 presents state-by-state total annual SO_2 emissions for CAIR and ARP electric utility plants for six years (1990, 1995, 2000, 2005, 2010, and 2011). 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 50 percent reductions in SO_2 emissions over the 22 years; the larger emitting states (Illinois, Indiana, Kentucky, Ohio, Pennsylvania, and West Virginia) reduced SO_2 emissions by more than 73 percent. The period 2005 through 2011 experienced sharp reductions in SO_2 emissions in several states as a result of CAIR requirements. For example, notable reductions were achieved in West Virginia (80 percent), North Carolina and Massachusetts (72 percent), and Florida (78 percent).

Annual NO_x emissions by state are depicted in Figure 1-6 for the same six 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 2011. For example, NO_x emissions from Ohio EGUs declined by 73 percent from 2000 to 2011. Declines in NO_x emissions from the larger emitting states ranged from 67 percent in Pennsylvania to 81 percent in Ohio over the entire 22 years.

Figure 1-5 Annual SO$_2$ Emissions (for CAIR and ARP Sources)

Annual Emissions of Sulfur Dioxide

- 1990
- 1995
- 2000
- 2005
- 2010
- 2011

Scale: Largest bar equals
2,212 thousand short
tons (Ohio, 1990).

Source: EPA Air Markets Program Data (2012c)

Figure 1-6 Annual NO$_x$ Emissions (for CAIR and ARP Sources)

Annual Emissions of Nitrogen Oxides

- 1990
- 1995
- 2000
- 2005
- 2010
- 2011

Scale: Largest bar equals
534 thousand short
tons (Ohio, 1990).
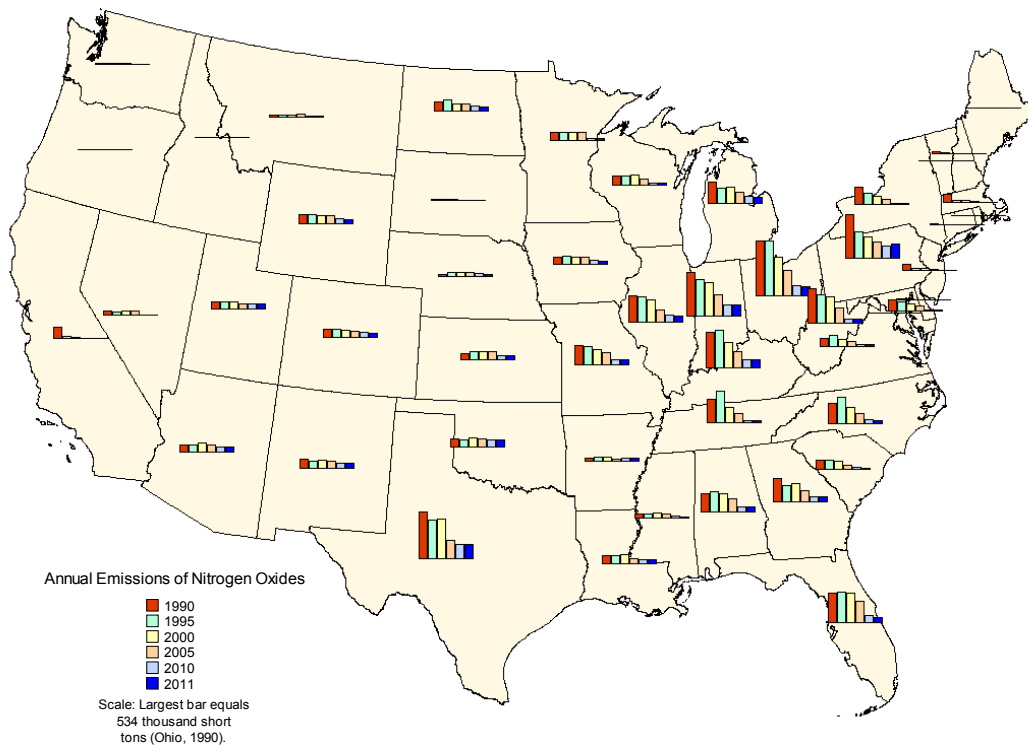
Source: EPA Air Markets Program Data (2012c)
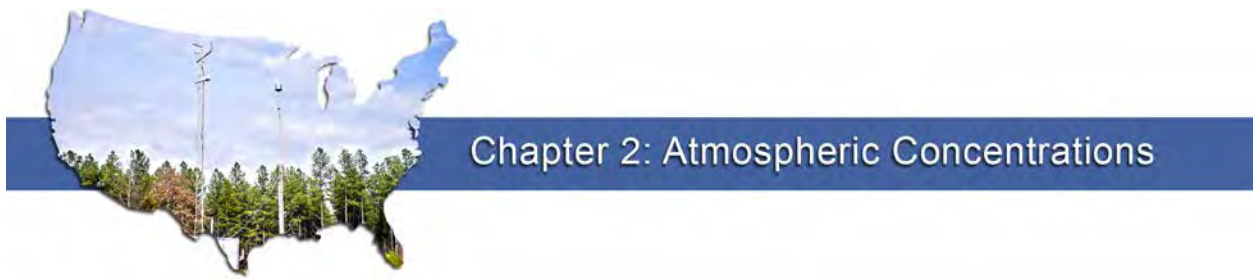
Chapter 2: Atmospheric Concentrations

Weekly average concentrations of SO_2, SO_4^{2-}, HNO_3, NO_3^-, NH_4^+, Cl^-, and 4 earth metals were measured at 83 CASTNET monitoring stations using 3-stage filter packs. Trends in mean annual SO_2, SO_4^{2-}, total NO_3, and NH_4^+ concentrations aggregated over 34 eastern and 17 western reference sites are shown using box plots for each year. All four sulfur and nitrogen parameters measured at the eastern sites declined over the 22-year period from 1990 through 2011. Measured annual mean concentrations of SO_2 and SO_4^{2-} have decreased steadily with a major reduction since 2005. Concentrations of total nitrate began to drop in 2000 in response to NO_x emission reduction programs and have continued to fall. SO_2, SO_4^{2-}, total NO_3, and NH_4^+ concentrations measured at the 17 western reference sites declined over the last 16 years.

Maps of 2011 annual mean concentrations of SO_2, SO_4^{2-}, total NO_3^- (HNO_3 + NO_3^-), and NH_4^+ are presented in this chapter. Additional maps are provided in CASTNET quarterly reports (AMEC, 2011a; 2011d; 2012a; 2012c). Trends in annual mean concentrations over the 22-year period (1990 through 2011) are presented using box plots derived from measurements from the 34 CASTNET eastern reference sites (Figure 1-2). Data from the 17 CASTNET western reference sites (Figure 1-2) were used to illustrate trends for the period 1996 through 2011. This chapter also includes information on the National Ambient Air Quality Standards (NAAQS) for particulate matter (PM), NH_3 measurements collected at five CASTNET sites, and final results from the Mountain Acid Deposition Program (MADPro).

Sulfur Dioxide

SO_2 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. Industrial facilities that fire fossil fuels and that extract metal from ore also emit SO_2. It is a major air pollutant that affects human health and plant ecosystems. SO_2 is a criteria pollutant, and, to be compliant under the SO_2 NAAQS, which was promulgated on June 2, 2010, 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 fine particulate matter ($PM_{2.5}$). Fine particles are also regulated by NAAQS since $PM_{2.5}$ adversely affects health and contributes to degradation of atmospheric visibility. See page 18 for a summary of the PM NAAQS. CASTNET does not measure $PM_{2.5}$, and CASTNET

SO_2 data are not used for attainment determinations. However, the results presented in this chapter depict long-term trends in the major components of $PM_{2.5}$. It should be noted that the regulatory monitoring networks such as State and Local Air Monitoring Stations (SLAMS) and National Air Monitoring Stations do not provide long-term, consistent data on trends in SO_2 and $PM_{2.5}$.

Annual mean SO_2 concentrations measured in 2011 are shown in Figure 2-1. Two sites in the eastern United States measured mean concentrations greater than 5.0 µg/m^3 of air. Quaker City, OH (QAK172) measured the highest concentration (6.5 µg/m^3). The other site with a level above 5.0 µg/m^3 was Oxford, OH (OXF122). SO_2 concentrations recorded in 2011 were lower than SO_2 levels measured in previous years. For comparison, the 3-state geographic average of mean SO_2 concentrations measured in 2011 at 10 monitoring stations in Indiana, Ohio, and Pennsylvania was 3.8 µg/m^3 versus a 3-state average of 4.4 µg/m^3 in 2010. Concentrations measured at the western sites in 2011 were generally lower than those measured at the eastern sites. Western concentrations were less than 1.0 µg/m^3 with the exception of the site at PAL190, TX which measured a 2011 annual mean SO_2 concentration equal to 1.0 µg/m^3.

Figure 2-1 Annual Mean SO$_2$ Concentrations (µg/m^3) for 2011
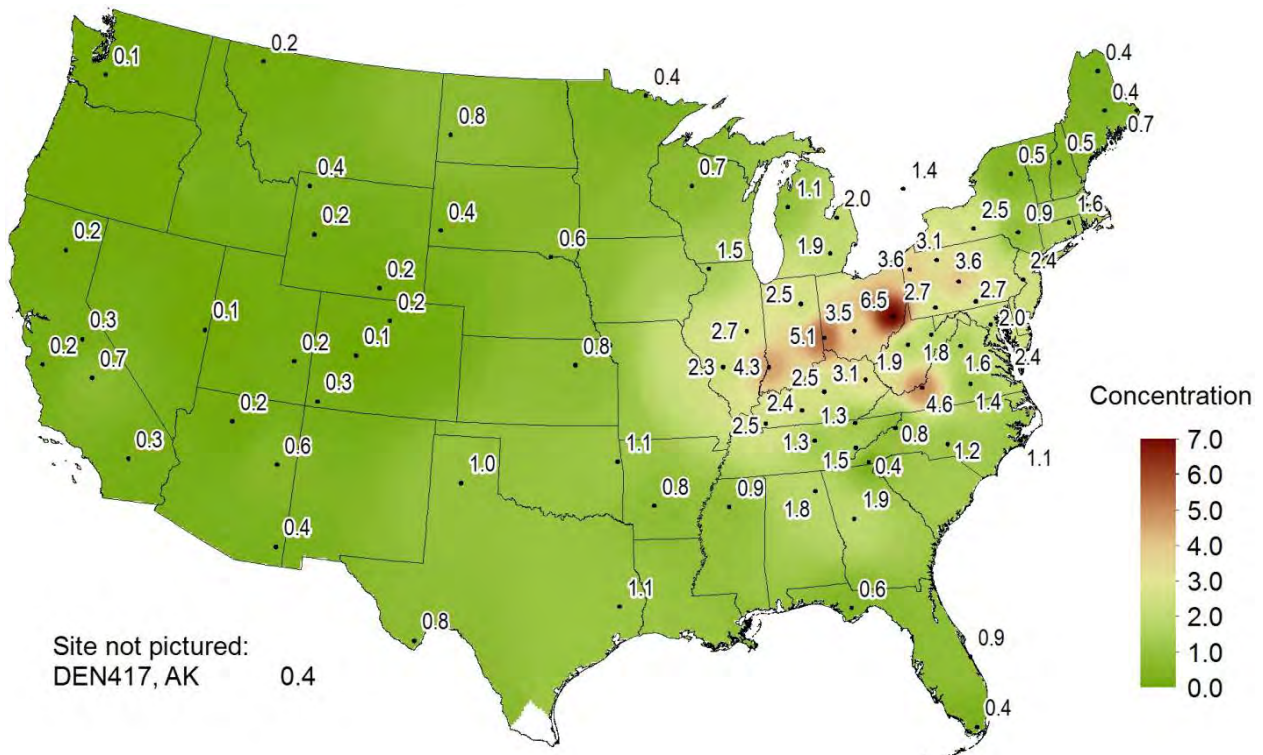
Figure 2-2 shows box plots of annual mean SO_2 concentrations aggregated over the 34 eastern reference sites from 1990 through 2011 (right side) and the 17 western reference sites from 1996 through 2011 (left side). Because concentrations measured at the western CASTNET

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. SO_2 levels also declined sharply from 2005 through 2011. Three-year mean concentrations for the eastern reference sites for 1990–1992 and 2009–2011 were 8.9 µg/m^3 and 2.5 µg/m^3, respectively. This change constitutes a 72 percent reduction in 3-year mean SO_2 concentrations between the two periods. The 2011 mean level of 2.1 µg/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 six 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 2009–2011 were 0.6 µg/m^3 and 0.3 µg/m^3, respectively. This change constitutes a 54 percent reduction in 3-year mean SO_2 concentrations over the 16 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)
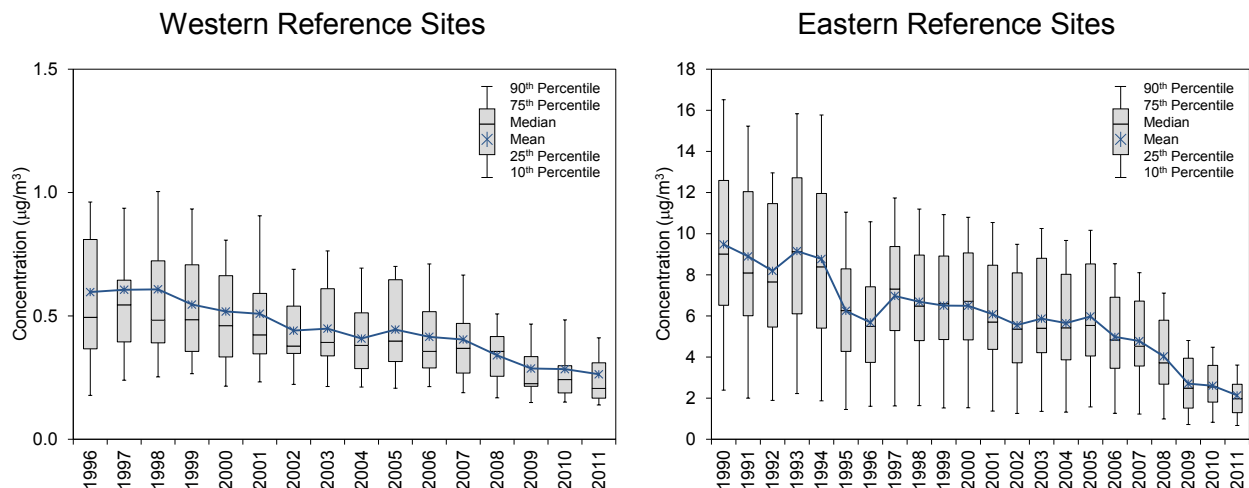
Quaker City, OH (QAK172)

National Ambient Air Quality Standards for Particulate Matter

On December 14, 2012, EPA strengthened the NAAQS for $PM_{2.5}$ while at the same time retaining the existing standard for coarse particulate matter (PM_{10}). $PM_{2.5}$ is comprised of $(NH_4)_2SO_4$, ammonium nitrate (NH_4NO_3), carbon aerosols, and other particles. $PM_{2.5}$ is formed when SO_2 and NO_x gaseous emissions from power plants, industrial facilities, and stationary diesel and gasoline engines react in the atmosphere. Other sources include fires and vehicles.

Annual standard *– EPA lowered the level of annual $PM_{2.5}$ concentrations from its previous level of 15 $\mu g/m^3$ to a level of 12 $\mu g/m^3$. An area will meet the standard if the 3-year average of its annual average $PM_{2.5}$ concentration is less than or equal to 12 $\mu g/m^3$.*

24-hour standards *– EPA retained the existing level of the 24-hour standard for $PM_{2.5}$ at 35 $\mu g/m^3$ along with the current framework of the standard. An area would meet the 24-hour standard if the 98th percentile of 24-hour $PM_{2.5}$ concentrations averaged over three years is less than or equal to 35 $\mu g/m^3$.*

EPA retained the existing 24-hour primary standard for PM_{10}, which is 150 $\mu g/m^3$. An area meets the 24-hour PM_{10} standard if it does not exceed the 150 $\mu g/m^3$ level more than once per year on average over a 3-year period.

24-hour secondary standards *– EPA retained the levels of the existing secondary standards for $PM_{2.5}$ and PM_{10}. An area meets the annual $PM_{2.5}$ secondary standard if the $PM_{2.5}$ concentration is less than or equal to 15 $\mu g/m^3$. An area meets the 24-hour $PM_{2.5}$ and PM_{10} secondary standard if the area does not exceed 35 $\mu g/m^3$ and 150 $\mu g/m^3$, respectively.*

Implementation *– EPA anticipates making final attainment/nonattainment designations by December 2014, with the designations becoming effective in early 2015. States will have until 2020 to meet the primary NAAQS. EPA intends to issue a final implementation rule in late 2014, about the same time as final designations.*

Particulate Sulfate

The transformation of SO_2 in the atmosphere through both gas and aqueous (cloud) phase reactions produces particulate SO_4^{2-}. Sulfate exists in the atmosphere primarily as $(NH_4)_2SO_4$, a major component of $PM_{2.5}$. Figure 2-3 depicts a map of annual mean particulate SO_4^{2-} concentrations measured during 2011. The map shows a fairly flat 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 four adjacent states (Kentucky, Indiana, Ohio, and Pennsylvania) plus the monitor at ALC188, TX measured SO_4^{2-} concentrations greater than or equal to 3.0 µg/m^3. Most of the filter pack samplers in the eastern United States measured SO_4^{2-} levels greater than or equal to 2.0 µg/m^3. Big Bend National Park, TX (BBE401); PAL190, TX; and Sequoia National Park, CA (SEK430) are the only three western sites that measured SO_4^{2-} concentrations greater than or equal to 1.0 µg/m^3.

Figure 2-3 Annual Mean SO_4^{2-} Concentrations (µg/m^3) for 2011
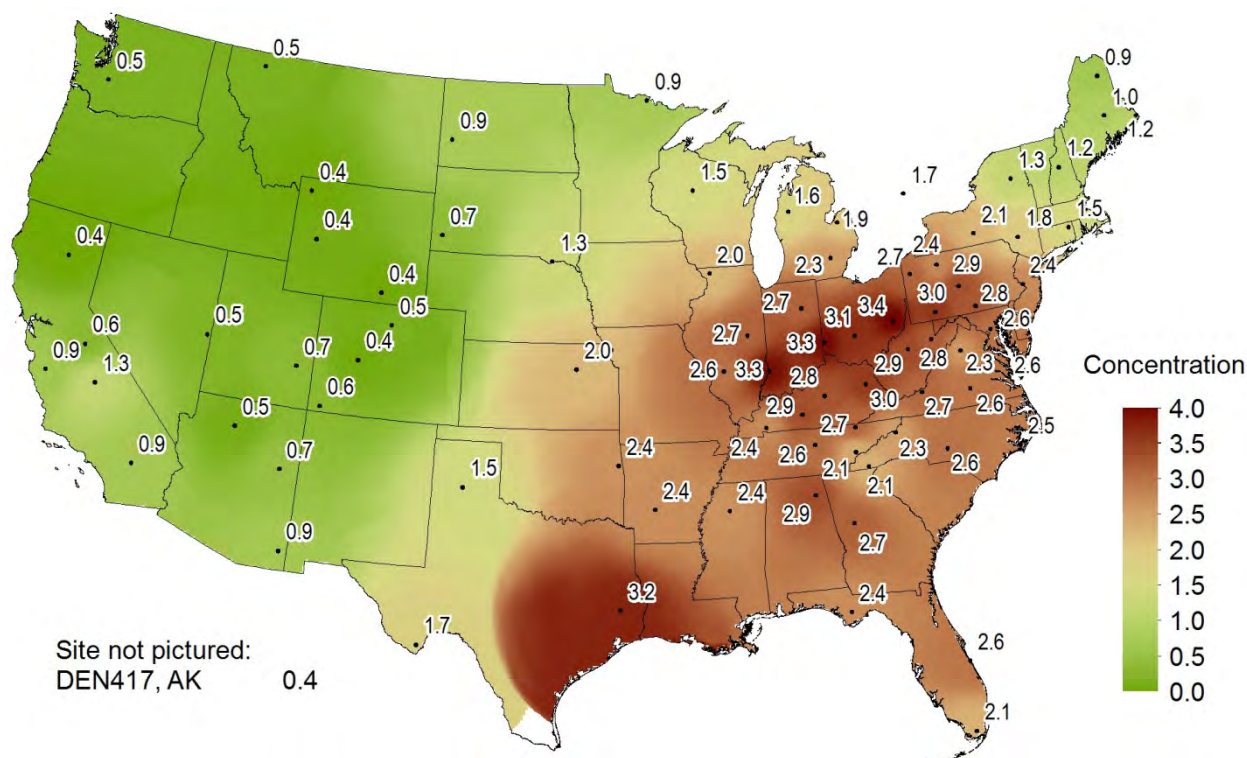
The right side of Figure 2-4 provides box plots of annual mean SO_4^{2-} concentrations from the 34 eastern reference sites. The figure shows a substantial decline in SO_4^{2-} over the 22 years, and, in particular, concentrations declined significantly from 2005 through 2011. The difference between 3-year means from 1990–1992 to 2009–2011 represents a 52 percent reduction in SO_4^{2-} from 5.4 µg/m^3 to 2.6 µg/m^3, respectively. The 2011 mean SO_4^{2-} level of 2.5 µg/m^3 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 21 percent reduction in annual mean SO_4^{2-} concentrations aggregated over the 17 sites, with 1996–1998 and 2009–2011 concentrations of 0.8 $\mu g/m^3$ and 0.6 $\mu g/m^3$, respectively.

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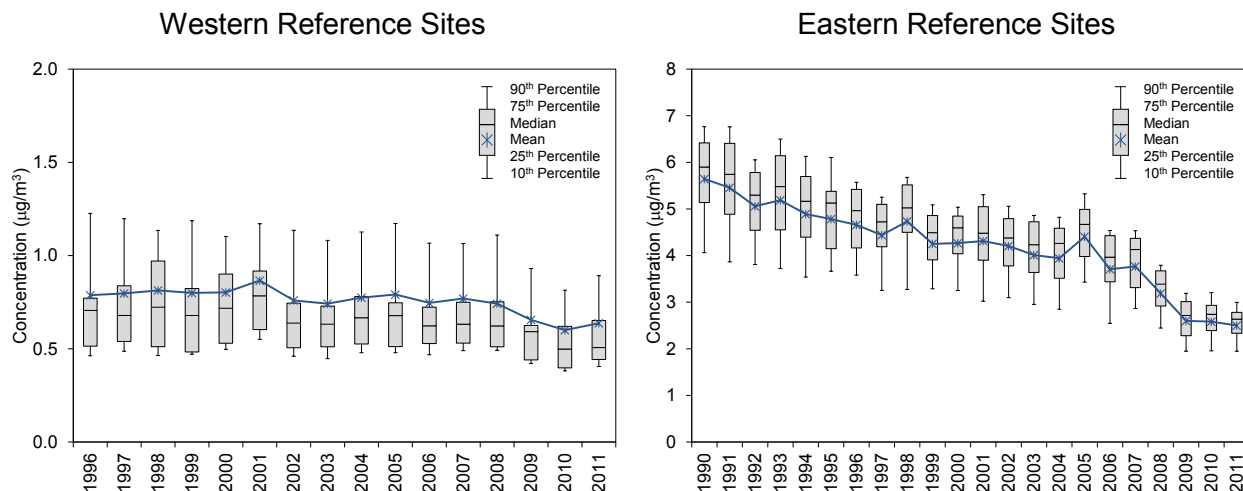
Total Nitrate

Total NO_3^- is the sum of HNO_3 and NO_3^-, which are formed in the atmosphere from NO_x emitted during the combustion of fossil fuels at high temperatures. Vehicular emissions (e.g., from 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. Lightning is a natural source of NO_x in the atmosphere. HNO_3 exists as a gas and contributes to acid deposition. NO_3^- is a component of $PM_{2.5}$ in the form of NH_4NO_3 and as larger particles such as sodium nitrate or calcium nitrate. Data on total NO_3^-, rather than HNO_3 and NO_3^- individually, are discussed because total NO_3^- is more representative of a response to changes in NO_x emissions than either of its constituents alone. Also, measurements of the individual constituents are thought to include significant uncertainties.

Figure 2-5 presents a map of annual mean total NO_3^- concentrations for 2011. The map shows annual mean concentrations greater than or equal to 3.0 $\mu g/m^3$ were measured in Illinois and Indiana. SEK430 and Joshua Tree National Park (JOT403) in California measured annual mean total NO_3^- concentrations greater than or equal to 2.0 $\mu g/m^3$. The BVL130, IL site measured the highest concentration (3.4 $\mu g/m^3$) in the network.

Figure 2-6 provides box plots of total NO_3^- levels for eastern sites for the years 1990 through 2011. 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 total NO_3^- levels began to decline in response to NO_x emission control programs. Three-year mean levels declined from 3.0 µg/m^3 to 2.0 µg/m^3 from 1990–1992 to 2009–2011, producing a 37 percent reduction in total NO_3^-. Total NO_3^- 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 1.9 µg/m^3 in 2011.

