

CASTNET

2012 ANNUAL REPORT

CLEAN AIR STATUS AND TRENDS NETWORK



**Clean Air Status and Trends Network
(CASTNET)**

2012 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

April 2014

Table of Contents

	Executive Summary	ii
Chapter 1	CASTNET Overview	1
	Background.....	1
	<i>Cooperating Networks</i>	4
	Locations of Monitoring Sites	5
	CASTNET Reference Sites.....	6
	Measurements Recorded at CASTNET Sites.....	8
	Estimating Dry and Wet Deposition.....	9
	Sulfur Dioxide and Nitrogen Oxides Emissions	9
Chapter 2	Atmospheric Concentrations	12
	Sulfur Dioxide	12
	Particulate Sulfate.....	14
	<i>Ambient Ammonia Measurements at Beaufort, NC</i>	16
	Total Nitrate	19
	Particulate Ammonium.....	20
	<i>Border 2020: U.S.-Mexico Environmental Program</i>	22
Chapter 3	Atmospheric Deposition	26
	<i>Hybrid Approach to Estimating Total Deposition</i>	27
	Sulfur Deposition.....	32
	<i>Total Reactive Oxides of Nitrogen Measurements at Beaufort, NC</i>	36
	Nitrogen Deposition	38
	<i>An Analysis of Critical Loads of Streams near Seven CASTNET Sites in Eastern United States</i>	42
Chapter 4	Ozone Concentrations	45
	<i>National Ambient Air Quality Standards for Ozone</i>	46
	Eight-Hour Ozone Concentrations	47
	<i>In-Canopy Measurements of Ozone and Other Gases and Particles at Howland Research Forest, ME</i>	52
	W126 Values for 2012	55
	<i>Ozone Monitoring System Performance Audits</i>	57
Chapter 5	Data Quality	62
	Summary of Data Quality Results	63
	Precision.....	63
	<i>Filter Pack Bias Comparison</i>	67
	Accuracy.....	76
	Completeness.....	78
	<i>Results for 2012 Environment Canada Proficiency Testing</i>	80
References	82
Appendix A	Locational and Operational Characteristics of CASTNET Sites	
Appendix B	Acronyms and Abbreviations	

Executive Summary

The EPA Clean Air Status and Trends Network (CASTNET) measures atmospheric pollution concentrations across the continental United States, Canada, and Alaska in order to evaluate the effectiveness of national and regional air pollution control programs. This report presents 2012 maps of the geographic distribution of sulfur and nitrogen pollutant concentrations, ozone (O₃) levels, and deposition fluxes and examines trends in air quality since 1990. CASTNET measured rural, regionally representative concentrations of sulfur and nitrogen species at 91 monitoring stations at 88 sites and measured O₃ at 83 sites in the United States and Canada during 2012.

Key Results and Highlights through 2012

- Mean annual sulfur dioxide (SO₂) and particulate sulfate (SO₄²⁻) concentrations have declined significantly over the 23-year period 1990 through 2012 and showed a substantive reduction since 2005. Three-year mean annual SO₂ levels declined 76 percent while SO₄²⁻ concentrations declined 56 percent at eastern reference sites from 1990 through 2012. SO₂ concentrations measured at western reference sites were reduced by 54 percent, and SO₄²⁻ levels dropped by 22 percent over the 17-year period (1996 through 2012).
- The three-year mean annual total (dry + wet) sulfur deposition estimated in the eastern United States declined by 63 percent from 1990–1992 through 2010–2012. Total sulfur deposition aggregated over western reference sites fell by 37 percent from 1996–1998 through 2010–2012.
- Three-year mean annual concentrations of total nitrate (NO₃⁻), which is comprised of nitric acid (HNO₃) plus particulate NO₃⁻, declined 39 percent at eastern sites over the 23-year period. Total NO₃⁻ levels measured at western reference sites dropped by 29 percent over the 17 years.
- Three-year mean total nitrogen deposition [particulate NO₃⁻ (dry + wet) and HNO₃] fell by 24 percent from 1990 through 2012 at eastern reference sites. Total nitrogen deposition estimated for western reference sites was reduced by 20 percent over the 17 years. However, total nitrogen deposition increased significantly at eastern reference sites from 2010 to 2011 because of increased nitrogen concentrations in precipitation and above-normal precipitation. In 2012 precipitation declined while the nitrogen concentration in precipitation increased slightly over the 2011 level. The net result was a decline in the total nitrogen deposition rate at eastern reference sites.
- The mean fourth highest daily maximum 8-hour average O₃ concentration for 2012 at eastern reference sites was 70 parts per billion (ppb) or, equivalently, 0.070 parts per million (ppm), which was higher than the 2011 value of 69 ppb and the 2009 concentration of 64 ppb, the lowest in the history of the network. Six eastern and three California sites plus the site at Rocky Mountain National Park, CO (ROM406) recorded exceedances of the 8-hour standard of 0.075 ppm during the most recent three-year period (2010 through 2012).

- Measurements from 2012 and historical data collected over the period 1990 through 2011 were analyzed relative to data quality indicators and their numerical measures, e.g., for precision, accuracy, completeness, bias, and comparability. The results of these analyses, which are discussed in Chapter 5, demonstrate that CASTNET data can be used with confidence and that CASTNET continues to produce information of the highest quality.
- In 2012, EPA operated 83 CASTNET sites that were compliant with the requirements of 40 CFR Parts 50, 53, and 58. The precision of O₃ data was evaluated as per Part 58 requirements.
- As with the 2011 CASTNET Annual Report, dry deposition estimates were based on the method developed by Bowker *et al.* (2011). This approach combines measured concentrations with deposition velocities modeled using the Multi-Layer Model (MLM) along with historical averages to replace missing values.
- For the wet deposition component of total 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. PRISM-based precipitation data were combined with measured values of concentrations in precipitation from the National Atmospheric Deposition Program's National Trends Network to obtain estimates of wet deposition.
- The MLM/Bowker estimates of dry deposition were combined with PRISM-adjusted values of wet deposition. The use of the MLM/Bowker approach and NTN/PRISM resulted in improved completeness of dry, wet, and total deposition estimates for 2012.

 **CHAPTER 1: CASTNET OVERVIEW**

The Clean Air Status and Trends Network (CASTNET) provides long-term monitoring of air quality in rural areas to determine trends in regional atmospheric sulfur, nitrogen, and ozone concentrations and deposition fluxes of sulfur and nitrogen pollutants. CASTNET is managed and operated by the Environmental Protection Agency's Clean Air Markets Division in cooperation with the National Park Service and other federal, state, and local partners. The Bureau of Land Management began operating four CASTNET sites in Wyoming in 2012. CASTNET was established under the 1990 Clean Air Act Amendments and continued and expanded the National Dry Deposition Network, which began in 1987. During 2012, the network operated 91 monitoring stations at 88 site locations throughout the contiguous United States, Alaska, and Canada. Measurements collected in 2012 show the continuing decline in sulfur and nitrogen pollutant concentrations. Ozone concentrations in the eastern United States increased relative to 2011. All pollutants have declined significantly over the last 23 years.

Background

The U.S. Congress directed the U.S. Environmental Protection Agency (EPA) to institute CASTNET under Title IX of the 1990 Clean Air Act Amendments (CAAA) in order to assess the effectiveness of the Acid Rain Program (ARP) as emission reductions became effective in 1995 and subsequent years. 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. CASTNET is sponsored by EPA and the National Park Service (NPS), which began its participation in 1994 and operated 26 sites in 2012. The Bureau of Land Management (BLM) began participation in CASTNET in late 2012 by operating four sites in Wyoming.

The U.S. Congress established the ARP under Title IV of the 1990 CAAA. The ARP was promulgated to reduce emissions of sulfur dioxide (SO₂) and nitrogen oxides (NO_x) from electric generating units (EGUs). The ARP has produced significant reductions in SO₂ and NO_x emissions from EGUs since 1995. The SO₂ program set a permanent cap on the total amount of SO₂ 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 SO₂. 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 equals the SO₂ 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 program was phased in with the final 2010 SO₂ emissions cap set at 8.95 million tons, a level about one-half of the total SO₂ emissions from the power sector in 1980. Actual SO₂ emissions from EGUs in 2012 were about 3.3 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 2012 were about 1.7 million tons. Although the ARP was responsible for a large portion of the 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), the Clean Air Interstate Rule (CAIR), and regional and state NO_x emission control programs.

CAIR was promulgated in 2005 and was designed to reduce emissions of SO₂ and NO_x in 27 eastern states and the District of Columbia. This rule created three separate trading programs: an annual NO_x program, an ozone (O₃) season NO_x program, and an annual SO₂ program. The CAIR O₃ seasonal and annual NO_x programs began in 2009 while the CAIR annual SO₂ program began in 2010. CAIR addresses regional interstate transport of O₃ and fine particles. CAIR benefits human health and results in improved visibility/visual quality in national parks and improved quality of freshwater ecosystems in the eastern United States.

In 2012, the network included 91 monitoring stations operated at 88 site locations throughout the contiguous United States, Alaska, and Canada. In mid-April 2012, NPS installed a collocated O₃ analyzer at Yosemite National Park (YOS204, CA). The Howland, ME (HOW132) site was closed at the end of October 2012. As of November 1, 2012, the 23.5-meter (m) inlet at the Howland, ME (HOW191) AmeriFlux site was designated as the primary filter pack measurement for the Howland area. During November, new filter pack measurement systems were established in Vermont, New York, and Wyoming. The specific start dates and other locational and operational information for these new sites can be found in Appendix A to this report. The four Wyoming sites are sponsored by BLM and are operated to support the Wyoming Air Resources Monitoring System (WARMS). The two new New York sites are sponsored by the New York State Department of Environmental Conservation (NYSDEC) and New York State Energy Research and Development Authority (NYSERDA). The site in Vermont is sponsored by EPA.