Figure 2-5 Annual Mean Total NO$_3^-$ Concentrations (µg/m^3) for 2011
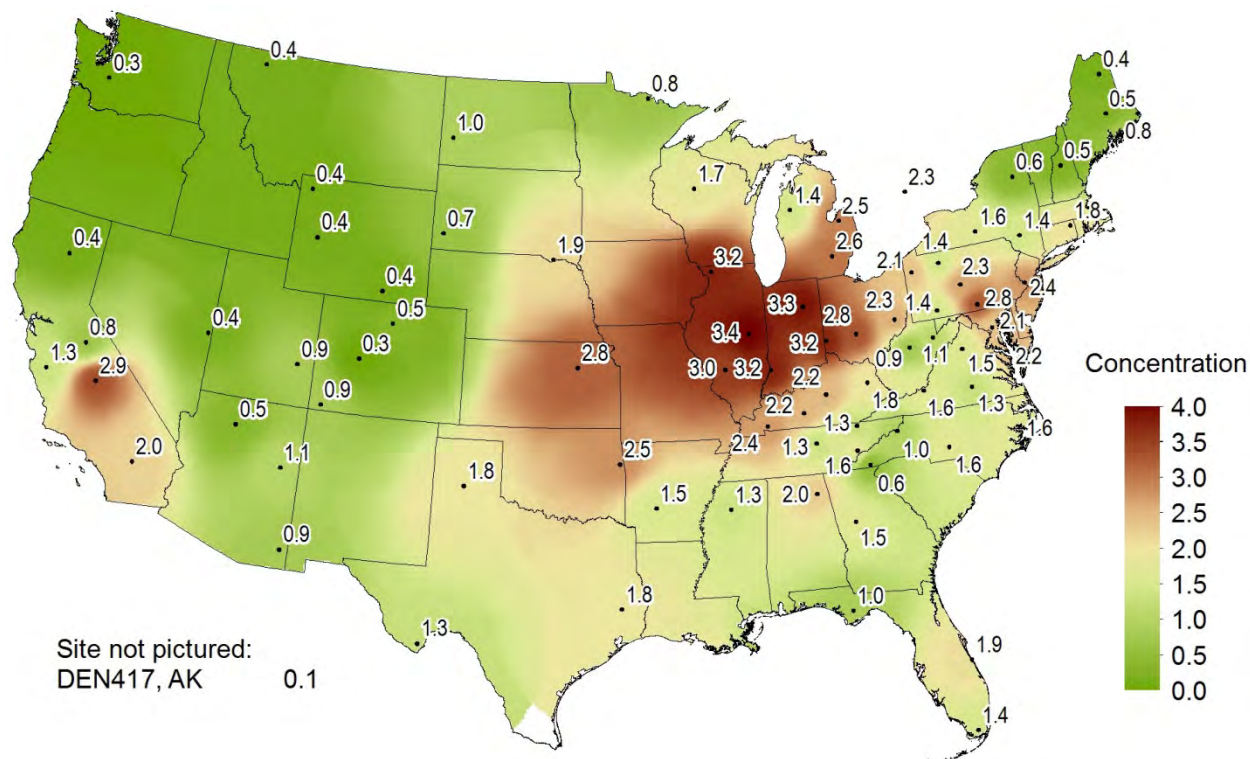
Data aggregated from the 17 western sites are shown on the left side of Figure 2-6. The 3-year mean total nitrate concentration for 2009–2011 was 29 percent lower than the corresponding 1996–1998 level with 3-year mean concentrations of 0.7 µg/m^3 and 1.0 µg/m^3, respectively.

Figure 2-6 Trend in Annual Mean Total NO$_3^-$ Concentrations (µg/m^3)

Western Reference Sites

Eastern Reference Sites
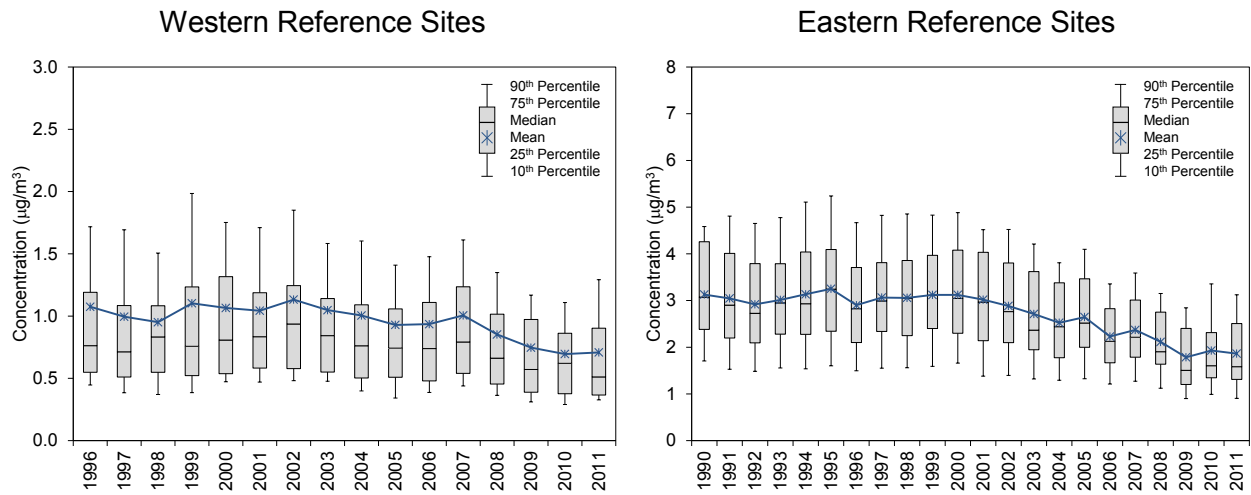
Bondville, IL (BVL130)

The CASTNET Ammonia Study and AMoN Ammonia Intercomparison

AMEC conducted a reactive nitrogen (Nr) inter-comparison study at five CASTNET sites over the period April 2010 through September 2011 (Rogers et al., 2012). This study is known as the Ammonia CASTNET Chemical Speciation Network (CSN) Study (ACCS). The current CASTNET 3-stage filter pack captures particulate NH_4^+ and NO_3^- on the first (Teflon) filter. There is a known bias of particulate NH_4^+ and particulate NO_3^- due to the volatilization of NH_4NO_3 during the typical 1-week sampling period. In addition to the bias introduced by volatilization, there is also an error introduced in the partitioning between particulate NO_3^- and gaseous HNO_3, which is collected on the second (nylon) filter.

The goals of the ACCS were to assess the weekly precision, accuracy, and bias of several different samplers, including passive NH_3 samplers (Radiello), a traditional CASTNET filter pack with an additional fourth stage filter impregnated with phosphorous acid (H_3PO_3) to collect atmospheric NH_3 and any volatilized NH_4^+ (an NH_x-filter), the Met One Super SASS mini-parallel plate denuder (MPPD) for NH_3, and the Met One Super SASS ion canisters, with duplicate annular denuder systems (ADS) as the reference method.

Study sites were selected based upon location, predicted or known nearby NH_3 emissions sources, site operator capability, and collocation with AMoN sites. AMoN sites are currently measuring NH_3 concentrations at 2-week intervals. During ACCS, concentrations were calculated as an average of results obtained from triplicate Radiello samplers. Currently 5 percent of AMoN sites measure triplicate NH_3 samples. The current AMoN protocol was followed for the passive samplers used in ACCS. The modified (4-stage) CASTNET filter pack was designed to run for two 1-week sampling periods at the same locations as the 3-stage filter pack. The Super SASS NH_3 denuder plus ion canisters and ADS (EPA modified Compendium Method I.O. 4.2) were run for two 1-week periods every six weeks. The passive samplers were analyzed by the NADP Central Analytical Laboratory and reported in the AMoN database, which is accessible via the NADP Web page (http://nadp.sws.uiuc.edu/AMoN/sites/data/). The Super SASS MPPD and annular denuders, which were operated in duplicate, were shipped to and analyzed by the AMEC CASTNET laboratory. The Super SASS ion canisters were shipped to the RTI International laboratory for analysis as part of the CSN contract.

Sampling Sites

Table 2a lists the primary sites within CASTNET that were selected for this study along with the types of samplers originally expected to be deployed at each site. Each of the sites selected for ACCS deployed a standard CASTNET 3-stage filter pack. The ACCS site locations can be seen on Figure 1-1.

Table 2a *CASTNET Sites Selected for Study*

Site ID	Sampler Configuration
CTH110, NY	AMoN passive sampler Single denuder NH_x only ADS
PAL190, TX	4-Stage CASTNET filter pack
ARE128, PA	AMoN passive sampler Two denuder ADS
CHE185, OK	4-Stage CASTNET filter pack Super SASS for NH_3
ROM206, CO	Super SASS CSN ion module

CTH110, NY

In addition to the primary sites, a test site was established at AMEC's Gainesville, FL office to test the equipment and sampling configurations.

Results

A test program was performed at the Gainesville test site from April 2010 to June 2010. Results of measurements at the test site showed problems with the 4-stage filter pack. NH_3 on the H_3PO_3-impregnated filter was expected but not found. Use of a 4-stage filter pack in high humidity environments was found to be not viable. Reaction of NH_3 with SO_2 collected by a hydrated K_2CO_3-impregnated filter prior to encountering the H_3PO_3-impregnated filter appeared to be responsible for the absence of NH_3 on the H_3PO_3-impregnated filter. A 3-stage filter pack with the K_2CO_3 filter replaced with a H_3PO_3 filter was successfully used to collect NH_3. Because of these results, 4-stage filter packs were not included during the ACCS field-sampling periods.

PAL190, TX

Following the test program, ACCS field sampling started at the end of August 2010 and continued through September 2011. Results from the field sampling component of the study are presented in Figures 2a through 2c. The results were used to evaluate the performance of the AMoN samplers and Super SASS MPPD.

In general, the AMoN passive sampler performed very well at all five sites compared with the ADS reference concentrations (Figures 2a–2c). Note that at ROM206/CO88, AMoN samples did not start until May 2011, and only four AMoN samples are currently included for comparison at that site.

Super SASS MPPD samples consistently collected less NH_3 than the reference ADS denuders (Figures 2b and 2c). This was especially evident at the high elevation site, ROM206 (Figure 2c). The CASTNET filter pack compared well with ADS-derived concentrations for all CASTNET analytes, but, as expected, CASTNET filter pack particulate NO_3^- concentrations were higher because of the collection of coarse-sized particles (Rogers et al., 2012).
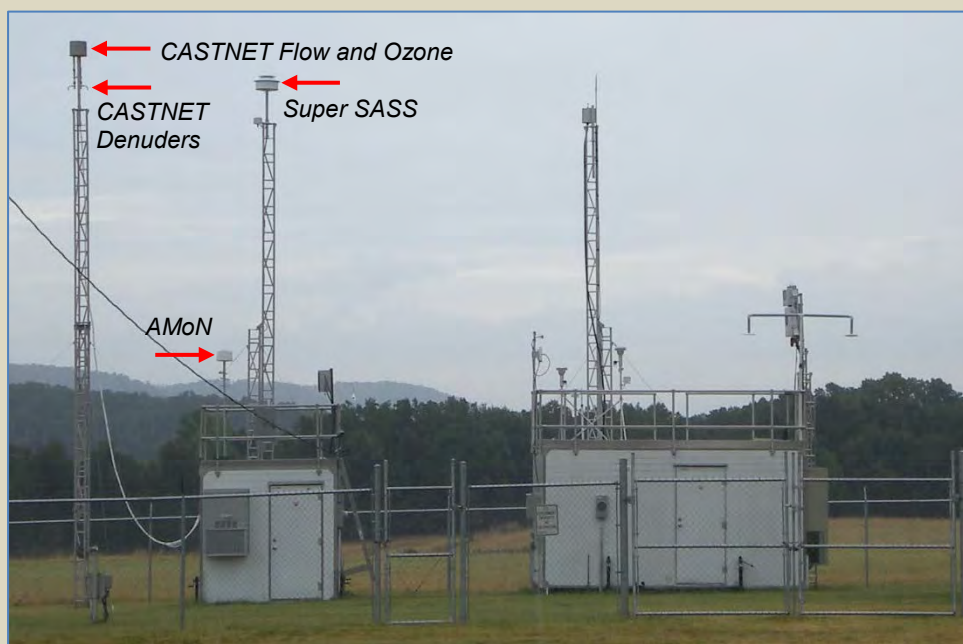
CHE185, OK

Figure 2a *Comparison between AMoN and ADS NH₃ Concentrations at PAL190/TX43*
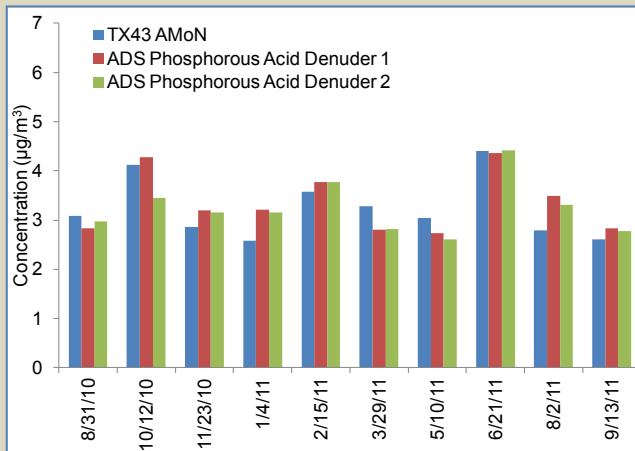
Note: TX43 is the AMoN site at Palo Duro Canyon State Park, TX.

Figure 2b *Comparison between AMoN, ADS, and Super SASS MPPD NH₃ Concentrations at ARE128/PA00*
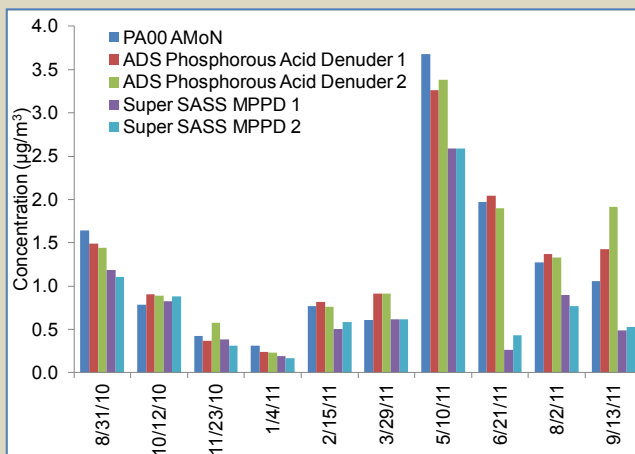
Note: PA00 is the AMoN site at Arendtsville, PA.

Figure 2c *Comparison between AMoN, ADS, and Super SASS MPPD NH₃ Concentrations at ROM206/CO88*
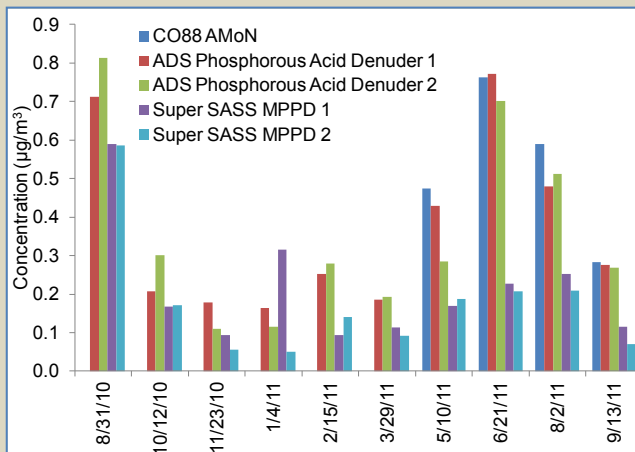
Note: CO88 is the AMoN site at Rocky Mountain National Park, CO.

Particulate Ammonium

Particulate NH_4^+ 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^-. The primary components of particulate NH_4^+ are from $(NH_4)_2SO_4$ and NH_4NO_3. Figure 2-7 provides a map of 2011 annual mean NH_4^+ concentrations. No monitors measured concentrations greater than 2.0 $\mu g/m^3$. The data show a relatively uniform geographic distribution across the central and eastern United States with more than half the sites reporting values less than or equal to 1.0 $\mu g/m^3$. Higher concentrations were measured in Illinois, Indiana, Ohio, Pennsylvania, Kentucky, and northern Alabama. The NH_4^+ concentrations measured at western sites were less than 1.0 $\mu g/m^3$.

Figure 2-7 Annual Mean NH_4^+ Concentrations ($\mu g/m^3$) for 2011
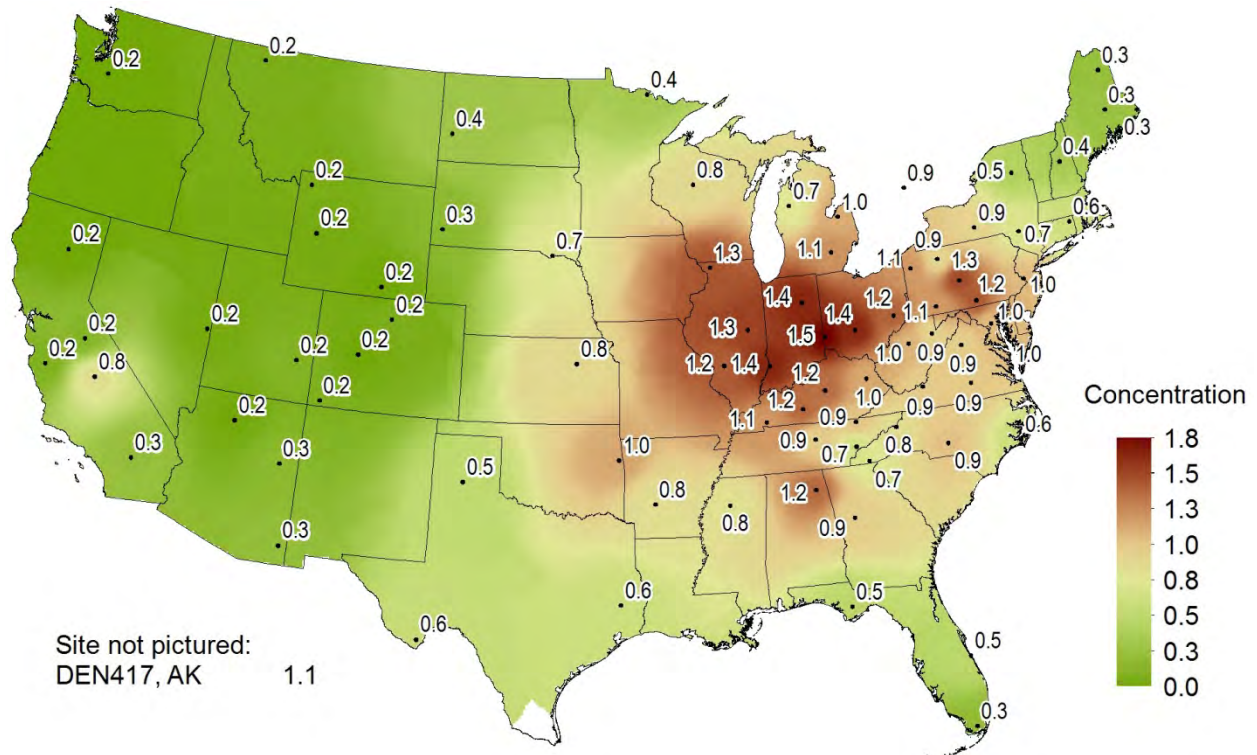
Figure 2-8 shows box plots of NH_4^+ concentrations. The trend diagram for the eastern sites shows a reduction in mean NH_4^+ levels from 1990–1992 to 2009–2011. The 1990–1992 mean concentration was 1.8 $\mu g/m^3$, and the 2009–2011 value was 1.0 $\mu g/m^3$, a 43 percent decline. The box plots characterizing the western sites show about an 18 percent reduction.

Figure 2-8 Trend in Annual Mean NH$_4^+$ Concentrations (µg/m^3)

Western Reference Sites

Eastern Reference Sites
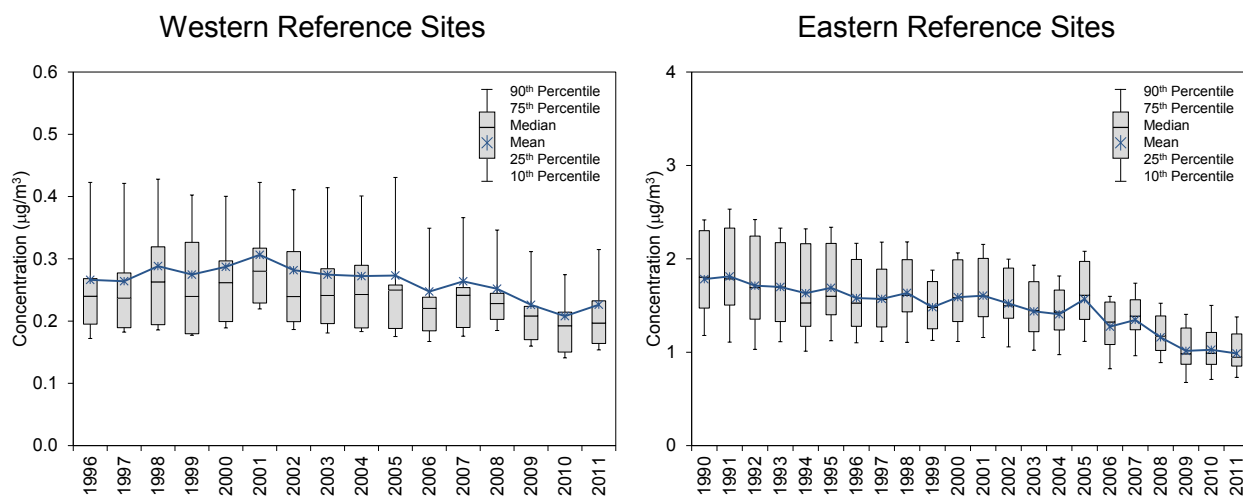
Cloud Deposition Monitoring at Clingmans Dome, TN

The Mountain Acid Deposition Program (MADPro) began in 1993 to support CASTNET's objective of gauging the impact of emission reductions on air pollution, atmospheric deposition, and ecological effects. Cloud water was measured at Clingmans Dome, TN (CLD303) in the Great Smoky Mountains National Park from 1993 through 2011, when the program was terminated. Monitoring stations were operated at other mountain locations in the early part of the program. Cloud water samples from MADPro were analyzed for their pollutant constituents and were used to estimate cloud deposition of these pollutants. During the last few years, MADPro was sponsored by the Tennessee Valley Authority (TVA) and EPA with infrastructure support from NPS.

For 2011, cloud water and meteorological parameters were measured at CLD303 (Figure 2d) atop a 50-m tower near the mountain summit. Ambient pollutant concentrations were sampled at the CASTNET site GRS420, TN in order to estimate dry deposition. Wet deposition was measured at Elkmont, TN (TN11), which is operated by NPS for NADP/NTN. The cloud water collector is depicted in Figure 2e. Atmospheric pollutant deposition experienced at mountain settings such as CLD303 results from the combined contributions of cloud, dry, and wet deposition.

Cloud deposition was modeled using the CLOUD model (Lovett, 1984). Cloud deposition depends on pollutant concentrations in cloud water, liquid water content (LWC), wind speed, and other parameters that were assumed fixed in the model simulations. LWC was measured using a particle volume monitor (Gerber PVM-100).

Figure 2f shows seasonal (June through September) cloud NO$_3^-$ concentrations, CLOUD-modeled NO$_3^-$ deposition fluxes, and NO$_x$ emissions from TVA power plants over the period 2000 through 2011. The figure shows an overall reduction in all three parameters. For example, the 3-year average NO$_3^-$ deposition declined from 42.3 kilograms per hectare (kg/ha) for 2000–2002 to 12.6 kg/ha for 2009-2011. NO$_x$ emissions declined from 270 thousand tons per year for 2000–2002 to about 64 thousand tons per year in 2009–2011.

Seasonal cloud SO$_4^{2-}$ concentrations, CLOUD-modeled SO$_4^{2-}$ deposition fluxes, and SO$_2$ emissions from TVA power plants over the period 2000 through 2011 are shown in Figure 2g. All three parameters were reduced significantly. The three-year average SO$_4^{2-}$ deposition declined from 70.4 kg/ha for

2000–2002 to 19.6 kg/ha for 2009–2011. SO_2 emissions declined from 630 thousand tons per year for 2000–2002 to about 210 thousand tons per year in 2009–2011.

Figures 2h and 2i show time series of cloud, wet (precipitation), and dry deposition fluxes of nitrogen and sulfur, respectively, for the period 2000 through 2011. The graphs show reductions in nitrogen and sulfur deposition fluxes associated with the three deposition mechanisms. Cloud deposition was the most significant pathway for deposition for CLD303, although the percentage contribution of cloud deposition decreased from about 90 percent at the beginning of the period to about 70 percent in 2011 (AMEC, 2012d).

Figure 2d *Clingmans Dome and Nearby Sampling Sites*

Figure 2e *Cloud Water Collector*
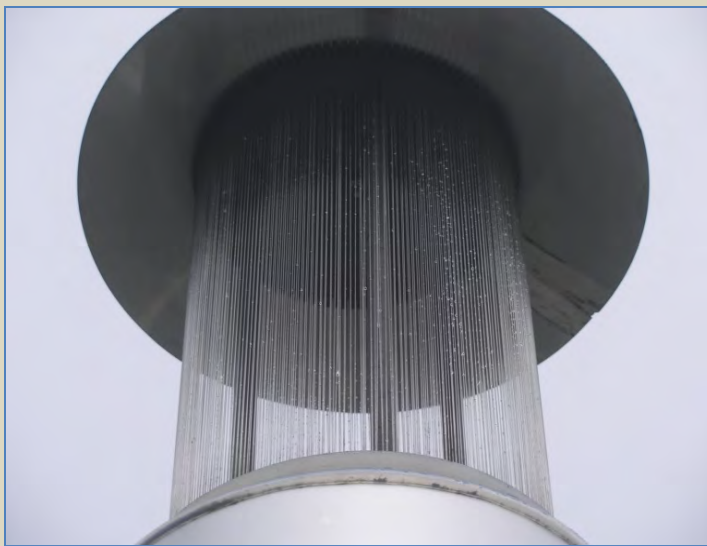
Figure 2f *Seasonal Cloud Water NO$_3^-$ Concentrations and Deposition and TVA Annual NO$_x$ Emissions*
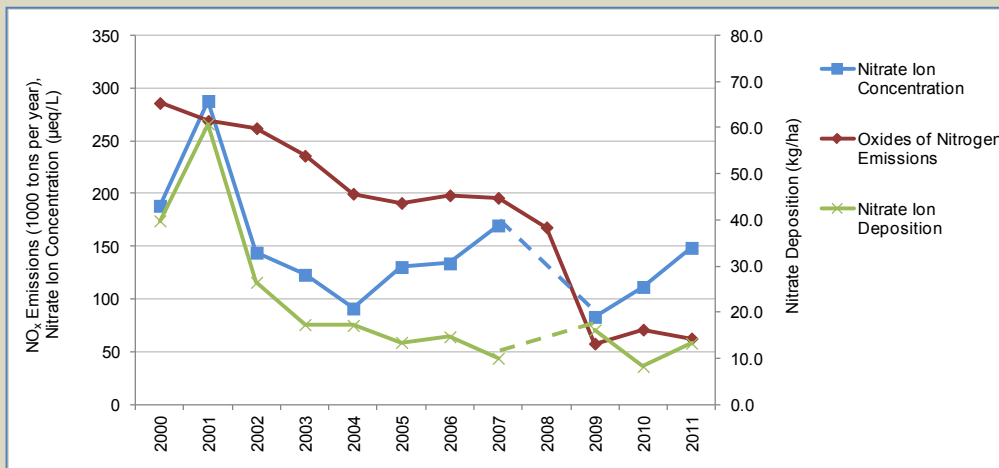
Figure 2g *Seasonal Cloud Water SO$_4^{2-}$ Concentrations and Deposition and TVA Annual SO$_2$ Emissions*
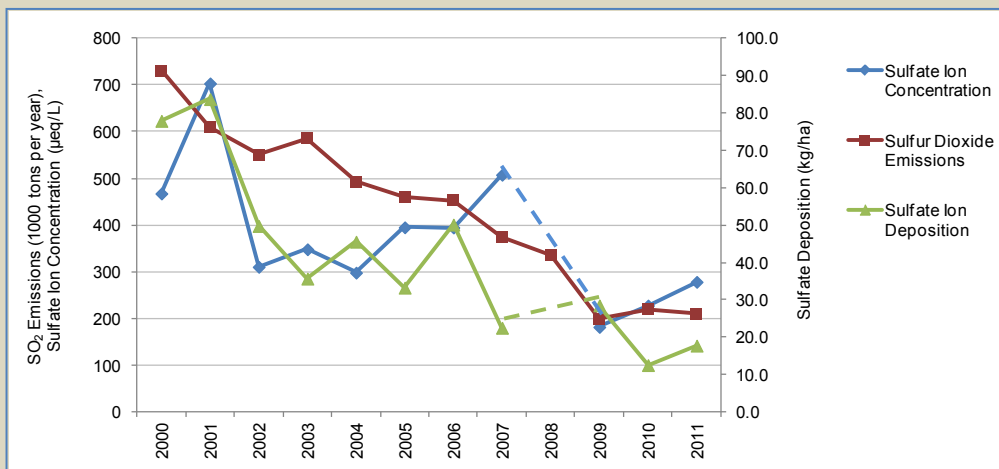
Figure 2h *Seasonal Nitrogen Deposition*
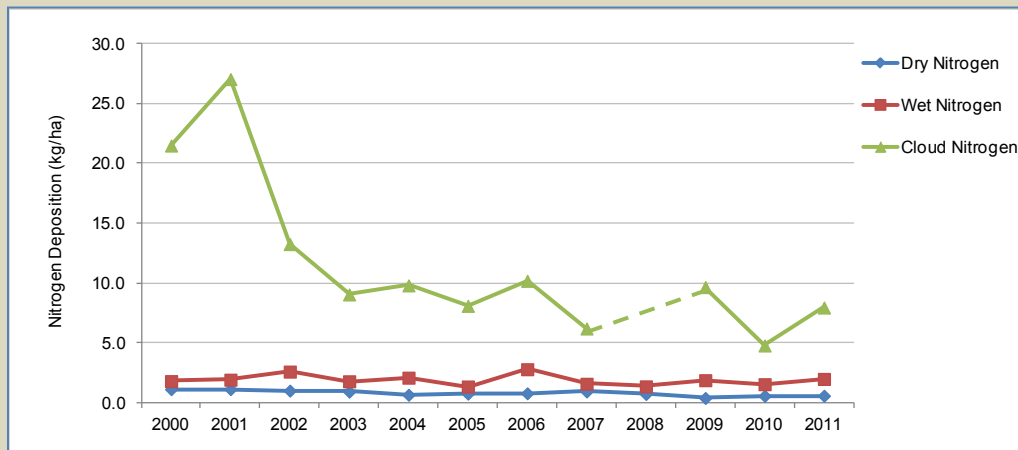
Figure 2i *Seasonal Sulfur Deposition*
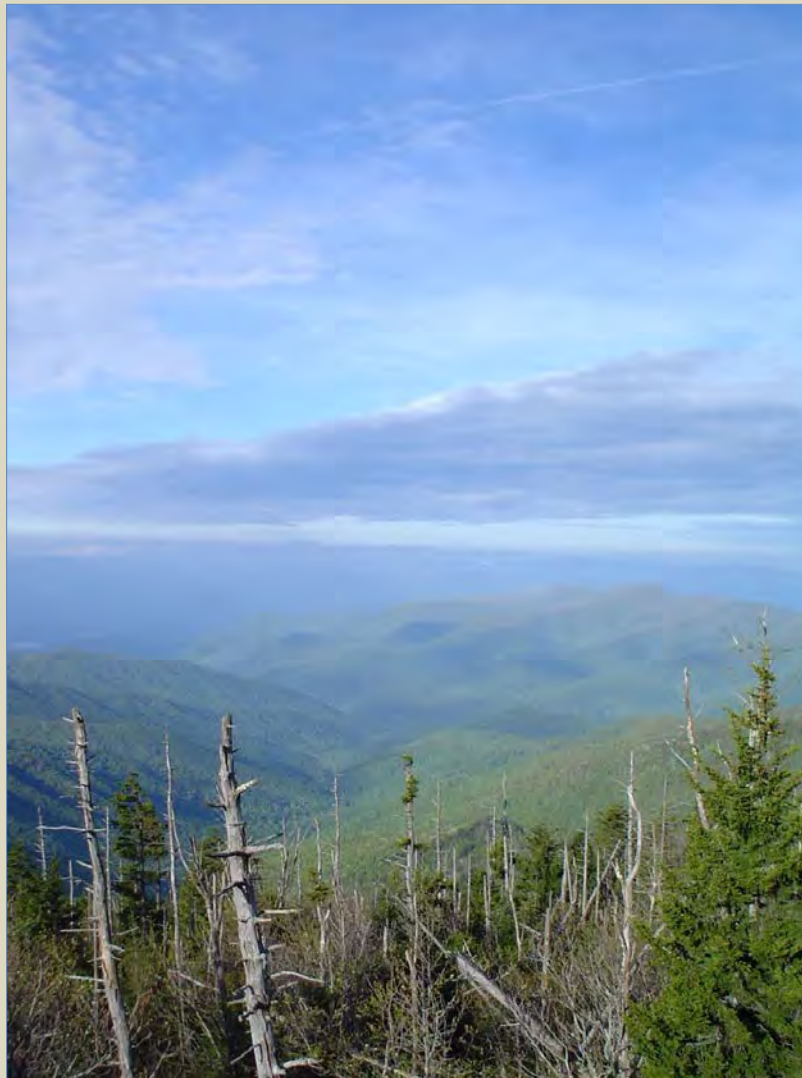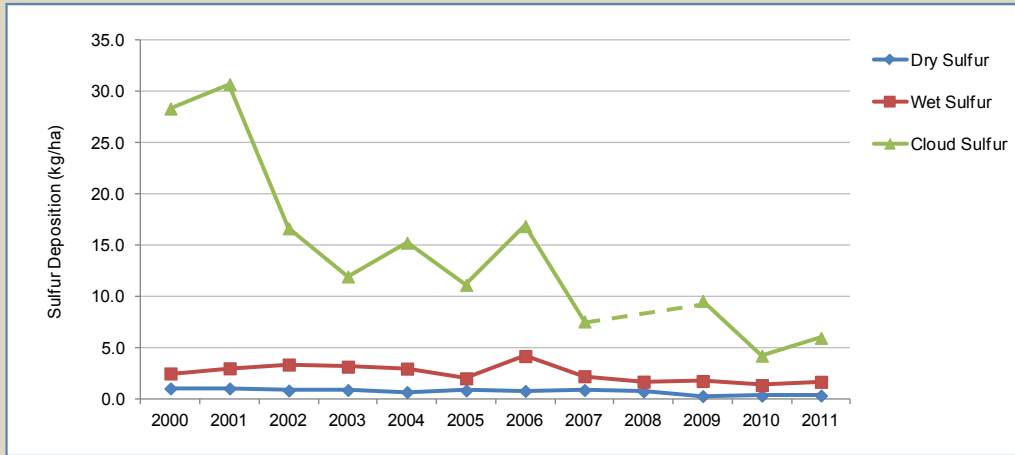
View from cloud water collection tower at CLD303

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 approach to estimate dry deposition by combining measured pollutant concentrations and modeled V_d. The MLM is used to calculate hourly V_d for each monitoring site based on meteorological measurements and information on the vegetative cover within 1 km of each site. Recently, CASTNET adopted a V_d data substitution method developed by Bowker et al. (2011) to fill in missing values of V_d with long-term averages. This method results in nearly 100 percent data completeness for V_d data. Dry deposition is calculated as the product of the measured pollutant concentration and modeled/substituted V_d. In order to improve estimates of wet deposition, the Parameter-elevation Regressions on Independent Slopes Model (PRISM) was selected in 2010 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 dry sulfur fluxes aggregated over the eastern reference sites declined by 68 percent over the period from 1990–1992 to 2009–2011. Three-year mean dry sulfur deposition estimated for 17 western sites declined by 41 percent over the period 1996–1998 to 2009–2011. Dry nitrogen deposition estimates declined 45 percent for the eastern reference sites and 36 percent at the western reference sites.

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 V_d. Recently, as summarized in the sidebar on the next page, CASTNET adopted a V_d data substitution method developed by EPA (Bowker *et al.,* 2011) to fill in missing values using long-term averages of V_d. This method results in nearly 100 percent data completeness for V_d data.

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.

EPA Method for Substituting Historical Hourly Deposition Velocity Values for Missing Hourly MLM Data

MLM calculations of hourly V_d values require hourly meteorological data plus information on vegetative cover as model input. This sidebar provides a synopsis of the analyses in the paper by Bowker et al. (2011) that are the bases for the data substitution method discussed herein. Historically, modeled V_d values have been about 70 percent complete for a given year. The discontinuance of meteorological measurements at all but five EPA-sponsored CASTNET sites coupled with 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 approach was developed to capture the site-specific diurnal and seasonal patterns in modeled V_d values and has resulted in long-term unbiased estimates of the annual mean V_d and total dry deposition.

The metric selected to describe the dry flux was the annual average V_d value for SO_2. The annual average V_d value depends on the year, the number of replaced values in the year, and distribution of missing values. The number of missing hours in a year was categorized by bins representing 10 percent intervals from 0 percent to 100 percent missing hours. The percent error (%E) and percent difference (%D) between the original data and substituted long-term hourly values was calculated for more than 5,000 pairs of annual V_d values. The formulas for the two measures of bias are given in Equations 3a and 3b.

Equation 3a $\quad \%E = \dfrac{1}{k} \sum_{j=1}^{k} \left(\dfrac{|Y - X|}{X} \right)_j x\ 100$ **Equation 3b** $\quad \%D = \dfrac{1}{k} \sum_{j=1}^{k} \left(\dfrac{Y - X}{X} \right)_j x\ 100$

The distribution and magnitude of the percent errors and percent differences are shown in Tables 3a and 3b. Both measures of bias were found to be site dependent. The %E increased generally with the percentage of missing data for each of the 11 sites selected for evaluation.

The %D showed both positive and negative average percent differences across the range of percent missing data. For a particular year at any given site, the annual mean V_d resulting from substitution was either higher or lower than the true mean and, consequently, showed little bias. That is, the substitution procedure did not have a large impact on the analysis of deposition trend. In addition, the results indicated that for the majority of the sites and missing data categories, the average percent difference was relatively small (less than ± 5 percent).
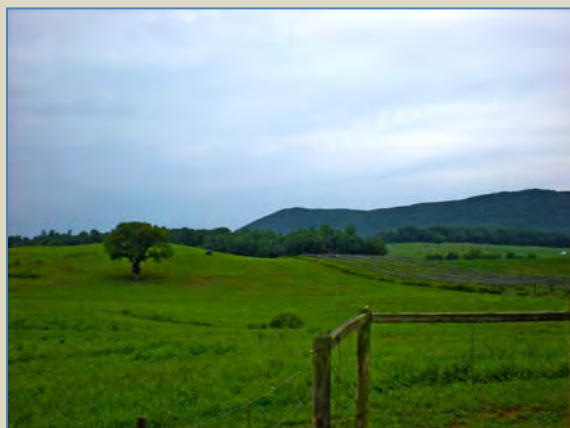
Speedwell, TN (SPD111)

Table 3a *Percent Error of Replaced Values for Each Selected Site and Percent Missing Hours*

	Percent Missing Data Categories									
SITE_ID	0-10%	11%-20%	21%-30%	31%-40%	41%-50%	51%-60%	60%-70%	71%-80%	81%-90%	90%-100%
ABT147, CT	0.50	1.52	1.97	3.32	4.62	5.66	5.31	3.15	0.00	7.21
ACA416, ME	0.58	1.58	3.23	4.41	5.75	8.85	7.02	9.85	0.00	11.84
CAD150, AR	0.46	0.93	1.99	2.12	2.82	3.42	4.83	3.47	1.64	5.10
DEN417, AK	0.93	2.48	4.47	6.23	6.35	8.73	7.67	11.54	0.00	14.56
DEV412, CA	0.06	0.12	0.18	0.19	0.22	0.21	0.31	0.40	0.00	0.54
GAS153, GA	0.61	1.89	3.03	4.29	4.55	4.85	6.53	6.21	1.09	7.37
GTH161, CO	0.38	0.95	1.72	1.65	2.02	1.43	2.81	2.52	1.70	4.49
NCS415, WA	0.42	1.06	1.12	2.19	2.25	1.86	3.58	2.82	3.39	3.71
PNF126, NC	0.38	1.28	1.76	1.87	2.25	3.24	3.22	3.62	0.00	3.33
PRK134, WI	0.93	3.30	5.49	7.43	8.64	10.92	10.73	12.72	0.00	17.80
WSP144, NJ	0.56	1.71	3.00	2.34	4.40	7.26	4.94	6.08	9.40	8.90

Table 3b *Percent Difference of Replaced Values for Each Selected Site and Percent Missing Hours*

	Percent Missing Data Categories									
SITE_ID	0-10%	11%-20%	21%-30%	31%-40%	41%-50%	51%-60%	60%-70%	71%-80%	81%-90%	90%-100%
ABT147, CT	0.10	0.50	0.63	0.48	1.89	1.94	1.24	2.89	0.00	1.95
ACA416, ME	-0.21	-0.88	-1.53	-1.84	-1.86	-6.09	2.66	-6.19	0.00	-4.76
CAD150, AR	-0.13	-0.22	-0.66	-1.23	-1.89	-0.70	-2.84	-2.52	-1.64	-2.93
DEN417, AK	-0.01	-0.03	0.11	-0.08	-0.47	0.33	1.37	-1.23	0.00	1.86
DEV412, CA	-0.03	-0.07	-0.09	-0.17	-0.19	0.09	-0.31	-0.40	0.00	-0.46
GAS153, GA	0.15	0.83	0.15	1.33	1.98	-1.11	1.53	1.85	1.09	1.38
GTH161, CO	0.07	-0.04	0.80	0.28	0.08	-0.79	1.16	0.03	-1.70	1.16
NCS415, WA	0.05	0.00	0.30	-0.07	0.02	-1.03	0.08	-0.13	3.39	0.83
PNF126, NC	-0.01	-0.35	0.04	0.57	-0.28	-1.37	-0.78	2.69	0.00	-0.86
PRK134, WI	-0.38	-1.77	-1.54	-3.80	-3.42	-5.37	-6.41	-1.92	0.00	-8.66
WSP144, NJ	0.04	0.17	0.55	-0.40	-0.95	-0.26	-2.20	1.60	9.40	-1.45

Consequently, for this annual report, the Bowker et al. (2011) substitution method was applied to the 1987 through 2011 database of hourly V_d values for all sites in order to improve V_d data completeness and to substitute for missing values. Consider the following example. A SO_2 V_d value for hour 10:00 (Eastern Standard Time) is missing on December 24, 2011, which is in the 51st week of the year, at Speedwell, TN (SPD111). SPD111 began operation on June 12, 1989. To obtain a V_d value for that hour, the substituted value was calculated as the mean of 7 hourly values, if valid, for hour 10:00 for week 51 for each year 1989 through 2010 plus 6 values, if valid, for hour 10:00 during week 51 for 2011, i.e., the mean of a

Speedwell, TN (SPD111)

possible 160 hourly V_d values. The substitution scheme resulted in nearly 100 percent completeness for all sites for the reporting period 1990 through 2011. The updated values of V_d were used to estimate dry deposition fluxes of individual sulfur and nitrogen species, which were then summed to obtain sulfur deposition as "S" ($SO_2 + SO_4^{2-}$) and nitrogen deposition as "N" ($HNO_3 + NO_3^- + NH_4^+$) and their trends for 1990 through 2011.

Sulfur Deposition

The MLM was run separately for SO_2 and SO_4^{2-}. The EPA substitution method was used to complete any missing flux values, resulting in 100 percent data completeness. The model calculations of SO_2 and SO_4^{2-} were summed to obtain the 2011 estimates of dry sulfur deposition (as S). Figure 3-1 shows a map of the estimated dry deposition fluxes. The magnitude of a deposition rate is illustrated by the size of the circle. The map shows three CASTNET sites in Indiana and Ohio with estimated fluxes greater than 3.0 kilograms per hectare per year (kg/ha/yr). The 3-state geographic average dry S deposition rate for Indiana, Ohio, and Pennsylvania was 2.5 kg/ha/yr compared to an average flux of 2.9 kg/ha/yr in 2010. The highest 2011 deposition rate was estimated for QAK172, OH with a flux of 5.2 kg/ha/yr compared to a flux of 5.5 kg/ha/yr in 2010. The highest estimated dry sulfur deposition rates coincided with the major SO_2 source region (Figures 1-5 and 2-1) and declined with distance from the source region. The dry deposition rates estimated for the western CASTNET sites were all less than 1.0 kg/ha/yr with all but the two west Texas sites with fluxes less than 0.5 kg/ha/yr.

Figure 3-1 Dry Sulfur ($SO_2 + SO_4^{2-}$) Deposition (kg/ha/yr) for 2011
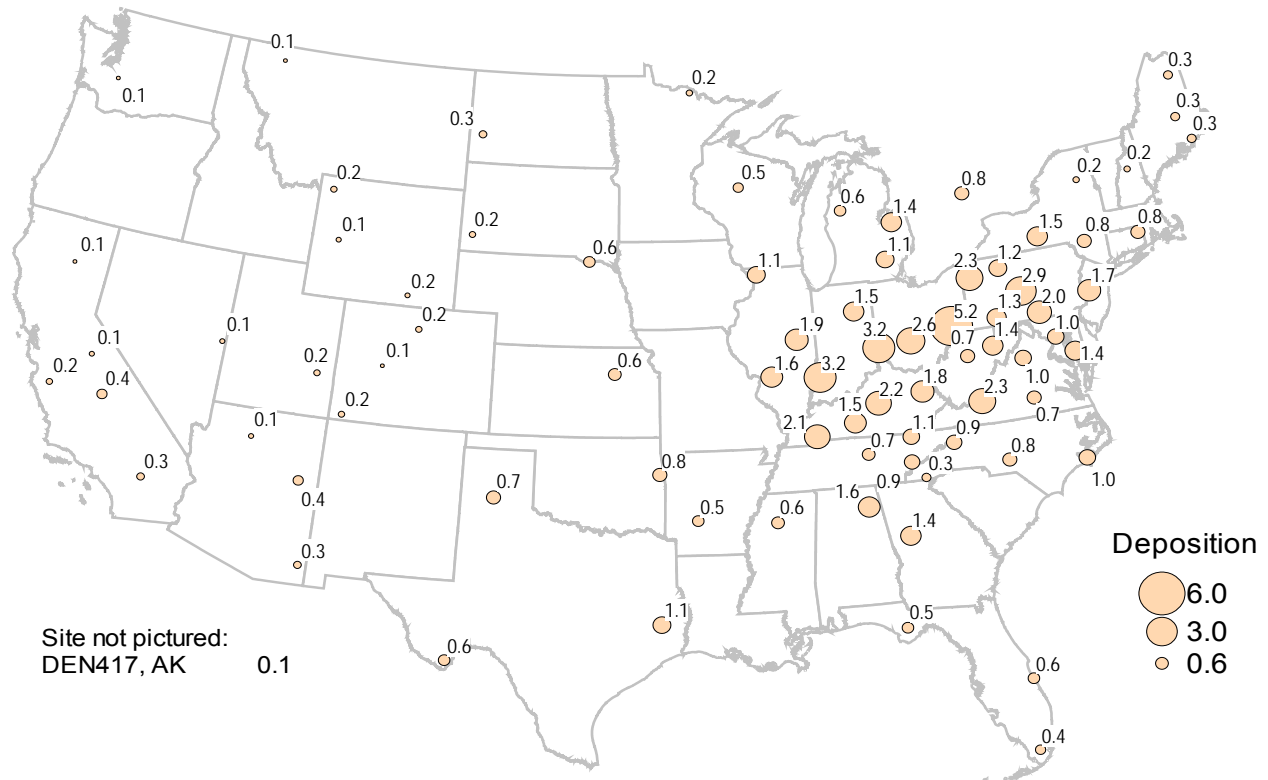
Wet deposition values used to estimate total deposition were based on a grid of PRISM-modeled precipitation amounts and gridded values of pollutant concentrations in precipitation. The concentrations were multiplied by precipitation rates to estimate wet fluxes. Wet flux data were interpolated to CASTNET sites.

A map of estimates of total sulfur deposition is given in Figure 3-2. 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. The values estimated for 2011 were higher than 2010 values due to the atypically high contribution from wet deposition in 2011. Ten CASTNET sites in the states of Indiana, Ohio, Pennsylvania, and Kentucky and in Ontario had total (dry + wet) sulfur deposition fluxes greater than 7.0 kg/ha/yr in 2011. The highest total sulfur deposition rate was estimated for QAK172, OH with a value of 13.0 kg/ha/yr. The total sulfur deposition value for this site was 9.8 kg/ha/yr in 2010 and 9.7 kg/ha/yr in 2009. Total sulfur deposition at western sites was less than or equal to 2.0 kg/ha/yr, which was the estimate for PAL190, TX.

Figure 3-2 Total (Dry + Wet) Sulfur Deposition (kg/ha/yr) for 2011
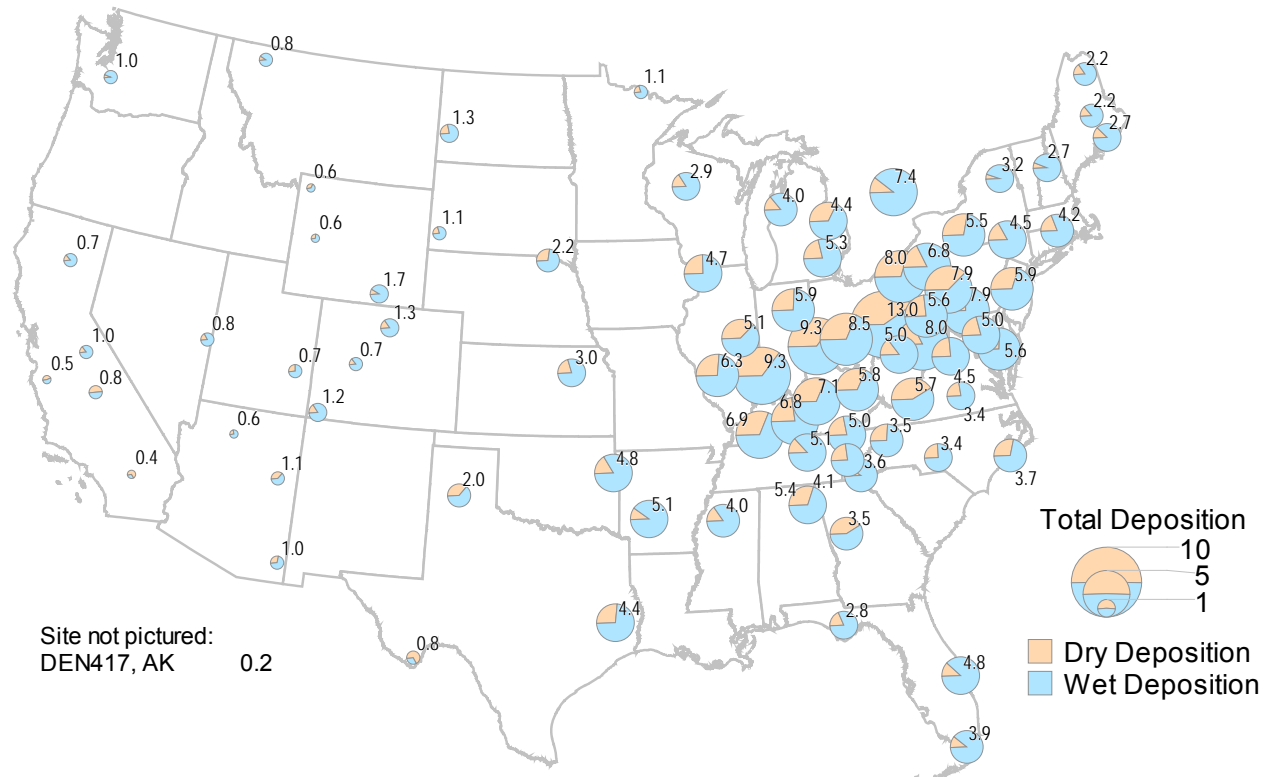
Figure 3-3 presents box plots that show the trend in dry sulfur deposition (as S) for the eastern (right side) and western (left side) reference sites. Figure 3-4 shows the trend in annual total (dry + wet) sulfur deposition (as S). The box plots were based on data obtained from the 34 CASTNET eastern reference sites for the period 1990 through 2011 and from the 17 western reference sites for 1996 through 2011. The y-axes on the two figures have different scales. Aggregated dry sulfur deposition declined considerably at the eastern and western reference sites over their respective periods. Overall, dry sulfur deposition declined at the eastern reference sites from a 1990–1992 mean of 5.1 kg/ha/yr to a 2009–2011 mean of 1.6 kg/ha/yr, a 68 percent reduction. Dry sulfur deposition declined at the western reference sites from a 1996–1998 mean of 0.3 kg/ha/yr to a 2009–2011 mean of 0.2 kg/ha/yr, a 41 percent reduction.