The three new eastern sites are small footprint, filter pack-only sites. These sites do not have traditional CASTNET shelters and use pole-mounted “boxes” instead. See the photographs on page 3 for an example of the equipment box used in place of a shelter at a small footprint site.

New Filter Pack Site Locations and Names

Eastern	Western
Nicks Lake, NY (NIC001)	Basin, WY (BAS601)
Underhill, VT (UND002)	New Castle, WY (NEC602)
Whiteface Mountain, NY (WFM105)	Buffalo, WY (BUF603)
	Sheridan, WY (SHE604)

Additionally, trace-level gas monitoring for SO₂, nitrogen oxide/total reactive oxides of nitrogen (NO/NO_y), and carbon monoxide (CO) continued during 2012. During the last half of 2012, trace-level gas monitoring was added to the BVL130, IL and HWF187, NY sites. The three CASTNET sites with trace-level gas monitoring are now using Teledyne Advanced Pollution Instrumentation. The trace-level gas analyzers and data validation procedures meet all regulatory requirements in Title 40 of the Code of Federal Regulations (CFR). Data are submitted to EPA’s Air Quality System (AQS). The sites and the parameters measured at each site include:

Trace-level Gas Monitoring Sites

Site Location and Name	Measurements
Bondville, IL (BVL130)	CO, SO ₂ and NO/NO _y
Huntington Wildlife Forest, NY (HWF187)	NO/NO _y
Beltsville, MD (BEL116)	SO ₂ and NO/NO _y

This report summarizes CASTNET monitoring activities and the resulting concentration and deposition data collected over the 23-year period from 1990 through 2012. Additional information, previous annual reports, other CASTNET documents, and the CASTNET database can be found on the EPA website, <http://www.epa.gov/castnet/>. The website provides a complete archive of concentration and deposition data for all EPA- and NPS-sponsored CASTNET sites.



Interior of box



Underhill, VT (UND002)

Cooperating Networks

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

- ▶ **National Atmospheric Deposition Program (NADP)** operates:
 - **National Trends Network (NTN)**, which includes 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.
 - **Mercury Deposition Network (MDN)**, which operates samplers to measure mercury in precipitation. MDN samplers are operated at several CASTNET sites.
 - **Ammonia Monitoring Network (AMoN)**, which operates passive ammonia (NH₃) samplers at about 40 CASTNET locations. AMoN, in operation for four years, provides information on 2-week average NH₃ concentrations.
 - **Atmospheric Mercury Network (AMNet)**, which measures atmospheric concentrations of gaseous oxidized, particulate-bound, and elemental mercury at about 18 locations in the continental United States, Canada, Hawaii, and Taiwan in order to estimate dry and total mercury deposition.

See NADP's website 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 website at <http://www.ec.gc.ca/rs-mn/default.asp?lang=En&n=752ce271-1>.
- ▶ **EPA's National Core Monitoring (NCore)** operates trace-level measurement systems for SO₂, NO/NO_y, and CO. NCore also collects O₃, particulate matter (PM), PM species, and meteorological measurements at approximately 80 sites.
- ▶ **BLM's Wyoming Air Resources Monitoring System (WARMS)** operates eight sites in Wyoming. Four of the WARMS sites are CASTNET-protocol sites.
- ▶ **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 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 partners that play a role in sponsoring individual sites include BLM, Native American tribes, universities, and government agencies. In all, CASTNET has more than 50 partners.

Locations of Monitoring Sites

The locations of CASTNET monitoring sites that were operational during 2012 are depicted in Figure 1-1. Ninety-one monitoring sites were operated at 88 distinct locations. To estimate precision across the network, collocated sites were operated at Mackville, KY (MCK131/231) and Rocky Mountain National Park, CO (ROM406/206) during 2012. The ROM406/206 monitors ensure consistency between the two sponsoring agencies, EPA and NPS, since EPA operates ROM206, and NPS operates ROM406. Of the two Rocky Mountain monitoring sites, ROM406 is considered the regulatory monitoring site for O₃. In 2012, NPS installed a collocated O₃ analyzer at YOS204, CA. 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, filter pack 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.



Parsons, WV (PAR107)

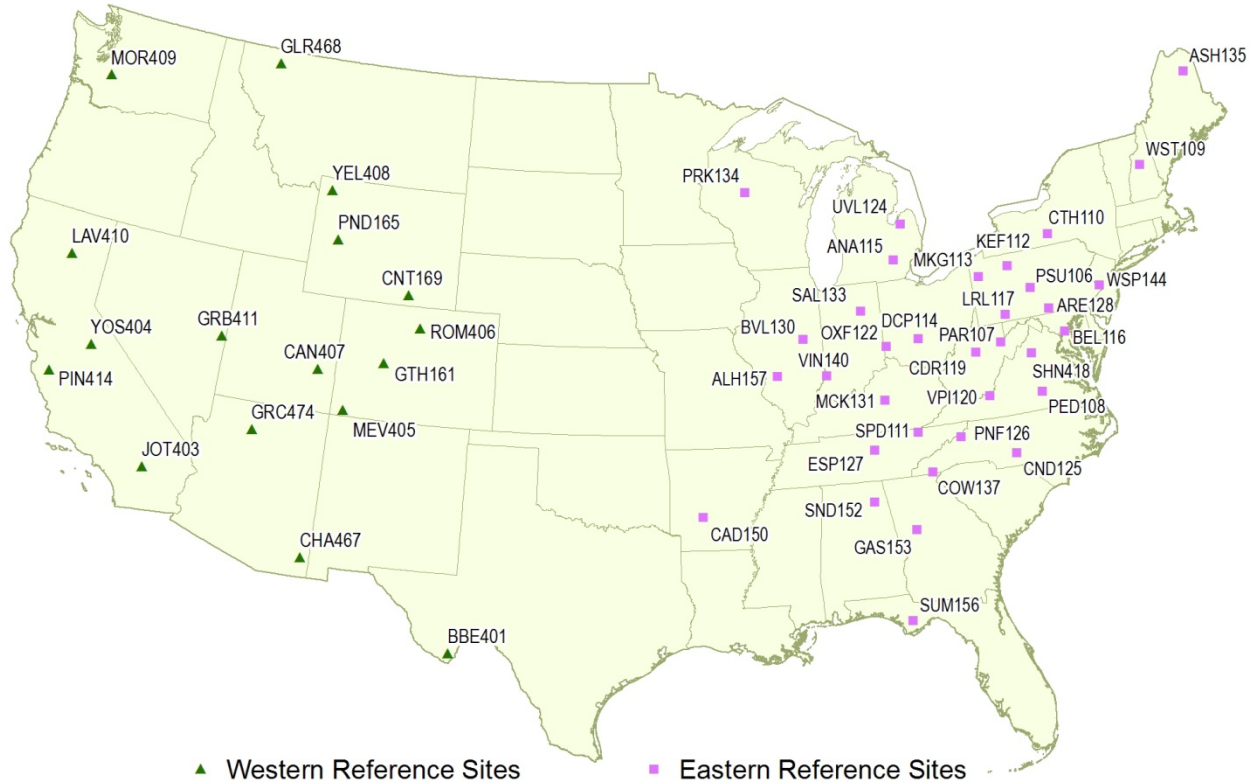
Figure 1-1 CASTNET Sites Operational During 2012



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



To determine trends in concentrations and rates of dry, wet, and total deposition, the data from the 34 eastern reference sites were aggregated and then presented using box plots (e.g., Figure 2-2) for the 23-year period 1990 through 2012. Data from the 17 western reference sites were aggregated and then presented using box plots for the period 1996 through 2012.



Centennial, WY (CNT169)

Measurements Recorded at CASTNET Sites

Each CASTNET site measures weekly concentrations of acidic pollutants, base cations, and chloride (Cl⁻) using a 3-stage filter pack with a controlled flow rate (AMEC, 2012d). The filter pack is changed out each Tuesday and shipped to the analytical chemistry laboratory for analysis. Most CASTNET sites also include a temperature controlled shelter and continuous O₃ monitoring system. The O₃ inlet and filter pack are located atop a 10-m tower.

Network Summary	
Number of Sites	91 at 88 locations
Weekly Ambient Measurements	
Gaseous	Sulfur dioxide (SO ₂) Nitric acid (HNO ₃)
Particulate	Sulfate (SO ₄ ²⁻) Nitrate (NO ₃ ⁻) Ammonium (NH ₄ ⁺) Base cations: magnesium (Mg ²⁺), calcium (Ca ²⁺), potassium (K ⁺), sodium (Na ⁺), Chloride (Cl ⁻)
Hourly Measurements	
	Ozone (O ₃) Shelter temperature 9-m temperature Trace-level SO ₂ * Trace-level carbon monoxide (CO)* nitrogen oxide/total reactive oxides of nitrogen (NO/NO _y)*
Other Meteorological Parameters** (1-hour averages)	
	2-m temperature Wind speed and direction Sigma theta Solar radiation Relative humidity Precipitation Surface wetness
* Measurements conducted at select locations.	
** Meteorological measurements were discontinued in 2010 at most EPA- sponsored CASTNET sites. In 2012, meteorological parameters were measured at 6 EPA-, 25 NPS- and 4 BLM- sponsored CASTNET sites.	