Figure 3-3 Trend in Dry Sulfur Deposition (kg/ha/yr)
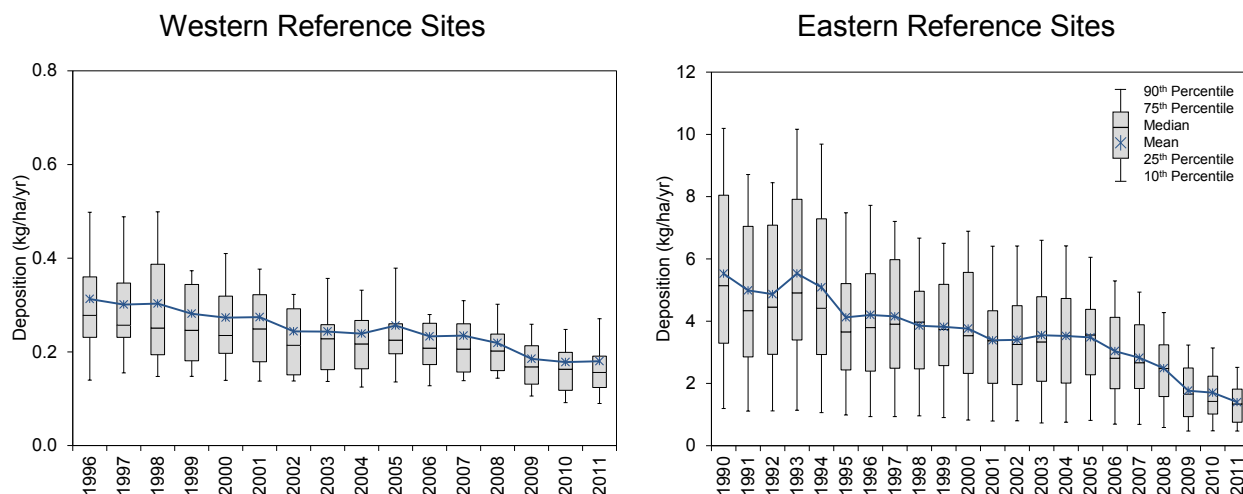
Figure 3-4 shows the trend in annual total (dry + wet) sulfur deposition (as S) at the reference sites. Aggregated sulfur deposition declined considerably at the eastern and western reference sites over their respective periods. Overall, total sulfur deposition declined at the eastern reference sites from a 1990–1992 mean of 12.9 kg/ha/yr to a 2009–2011 mean of 5.3 kg/ha/yr, a 59 percent reduction. Total sulfur deposition declined at the western reference sites from a 1996–1998 mean of 1.3 kg/ha/yr to a 2009–2011 mean of 0.8 kg/ha/yr, a 35 percent reduction. The total sulfur flux for the eastern reference sites was higher in 2011 than in 2010. Wet deposition in 2011 was a major component of sulfur flux with a contribution of 75 percent.

Figure 3-5 presents estimates of trends in dry, wet, and total deposition of sulfur (as S) for the western and 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 3-5. The solid line shows total deposition, which depends on sulfur concentrations in precipitation and precipitation amounts. The dotted line shows concentrations in precipitation, which are independent of

precipitation amount. The figure shows wet, dry, and total sulfur depositions have all declined significantly. However, total sulfur deposition estimated for the eastern sites in 2011 increased relative to 2010, and the sulfur concentration in precipitation for the western sites increased in 2011.

Figure 3-4 Trend in Total Sulfur Deposition (kg/ha/yr)
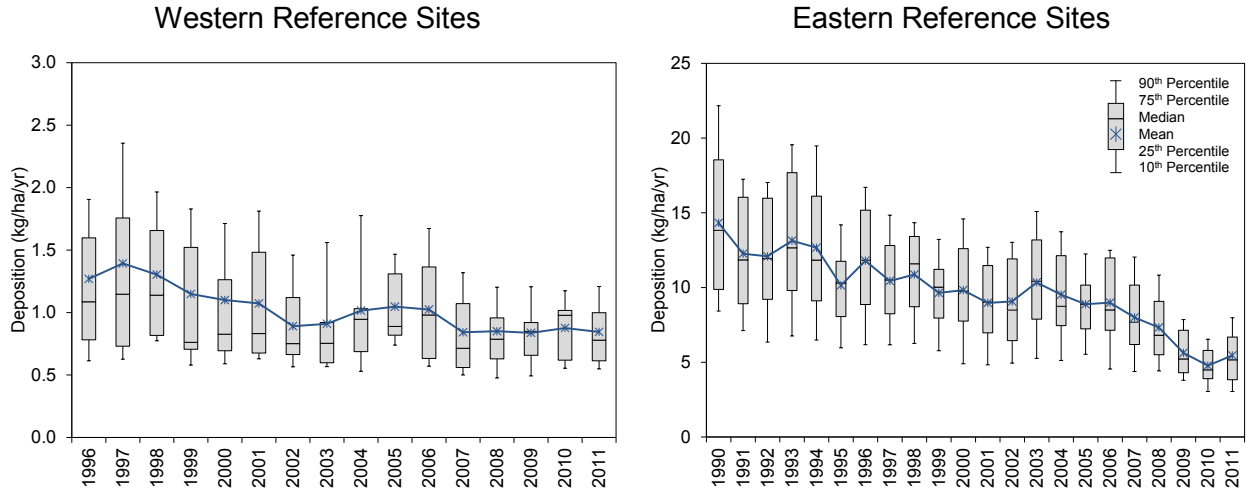
Figure 3-5 Trend in Sulfur Deposition (kg/ha/yr) with Concentrations in Precipitation [milligrams per liter (mg/l)]
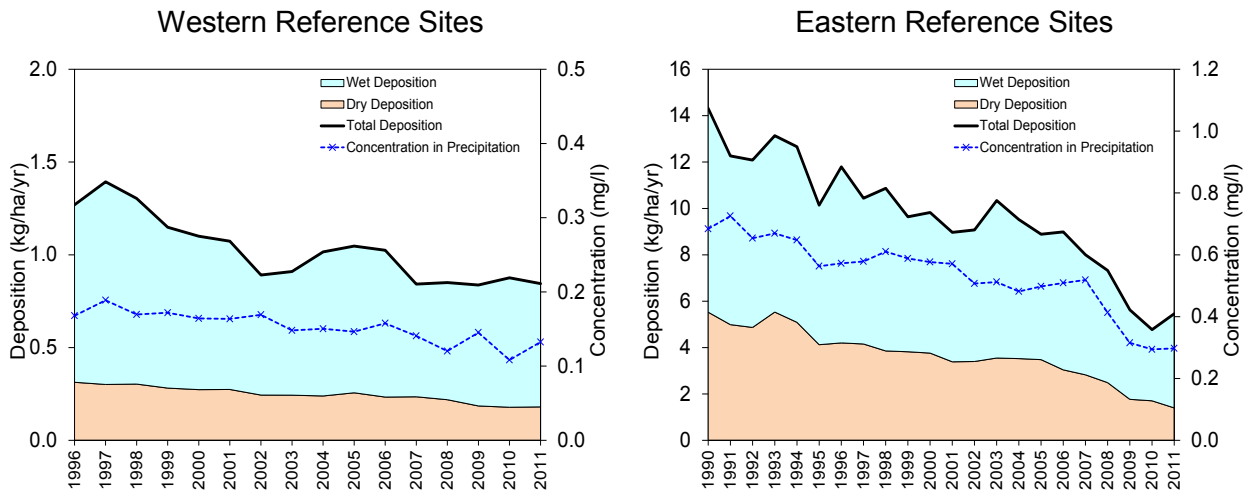
The Effect of Differences in Annular Denuder System and CASTNET Filter Pack Concentration Data Relative to Estimates of Atmospheric Deposition

The primary purpose of the Ammonia CASTNET CSN Study (ACCS) was to conduct a Nr inter-comparison study at five CASTNET sites for one year (Rogers et al*., 2012). See the sidebar on page 23 in Chapter 2 for a synopsis of ACCS.*

While the primary purpose of ACCS was to evaluate NH_3 samplers and their bias, one of the benefits of ACCS was an increased understanding of how well the standard CASTNET filter pack performed relative to ADS (EPA Modified Compendium Method I.O. 4.2) in terms of estimating atmospheric deposition of sulfur and nitrogen species.

Results from ACCS (Rogers et al*., 2012) show that, in general, the current CASTNET filter packs compared favorably with the ADS when measuring SO_2, total NO_3^-, SO_4^{2-}, and NH_4^+. Both systems consistently measured these standard CASTNET analytes. Total NO_3 measurements were slightly higher for the CASTNET filter pack compared with the ADS because the CASTNET filter pack has an open face while the ADS has a 2.5 micrometer size cut cyclone separator. The cyclone feature allows coarse-sized NO_3^- particles (e.g., sodium and calcium nitrate) to be removed prior to sampling by the ADS. The filter pack samples are without size restriction, which results in the collection of both coarse and fine particles.*

Comparisons of sulfur species were consistently better than for nitrogen species. Figure 3a shows the comparison for SO_2 between the CASTNET filter pack and two ADS at the Arendtsville, PA (ARE128) CASTNET site. The results between the two systems were very consistent. Similar results were also found when comparing SO_4^{2-} concentrations. Sulfur species are not subject to the volatilization and partitioning found with nitrogen species. In addition, particulate sulfur species are dominated by fine particles, which are less affected by the size restriction imposed by the cyclone on the ADS. As a consequence, estimates of deposition of sulfur species based on either the CASTNET filter pack or the ADS data are similar.

Figure 3a *Comparison between CASTNET Filter Pack and ADS SO_2 Concentrations at the ARE128, PA Site*
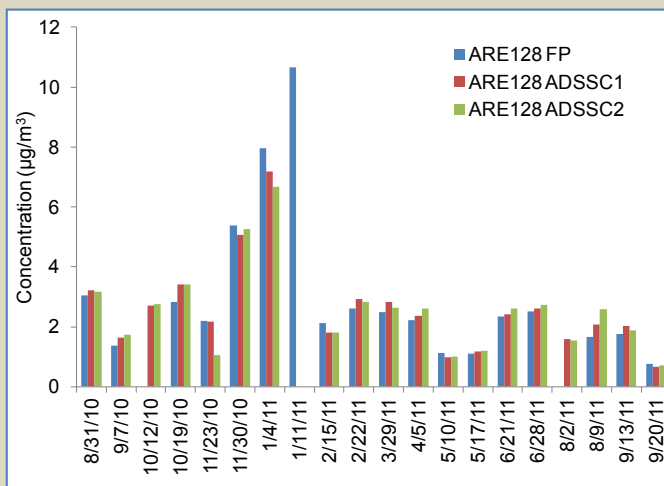
Note: FP = filter pack

ADSSC = sodium carbonate-impregnated ADS

Results for nitrogen species are more uncertain. The use of a cyclone by the ADS to remove coarse particulate nitrogen affects the concentration levels. However, the bigger issue is that the absence of ammonia has historically been a major missing component of total deposition. The AMoN data resolve that problem; the results summarized in the ACCS sidebar on page 23 in Chapter 2 provide confidence in ammonia measurements. Figure 3b shows the comparison between CASTNET filter pack and ADS NH_4^+ concentrations. Figure 3b also includes results from the Super SASS system used in the CSN. The figure shows that, relative to the ADS, the CASTNET filter pack measures higher concentrations of NH_4^+.

Figure 3b *Comparison between CASTNET Filter Pack, ADS, and Super SASS Ion Module NH_4^+ Concentrations at the ARE128, PA Site*
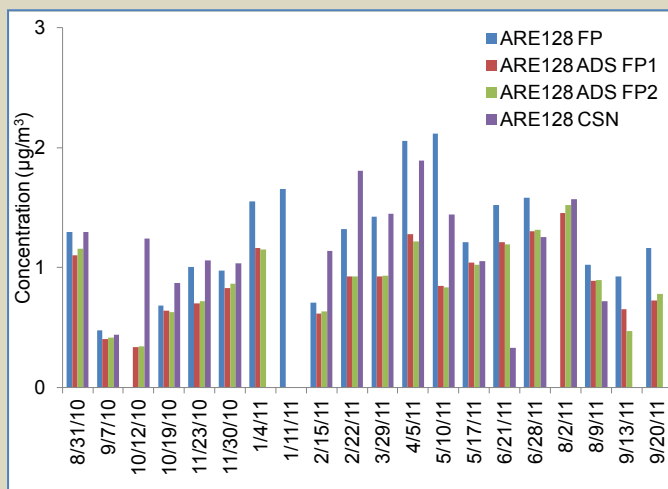
Note: FP = filter pack

Figure 3c shows similar data for total NO_3^-. The results are not as consistent relative to the CASTNET filter pack versus the ADS. In some cases the values are higher; in others the values are lower. This is largely the result of the volatilization and partitioning of the nitrogen compounds on the filters of the CASTNET filter pack.

Figure 3c *Comparison between CASTNET Filter Pack and ADS Total NO_3^- Concentrations at the ARE128, PA Site*
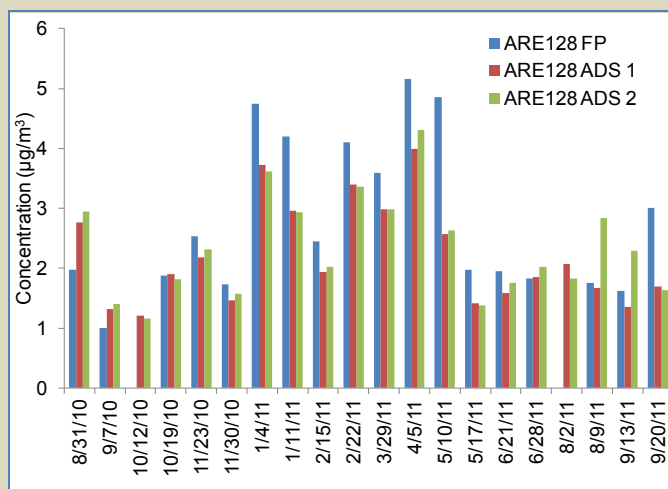
Note: FP = filter pack

Nitrogen Deposition

Figure 3-6 illustrates estimates of dry fluxes of nitrogen (as N) for 2011. These fluxes are the sum of fluxes of $HNO_3 + NO_3^- + NH_4^+$, based on the individual MLM simulations or substituted values 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 sites had deposition rates greater than or equal to 2.0 kg/ha/yr. QAK172, OH had an estimated dry nitrogen flux of 2.1 kg/ha/yr, the highest value at eastern sites. The highest value for western sites was calculated for the CASTNET site at JOT403, CA with a dry nitrogen flux of 1.9 kg/ha/yr.

Figure 3-6 Dry Nitrogen ($HNO_3 + NO_3^- + NH_4^+$) Deposition (kg/ha/yr) for 2011
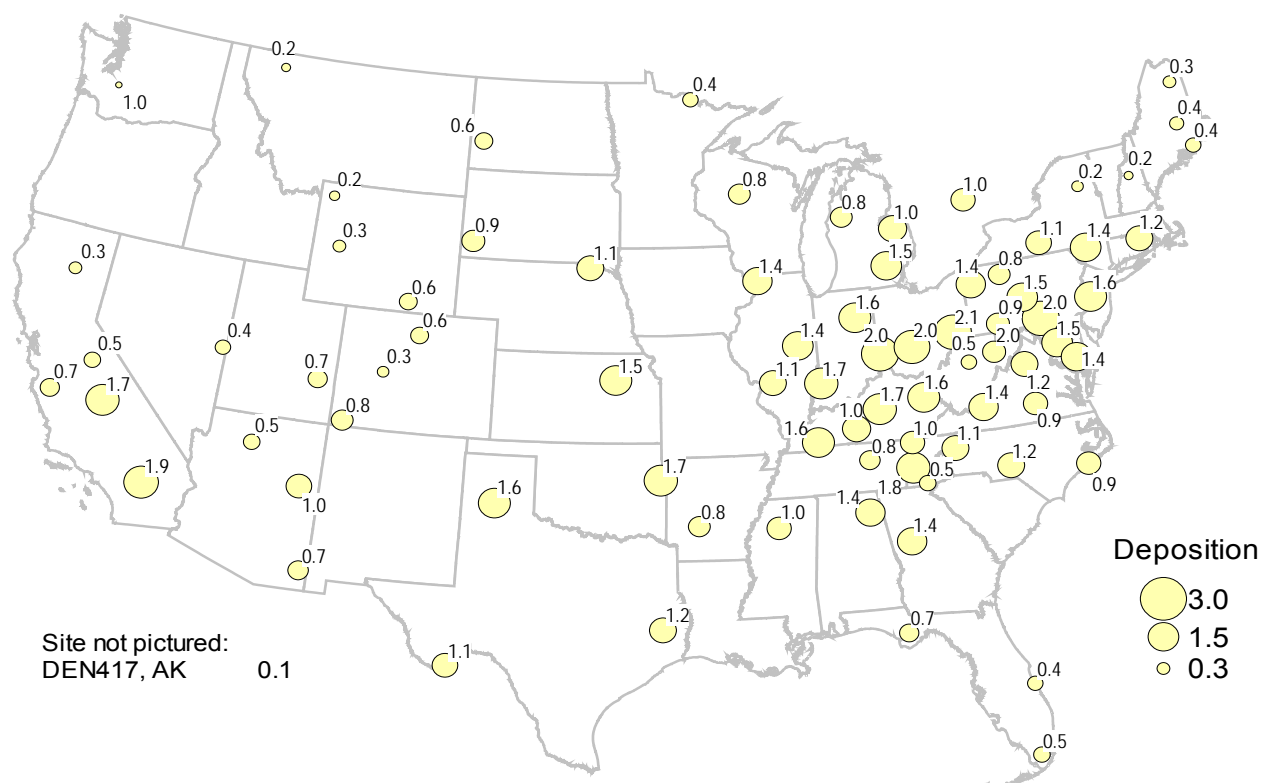
A map of total nitrogen deposition (as N) for 2011 is given in Figure 3-7. The map was constructed by summing the estimates of dry (light shading) and wet (dark shading) deposition. The figure shows that a majority of the eastern sites had estimated deposition rates greater than 5.0 kg/ha/yr. The site at ARE128, PA recorded the highest total nitrogen flux (10.6 kg/ha/yr). Most of the western sites had estimated total nitrogen deposition rates below 3.0 kg/ha/yr. The CASTNET site at Wind Cave National Park, SD (WNC429) had the highest total nitrogen flux for the western sites with an estimated flux of 3.7 kg/ha/yr. Five other western sites in California,

North Dakota, Wyoming, Colorado, and Texas had estimated total nitrogen fluxes greater than or equal to 3.0 kg/ha/yr.

Dry nitrogen deposition contributed less than 50 percent of total deposition at the eastern and at the majority of western CASTNET sites. On the other hand, dry nitrogen deposition contributed more than half of total nitrogen deposition at two of the four monitors in California and at the two western monitors in Texas. The two California sites are in a region with elevated concentrations of nitrogen species and limited rainfall. Dry nitrogen deposition contributed about 80 percent of the total nitrogen deposition at JOT403, CA. Dry nitrogen deposition also contributed a minimum of 50 percent of total deposition in western Texas, which is also a region with limited rainfall. The site at BBE401, TX received a contribution of about 75 percent of dry nitrogen.

Figure 3-7 Total (Dry + Wet) Nitrogen Deposition (kg/ha/yr) for 2011
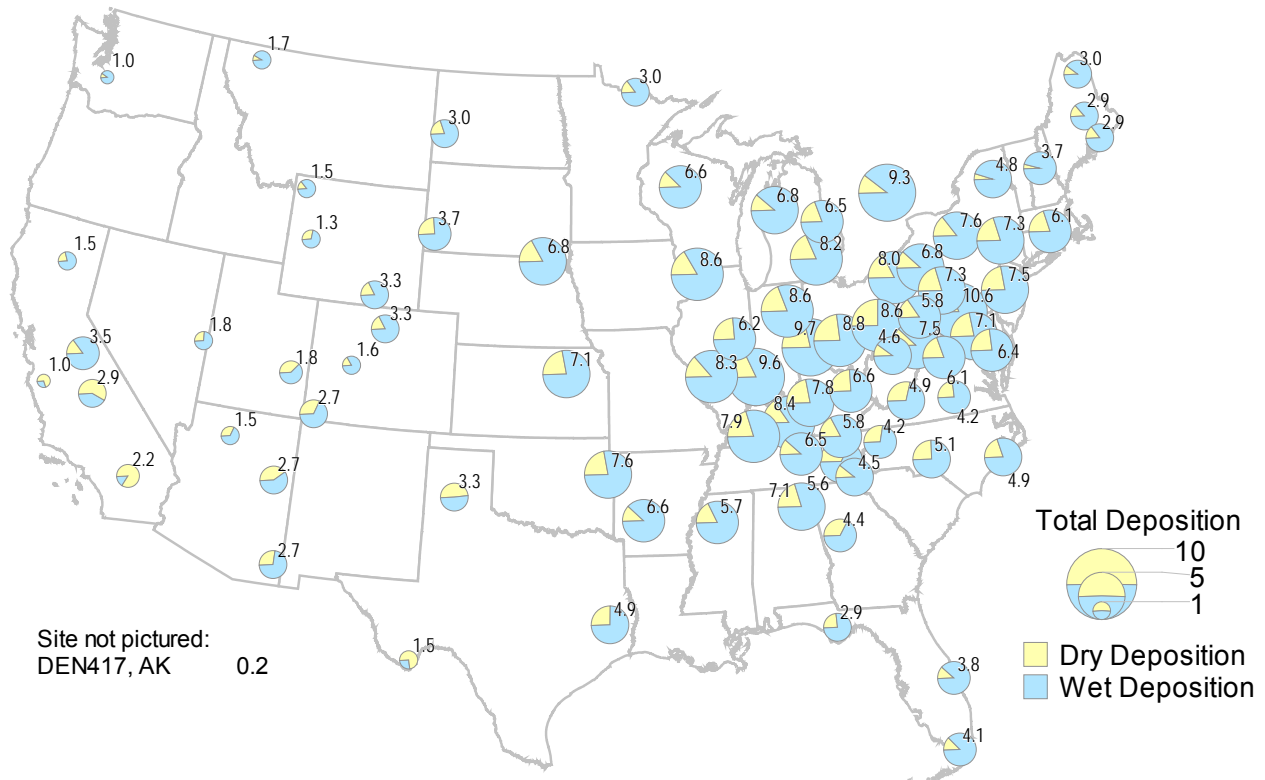
Figure 3-8 presents box plots that were constructed using data from the 34 eastern reference sites over the period 1990 through 2011 (right side) and 17 western reference sites for 1996 through 2011 (left side). The box plots show the trends in dry nitrogen deposition (as N). The box plots for the eastern sites in Figure 3-8 show a reduction in dry nitrogen deposition beginning in 1999. Three-year mean fluxes declined from 2.2 kg/ha/yr for 1990–1992 to 1.2 kg/ha/yr for 2009–2011, a 45 percent reduction over the 22 years. The box plots for the

western sites show a 36 percent decline, a change from a mean of 0.9 kg/ha/yr for 1996–1998 to 0.6 kg/ha/yr for 2009–2011.

Figure 3-9 depicts the trends in annual total (dry + wet) nitrogen deposition for the eastern (right side) and western (left side) reference sites. The figure shows that total nitrogen flux in the eastern United States has decreased since 1996 with a substantial decline from 2003 through 2010. Total nitrogen flux increased significantly in 2011. Total nitrogen flux for the western sites shows a relatively flat distribution. Estimates of trends in wet, dry, and total deposition of atmospheric nitrogen (as N) are presented in Figure 3-10 for both eastern and western reference sites. The trend line (dotted) for precipitation-weighted mean nitrogen concentrations in precipitation measured at eastern sites shows an overall slow downward trend since 1998 with increases in 2010 and 2011. This trend line is reasonably representative of the effect of changes in NO_x emissions because it does not depend on precipitation amounts. Total N deposition declined 26 percent in the East over the 22 years and 22 percent for the aggregated western sites over the 16-year period. However, total N deposition at eastern sites increased by 33 percent from 2010 to 2011. This significant increase can be explained by an increase in N concentration in precipitation and the highest average annual rainfall rate (138 centimeters) at eastern sites over the 22-year period.

Figure 3-8 Trend in Dry Nitrogen Deposition (kg/ha/yr)
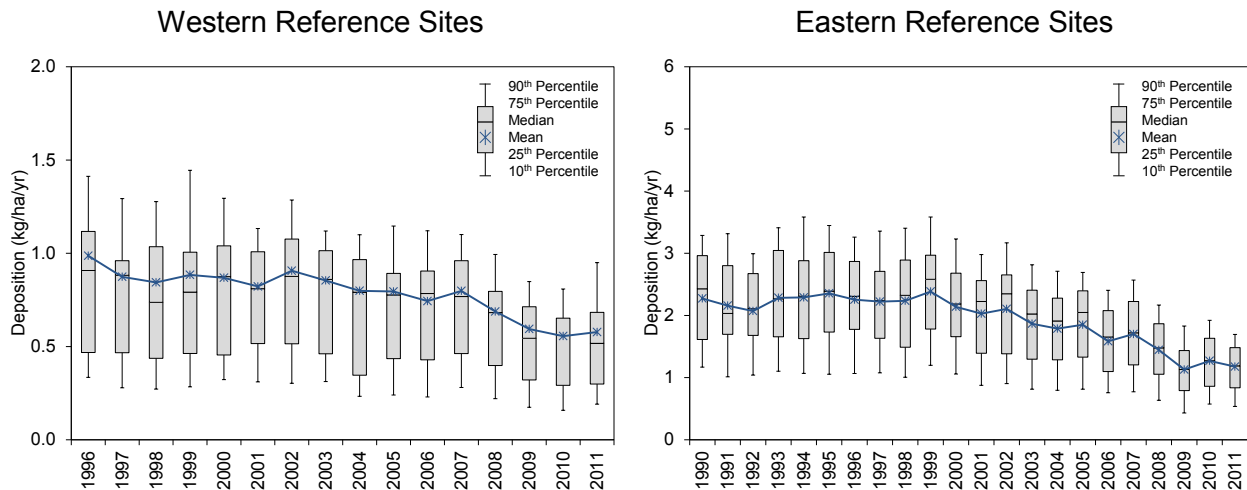
Abington, CT (ABT147)

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

Western Reference Sites

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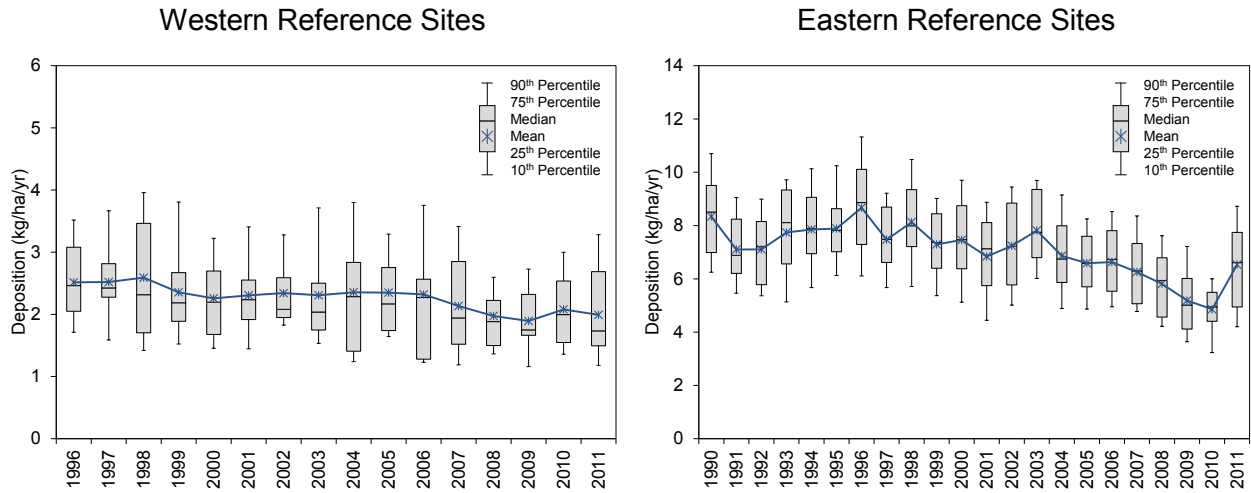
Figure 3-10 Trend in Nitrogen Deposition (kg/ha/yr) with Concentrations in Precipitation (mg/l)

Western Reference Sites

Eastern Reference Sites
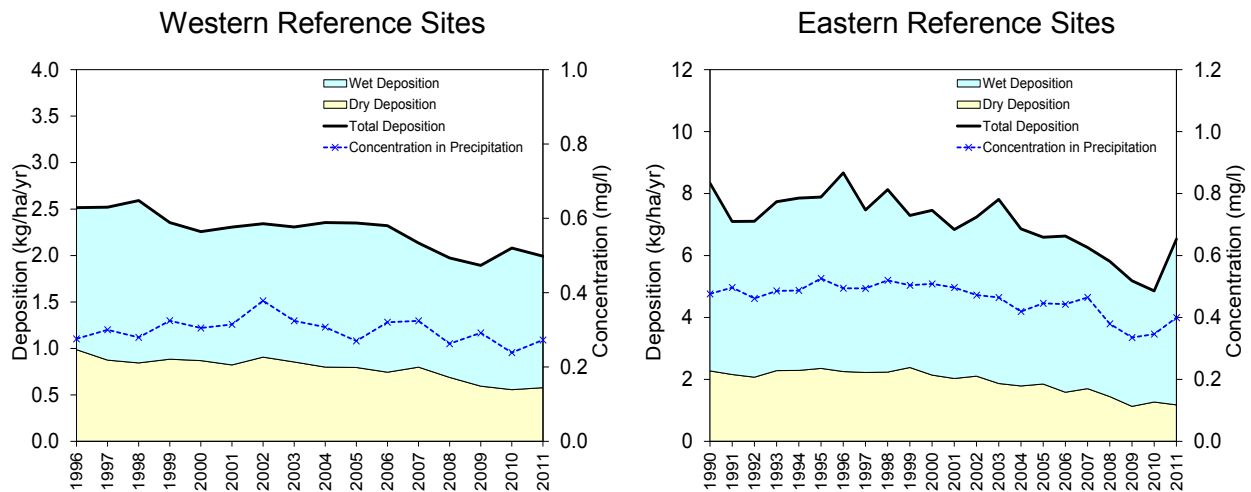
Arendtsville, PA (ARE128)

Estimates of Critical Loads throughout the United States

The critical load approach is an assessment tool that can help determine the degree to which acidic deposition may be affecting the ecological health of surface waters. The 2011 NAPAP Report to Congress (Burns et al., 2011) used critical loads to gauge the effectiveness of emission reductions associated with the ARP and other programs by assessing a selected number of sensitive lakes and streams in the eastern United States affected by acidification.

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. An exceedance indicates the ecosystem continues to be exposed to damaging levels of S and N deposition.

This critical load assessment examined selected lakes and streams within 25 km of 30 CASTNET monitoring locations in the United States (Figures 3d and 3e). Critical loads were obtained for 600 lakes and streams from the National Critical Load Database, developed in conjunction with the NADP Critical Loads of Atmospheric Deposition (CLAD) science committee. Critical loads were estimated using the Steady-State Water Chemistry mass-balance model (Henriksen et al., 2002). The critical load assumed 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 microequivalents per liter (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 S and N deposition were determined for each lake and stream. Wet deposition for SO_4^{2-}, NO_3^-, and NH_4^+ was based on PRISM-corrected NADP estimates. Dry deposition of SO_2, SO_4^{2-}, NO_3^-, HNO_3, and NH_4^+ was based on CASTNET modeled values for each CASTNET monitoring location. At CASTNET sites with AMoN monitors, dry NH_3 deposition values were calculated using AMoN's air concentration and a V_d from a 2002 Community Multiscale Air Quality Modeling System (CMAQ) model run (EPA, 2011). For CASTNET sites without AMoN monitors, dry NH_3 was determined using a dry NH_3 to wet NH_4^+ concentration ratio (NH_3/NH_4^+) calculated for AMoN monitoring locations and applied to CASTNET locations.

Critical load estimates for surface water acidification for selected lakes and streams within 25 km of selected CASTNET locations are shown in Figures 3d and 3e. 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 15 percentile critical load and total S and N deposition for years 2010 and 2011 at CASTNET locations. On the graphs, dark and light red bars represent the maximum critical load (CLmaxS) of S and the amount (CLminN) of N 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 N and S deposition, respectively. Figures 3d and 3e show a comparison between the 15 percentile critical load for lakes and streams within 25 km of a CASTNET location and total average N and S deposition.

The 15 percentile critical load represents the lakes and streams most vulnerable to acidic deposition near the CASTNET monitoring locations. Many of these vulnerable lakes and streams are in pristine natural areas that are located within national parks, wilderness areas, and other protected areas. For the 30 selected CASTNET locations, 16 of them received total S and N deposition greater than the 15 percentile critical load. The greatest density (7 of 16 lakes and streams that exceed the 15 percentile critical load) is located along the Appalachian Mountain chain from Pennsylvania to North Carolina, despite significant reductions of upwind emissions of NO_x and SO_2 since 1990. This analysis also shows that lakes and streams near CASTNET monitoring sites in the central Rocky Mountains and Sequoia, Lassen Volcanic, and Mount Rainier National Parks are at risk of acidification.

Figure 3d *Critical Load Estimates for Selected Lakes and Streams within 25 km of Eastern CASTNET Sites (2010–2011)*
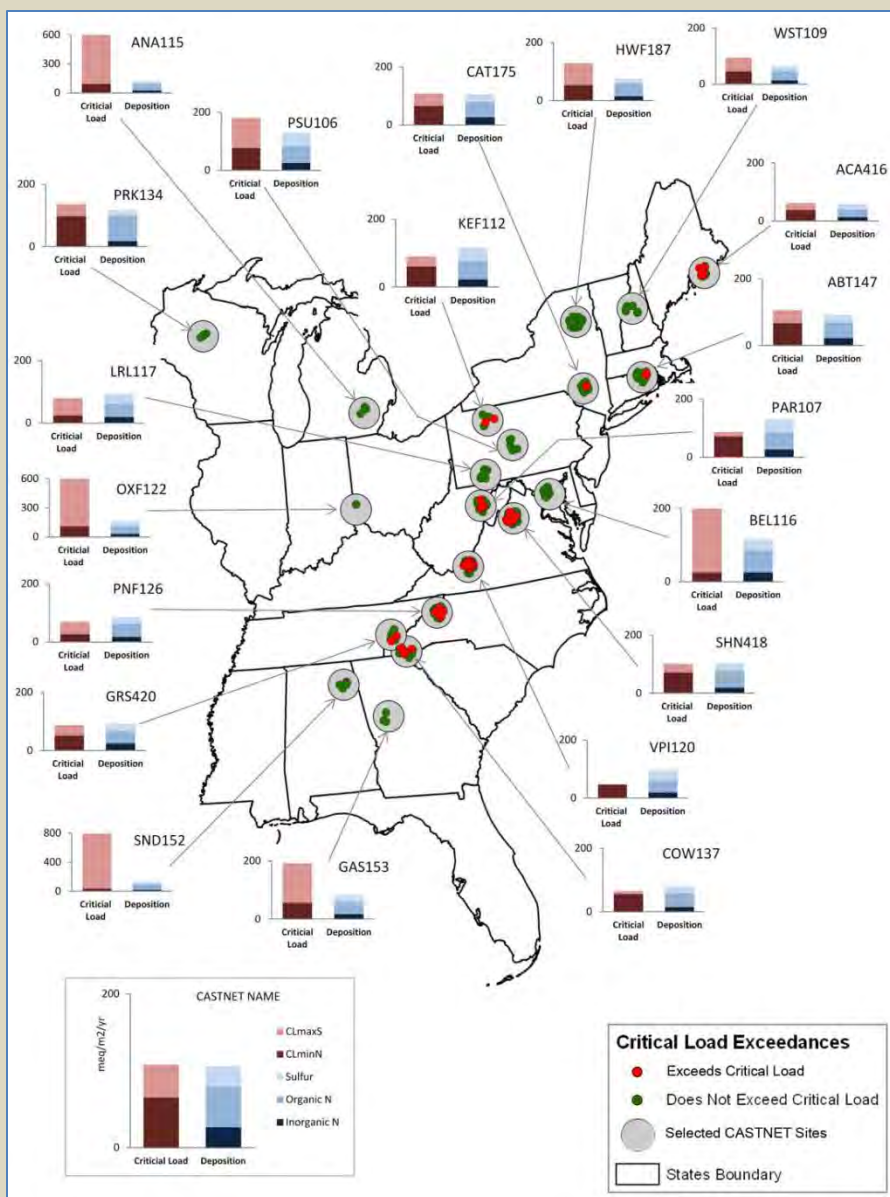
Source: J. Lynch

Figure 3e *Critical Load Estimates for Selected Lakes and Streams within 25 km of Western CASTNET Sites (2010–2011)*
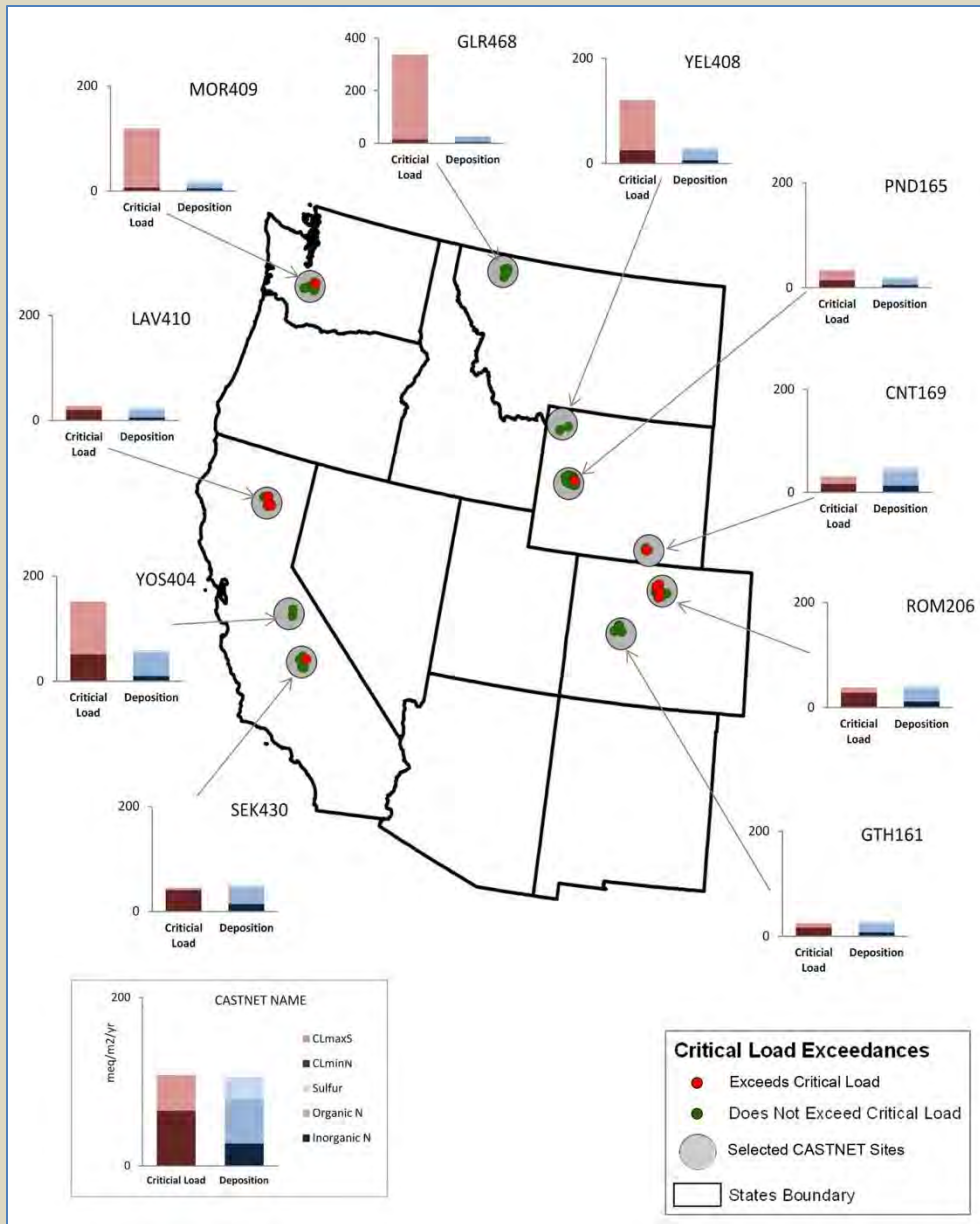
Source: J. Lynch

Chapter 4: Ozone Concentrations

CASTNET is the principal network for monitoring rural, ground-level O_3 concentrations in the United States. The network provides critical information on geographic patterns in rural O_3 levels as well as O_3 data for evaluation of compliance with NAAQS. CASTNET was not originally designed to operate as a regulatory network. However, during 2010 and 2011, CASTNET O_3 monitoring systems were upgraded in order to comply with regulatory monitoring requirements, and data collected during the 2011 O_3 season were submitted to EPA's AQS. In this report, O_3 measurements collected during 2009–2011 were evaluated with respect to the current NAAQS (EPA, 2008a) of 0.075 parts per million (ppm). For the 2009–2011 period, three California and four eastern sites recorded exceedances of the 0.075 ppm standard.

Most CASTNET sites operate an O_3 analyzer that measures hourly concentrations, which are archived in the CASTNET database and delivered to AQS. At the end of 2011, 80 ozone analyzers were operated throughout the network. Data from these sites, with the exception of ROM206, CO and HOW191, ME, which are designated as non-regulatory, will be used to calculate design values as three years of Part 58-compliant data become available. CASTNET's geographic coverage of the United States provides data that are essential 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. Maps of 2011 dry O_3 fluxes and W126 values are also presented. Additional maps of O_3 concentrations from the NPS Air Atlas can be viewed at http://nature.nps.gov/air/maps/airatlas/index.cfm.

Ground-level O_3 is an air pollutant of major concern that can cause adverse effects to the human respiratory system, damage to vegetation and ecosystems, and reduce crop yield and quality. O_3 is formed in the lower atmosphere when volatile organic compounds (VOCs) and NO_x react in the presence of sunlight. O_3 is the main component of smog. Emissions from motor vehicle exhaust, industrial facilities, chemical solvents, surface coatings, 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 geographical region. Ozone concentrations typically increase during daylight and peak in the late afternoon after temperature and sunlight intensity peak.

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, and CAIR. On May 1, 2009, the CAIR NO$_x$ O$_3$ 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. VOC 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 sidebar. 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 set at a level of 0.075 ppm averaged over 8 hours. EPA is in the midst of its regularly scheduled review of the O$_3$ NAAQS.

O$_3$ concentrations can also be 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. See page 60 for an additional discussion of W126.

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).

Assessing Compliance with NAAQS

EPA and other federal, tribal, and state agencies collect O$_3$ measurements on an hourly basis through national and local monitoring networks. AMEC followed EPA procedures (1998) to use CASTNET data to estimate O$_3$ design values and 2011 fourth-highest DM8A O$_3$ concentrations. It should be noted that CASTNET O$_3$ data will not be used to gauge compliance with NAAQS until Part 58 compliant data are available for three years.

- *Hourly O_3 measurements were used to compute 8-hour average concentrations.*

  Running 8-hour averages were computed from the hourly O_3 concentration data for each hour of the year, and the result was stored in the first, or start, hour of each 8-hour period. In the event that only 6 (or 7) hourly averages were available, the 8-hour average was computed using 6 (or 7) as the divisor.

  When more than two hours of monitoring data were missing, the 8-hour average concentration was computed by substituting one-half the minimum detectable limit for the missing hourly concentrations and using 8 as the divisor. In this case, if the computed 8-hour average concentration was greater than 0.075 ppm, it was retained; otherwise, the 8-hour concentration for this 8-hour period was considered to be missing.

  In all cases, the computed 8-hour average O_3 concentration was reported in ppm to three decimal places.

- *The daily maximum 8-hour average was recorded for each day.*

  An O_3 monitoring day was counted as a valid O_3 monitoring day if 8-hour averages were available for at least 18 of the 24 possible 8-hour average periods that start within the day, or if the DM8A O_3 concentration for the day was greater than 0.075 ppm.

- *For each year, the fourth highest DM8A concentration was calculated for the designated O_3 monitoring season for each CASTNET site. The designated O_3 monitoring seasons are listed by state in 40 CFR 58, Appendix D (Table D-3). The listed O_3 seasons were used to compute the data completeness requirements.*

- *The annual fourth highest daily DM8A O_3 concentrations were averaged over 3-year periods to compute design values.*

  For the purpose of judging compliance with the standard, a valid year had to have valid DM8A O_3 concentrations for at least 75 percent of the required monitoring days in the O_3 season unless the fourth highest DM8A was above 0.075 ppm, in which case completeness was not considered, and the year was automatically considered valid. A design value requires that all three years be valid and that the combined data completeness for the 3-year period has to average at least 90 percent to demonstrate attainment.

If the 3-year average of DM8A O_3 concentrations exceeded 0.075 ppm (or 75 ppb), the site was considered nonattainment. EPA (2012b) made final designations using air quality monitoring data from 2008, 2009, and 2010, generally the most recent three years of certified data available, and in some cases using data from 2009, 2010, and 2011. EPA considered data through 2011 if a state certified them complete and submitted the data for consideration by February 29, 2012. Based on 2008 through 2010 or 2009 through 2011 data, EPA designated 46 areas nonattainment.
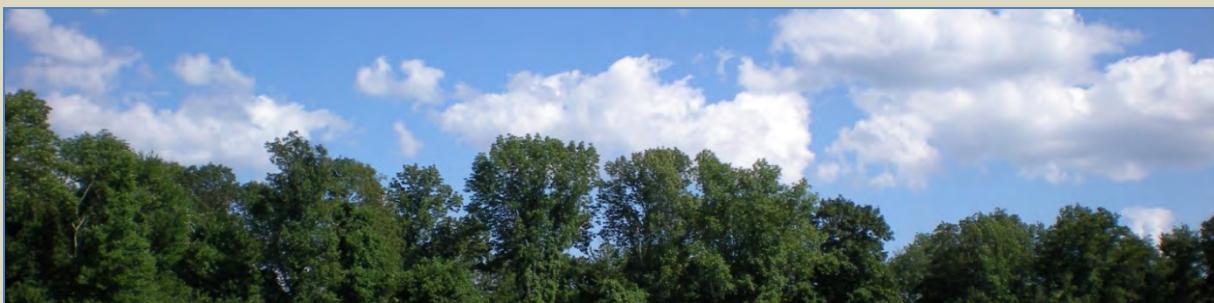
Eight-Hour Ozone Concentrations

Figure 4-1 presents 3-year averages of the fourth highest DM8A O_3 concentrations for 2009–2011. If the 3-year average was not available because of incomplete data (see the discussion in the sidebar beginning on page 48), the results were not included on the maps in this chapter. Sites with no O_3 concentrations are shown as dots with no value. During this period, 3-year averages of the three highest DM8A O_3 concentrations were greater than 75 ppb at four eastern sites and three sites in California. The eastern sites include Washington Crossing, NJ (WSP144); BEL116, MD; Blackwater National Wildlife Refuge (BWR139); and GRS420, TN. The three California sites include Yosemite National Park (YOS404), SEK430, and JOT403. Three-year average concentrations were generally lower in 2009–2011 than in 2008-2010.

The 2009–2011 3-year averages of fourth highest DM8A O_3 concentrations shown on Figure 4-1 provide examples of the design value for achieving the DM8A O_3 NAAQS if CASTNET 2009 and 2010 O_3 data were Part 58 compliant. 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 used to classify nonattainment areas, assess progress towards meeting the NAAQS, and develop control strategies to achieve the NAAQS. For example, the value of 96 ppb at SEK430 that was measured during 2009–2011 would have to be reduced to 75 ppb to achieve the level of the current standard. Similarly, the concentration of 78 ppb at BEL116 would have to be reduced to 75 ppb to meet the NAAQS.

Beltsville, MD (BEL116)

Figure 4-1 Three-year Average of Fourth Highest DM8A Ozone Concentrations (ppb) for 2009–2011

Site not pictured:
DEN417, AK   53
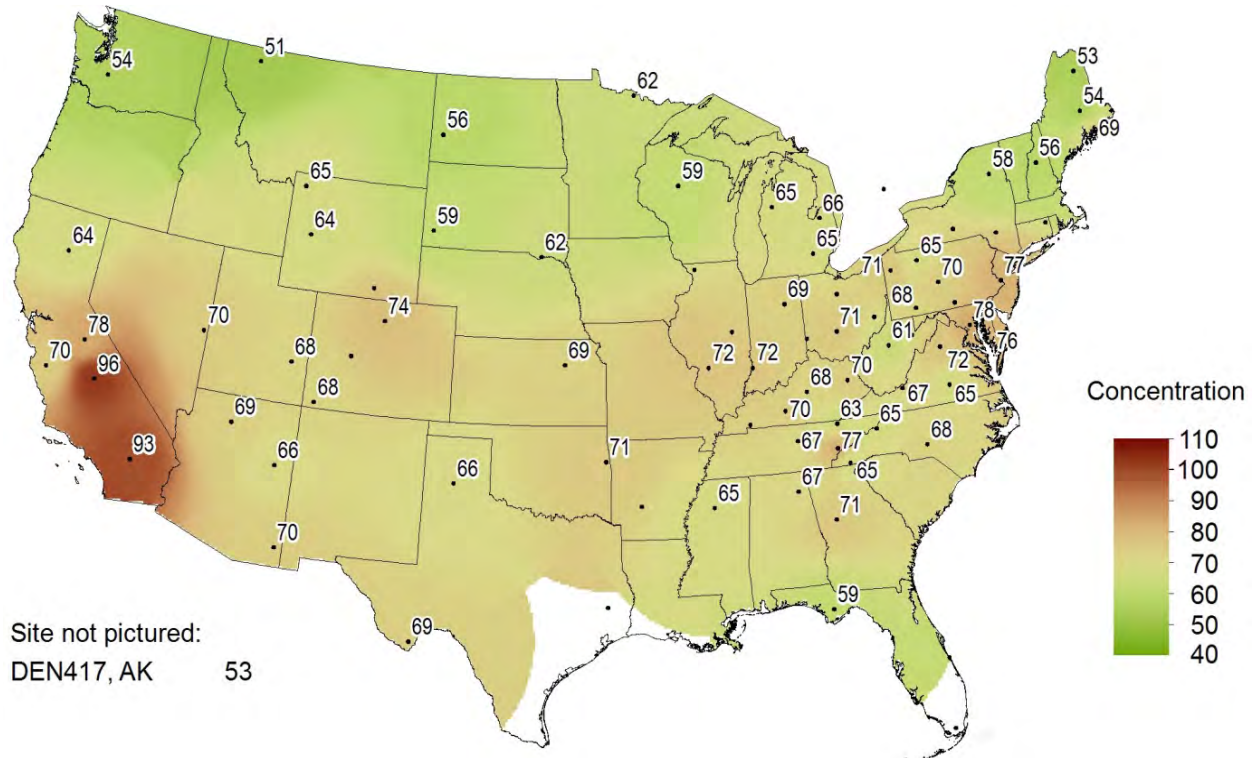
Figure 4-2 Three-year Average of Fourth Highest DM8A Ozone Concentrations (ppb) for 2000–2002

Site not pictured:
DEN417, AK   49
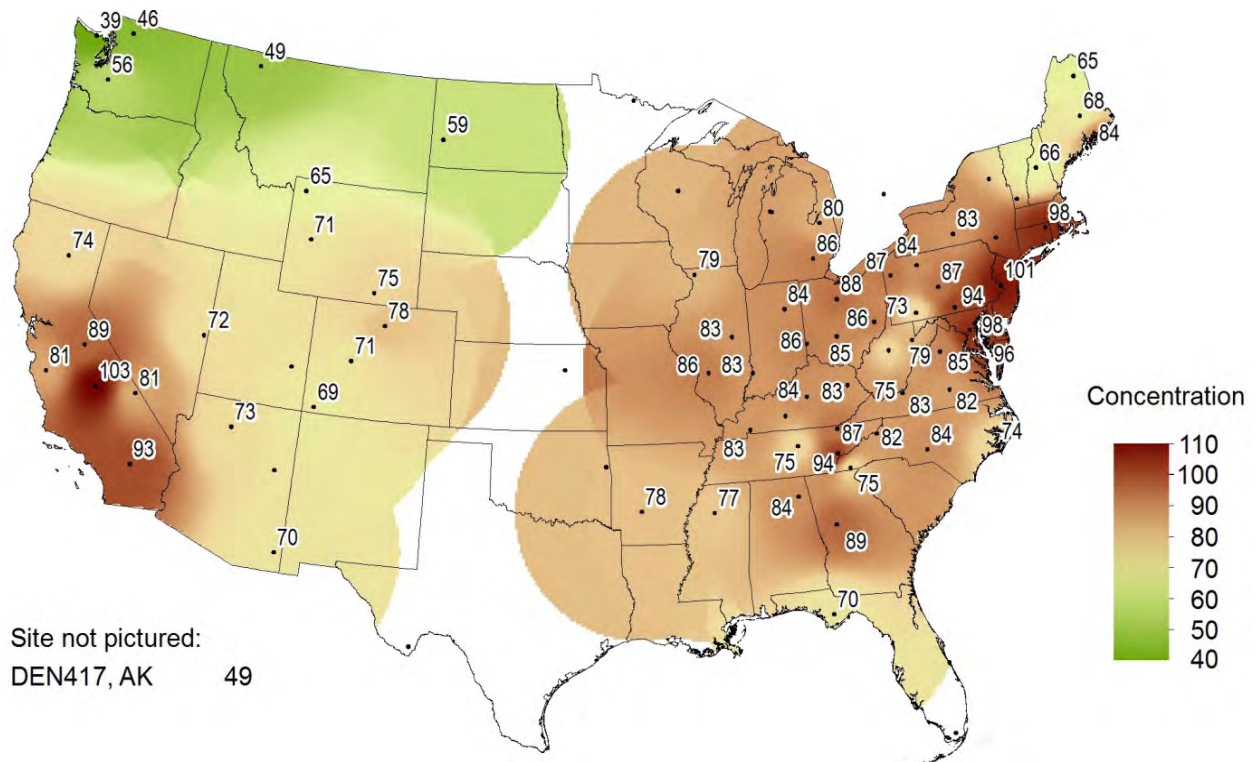
Three-year averages of the fourth highest DM8A O_3 concentrations for 2000–2002 are presented in Figure 4-2 for comparison with the 2009–2011 design values shown in Figure 4-1. The period 2000–2002 was selected because the NO_x SIP Call/NBP began in 2003 for the eastern United States. The changes in O_3 concentrations from 2000–2002 to 2009–2011 illustrate the effectiveness of the emission reduction programs. Based on the 75 ppb NAAQS level, almost all eastern sites recorded 3-year averages greater than 75 ppb during 2000–2002. Five monitors in California and the site at ROM406, CO also recorded concentrations greater than 75 ppb. The regions with relatively low DM8A O_3 concentrations in the East were located in northern New England and in Florida.