Estimating Dry and Wet Deposition

Dry deposition for 2012 was estimated using the method developed by Bowker *et al.* (2011), which was summarized in the 2011 CASTNET Annual Report (AMEC, 2013a). This approach combines measured concentrations with deposition velocities modeled using the Multi-Layer Model (MLM). When deposition velocities are unavailable due to data completeness or validity issues, historical deposition velocities are used as a substitute. The new hybrid approach (EPA, 2013d), which incorporates air quality monitoring data with Community Multiscale Air Quality Modeling System (CMAQ) output, will be used for future spatial analyses of total deposition. The hybrid approach is summarized in the first callout in Chapter 3.

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 (km) resolution grid. Pollutant concentrations in precipitation were provided by NADP/NTN. The precipitation amount and pollutant concentration 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. Dry and wet deposition fluxes were added to obtain the estimates of total deposition that are discussed in Chapter 3.

Sulfur Dioxide and Nitrogen Oxides Emissions

The ARP was designed to reduce the effects of acid deposition by requiring major reductions of SO₂ and NO_x emissions from the electric power industry. EPA issues annual progress reports (e.g., EPA, 2013b; 2013c; 2012b) on the effects of the ARP and related programs such as the CAIR and the NBP.

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 SO₂ 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 O₃ season. These programs include the OTC NO_x Budget Program, the NO_x SIP Call/NBP, and the CAIR.

The ARP is comprised of two phases for the reduction of SO₂ and NO_x. Phase I required substantive SO₂ emission reductions from the largest 435 coal-fired EGUs from 1995 through 1999 and from 1996 through 1999 for NO_x emissions. Phase II for both pollutants began in 2000. In 2012, the Phase II ARP SO₂ requirements affected 3,652 operating units. The Phase II ARP NO_x requirements applied to 900 of those operating units that exceeded 25 megawatts and burned coal between 1990 and 1995 (EPA, 2013b). The CAIR NO_x O₃ season program affected 3,273 units in 2012, and the NO_x and SO₂ annual programs affected 3,336 units. Under the ARP's and CAIR's emission reduction requirements, total SO₂ emissions from affected sources

were 3.3 million tons in 2012; total annual NO_x emissions from ARP and CAIR sources were 1.7 million tons.

Figure 1-3 presents state-by-state total annual SO₂ emissions for CAIR and ARP electric utility plants for six years (1990, 1995, 2000, 2005, 2010, and 2012). The states with the highest emitting sources in 1990 have typically seen the greatest reductions in SO₂ emissions under the ARP, and this trend has continued under CAIR. From 1990 to 2012, annual SO₂ emissions dropped in 43 states and D.C. by a total of approximately 12 million tons. The most significant reductions in SO₂ emissions achieved between 2005 and 2012 were realized in Massachusetts (91 percent), North Carolina (89 percent), Florida (86 percent), and West Virginia (83 percent).

Annual NO_x emissions by state are depicted in Figure 1-4 for the same six years. Between 1990 and 2012, all states participating in the CAIR NO_x annual program decreased their NO_x emissions. The greatest NO_x emissions reductions between 2000 and 2012 were realized in Ohio (78 percent reduction).



Oxford, OH (OXF122)

Figure 1-3 Annual SO₂ Emissions (for CAIR and ARP Sources)

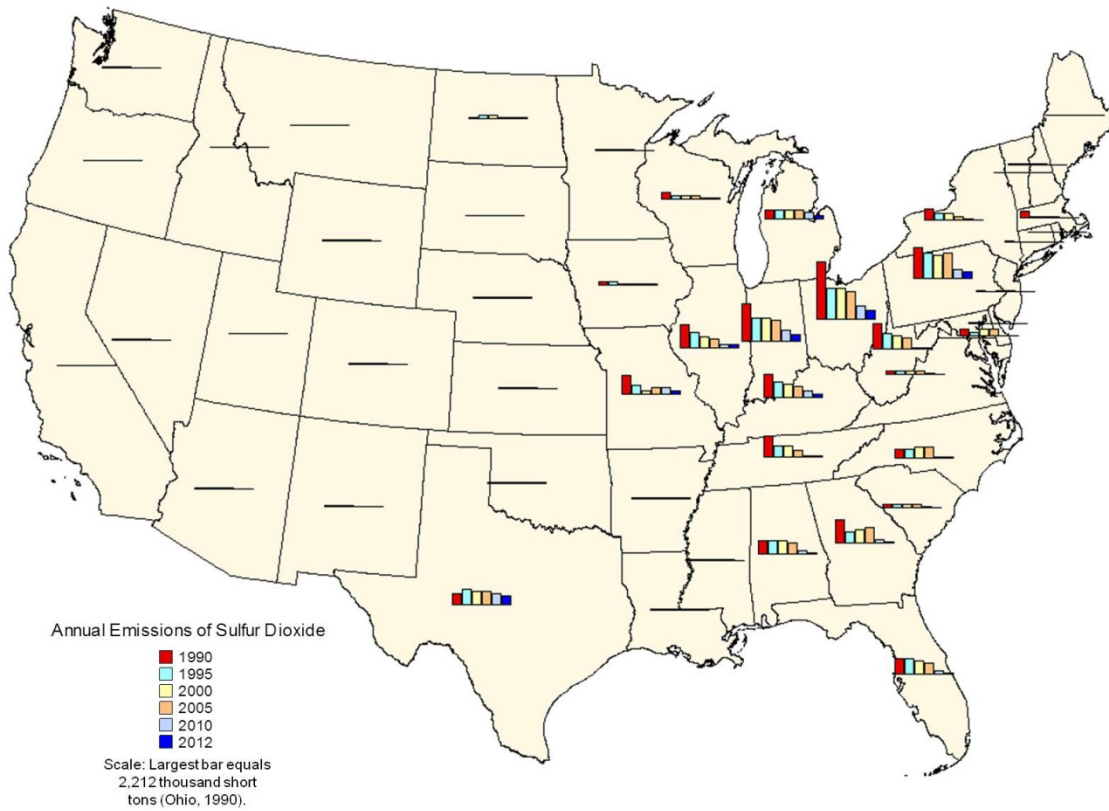
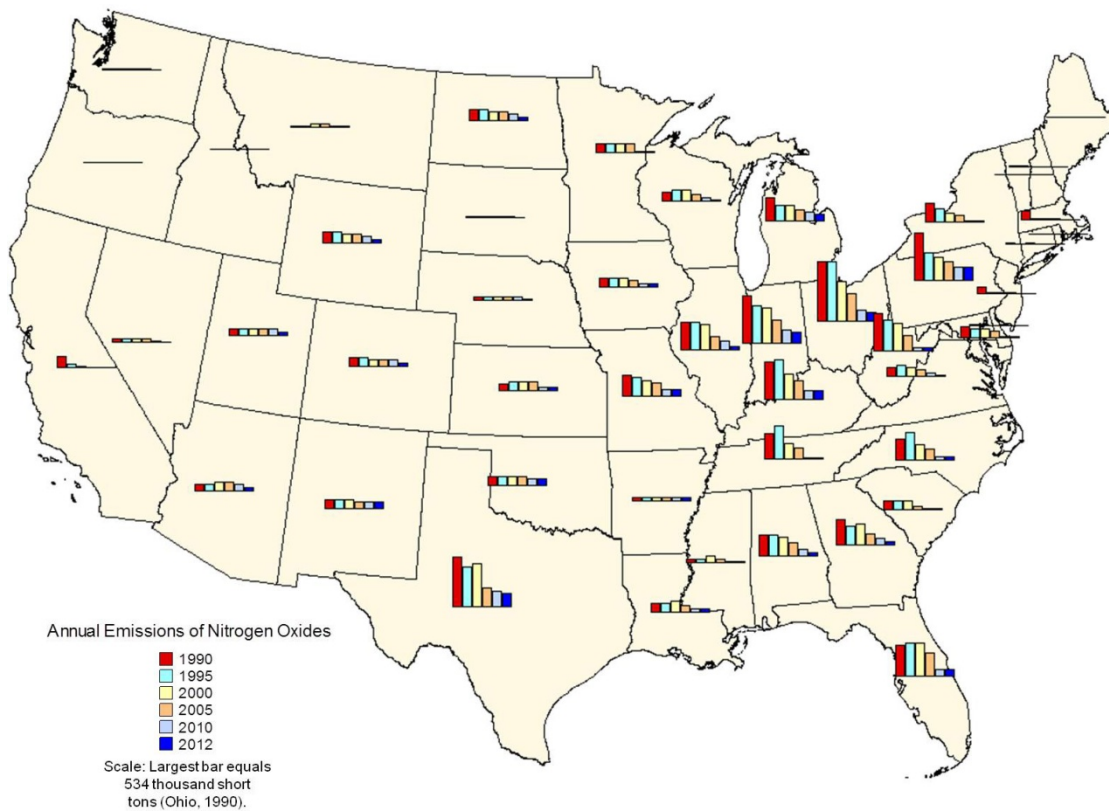


Figure 1-4 Annual NO_x Emissions (for CAIR and ARP Sources)



CHAPTER 2: ATMOSPHERIC CONCENTRATIONS

Three-stage filter packs were used to sample weekly average concentrations of SO_2 , SO_4^{2-} , HNO_3 , NO_3^- , NH_4^+ , Cl^- , and 4 base cations at 91 CASTNET monitoring stations in 88 locations. HNO_3 and particulate NO_3^- were summed to estimate total NO_3^- . The sulfur and nitrogen pollutants measured at the 34 eastern reference sites declined over the 23-year period from 1990 through 2012. Measured annual mean concentrations of SO_2 and SO_4^{2-} have decreased steadily with major annual reductions 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 17 years.