O_3 concentrations for 2011 are shown in Figure 4-3. These data comply with Part 58 requirements. All valid data are included, and exceptional events are not excluded. Three California, three other western, and nine eastern CASTNET sites measured fourth highest DM8A O_3 concentrations above 75 ppb. The geographic extent of measured fourth highest DM8A O_3 concentrations above 75 ppb was greater in 2011 than in 2010 for both the western and eastern sites. The highest western concentration of 98 ppb was measured at SEK430, CA, and the highest eastern level of 84 ppb was measured at BEL116, MD.

In 2011, CASTNET sites at BBE401, TX; PAL190, TX; and CHE185, OK all measured a fourth highest DM8A O_3 concentration greater than the NAAQS for the first time in the last five years. Also, two other southwestern sites measured relatively high concentrations: Chiricahua National Monument, AZ (CHA467) – 75 ppb and Grand Canyon National Park, AZ (GRC474) – 74 ppb. The following concentration data illustrate fourth highest DM8A O_3 concentrations over the last five years for the five sites.

	2011	2010	2009	2008	2007
BBE401, TX	80	64	65	65	68
PAL190, TX	76	61	63	65	65
CHE185, OK	78	71	64	68	73
CHA467, AZ	75	71	65	68	67
GRC474, AZ	74	69	66	71	69

The high DM8A levels measured at these five sites were likely influenced by frequent wildfires in Texas and Arizona during the 2011 summer and fall fire season. The National Oceanic and Atmospheric Administration (2012) and the National Climatic Data Center (2012) reported extensive fires in Arizona, New Mexico, Texas, and Oklahoma throughout the 2011 summer O_3 season. These wildfires affected air quality locally, as indicated by the preceding O_3 data, as well as throughout the eastern United States all the way to the Baltimore-Washington metropolitan area.

Figure 4-3 Fourth Highest DM8A Ozone Concentrations (ppb) for 2011
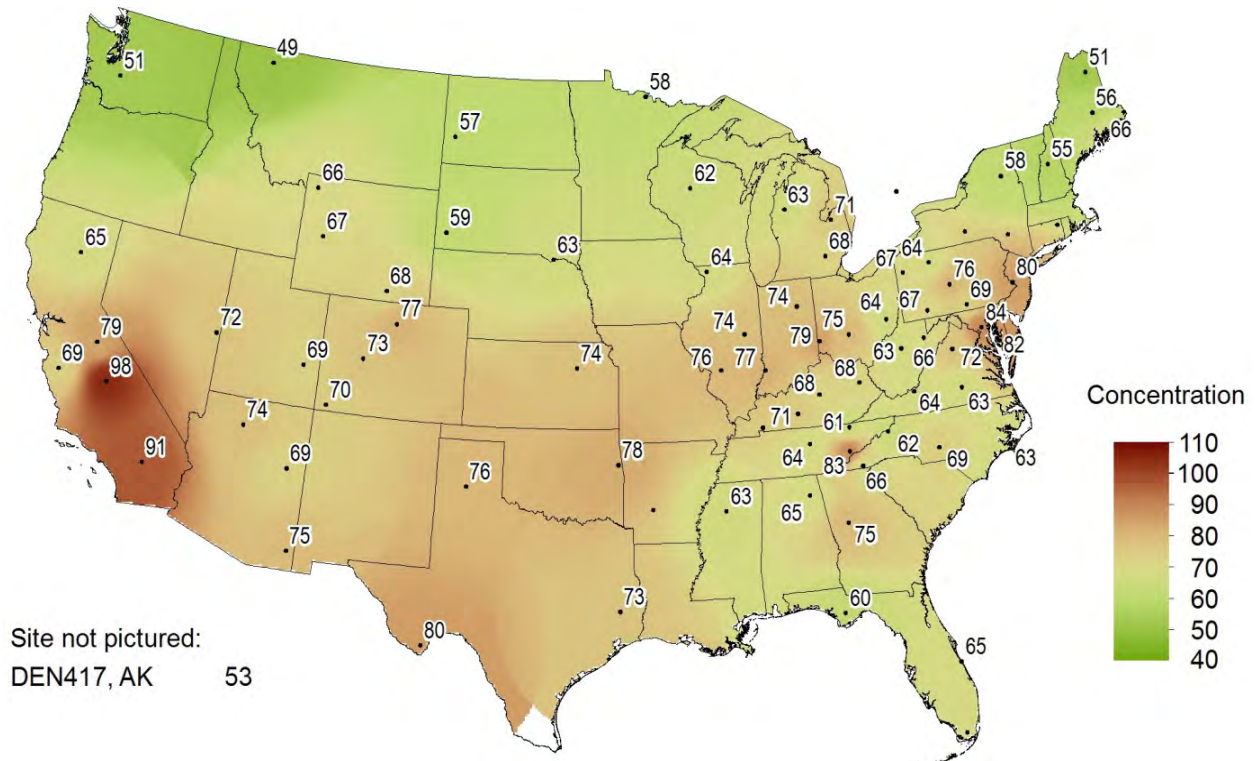
Figure 4-4 provides box plots depicting trends in fourth highest DM8A O$_3$ concentrations from the 34 CASTNET eastern reference sites (right side) and 17 western reference sites (left side). The eastern O$_3$ data show an overall reduction since 2003. The mean aggregated value (68 ppb) for the eastern reference sites for 2011 was the second lowest in the history of the network and shows a small decline from the 2010 level of 69 ppb. The concentrations measured in 2009 through 2011 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 2009–2011 average of the fourth highest DM8A O$_3$ concentrations for the western reference sites was 68 ppb.

Washington Crossing, NJ (WSP144)

Figure 4-4 Trend in Fourth Highest DM8A Ozone Concentrations (ppb)
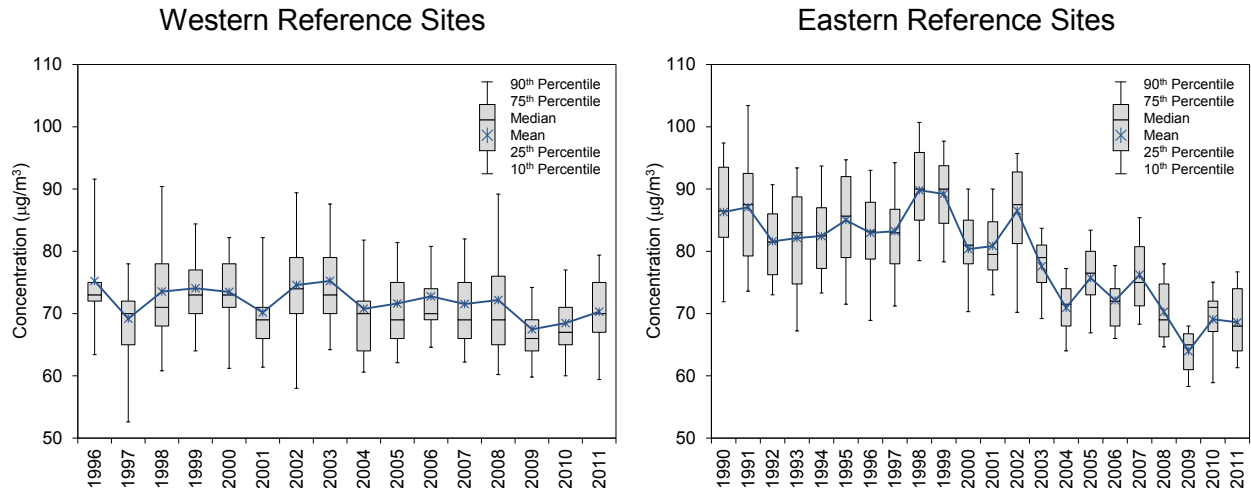
Georgia Station, GA (GAS153)

Ozone and Filter Pack Concentrations at the Maine Howland Research Forest

CASTNET began collecting O_3 and filter pack measurements at the Howland Research Forest AmeriFlux site (designated HOW191) in Maine in September 2011. This study represents the first collaboration between the two long-standing national networks. AmeriFlux's goal is to measure ecosystem level exchanges of carbon dioxide, water, energy, and momentum. AmeriFlux sites use a 30-m tower to enable flux measurements in the lower boundary layer. CASTNET is interested in similar atmospheric processes for O_3 and sulfur and nitrogen species.

Hourly average O_3 concentrations were collected at eight elevations on a 30-m scaffold tower during fourth quarter 2011 at the HOW191 site. The tower is located in a 20-m natural canopy of hemlock-spruce-fir (66 percent), aspen-birch (23 percent), and hemlock-hardwood (11 percent) mixtures. The site is situated in a mature, lowland evergreen forest with trees between 40 and 160 years old. O_3 concentrations are measured at 2, 6, 10, 14, 17, 20.5, 23.5, and 28 m. The inlet for the sampler at 28 m is above the canopy, and the inlet at 23.5 m is near the top of the canopy. All other sampler inlets are located within the canopy. Filter pack sampling systems are operated at 2 and 23.5 m.

Design for the O_3 system centered on the use of a single O_3 analyzer and site transfer standard in conjunction with a solenoid system to allow for all eight levels to be measured using the same analyzer (Figure 4a). Even though the measurement heights vary from 2 m to more than 28 m above the ground, the residence times for all levels are less than 20 seconds, and there are no indications of line loss. Although not a regulatory O_3 site, the analyzer is challenged in a similar manner by performing daily checks using a calibration gas created by the site transfer standard and delivered through-the-probe at the 23.5-m inlet.

Figure 4a *O_3 Sampling System*
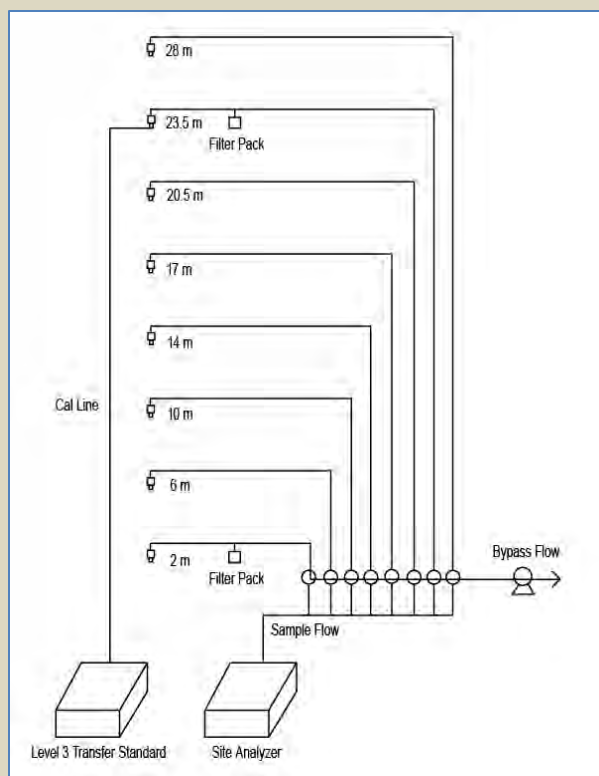
Data from fourth quarter 2011 are presented in this report. Figure 4b depicts three plots of aggregated O_3 concentrations versus height. The graphs were constructed from measurements at the eight sampling heights. The blue diamonds show concentrations aggregated over all hours of the day for the entire quarter. These data show a decrease in concentrations with decreasing elevation throughout the canopy and fit a conceptual model of the distribution of reactive pollutants in a treed canopy. The red boxes show concentrations aggregated for the hour 0600. As expected, the early morning concentrations were lower than midday values, likely because of nighttime scavenging. Finally, the green triangles show concentrations by elevation for the hour 1400. The afternoon values were higher than the other two sets and were more uniformly distributed with height. The magnitude and distribution of the 1400 values were influenced by daytime O_3 production and atmospheric mixing of O_3 from aloft.

Figure 4b *Aggregated O₃ Concentrations for Fourth Quarter 2011 for Specific Hours at HOW191, ME*
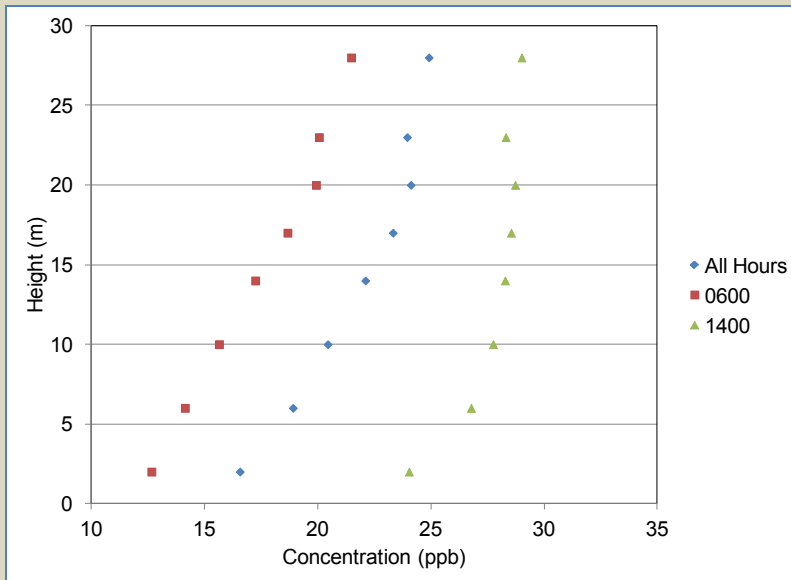
HOW191 site tower

HOW191 site shelter

Figure 4c *SO₂ Concentrations for Fourth Quarter 2011 for HOW191, ME Above and Below Canopy and HOW132, ME Standard 10-m Filter Packs*
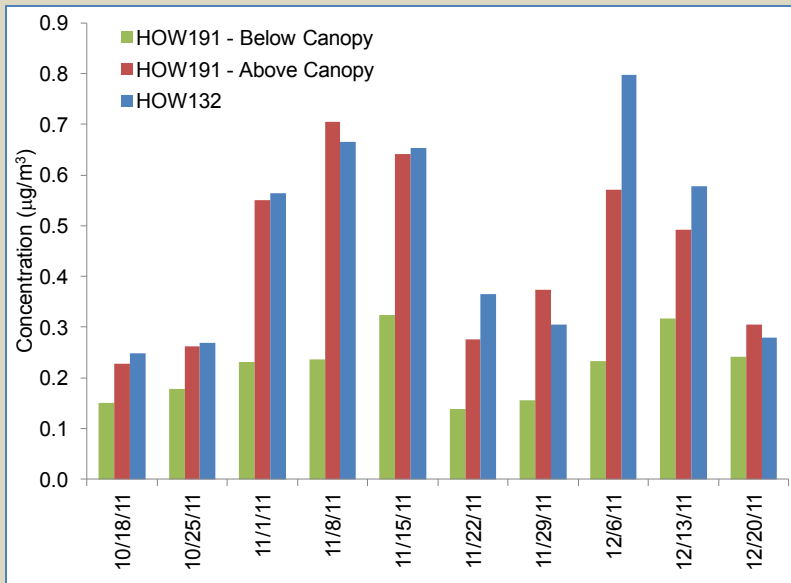
HOW191 O₃ sampling solenoid system

A standard CASTNET sampling tower is located in a clearing approximately 5 km east of HOW191 at the HOW132 site. O_3 concentrations aggregated over the entire quarter and measured at the standard 10-m level at HOW132, ME conform to the 28-m values measured at HOW191.

	All Hours (ppb)	*0600 (ppb)*	*1400 (ppb)*
HOW132, ME (10 m)	*33.0*	*28.3*	*36.9*
HOW191, ME (28 m)	*34.0*	*30.8*	*37.0*

SO_2 concentrations from the two sampling heights at HOW191 and from the 10-m height at HOW132 are shown in Figure 4c using a time series of bars to illustrate how concentrations compared during the fourth quarter. The chart shows the above-canopy concentration values from HOW191 and the 10-m values from HOW132 are comparable. The SO_2 concentrations measured at 2 m were noticeably lower than the above-canopy values, indicating depletion by deposition near the ground. Similar results were found for measured total NO_3^- concentrations.

These data collected from HOW191 provide insight into the deposition and scavenging mechanisms that exist within a forest canopy. Hourly O_3 concentrations show evidence of episodic within-canopy nighttime loss events. Deposition is also evident in the above- and below-canopy filter pack concentrations. The below-canopy SO_2 concentrations are approximately 60 percent of the above-canopy concentration values, and the below-canopy total NO_3^- concentrations, which include gaseous HNO_3, are approximately 64 percent of the above-canopy concentrations. As would be expected, concentrations of particles, such as SO_4^{2-} and NH_4^+, show that deposition rates of particles within the canopy are slower than for gaseous species.

HOW191 tower looking down inlets

Ozone Flux Values for 2011

Recent research (Klingberg *et al.*, 2011) has concluded that the effects of O_3 on vegetation depend more on the flux of O_3 to the plant than on ambient O_3 concentrations. In particular, damage to vegetation is related to the uptake of O_3 through the stomata. The MLM modeling approach was used to simulate dry O_3 deposition. Figure 1-4 illustrates the MLM used for O_3 dry deposition modeling. The EPA data substitution method was used to fill in long-term averages of O_3 V_d for missing values. A map of modeled 2011 annual O_3 fluxes is presented in Figure 4-5. These estimates represent the dry deposition of O_3 to the environment. Dry deposition fluxes greater than 50.0 kg/ha/yr were simulated for 12 CASTNET sites in 10 states, including North Carolina, Tennessee, Kentucky, Virginia, Ohio, Kansas, Oklahoma, Texas, Arizona, and California. The highest flux (68.3 kg/ha/yr) was modeled for GRS420, TN and the lowest (7.7 kg/ha/yr) for the site at Indian River Lagoon, FL (IRL141).

Figure 4-5 Modeled Annual O$_3$ Flux (kg/ha/yr) for 2011
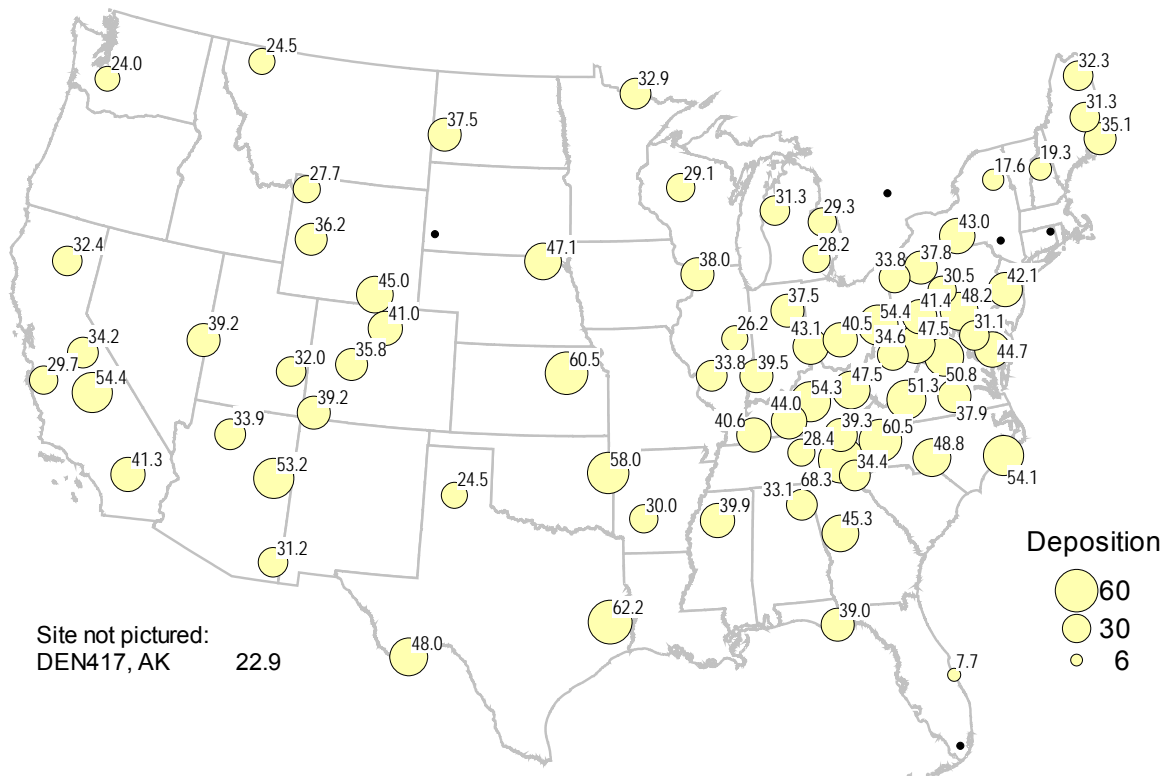
W126 Values for 2011

The W126 O_3 exposure index is a biologically-based, cumulative peak-weighted exposure index (Lefohn and Runeckles, 1987; EPA, 1996; 2006) for relating reduced vegetation yields to O_3 exposure. Many scientists (e.g., Musselman *et al*., 2006) concluded that both cumulative effects and peak concentrations are important in relating atmospheric O_3 to vegetation damage. Consequently, W126 was developed as a seasonal measure from the sum of weighted hourly values measured during the approximately 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 is used to characterize high O_3 concentrations over a seasonal, 3-month exposure period. The highest rolling 3-month W126 is presented.

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:

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

Where:

w_i = weighting value for hourly concentration c_i, and

c_i = hourly concentration in ppb for period i.

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:

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

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 2011. 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 2011 are presented in Figure 4-6. The higher W126 values were measured in California, at western sites in high terrain, and at eastern sites with relatively high DM8A O_3 concentrations. The highest W126 value (61.5 ppm-hour) was measured at SEK430, CA. O_3 concentrations measured at high elevation sites (AMEC, 2003) typically persist during the night because dry deposition and scavenging of O_3 by nitric oxide are low at night, resulting in the persistence of daytime values. 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. The 2011 W126 values were higher than values in 2010, reflecting higher ambient concentrations in 2011. For example, GRS420 measured a W126 value of 22.3 ppm-hour in 2011 versus a value of 13.7 ppm-hour in 2010. W126 values observed at southwestern CASTNET sites were higher in 2011, consistent with higher ambient O_3 concentrations associated with frequent wildfires in Texas and Arizona during the summer and fall fire season.

Figure 4-6 W126 Values (ppm-hour) for 2011
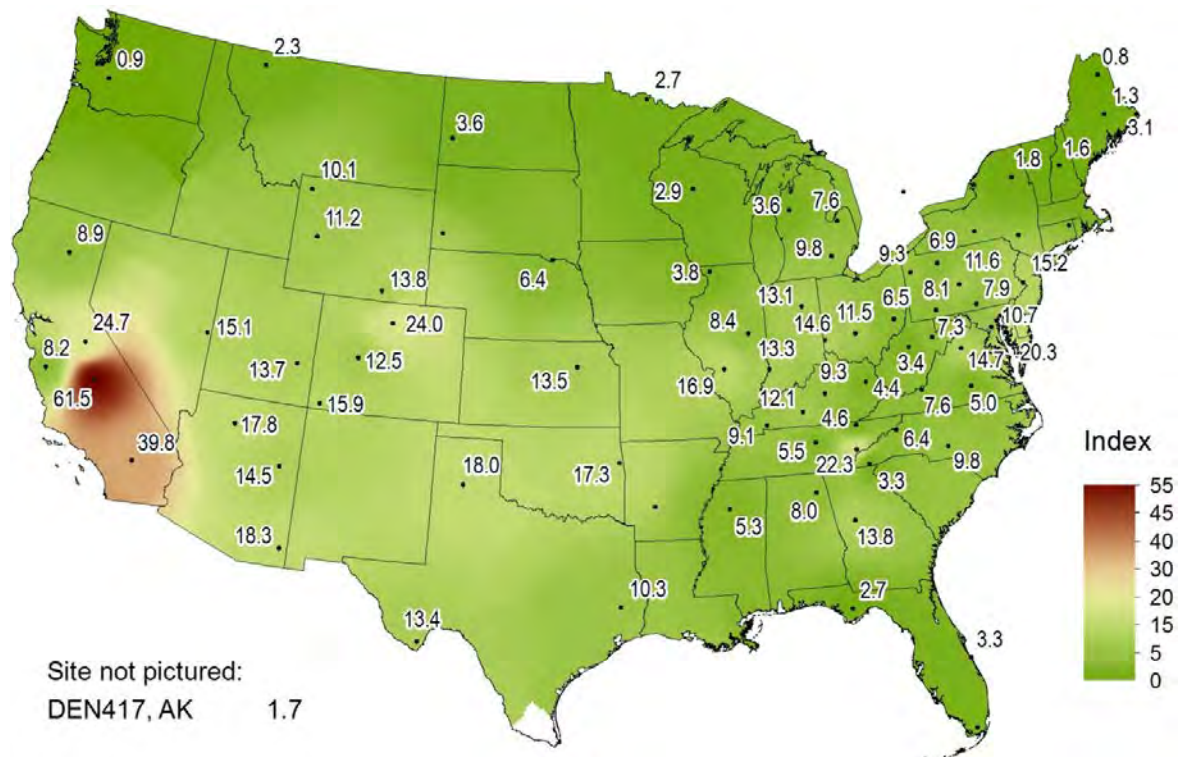
Air Quality in Western North Dakota

North Dakota has surpassed Alaska and California as the nation's second highest oil producing state. The state is drawing oil and gas from the Bakken shale formation in the northwest corner of North Dakota and eastern Montana. About 7,000 wells currently operate in an area centered on Williston, ND. Oil production increased from 28 million barrels in 2008 to 86 million barrels in 2010. Many more wells are under construction, and oil production is growing rapidly. The Bakken field is producing domestic energy for the United States, creating jobs, and generating royalty revenues for the state, tribes, and taxpayers.

The Bureau of Land Management, which is the lead agency for permitting and enforcement, and the general public have expressed concern that Class I areas in the region may experience a deterioration in visibility and air quality in addition to an increase in O_3 concentrations as the result of the development of the Bakken field. The North Dakota Department of Health, Division of Air Quality, operates and maintains a network of ambient air quality monitors in North Dakota. Eight department-operated sites are shown in Figure 4d. The Theodore Roosevelt National Park (TRNP) – South Unit (Painted Canyon) site is also a CASTNET site (THR422) sponsored by NPS. The North Dakota Division of Air Quality operates and maintains SO_2, O_3, and continuous $PM_{2.5}$ analyzers at the THR422 site in addition to the CASTNET filter pack sampling system.

Fourth highest DM8A O_3 concentrations from the eight North Dakota monitors are shown in Table 4a for 2011. Three-year averages of the fourth highest DM8A values are also shown in the table. The measurements show O_3 concentrations are below the NAAQS. Figure 4e illustrates changes in sulfur and nitrogen pollutants and O_3 at the THR422 site over the period 1999 through 2011. The figure shows annual mean concentrations of SO_2 and total NO_3^- and fourth highest DM8A O_3 levels for the 13 years. The plots suggest no significant change in O_3 or total NO_3^- concentrations and a 21 percent reduction in 3-year mean SO_2 levels from 1999–2001 to 2009–2011.

Figure 4d *Air Quality Monitoring Sites*
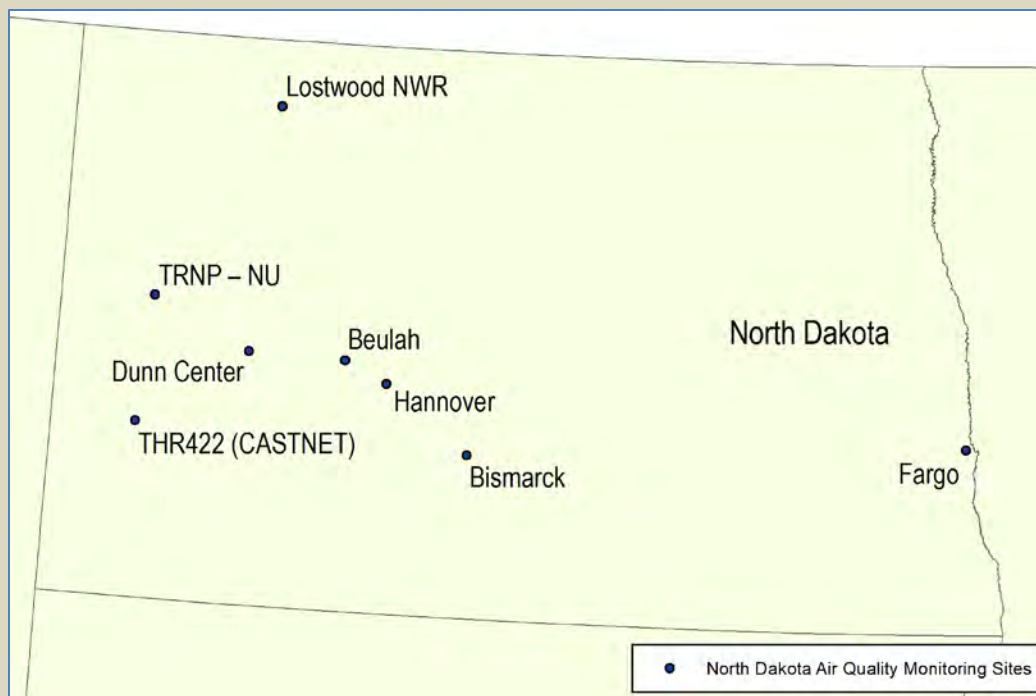
Table 4a *2011 O$_3$ Concentrations in North Dakota*

Pollutant: O$_3$ (ppb)*   M A X I M A

Location	Year	Valid Days	1 – Hour 1st	2nd	8 – Hour 1st	2nd	3rd	4th	3yr Avg	1HR #>120	8HR #>75
Beulah North	2011	151	66	64	62	62	59	59	58	0	0
Bismarck Residential	2011	146	63	63	62	60	58	56	57	0	0
Dunn Center	2011	152	60	60	58	57	54	54	55	0	0
Fargo NW	2011	128	66	64	61	60	58	57	59	0	0
Hannover	2011	139	78	65	62	62	60	58	58	0	0
Lostwood NWR	2011	149	68	65	65	62	61	60	60	0	0
TRNP - NU	2011	142	65	64	62	62	60	58	59	0	0
THR422	2011	151	65	63	59	59	58	57	56	0	0

    * The air quality standards for O$_3$ are:

    STATE – 75 ppb three year average of the annual 4th highest daily maximum 8-hour concentrations.

    FEDERAL – 75 ppb three year average of the annual 4th highest daily maximum 8-hour concentrations.

    NW = northwest, NWR = national wildlife refuge, NU = north unit

Source: North Dakota Department of Health, Division of Air Quality (2012)

Figure 4e *Trend in Pollutant Concentrations at THR422, ND*
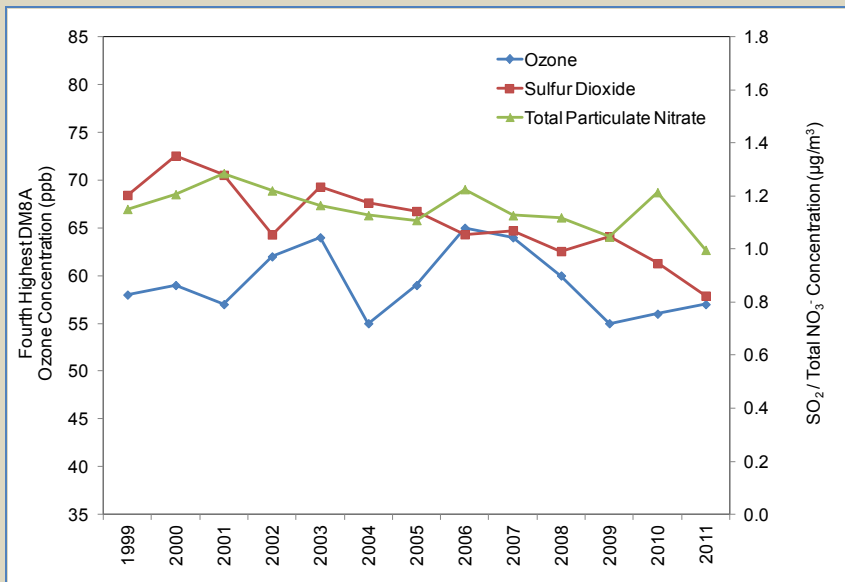
Theodore Roosevelt National Park, ND (THR422)

Chapter 5: Data Quality

CASTNET measurements and supporting activities are assessed routinely in order to provide high-quality data to meet project objectives. The CASTNET quality assurance program is based on data quality objectives that are evaluated using data quality indicators (DQI) such as precision, accuracy, and completeness. Measurements taken during 2011 and historical data collected over the period 1990–2010 were analyzed relative to DQI and their associated measures. These analyses demonstrate that CASTNET data can be used with confidence and that CASTNET continues to produce information of the highest quality.

The CASTNET Quality Assurance (QA) program was designed to ensure that all reported data are of known and documented quality in order to meet CASTNET objectives and to be reproducible and comparable with data from other monitoring networks and laboratories. The 2011 QA program elements are documented in the CASTNET Quality Assurance Project Plan (QAPP), Revision 7.0 (AMEC, 2011c). The QAPP is comprehensive and includes standards and policies for all components of project operation from site selection through final data reporting. The QAPP contains a project overview and sections on field measurements, chemical analysis of field samples, data management, and QA (e.g., assessments and response actions). The appendices provide standard operating procedures (SOPs), plans, and other procedures for all aspects of CASTNET operations.

DQI are quantitative statistics and qualitative descriptors used to interpret 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 2011 data were analyzed and compared with historical data collected during the period 1990 through 2010. The information in this report is supplemented by analyses that are discussed in quarterly QA reports (AMEC, 2011b; 2011e; 2011f; 2012b). These QA reports are produced four times per year with the fourth quarter report including an annual summary.

To estimate precision across the network, collocated sites were operated at Mackville, KY (MCK131/231) and at Rocky Mountain National Park, CO (ROM406/ROM206) during 2011. The ROM406/206 monitors are operated independently and also ensure consistency between the two sponsoring agencies, NPS and EPA, respectively. ROM406 is considered the regulatory monitoring site. Beginning with 2012 measurements, precision of O_3 measurements will be

estimated based on requirements in 40 CFR Part 58 and the EPA QA Handbook for Air Pollution Measurement Systems, Volume II, Appendix D (2008b). In other words, precision of O_3 measurements will be calculated based on single instrument data, not collocated data. Precision of filter measurements will continue to be estimated from collocated data.

Meteorological measurements (excluding temperature) were discontinued at all but five EPA-sponsored sites by the end of 2010. Meteorological data collection is continuing at all NPS sites. However, NPS discontinued measurements of 2-m temperature and surface wetness at all but three sites. Precision was calculated for 2011 O_3, flow, and temperature data, only, because the other continuous measurements were terminated at EPA-sponsored collocated sites. Accuracy was estimated for all parameters.

Precision

Exposed Filter Concentrations

Historical (1990 through 2010) mean absolute relative percent difference (MARPD) data for all 11 collocated site pairs operated over the history of the network and the 2011 data for the current collocated sites at MCK131/231 and ROM406/206 are provided in Figure 5-1. Precision estimates for trace cations and Cl⁻ are shown later in Figure 5-2. Table 5-1 lists the precision and accuracy criteria for laboratory filter pack measurements.

Figure 5-1 Historical and 2011 Precision Data for Atmospheric Concentrations
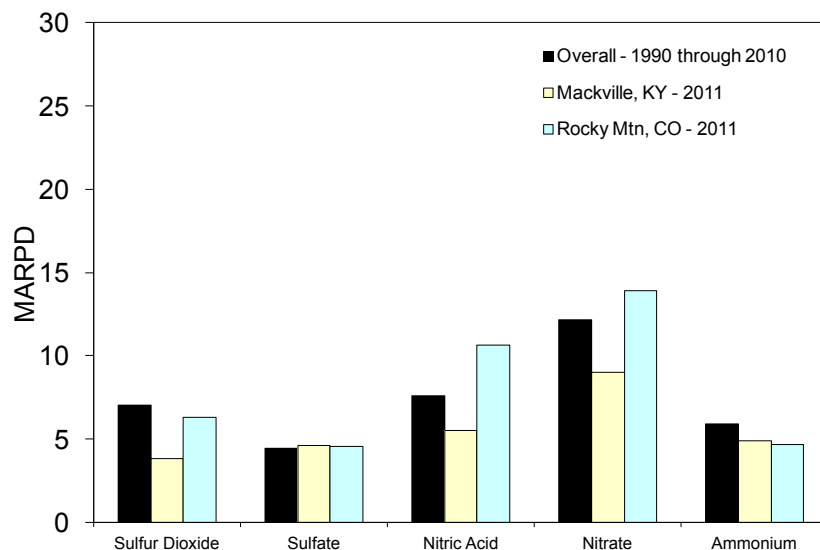
Table 5-1 Data Quality Indicator Criteria for CASTNET Laboratory Measurements

Analyte	Method	Precision[1] (MARPD)	Accuracy[2] (%)	Nominal Reporting Limits mg/l	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

Values are rounded according to American Society for Testing and Materials (Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications E 29).

For more information on analytical methods and associated precision and accuracy criteria, see the CASTNET QAPP, Revision 7.0 (AMEC, 2011c)

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 2011 met the 20 percent criterion for the CASTNET filter pack measurements shown in Table 5-1. The precision of historical and 2011 NO_3^- measurements was consistently worse than for the other analytes, largely because NO_3^- concentrations include sampling artifacts as discussed in Chapter 2.

The 2011 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, except SO_4^{2-}. The 2011 results for ROM406/206 showed better precision than historical precision for SO_2 and NH_4^+. All the 2011 filter pack concentration data met the 20 percent criterion. The MARPD results were higher for ROM406/206 than for MCK131/231 because of lower concentrations measured at this site. Overall, the filter pack precision estimates for MCK131/231 were about the same in 2011 as in 2010. The precision values for ROM406/206 showed improvement in 2011.

Historical and 2011 precision statistics for four metal cations and Cl^- are summarized in Figure 5-2. The historical and 2011 MARPD statistics for both MCK131/231 and ROM406/206 met the DQI criterion of 20 percent. The MARPD values for K^+ were higher than for the other ions at ROM406/206. In 2009 and 2010, the MARPD values for K^+ exceeded the DQI criterion. The precision of the K^+ concentration data was improved by ensuring SOPs for filter pack

assembly and disassembly, extraction and analysis, and impregnation of the potassium carbonate filters were followed carefully; by refining existing procedures for isolating the room where filters are handled to avoid filter contamination; and by improving air handling in the filter room. The 2011 precision results for the four metal cations and Cl⁻ were about the same as 2010 at MCK131/231 and showed improvement at ROM406/206.

Table 5-2 summarizes 2011 precision results by quarter for the two sets of collocated sites. See the 2011 Quarterly Data Reports (AMEC, 2011a; 2011d; 2012a; 2012c) and QA Quarterly Reports (AMEC, 2011b; 2011e; 2011f; 2012b) for discussions of quarterly precision data.

Figure 5-2 Historical and 2011 Precision Data for Cation and Cl⁻ Concentrations
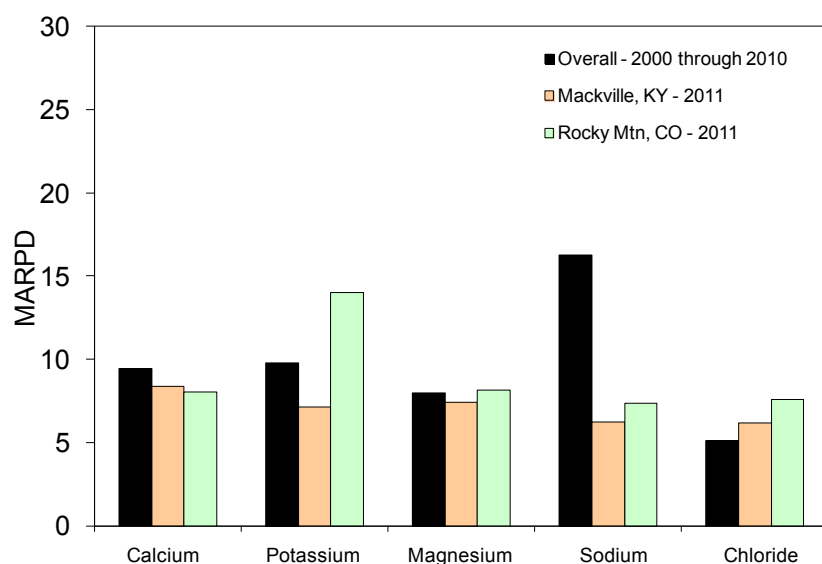
Table 5-2 Collocated Precision Results (MARPD) for 2011 Filter Pack Data by Quarter

Sampling Period	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	2.21	4.46	2.15	7.76	6.69	5.02	5.25	8.46	5.63	2.47	3.98
Quarter 2	6.02	10.67	6.28	9.03	7.32	7.17	6.77	6.08	4.76	4.76	6.78
Quarter 3	3.91	10.68	3.92	6.80	5.51	4.81	7.72	1.78	5.57	4.28	5.70
Quarter 4	6.29	10.22	7.34	9.85	10.24	7.88	8.89	8.35	5.99	3.86	6.55
2011	4.61	9.01	4.92	8.36	7.44	6.22	7.16	6.17	5.49	3.84	5.75
ROM406/ROM206, CO											
Quarter 1	4.74	11.69	4.97	11.29	9.74	10.98	19.26	2.46	7.66	5.56	6.38
Quarter 2	3.37	12.95	3.93	5.99	7.55	4.16	12.64	7.08	10.66	6.22	8.66
Quarter 3	3.30	11.21	3.47	3.57	4.83	4.01	10.71	3.35	12.64	4.46	11.11
Quarter 4	6.75	19.90	6.41	11.31	10.47	10.37	13.51	17.53	11.63	9.03	9.18
2011	4.54	13.94	4.70	8.04	8.15	7.38	14.03	7.61	10.65	6.32	8.83

The 2011 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 (2011)
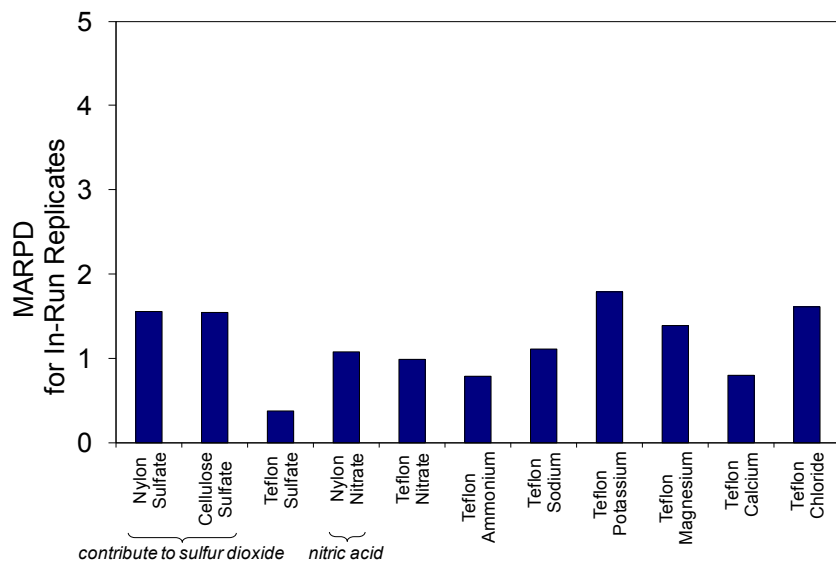
Ozone Concentrations

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 SLAMS monitoring (EPA, 2010a). Consequently, EPA directed AMEC to update EPA-sponsored CASTNET O_3 monitoring to meet 40 CFR Part 58 monitoring requirements. This effort was completed in 2011.

In September 2011, AMEC began submitting O_3 data collected at EPA-sponsored CASTNET sites to the EPA AQS database. The beginning of the data record in AQS was determined by the date of conversion to 40 CFR Part 58 O_3 monitoring protocols for a given site, the earliest of which occurred in late 2010. Approximately one third of EPA-sponsored CASTNET sites have an AQS data record that starts January 1, 2011. The second group of sites has a start date of April 1, 2011, and the final third of the sites has a start date of June 1, 2011. Data are now uploaded to the AQS database monthly. One month of data from all EPA-sponsored CASTNET sites is submitted no later than 90 days after the end of a given month (e.g., August 2011 data for all sites were uploaded in November 2011). NPS-sponsored CASTNET sites and CHE185, OK, which is operated in partnership with the Cherokee Nation, have been configured as

40 CFR Part 58 protocol sites since the beginning of site operation, and their entire data records are in AQS. Submittal schedules of O_3 data to AQS are similar for these sites.

Beginning in 2012, O_3 data quality will be evaluated in terms of AQS-protocol O_3 quality control (QC) criteria (e.g. precision will be calculated as per 40 CFR Part 58 instead of using MARPD of collocated sites). In any event, despite historical 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.

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

Measurement			Criteria*	
Parameter	Method	MARPD/MAD	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 flow.
Mean absolute difference (MAD) is the precision measure for difference criteria such as temperature.

°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. Precision was calculated for only ozone, flow, and temperature because the other continuous measurements were terminated at MCK131, KY; MCK231, KY; and ROM206, CO. Accuracy was estimated for all parameters.

[†] For target value of 0.50 inch

MARPD statistics were calculated from hourly O_3 measurements obtained from the collocated sites MCK131/231 and ROM406/206 during 2011. In addition, quarterly historical precision statistics were compiled for all collocated sites. The historical data were based on the operation of 11 collocated site pairs over the history of the network. Quarterly precision results are summarized in Figure 5-4. Table 5-4 provides precision results for O_3 concentrations by quarter for 2011. The data show the historical and MCK131/231 2011 results met the 10 percent criterion. However, the 2011 MARPD values for first and second quarter 2011 at ROM406/206 did not meet the criterion. The high MARPD values were caused by an erroneous calibration, which dropped readings by about 2 ppb, as well as ongoing differences in systems and

procedures at the two independently operated sites. Also, the completeness of the O_3 concentrations combined from the two monitoring stations at ROM406/206 was only 63 percent in the first quarter. The relatively low completeness was caused by ice in the sample line at ROM206. This resulted in a corresponding inability to perform zero/precision/span checks over an extended period in early 2011.

Scatter plots of the hourly O_3 concentrations measured at the MCK131/231 and ROM406/206 collocated site pairs during 2011 are presented in Figure 5-5. The results from MCK131/231 were excellent with an R^2 of 0.9982 and small y-intercept of 0.48. The ROM406/206 regression line shows a consistent bias between ROM406 and ROM206 O_3 measurements with ROM406 measuring higher concentrations with a slope of 0.9224 and a y-intercept of 1.04. Efforts are underway to eliminate the bias by reducing differences in hardware configuration, systems, and procedures between the two networks. In any event, ROM206 is considered a special study site and ROM206 O_3 data are not used to gauge compliance.

Figure 5-4 Historical and 2011 Precision Data by Quarter for Ozone Concentrations
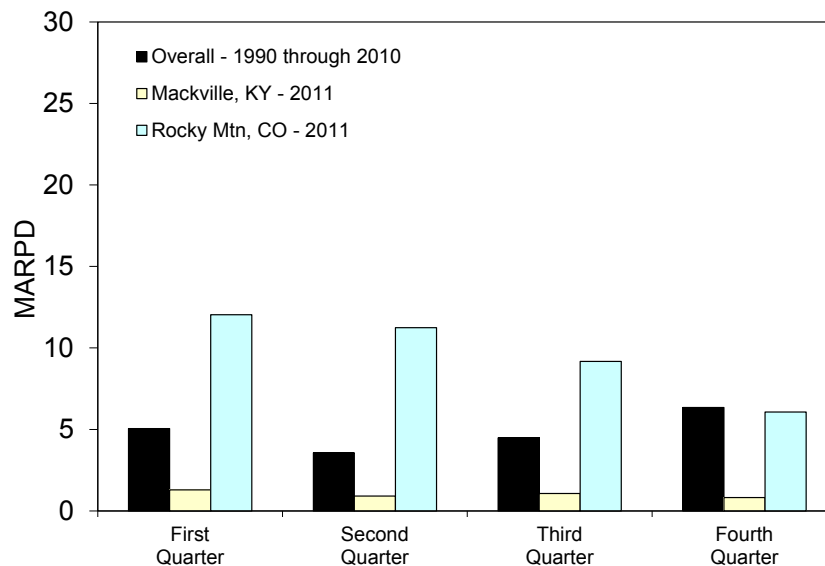
**Table 5-4 Collocated Precision Results (MARPD) for 2011 Ozone Concentrations
by Quarter**

Sampling Period	MCK131/231, KY	ROM406/206, CO
Quarter 1	1.29	12.03
Quarter 2	0.91	11.24
Quarter 3	1.07	9.17
Quarter 4	0.83	6.07
2011	1.03	9.63

Figure 5-5 2011 Hourly Ozone Concentrations at Collocated Sites
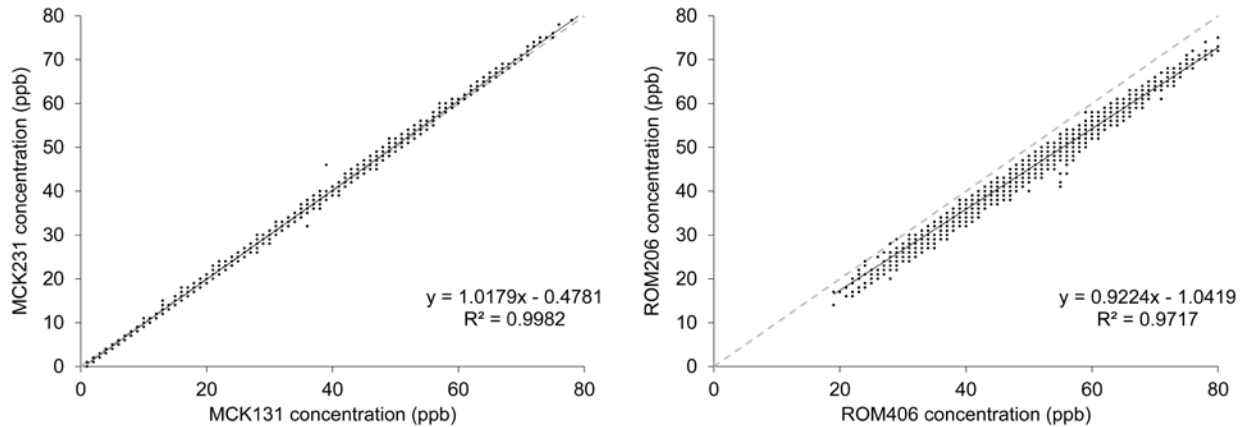
Continuous Measurements

Precision criteria for the continuous measurements are listed in Table 5-3. Because continuous measurements, excluding O_3, flow, and temperature, were discontinued at all but five EPA sites at the end of 2010, including MCK131, MCK231, and ROM206, precision estimates were made only for flow and temperature data. Figure 5-6 provides precision results for flow and temperature for historical data (1990 through 2010) at all collocated site pairs and 2011 precision statistics at the two current collocated site pairs. Precision was calculated in terms of the MARPD or mean absolute difference (MAD) of hourly measurements. All historical and 2011 precision results met the DQI criteria. Table 5-5 gives precision data by quarter for 2011 for flow and temperature for the two collocated sites. The results show overall good instrument precision with all annual and quarterly precision results meeting the DQI criteria.