This chapter presents maps of 2012 annual mean concentrations of SO_2 , SO_4^{2-} , total NO_3^- ($\text{HNO}_3 + \text{NO}_3^-$), and NH_4^+ . Additional maps are provided in CASTNET quarterly reports (AMEC, 2012b; 2012e; 2013b; 2013e). Trends in annual mean concentrations over the 23-year period (1990 through 2012) were derived from measurements from the 34 CASTNET eastern reference sites (Figure 1-2) and for the period 1996 through 2012 from data collected at 17 CASTNET western reference sites (Figure 1-2). This chapter also includes information on NH_3 measurements collected at Beaufort, NC (BFT142) and summarizes the United States-Mexico Border 2020 Program.

Sulfur Dioxide

SO_2 is a major air pollutant that affects human health and plant ecosystems. It is emitted during the combustion of coal, oil, and other fossil fuels that contain sulfur. EGUs constitute the largest source (69 percent) of SO_2 in the United States (EPA, 2013a). Industrial facilities that fire fossil fuels and extract metal from ore compose another source (20 percent) of SO_2 emissions (EPA, 2013a). Some transportation sources that combust high sulfur fuels, such as ships, locomotives, and off-road equipment, also discharge SO_2 .

Since SO_2 is a criteria pollutant, concentrations are required to not exceed the National Ambient Air Quality Standard (NAAQS), which was promulgated on June 2, 2010. For compliance, 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 ($\mu\text{g}/\text{m}^3$) of air]. Gas phase SO_2 reacts in the atmosphere to form various acidic compounds including sulfuric acid (H_2SO_4), a significant contributor to acid rain, and ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$], a major component of fine particulate matter ($\text{PM}_{2.5}$). Fine particles are also regulated by NAAQS since $\text{PM}_{2.5}$ adversely affects health and contributes to degradation of atmospheric visibility.

Annual mean SO₂ concentrations measured in 2012 are shown in Figure 2-1. No sites in the eastern United States measured mean concentrations greater than 5.0 µg/m³ of air. Quaker City, OH (QAK172) and Horton Station, VA (VPI120) measured the highest concentration of SO₂ at 3.8 µg/m³. SO₂ concentrations recorded in 2012 were lower than SO₂ levels measured in previous years. One simple comparison is to calculate the average of annual mean SO₂ concentrations measured in 2012 versus 2011 at 10 monitoring stations in Indiana, Ohio, and Pennsylvania. The 2012 average concentration for these 10 sites was 2.6 µg/m³ versus an average concentration of 3.8 µg/m³ in 2011. Concentrations measured at the western sites in 2012 were generally lower than those measured at the eastern sites with no SO₂ concentrations greater than 1.0 µg/m³.

Figure 2-1 Annual Mean SO₂ Concentrations (µg/m³) for 2012

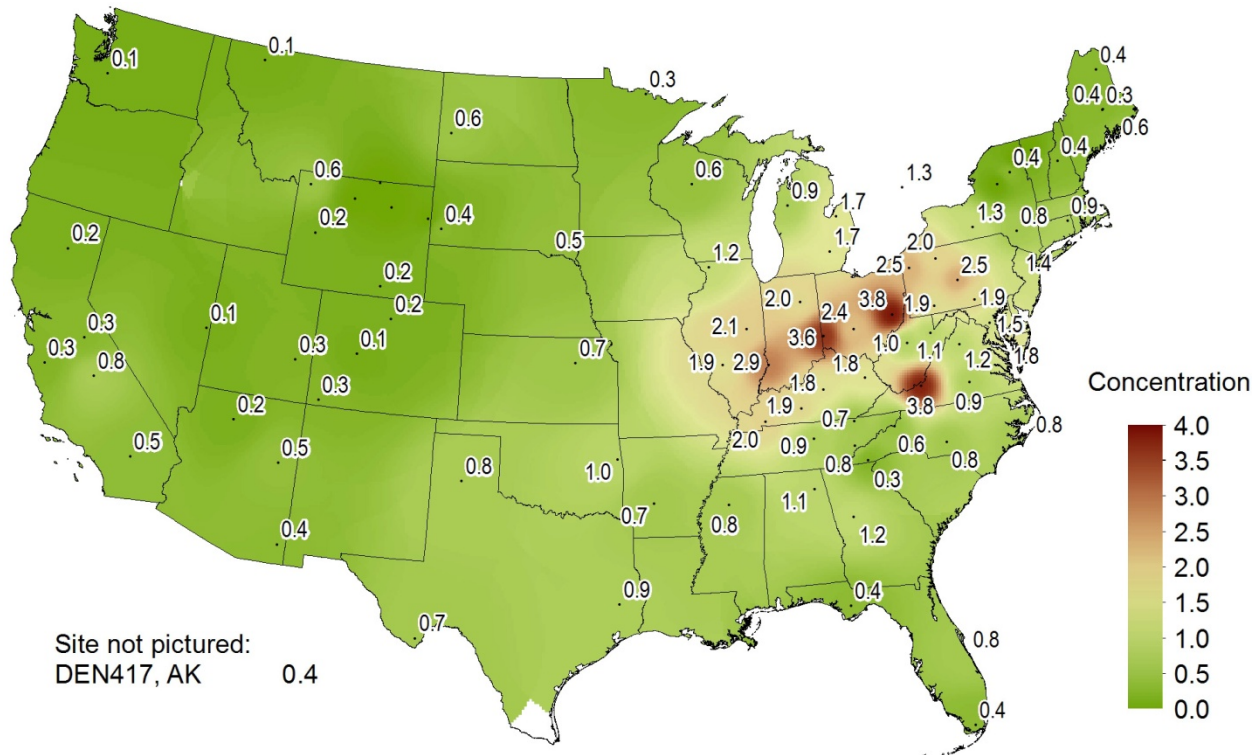


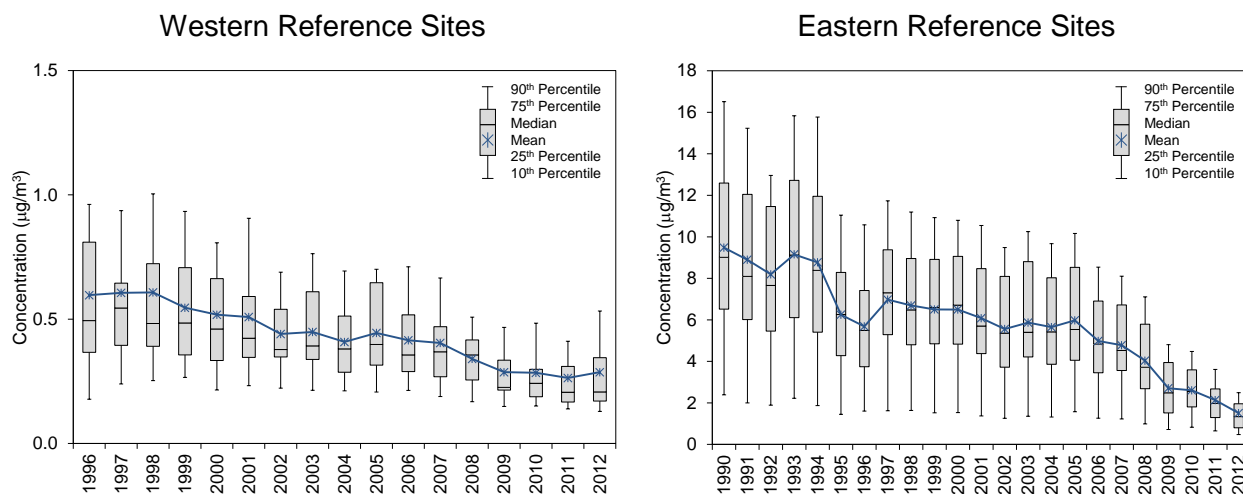
Figure 2-2 shows box plots of annual mean SO₂ concentrations aggregated over the 34 eastern reference sites from 1990 through 2012 (right side) and the 17 western reference sites from 1996 through 2012 (left side). Because concentrations measured at the western CASTNET sites were much lower than concentrations 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 SO₂ was recorded in 1995 at the beginning of the ARP. SO₂ levels also declined sharply from 2005 through 2012. Three-year mean concentrations for the eastern reference sites for

1990–1992 and 2010–2012 were $8.9 \mu\text{g}/\text{m}^3$ and $2.1 \mu\text{g}/\text{m}^3$, respectively. This change constitutes a 76 percent reduction in 3-year mean SO_2 concentrations between the two periods. The 2012 mean level of $1.5 \mu\text{g}/\text{m}^3$ was the lowest mean value measured by the eastern reference sites in the history of the network and represents a significant decline over the seven years from the 2005 concentration of $6.1 \mu\text{g}/\text{m}^3$.