Figure 5-6 Historical and 2011 Precision Data for Flow and Temperature Measurements
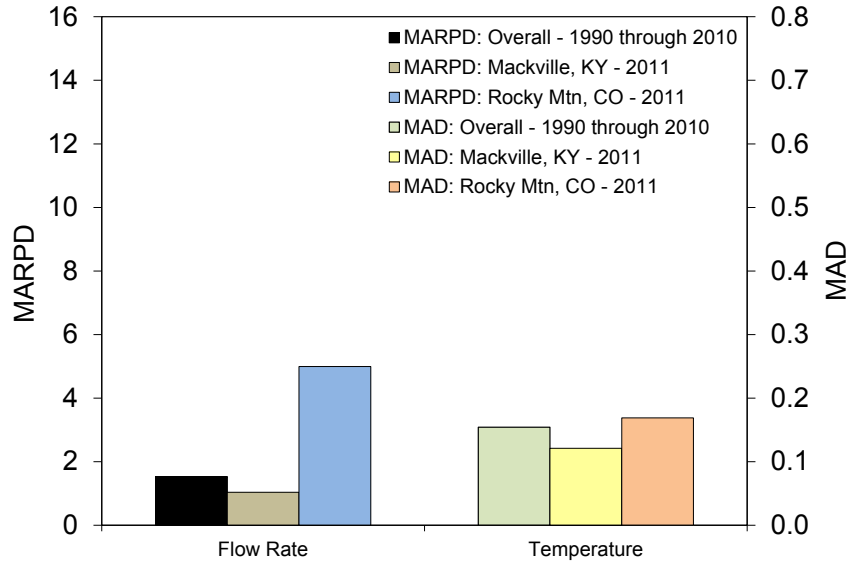
Note: The left y-axis indicates MARPD for flow (Table 5-3), and the right y-axis indicates MAD for temperature (Table 5-3).

Table 5-5 Collocated Precision Results for 2011 Continuous Measurements by Quarter

Sampling Period	MARPD	MAD
	Flow Rate	Temperature
MCK131/231, KY		
Quarter 1	0.08	0.09
Quarter 2	0.12	0.13
Quarter 3	0.08	0.10
Quarter 4	3.88	0.16
2011	1.04	0.12
ROM406/206, CO		
Quarter 1	0.68	0.14
Quarter 2	6.64	0.14
Quarter 3	4.59	0.17
Quarter 4	8.07	0.23
2011	4.99	0.17

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 the National Institute for Standards and Technology (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 are analyzed every tenth sample to verify that instrument calibration has not drifted beyond established limits. Table 5-6 presents the percent recoveries and standard deviations for reference samples and CCV relative to target concentrations for 2011. The table shows that the DQI goals (see Table 5-1) were met in 2011.

Table 5-6 Filter Pack Quality Control Summary for 2011

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-}	98.97	1.49	130	99.72	1.41	661	0.37	0.56	310
	NO_3^-	100.85	0.91	130	100.51	1.12	661	0.99	1.18	326
	NH_4^+	102.96	2.34	132	101.32	2.18	677	0.78	0.91	347
	Ca^{2+}	99.18	2.34	133	100.45	0.94	678	0.80	0.81	312
	Mg^{2+}	103.41	1.29	133	100.03	0.88	678	1.39	1.61	312
	Na^+	99.96	1.66	133	100.01	0.96	678	1.11	1.48	312
	K^+	100.80	2.23	133	100.03	0.78	678	1.79	2.21	312
	Cl^-	103.48	0.83	130	100.83	1.59	661	1.61	1.78	296
Nylon	SO_4^{2-}	98.83	1.27	129	99.97	1.59	651	1.55	2.20	298
	NO_3^-	100.54	1.16	129	100.72	1.17	651	1.07	1.19	312
Cellulose	SO_4^{2-}	98.28	1.49	170	99.42	1.58	671	1.54	2.19	337

Note: % R = percent recovery
RPD = relative percent difference
[1] Results of reference sample analyses provide accuracy estimates
[2] Results of replicate analyses provide precision estimates
[3] Number of quality control samples

Continuous Measurements

Table 5-7 presents field accuracy results for 2011 based on instrument challenges performed using independent reference standards during site calibration visits. CASTNET sites were calibrated every six months with NIST-traceable standards. The calibration results were evaluated using the accuracy criteria listed in Table 5-3. Each parameter was within its criterion with at least 90 percent frequency with the exception of wind direction north at 87.5 percent and solar radiation at 87.5 percent. However, these results did not adversely affect data collection because data are not considered invalid unless criteria are exceeded by more than two times the criterion. Using the two times standard, the two parameters passed with 100.0 percent frequency. The 2011 results for flow rate accuracy were lower than for 2010.

Table 5-7 Accuracy Results for 2011 Field Measurements

Parameter	Percent Within Criterion	Parameter	Percent Within Criterion
Flow Rate	90.9 percent	Temperature (ambient)	97.1 percent
Ozone Slope	97.0 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	100.0 percent
Wind Speed ≥ 5 m/s	100.0 percent	Precipitation	100.0 percent
*Wind Direction North	87.5 percent	*Solar Radiation	87.5 percent
Wind Direction South	100.0 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).

Cedar Creek State Park, WV (CDR119)

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. For 2011 all the parameters listed in Figure 5-7 were measured at the five EPA-sponsored sites with continuing meteorological measurements. All parameters, except delta temperature and wetness, were measured at NPS-sponsored sites. Ozone concentrations were measured at 80 of 83 sites. Atmospheric concentrations, filter pack flow, and ambient temperature were measured at all sites. Delta temperature was measured at the five EPA sites plus ACA416, ME; GRS420, TN; and ROM406, CO. Surface wetness was measured at the five EPA sites plus GRS420, TN. Figure 5-7 presents historical (black) and 2011 completeness data for all sites for measured filter concentrations and continuous measurements. The figure shows that the 2011 direct measurements met the 90 percent completeness goal, and four meteorological measurements and filter pack flow exceeded 95 percent. Atmospheric concentrations also exceeded 95 percent.

Figure 5-7 Historical and 2011 Percent Completeness of Measurements (black bars are 1990–2010)
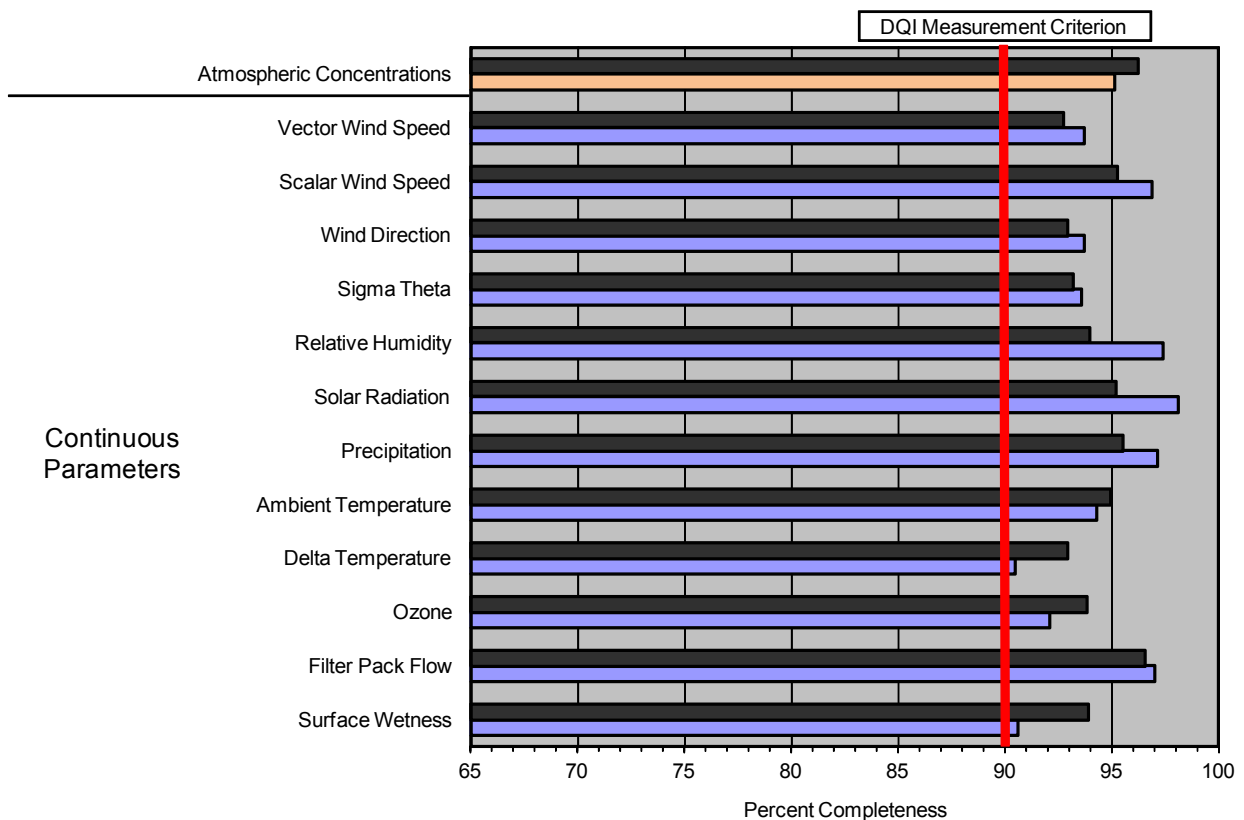
Results for 2011 Environment Canada Proficiency Testing

During 2011, the 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 32 laboratories that participated in the 2011 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 6 months. The laboratory reported the eight CASTNET parameters for samples in two studies (study codes 0098 and 0099) during 2011.

The results reported by the 32 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 (R-σ) 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; 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 2011 ECAN results for the eight CASTNET parameters are presented in Table 5a. All scored parameters received the highest possible rating of "ideal" indicating an unbiased score in study 0098. Two of 10 individual results for NH_3 were flagged "warning high" for study 0099, indicating that the flagged results were between 2 and 3 R-σ from their assigned values. Both of these results were at concentrations below 3 times the method reporting limit. Investigation by the laboratory revealed the root cause for these results to be a slightly degraded low-level standard. Corrective action was implemented to require an acceptance criterion of ±5 percent of the expected value for each point in a calibration curve.

Table 5a *AMEC Results for Studies 0098 and 0099*

Test Parameter	Analytical Method	Reference Method	Laboratory Performance Rating	
			Study 0098 Summer 2011	*Study 0099 Winter 2011*
NH_3	AC	EPA Method 350.1	Insufficient Data*	Biased High
Ca^{2+}	ICP-AES	EPA Method 6010	Ideal	Ideal
Cl^-	IC	EPA Method 300.0	Ideal	Ideal
Mg^{2+}	ICP-AES	EPA Method 6010	Ideal	Ideal
$NO_3^- + NO_2^-$	IC	EPA Method 300.0	Ideal	Ideal
K^+	ICP-AES	EPA Method 6010	Ideal	Ideal
Na^+	ICP-AES	EPA Method 6010	Ideal	Ideal
SO_4^{2-}	IC	EPA Method 300.0	Ideal	Ideal

Note: * Fewer than five samples above method reporting limit.

Source: Environment Canada (2012)

The overall laboratory performance rating was "Very Good" for study 0098 and "Good" for study 0099. The overall laboratory rating indicates a percent score as described in Table 5b.

Table 5b *Laboratory Performance Rating*

Laboratory Performance Rating	
Rating	*% Score**
Very Good	*0 - 5*
Good	*> 5 - 12.5*
Fair	*> 12.5 - 30*
Poor	*> 30*

Note: * *Sum of Parameters Biased and Results Flagged*

Source: Environment Canada (2012)

The report for study 0099 included a summary of the laboratory's performance over the last five years. The laboratory achieved the highest possible rating for 9 of the 10 studies conducted during that period. The results are listed below in Table 5c.

Table 5c *Five-Year Historical Laboratory Performance*

Study No. / Date	Score*
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*
No. 0098, Summer 2011	*0.0*
No. 0099, Winter 2011	*6.0*
5-Year Median	*1.5*

Note: * *Sum of Parameters Biased and Results Flagged*

Source: Environment Canada (2012)

Mackville, KY (MCK131/231)

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 2011 with the exception of O_3 measurements at ROM406/206, CO. The O_3 concentrations measured at ROM406 were consistently higher than ROM206. However, ROM206 is considered a special study site, and ROM206 O_3 data are not used to gauge compliance with NAAQS.

Historical and 2011 precision data for filter pack parameters are considered acceptable. The 2011 precision data for O_3 concentrations met the 10 percent DQI criterion for six of the eight quarters. The 2011 O_3 MARPD values for the first and second quarter 2011 at ROM406/206 did not meet the criterion. The precision of quarterly and annual flow and temperature measurements for 2011 was good with all quarterly and annual results meeting the DQI criteria.

Accuracy data met the established criteria for field and laboratory parameters. Completeness criteria were met for all parameters in 2011. Completeness results for 2011 are considered excellent. ECAN proficiency test studies (0098 and 0099) showed that the CASTNET laboratory performed well for the interlaboratory chemical analyses.

Rocky Mountain National Park, CO (ROM406/206)

References

AMEC Environment & Infrastructure, Inc. (AMEC). 2012a. *Clean Air Status and Trends Network (CASTNET) Fourth Quarter 2011 Data Report.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. EP-W-09-028. Gainesville, FL.

AMEC Environment & Infrastructure, Inc. (AMEC). 2012b. *Clean Air Status and Trends Network (CASTNET) Fourth Quarter 2011 Quality Assurance Report with 2011 Annual Summary.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. EP-W-09-028. Gainesville, FL. http://java.epa.gov/castnet/documents.do.

AMEC Environment & Infrastructure, Inc. (AMEC). 2012c. *Clean Air Status and Trends Network (CASTNET) Third Quarter 2011 Data Report.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. EP-W-09-028. Gainesville, FL.

AMEC Environment & Infrastructure, Inc. (AMEC). 2012d. *Cloud Deposition Monitoring, Clingmans Dome, TN, Great Smoky Mountains National Park, 2011*. Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. EP-W-09-028. Gainesville, FL. http://java.epa.gov/castnet/documents.do.

AMEC Environment & Infrastructure, Inc. (AMEC) [*]. 2011a. *Clean Air Status and Trends Network (CASTNET) First Quarter 2011 Data Report.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. 68-D-03-052. Gainesville, FL.

AMEC Environment & Infrastructure, Inc. (AMEC) [*]. 2011b. Clean Air Status and Trends Network (CASTNET) First Quarter 2011 Quality Assurance Report. Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. 68-D-03-052. Gainesville, FL. http://java.epa.gov/castnet/documents.do.

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[*] Formerly known as MACTEC Engineering and Consulting, Inc.

References (continued)

AMEC Environment & Infrastructure, Inc. (AMEC) [*]. 2011c. *Clean Air Status and Trends Network (CASTNET) Quality Assurance Project Plan (QAPP) Revision 7.0*. Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. EP-W-09-028. Gainesville, FL. http://java.epa.gov/castnet/documents.do.

AMEC Environment & Infrastructure, Inc. (AMEC) [*]. 2011d. *Clean Air Status and Trends Network (CASTNET) Second Quarter 2011 Data Report*. Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. EP-W-09-028. Gainesville, FL.

AMEC Environment & Infrastructure, Inc. (AMEC) [*]. 2011e. *Clean Air Status and Trends Network (CASTNET) Second Quarter 2011 Quality Assurance Report*. Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. 68-D-03-052. Gainesville, FL. http://java.epa.gov/castnet/documents.do.

AMEC Environment & Infrastructure, Inc. (AMEC) [*]. 2011f. *Clean Air Status and Trends Network (CASTNET) Third Quarter 2011 Quality Assurance Report*. Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. EP-W-09-028. Gainesville, FL. http://java.epa.gov/castnet/documents.do.

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

AmeriFlux Network. 2012. AmeriFlux. http://public.ornl.gov/ameriflux/ (accessed May 2012).

Bowker, G.E., Schwede, D.B., Lear, G.G., Warren-Hicks, W.J., and Finkelstein, P.L. 2011. Quality Assurance Decisions with Air Models: A Case Study of Imputation of Missing Input Data Using EPA's Multi-Layer Model. *Water, Air, & Soil Pollution* DOI 10.1007/s11270-011-0808-7.

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[*] Formerly known as MACTEC Engineering and Consulting, Inc.

References (continued)

Burns, D.A., Lynch, J.A., Cosby, B.J., Fenn, M.E., Baron, J.S., US EPA Clean Air Markets Div. 2011. *National Acid Precipitation Assessment Program Report to Congress 2011: An Integrated Assessment*. National Science and Technology Council, Washington, DC http://ny.water.usgs.gov/projects/NAPAP/

Environment Canada (ECAN) Water Science and Technology Directorate. 2012. *Rain and Soft Waters PT Studies 0098 and 0099 Report.* Proficiency Testing Program, Burlington, Ontario, Canada. Prepared for AMEC Environment & Infrastructure, Inc.

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

Henriksen, A., Dillon, P.J, Aherne, J. 2002. Critical Loads of Acidity for Surface Waters in South-central Ontario, Canada: Regional Application of the Steady-State Water Chemistry (SSWC) Model. *Can. J. Fish. Aquat. Sci*. 59: 1287–1295.

International Organization for Standardization (ISO). 2005. *Statistical Methods for the Use in Proficiency Testing by Interlaboratory Comparisons, Annex C, Robust Analysis, Section C.1: Algorithm A*. Standard 13528. ISO 13528:2005(E).

Klingberg, J., Engardt, M., Uddling, J., Karlsson, P.E., and Pleijel, H. 2011. Ozone Risk for Vegetation in the Future Climate of Europe Based on Stomatal Ozone Uptake Calculations. *Tellus*. 63A, 174-187.

Lefohn, A.S., Lawrence, J.A., and Kohut, R.J. 1988. A Comparison of Indices that Describe the Relationship between Exposure to Ozone and Reduction in the Yield of Agricultural Crops. *Atmos. Environ*., 22:1229-1240.

Lefohn, A.S. and Runeckles, V.C. 1987. Establishing a Standard to Protect Vegetation - Ozone Exposure/Dose Considerations. *Atmos. Environ*., 21:561-568.

Lovett, G.M. 1984. Rates and Mechanisms of Cloud Water Deposition to a Subalpine Balsam Fir Forest. *Atmos. Environ*. 18:361-371.

References (continued)

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

Musselman, R.C., Lefohn, A.S., Massman, W.J., and Heath, R.L. 2006. A Critical Review and Analysis of the Use of Exposure and Flux-Based Ozone Indices for Predicting Vegetation Effects. *Atmos. Environ*., 40:1869-1888.

National Climatic Data Center. 2012. State of the Climate, Wildfires, September 2011. http://www.ncdc.noaa.gov/sotc/fire/2011/9 (accessed January 2012).

National Oceanic and Atmospheric Administration. 2012. Texas, New Mexico, Arizona Wildfires, Spring-Fall 2011. http://www.noaa.gov/extreme2011/wildfire.html (accessed January 2012).

National Park Service (NPS). 2012. *Data Quality Assurance Report 2011, Gaseous Pollutant Monitoring Program*. National Park Service Air Resources Division, Lakewood, CO. http://www.nature.nps.gov/air/Pubs/pdf/ads/2011/NPS_GPMP_Annual_Data_Summary_2011_1-31-2013.pdf

Nilsson, J., and Grennfelt, P. (Eds). 1988. *Critical Loads for Sulphur and Nitrogen.* UNECE/Nordic Council workshop report, Skokloster, Sweden. March 1988. Nordic Council of Ministers: Copenhagen.

North Dakota Department of Health, Division of Air Quality. 2012. 2011 Ozone Concentrations. http://www.ndhealth.gov/aq/ (accessed April 2012).

Ray, J.D. 2013. *Annual Data Summary 2011: Gaseous Pollutant Monitoring Program*, Natural Resource Data Series, NPS/NRSS/ARD/NRDS—2013/443. National Park Service, Denver, Colorado. http://www.nature.nps.gov/air/Pubs/pdf/ads/2011/NPS_GPMP_Annual_Data_Summary_2011_1-31-2013.pdf

Rogers, C.M., Mishoe, K.P., Stewart, M.O., Smith, M.J., Price, G.L., Howell, H.K. 2012. *Results from the CASTNET Ammonia Special Study*. Paper 2012-A-528-AWMA. Proceedings of the AWMA Annual Meeting, San Antonio, TX, June 19-22.

References (continued)

U.S. Environmental Protection Agency (EPA). 2012a. *Clean Air Interstate Rule, Acid Rain Program and Former NO$_x$ Budget Trading Program, 2011 Progress Reports:* http://www.epa.gov/airmarkets/progress/ARPCAIR11.html

U.S. Environmental Protection Agency (EPA). 2012b. *Clean Air Interstate Rule, Acid Rain Program and Former NO$_x$ Budget Trading Program, 2010 Progress Reports: Environmental and Health Results*. http://www.epa.gov/airmarkets/progress/ARPCAIR10_02.html (accessed June 2012).

U.S. Environmental Protection Agency (EPA). 2012c*. Office of Air & Radiation, Clean Air Markets Division, Air Markets Program Data.* http://ampd.epa.gov/ampd/QueryToolie.html (accessed August 2012).

U.S. Environmental Protection Agency (EPA). 2011. *Estimates of Atmospheric Deposition Using the Community Multiscale Air Quality Model (CMAQ)*, http://www.epa.gov/AMD/EcoExposure/depositionMapping.html (accessed November 2012).

U.S. Environmental Protection Agency (EPA). 2010a. Appendix A to Part 58 – Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS), Special Purpose Monitors (SPMs), and Prevention of Significant Deterioration (PSD) Air Monitoring. 40 *CFR* Part 58.

U.S. Environmental Protection Agency (EPA). 2010b. *Proposed Revisions to National Standards for Ground-Level Ozone*. http://www.epa.gov/air/ozonepollution/actions.html (accessed June 2012).

U.S. Environmental Protection Agency (EPA). 2008a. National Ambient Air Quality Standards for Ozone; Final Rule. *Federal Register* 73, No. 60 (March). EPA-HQ-OAR-2005-0172.

U.S. Environmental Protection Agency (EPA). 2008b. *Quality Assurance Handbook for Air Pollution Measurement Systems*, Volume II, Ambient Air Quality Monitoring Program. EPA-454/B-08-003, December.

U.S. Environmental Protection Agency (EPA). 2006. *Air Quality Criteria for Ozone and Related Photochemical Oxidants*. Report No. EPA/600/R-05/004af. ORD, Research Triangle Park, NC.

References (continued)

U.S. Environmental Protection Agency (EPA). 2000. *National Air Quality and Emissions Trends Report, 1998.* Report No. EPA-454-R-00-003. OAQPS, Research Triangle Park, NC 27711.

U.S. Environmental Protection Agency (EPA). 1998. *Guideline on Data Handling Conventions for the 8-Hour Ozone NAAQS*. EPA-454/R-98-017. OAQPS, Research Triangle Park, NC 27711.

U.S. Environmental Protection Agency (EPA). 1996. *Air Quality Criteria for Ozone and Related Photochemical Oxidants*. EPA Report No. EPA/600/P-93/004bF. ORD, Research Triangle Park, NC.

Youden, W.J. (Ku, H.H., ed). 1969. *Precision Measurement and Calibration*. NBS Special Publication 300-Volume 1. U.S. Government Printing Office, Washington, DC.

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												
JOT403	Joshua Tree National Park	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
HOW191	Howland AmeriFlux	09/16/2011	45.2041	68.7402	60	•	•	ME09	Forested	Rolling	N	EPA

Table A-1 Locational and Operational Characteristics of CASTNET Sites

Site ID	Site Name	Start date	Latitude (°N)	Longitude (°W)	Elevation (m)	Deposition Filter Pack[1]	Ozone and Meteorology[2]	Nearby NADP Site	Primary Land Use	Terrain	Representative to the MLM[3]	Sponsor
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 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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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
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
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 $\quad = \quad SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, K^+, Na^+, Mg^{2+}, Ca^{2+}$

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

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

2. Temperature is measured at all sites. Other meteorological measurements have been discontinued at all 100 and 200 series sites with the exception of PAL190,TX; CHE185, OK; BVL130, IL, BEL116, MD; and BFT142, NC. Delta temperature was discontinued at all 400 series sites with the exception of ACA416, ME; GRS420, TN; and ROM406, CO. Surface wetness was discontinued at all 400 series sites with the exception of GRS420. Meteorological sensors include: 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

ACCS	Ammonia CASTNET Chemical Speciation Network Study
ADS	annular denuder system
AMEC	AMEC Environment & Infrastructure, Inc.
AMNet	Atmospheric Mercury Network
AMoN	Ammonia Monitoring Network
ANC	acid neutralizing capacity
AQS	EPA's Air Quality System
ARP	Acid Rain Program
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
CFR	Code of Federal Regulations
CCV	continuing calibration verification samples
Cl^-	particulate chloride ion
CLAD	Critical Loads of Atmospheric Deposition science committee
CLD303	Clingmans Dome, TN cloud sampling site
CLmaxS	maximum critical load of sulfur
CMAQ	Community Multiscale Air Quality Modeling System
CLminN	nitrogen removed by an ecosystem
CSAPR	Cross-State Air Pollution Rule
CSN	Chemical Speciation Network
%D	percent difference
DM8A	daily maximum 8-hour average
DQI	data quality indicator
%E	percent error
ECAN	Environment Canada
EGU	electric generating unit
EPA	U.S. Environmental Protection Agency
H_2SO_4	sulfuric acid
HNO_3	nitric acid
H_3PO_3	phosphorous acid
IC	ion chromatography
ICP-AES	inductively coupled plasma-atomic emission spectrometry
IDW	inverse distance weighting
IMPROVE	Interagency Monitoring of Protected Visual Environments

List of Acronyms and Abbreviations (continued)

ISO	International Organization for Standardization
K^+	particulate potassium ion
K_2CO_3	potassium carbonate
kg/ha	kilograms per hectare
kg/ha/yr	kilograms per hectare per year
km	kilometer
LAI	leaf area index
lpm	liters per minute
LWC	liquid water content
m	meter
MAD	mean absolute difference
MADPro	Mountain Acid Deposition Program
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
MPPD	mini-parallel plate denuder
N	nitrogen ($HNO_3 + NO_3^- + NH_4^+$)
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
NDDN	National Dry Deposition Network
NH_3	ammonia
NH_4^+	particulate ammonium
NH_4NO_3	ammonium nitrate
$(NH_4)_2SO_4$	ammonium sulfate
NH_x	NH_3 + volatilized NH_4^+
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
Nr	reactive nitrogen
NTN	National Trends Network

List of Acronyms and Abbreviations (continued)

O_3	ozone
OTC	Ozone Transport Commission
PM	particulate matter
PM_{10}	coarse particulate matter
$PM_{2.5}$	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
R-σ	robust standard deviation
RTI	RTI International, Inc.
S	sulfur (SO_2 + SO_4^{2-})
SIP	State Implementation Plan
SLAMS	State and Local Air Monitoring Stations
SO_2	sulfur dioxide
SO_4^{2-}	particulate sulfate
SOP	standard operating procedure
TN11	Elmont, TN wet deposition monitoring site
total NO_3^-	gaseous nitric acid (HNO_3) + particulate nitrate (NO_3^-)
TRNP	Theodore Roosevelt National Park
TVA	Tennessee Valley Authority
µeq/L	microequivalents per liter
µg/m^3	micrograms per cubic meter
V_d	deposition velocity
VOCs	volatile organic compounds

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

www.epa.gov/airmarkets

www.epa.gov