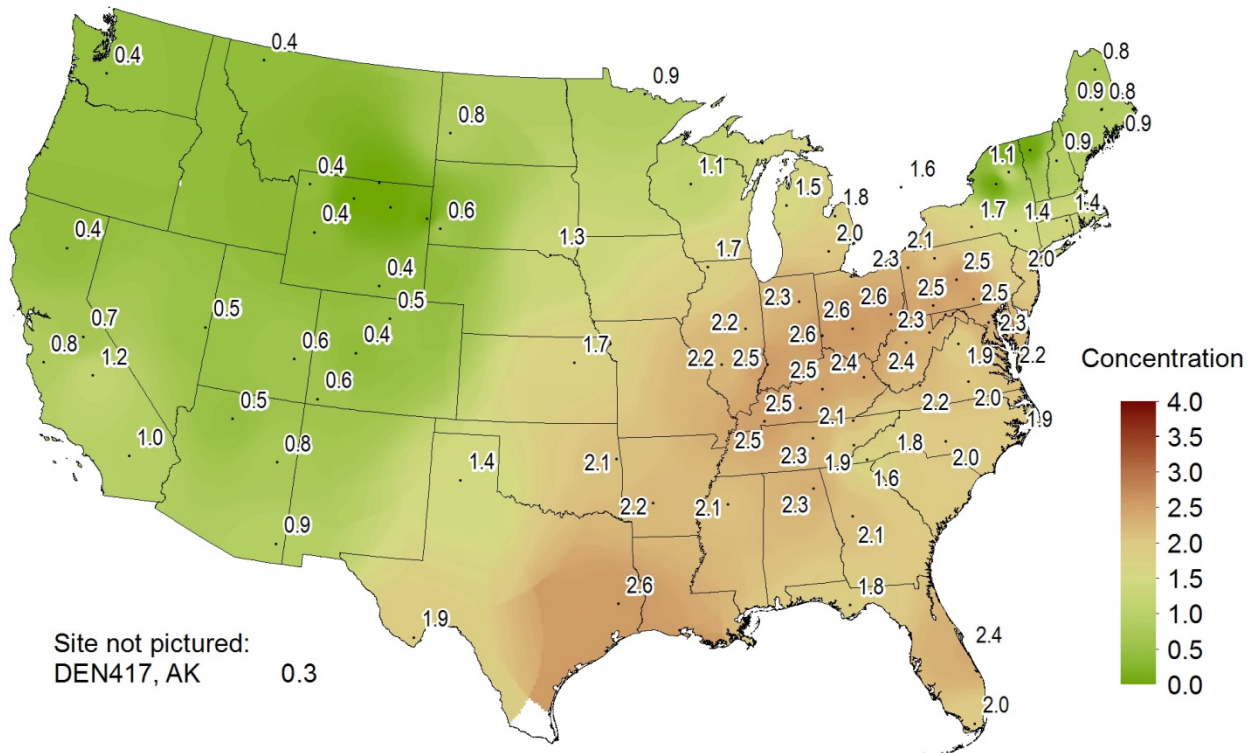
The box plots for the western reference sites indicate a decline in annual mean SO_2 concentrations aggregated over the 17 sites. Three-year mean SO_2 concentrations for 1996–1998 and 2010–2012 were $0.6 \mu\text{g}/\text{m}^3$ and $0.3 \mu\text{g}/\text{m}^3$, respectively. This change constitutes a 54 percent reduction in 3-year mean SO_2 concentrations over the 17 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 ($\mu\text{g}/\text{m}^3$)



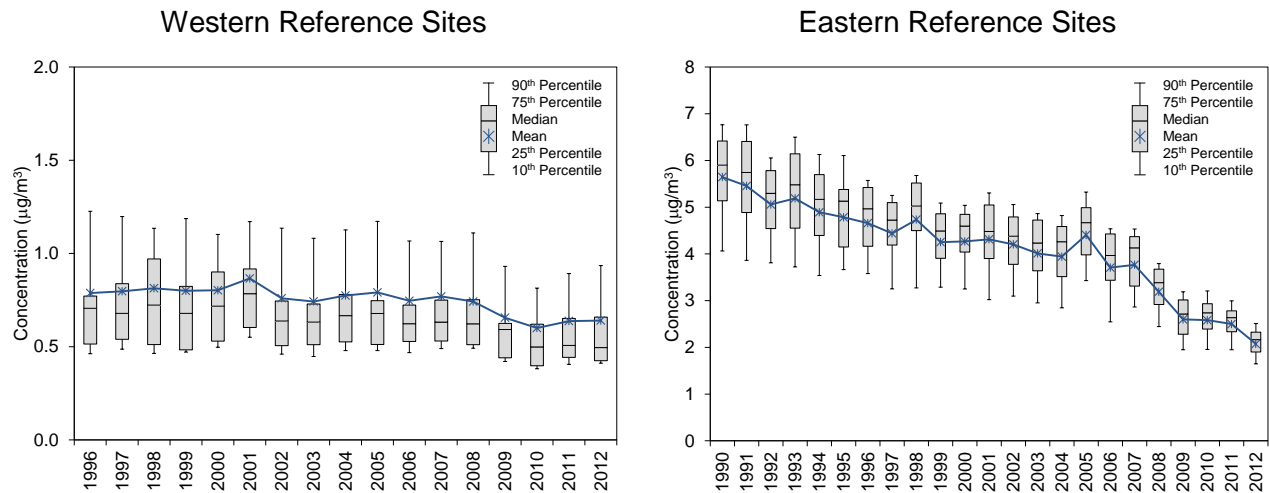
Particulate Sulfate

Sulfate exists in the atmosphere primarily as $(\text{NH}_4)_2\text{SO}_4$, a major component of $\text{PM}_{2.5}$. Particulate SO_4^{2-} is produced by the transformation of SO_2 in the atmosphere through both gas and aqueous (cloud) phase reactions. A map of annual mean particulate SO_4^{2-} concentrations measured during 2012 is shown in Figure 2-3. The map shows the highest SO_4^{2-} concentrations were measured in or near the Ohio River Valley. A majority of the CASTNET filter pack samplers in the eastern United States measured SO_4^{2-} levels greater than or equal to $2.0 \mu\text{g}/\text{m}^3$. SO_4^{2-} concentrations measured at the eastern CASTNET sites were higher than those measured at western sites. In the West, Big Bend National Park, TX (BBE401); Palo Duro Canyon State Park, TX (PAL190); Joshua Tree National Park, CA (JOT403); and Sequoia National Park, CA (SEK430) measured SO_4^{2-} concentrations greater than or equal to $1.0 \mu\text{g}/\text{m}^3$.

Figure 2-3 Annual Mean SO₄²⁻ Concentrations (µg/m³) for 2012

The right side of Figure 2-4 provides box plots of annual mean SO₄²⁻ concentrations from the 34 eastern reference sites. The figure shows a substantial decline in SO₄²⁻ over the 23 years, and, in particular, concentrations declined significantly from 2005 through 2012. The difference between 3-year means from 1990–1992 to 2010–2012 represents a 56 percent reduction in SO₄²⁻ from 5.4 µg/m³ to 2.4 µg/m³, respectively. The 2012 mean SO₄²⁻ level of 2.1 µg/m³ 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 22 percent reduction in annual mean SO₄²⁻ concentrations aggregated over the 17 sites with 1996–1998 and 2010–2012 concentrations of 0.8 µg/m³ and 0.6 µg/m³, respectively.

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

Ambient Ammonia Measurements at Beaufort, NC

CASTNET collected measurements of ambient ammonia (NH_3) at Beaufort, NC (BFT142) in order to supplement filter pack and AMoN measurements. The goals of the Beaufort study were to continue and expand analyses started during the Ammonia CASTNET CSN Study (ACCS). The Beaufort location expanded ACCS to include a coastal site located in an area of interest for NH_3 monitoring because of the proximity to agricultural sources (animal and crop production) in eastern North Carolina.

Reference ammonia concentrations were measured using a modified annular denuder system (ADS) that included a phosphorus acid-coated annular denuder for collecting gaseous NH_3 . The Beaufort sampling included:

- Seven daily ADS (one for each day) that ran only for the first week of the 2-week sampling period,
- One field blank, and
- Two weekly ADS (one for each week) that ran for one week in conjunction with the daily ADS and then for a second consecutive week for comparison with AMoN.

The ADS was designed for automated and unattended operation and required only a weekly site operator visit. The weekly ADS samples were run using a flow rate of 3.0 lpm compared with a flow rate of 16.7 lpm normally used for daily ADS sampling. The denuders were analyzed by automated colorimetry using distilled water as the extraction fluid. Chemical analysis of the denuders was performed by the CASTNET laboratory.

ADS sampling began in May 2011 and was completed in November 2012. Similar to ACCS, the Beaufort sampling included exposing a weekly ADS for two consecutive 1-week periods during the designated measurement weeks. The daily ADS ran for a 24 hour period at 16.7 lpm each day of the first week of each 2-week measurement period to provide better temporal resolution. The ADS used a cyclonic separator with a 2.5 micrometer (μm) size cut to remove larger particles. The ADS (daily, weekly, and field blanks) were installed and operated at 10 m. Figure 2a provides photographs of the BFT142 site configuration.

Figure 2b shows the weekly and daily ADS NH_3 concentrations from the Beaufort study along with AMoN NH_3 concentrations. The figure also shows ADS concentrations that were averaged from daily to weekly values. The daily ADS samples (black diamonds) showed greater variability than the weekly integrated samples. Daily ADS concentrations averaged over a week (red x) matched the weekly ADS levels (green squares) very well, indicating that weekly ADS run at reduced flow rates is a viable sampling method.

The 2-week average ADS NH_3 concentrations also showed good agreement with the integrated concentration measurements made at the AMoN site (NC06) as shown in Figure 2b. A linear regression based on ADS values aggregated to two weeks versus the 2-week NC06 values gives a regression equation of

$$y = 0.7792x + 0.0963,$$

with an R^2 value of 0.8178. This comparison demonstrates that AMoN provides viable measurements of atmospheric NH_3 concentrations.

Figure 2a Annular Denuder System and Related Sampling Systems at the BFT142 Site



ADS tower configuration

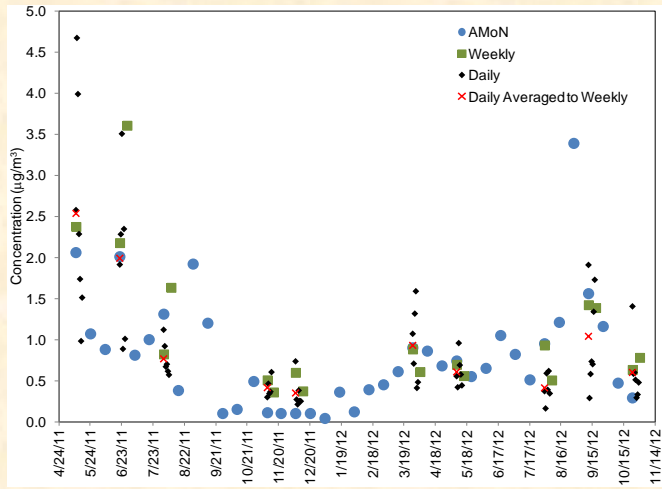
Solenoids used to control ADS flow



Beaufort, NC (BFT142)

Note: 1 NADP/NTN precipitation sampling systems
 2 AMoN sampler
 3 Meteorological tower
 4 NO_y converter tower
 5 Filter pack and ADS tower

Figure 2b Time Series of Measured NH_3 Concentrations ($\mu\text{g}/\text{m}^3$)



Yosemite National Park, CA (YOS404)

Total Nitrate

The sum of HNO_3 and particulate NO_3^- is defined herein as total NO_3^- . HNO_3 and NO_3^- 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 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 $\text{PM}_{2.5}$ in the form of ammonium nitrate (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 its constituents are in equilibrium with each other and total NO_3^- is considered to be 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.

A map of annual mean total NO_3^- concentrations for 2012 is provided in Figure 2-5. The map shows annual mean concentrations greater than $3.0 \mu\text{g}/\text{m}^3$ were sampled in Illinois and Indiana. In the West, the highest concentrations ($2.7 \mu\text{g}/\text{m}^3$ and $2.3 \mu\text{g}/\text{m}^3$) were measured in California at SEK430 and JOT403, respectively. The Salamonie Reservoir, IN (SAL133) site measured the highest concentration ($3.4 \mu\text{g}/\text{m}^3$) in the network.

Figure 2-5 Annual Mean Total NO_3^- Concentrations ($\mu\text{g}/\text{m}^3$) for 2012

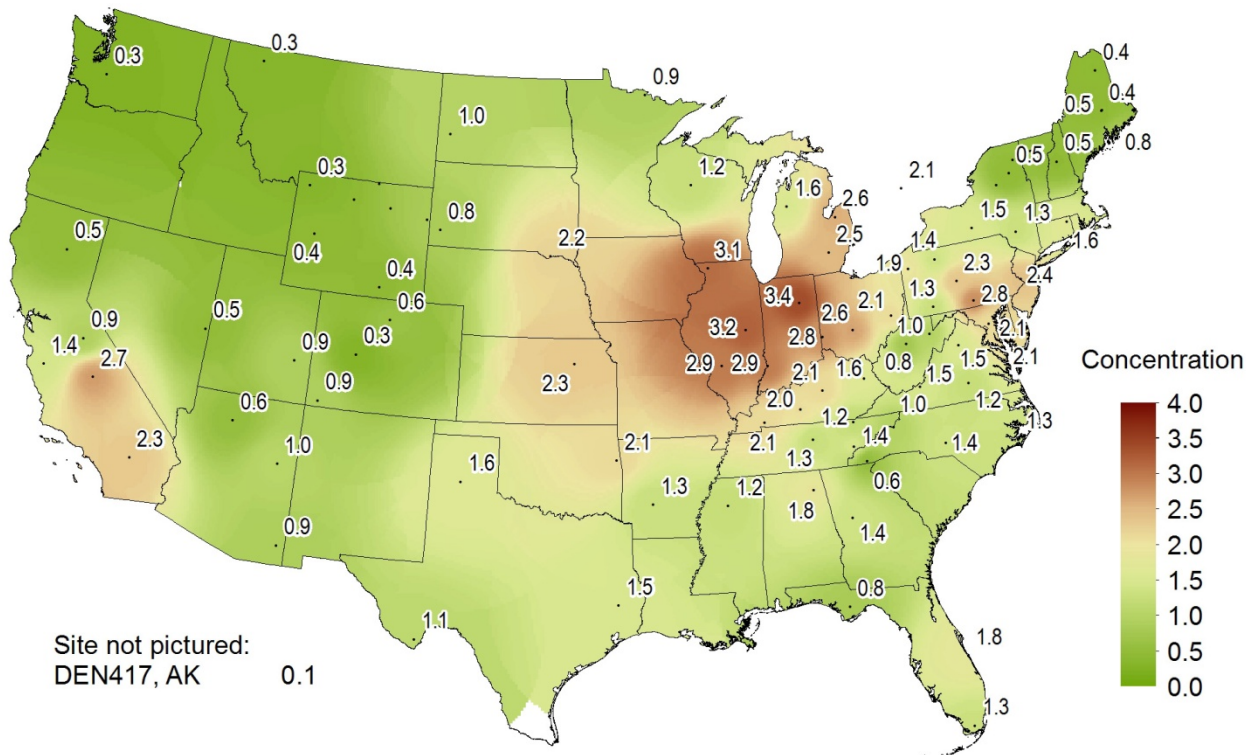
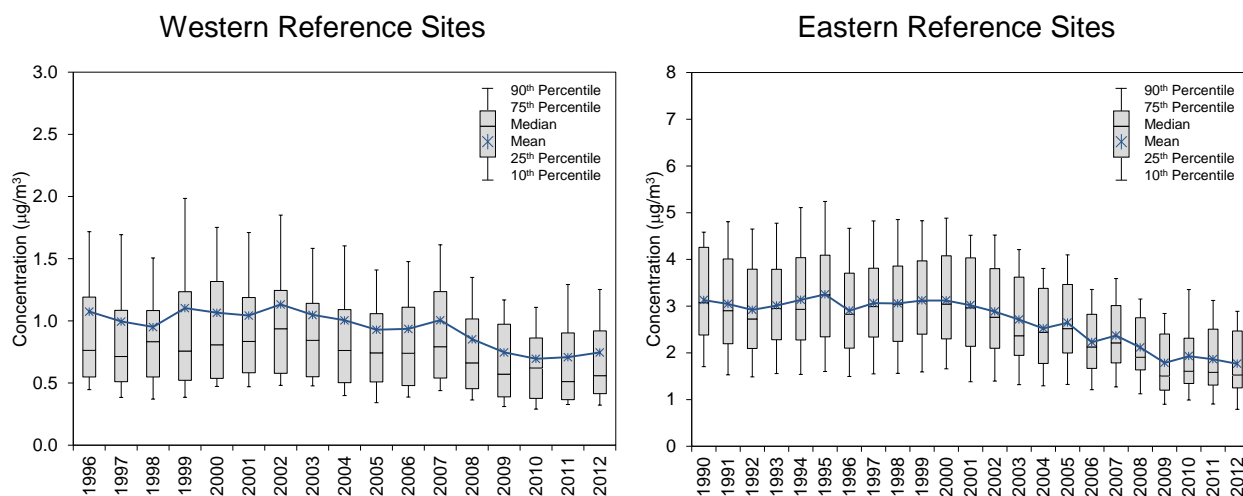


Figure 2-6 provides box plots of total NO_3^- levels for the eastern and western reference sites through 2012. The data shown on the right side of the figure were aggregated from the 34 eastern reference sites. The data show no trend in mean concentrations until 2000 when total NO_3^- levels began to decline in response to NO_x emission control programs. Three-year mean levels declined from 1990–1992 to 2010–2012, from $3.0 \mu\text{g}/\text{m}^3$ to $1.8 \mu\text{g}/\text{m}^3$, producing a 39 percent reduction in total NO_3^- . Total NO_3^- levels measured at the eastern reference sites declined from a mean value of $3.1 \mu\text{g}/\text{m}^3$ in 2000 to a mean value of $1.8 \mu\text{g}/\text{m}^3$ in 2012.

Data aggregated from the 17 western sites are shown on the left side of Figure 2-6. The 3-year mean total NO_3^- concentration for 2010–2012 was 29 percent lower than the corresponding 1996–1998 level with 3-year mean concentrations of $0.7 \mu\text{g}/\text{m}^3$ and $1.0 \mu\text{g}/\text{m}^3$, respectively.

Figure 2-6 Trend in Annual Mean Total NO_3^- Concentrations ($\mu\text{g}/\text{m}^3$)



Particulate Ammonium

Particulate NH_4^+ is formed when gaseous NH_3 reacts with acidic gases, including HNO_3 and H_2SO_4 , in the atmosphere. The primary components of particulate NH_4^+ are $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 . A map of 2012 annual mean NH_4^+ concentrations is given in Figure 2-7. No monitors measured concentrations greater than $2.0 \mu\text{g}/\text{m}^3$. The data show a relatively uniform geographic distribution across the central and eastern United States with more than two-thirds of the sites reporting values less than or equal to $1.0 \mu\text{g}/\text{m}^3$. Higher concentrations were measured at eastern CASTNET sites in Illinois, Indiana, Michigan, Ohio, Pennsylvania, and Kentucky. The NH_4^+ concentrations measured at western CASTNET sites were less than $1.0 \mu\text{g}/\text{m}^3$.

Figure 2-7 Annual Mean NH_4^+ Concentrations ($\mu\text{g}/\text{m}^3$) for 2012

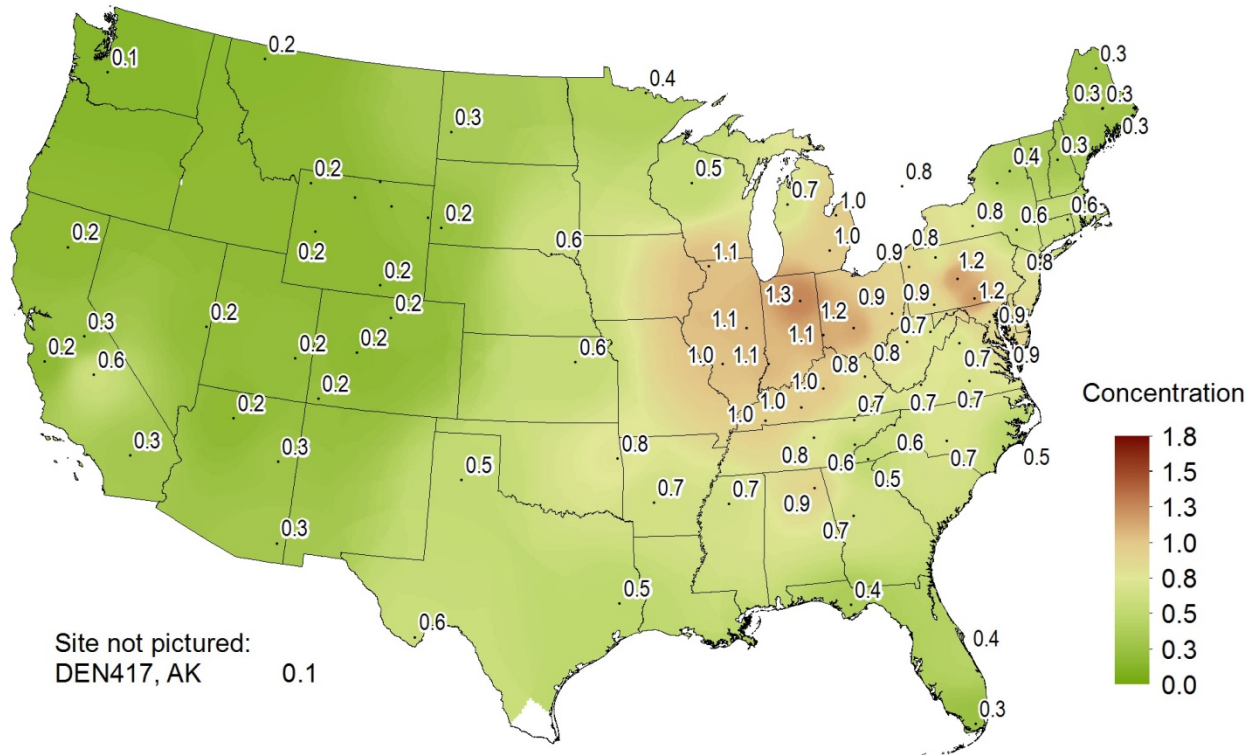
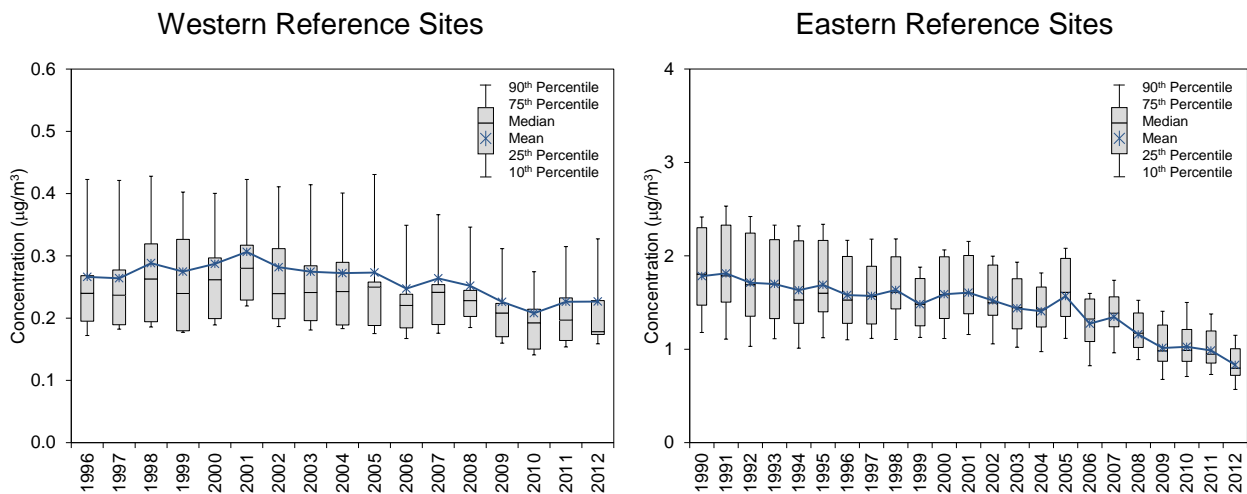


Figure 2-8 shows box plots of NH_4^+ concentrations. The trend diagram for the eastern sites shows a reduction in mean NH_4^+ levels from 1990–1992 to 2010–2012. The 1990–1992 mean concentration was $1.8 \mu\text{g}/\text{m}^3$, and the 2010–2012 value was $0.9 \mu\text{g}/\text{m}^3$, a 46 percent decline. The box plots characterizing the western sites show about an 18 percent reduction from 1996–1998 to 2010–2012.

Figure 2-8 Trend in Annual Mean NH_4^+ Concentrations ($\mu\text{g}/\text{m}^3$)



Border 2020: U.S.-Mexico Environmental Program

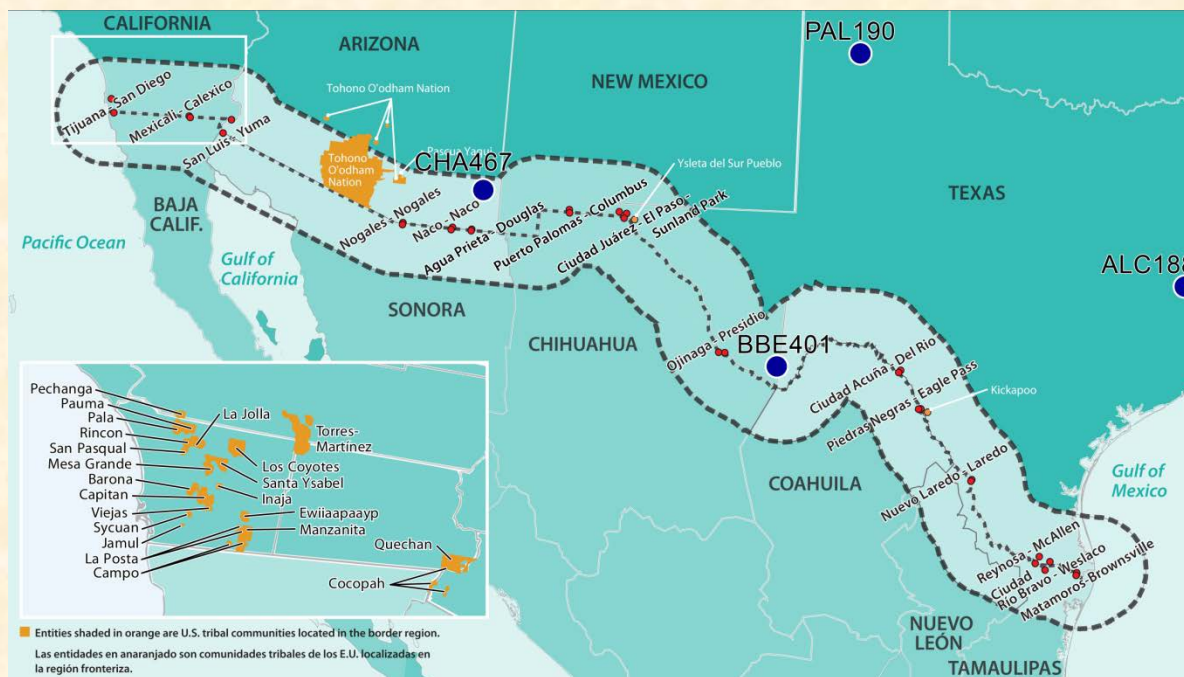
In 2012, the United States and Mexico established Border 2020: U.S.-Mexico Environmental Program to address the environmental and public health problems in the U.S.-Mexico border region. Border 2020 is a continuation of the Border 2012 program. Border 2020 established six strategies and five long-term goals (EPA, 2012c). The goals are:

1. Reduce air pollution,
2. Improve access to clean and safe water,
3. Promote materials and waste management and clean sites,
4. Enhance joint preparedness for environmental response, and
5. Assure environmental compliance and stewardship.

This discussion focuses on the first goal and describes air quality data collected in the border region and their trends.

Figure 2c provides a map of the border region and shows the locations of four nearby CASTNET sites. Chiricahua National Park (CHA467) is located in southeastern Arizona and has been operating since April 25, 1989. Big Bend National Park, TX (BBE401) and Alabama-Coushatta, TX (ALC188) have been operating since July 18, 1995 and April 2, 2004, respectively. Palo Duro Canyon State Park, TX (PAL190) has been operating since April 24, 2007. CHA467 and BBE401 also operate IMPROVE visibility-related monitoring sites. CHA467 and BBE401 are located within the designated border region.

Figure 2c U.S.-Mexico Border Region



Source: EPA

A field data collection and data analysis study (Pitchford *et al.*, 2004) was performed from July through October 1999 to understand atmospheric haze in Big Bend National Park (BBNP). The study was titled, “Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study,” and it was sponsored by NPS, EPA, and the Texas Commission on Environmental Quality (TCEQ). BRAVO scientists

concluded that SO_4^{2-} particles were the single largest contributor to haze in BBNP. The haze in the park peaked in the spring months when both SO_4^{2-} and carbonaceous particles contributed to the haze and in the early fall months (August–October) when SO_4^{2-} particles dominated. Key BRAVO findings can be found in the 2004 report (Pitchford *et al.*, 2004).

The findings include:

- Eastern United States and eastern Texas sources of SO_2 were the largest contributors to peak SO_4^{2-} episodes during BRAVO.
- On average, Mexican sources contributed about one-fifth of the total SO_4^{2-} . In particular, the Carbon I and II power plants, which are located at Nava, Coahuila, Mexico, contributed to SO_4^{2-} levels during easterly winds toward BBNP.
- The least hazy days at BBNP were produced during westerly winds.

The CASTNET sites CHA467 and BBE401 began operating before BRAVO began and provide a good record of trends in sulfur and nitrogen pollutants and O_3 in the border region. Figure 2d depicts 3-month (August–October) average SO_4^{2-} concentrations for the two border region CASTNET sites plus ALC188 and PAL190. ALC188 reported the highest August–October SO_4^{2-} concentrations. Figure 2e shows annual average concentrations of total NO_3^- for the sites; Figure 2f provides fourth highest daily maximum 8-hour average (DM8A) O_3 concentrations over the histories of the sites.

Figure 2d shows overall reductions in 3-month average SO_4^{2-} concentrations over the lifetime of the monitoring at the sites. Data from the two sites (BBE401 and CHA467) in the border region are presented using solid lines. Data from the other sites are presented using dashed lines. PAL190 data were not analyzed for trends because of its limited data record. The percent declines were 26 percent for CHA467, 16 percent for BBE401, and 35 percent for ALC188. The downward trends in 3-month average SO_4^{2-} concentrations resulted from SO_2 emission reductions in Texas and nearby states (Figure 1-3).

The data from two of the monitoring sites (Figure 2e) show decreases in total NO_3^- : 12 percent for BBE401 and 11 percent for ALC188. An 18 percent increase was measured at CHA467.

Trends in fourth highest DM8A O_3 concentrations for the sites are shown in Figure 2f. The 75 ppb NAAQS is identified in the figure by a black line. Fourth highest DM8A O_3 concentrations averaged less than 75 ppb with the exception of 78 ppb at ALC188 in 2008 and 80 ppb at BBE401 in 2011, both during periods with extensive wildfires.

Relatively high annual mean total NO_3^- and fourth highest DM8A O_3 concentrations were observed in 2011 with moderate declines in 2012. The high 2011 annual total NO_3^- and DM8A O_3 concentrations measured at the sites were likely influenced by frequent wildfires over Texas and Arizona during the summer and fall fire season (AMEC, 2013a). 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 O_3 season. The fires continued into the 2012 fire season. These wildfires affected air quality in the southwestern states and the border region; some plumes were transported all the way to the Baltimore-Washington metropolitan area (AMEC, 2013a).

Figure 2d Three-month (August–October) Average SO_4^{2-} Concentrations

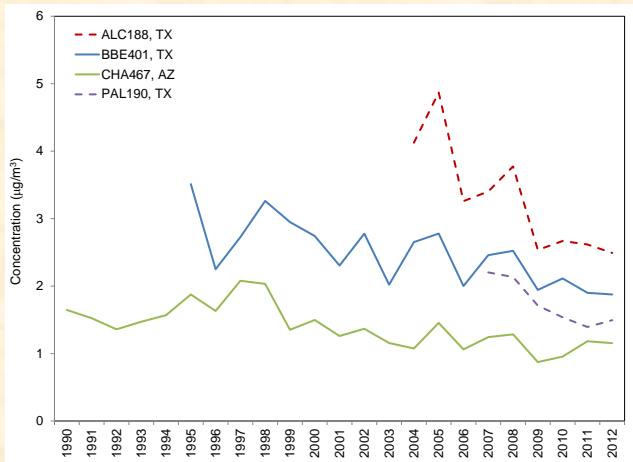
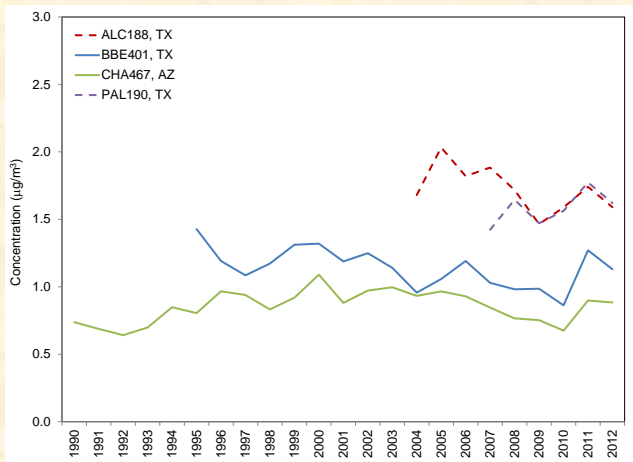
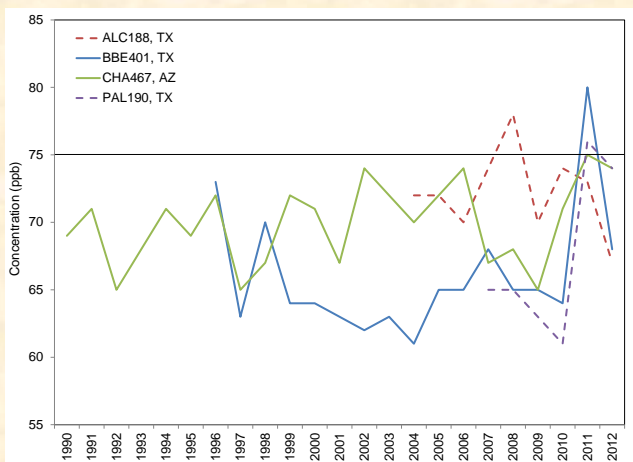


Figure 2e Annual Average Concentrations of Total NO_3^- ($\text{HNO}_3 + \text{NO}_3^-$)



Note: Total NO_3^- concentrations measured at all four sites were influenced by wildfires in 2011.

Figure 2f Fourth Highest DM8A O_3 Concentrations



Note: Fourth highest DM8A O_3 concentrations measured at BBE401, PAL190, and CHA467 in 2011 were influenced by wildfires.

CASTNET measurements have shown that SO_4^{2-} concentrations have declined in the border region. Total NO_3^- levels declined at BBE401 and ALC188 and increased at CHA467. Fourth highest DM8A O_3 concentrations remained fairly steady over the monitoring periods. Both NO_3^- and O_3 levels were elevated during periods with frequent wildfires.



Alabama-Coushatta, TX (ALC188)



Big Bend National Park, TX (BBE401)



Chiricahua National Park, AZ (CHA467)

 **CHAPTER 3: ATMOSPHERIC DEPOSITION**

CASTNET was designed to provide estimates of the dry deposition of sulfur and nitrogen pollutants across the United States. CASTNET currently estimates dry deposition by combining measured pollutant concentrations and modeled deposition velocities (V_d). The MLM/Bowker method was used to produce values of hourly V_d , which were combined with values of air pollutant concentrations to produce dry deposition fluxes. PRISM was used 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 73 percent over the period from 1990–1992 to 2010–2012. Three-year mean dry sulfur deposition estimated for the 17 western reference sites declined by 40 percent over the period 1996–1998 to 2010–2012. Dry nitrogen deposition estimates declined 46 percent for the eastern reference sites and 36 percent at the western reference sites. In summary, sulfur and nitrogen deposition are at historic lows.

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. Dry flux values were estimated as the product of V_d estimates produced by the MLM and measured concentration data. In 2012, CASTNET adopted a V_d data substitution method developed by Bowker *et al.* (2011) to fill in long-term averages of V_d for missing values to improve data completeness. This method resulted 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. The grid of wet deposition data was combined with the MLM/Bowker point estimates of dry deposition data to estimate total deposition.

The MLM/Bowker and NTN/PRISM approaches were used to produce the deposition data to generate the maps and trends analyses for this annual report. For future spatial analyses of total deposition, the hybrid model, which is also called the Total Deposition Science Committee (TDEP) model (EPA, 2013d), will be used. The hybrid model is summarized in the first callout in this chapter.

Hybrid Approach to Estimating Total Deposition

A hybrid approach has been developed for estimating total deposition of nitrogen and sulfur and producing data products of deposition for use by the scientific community. The development of the hybrid approach and map production efforts are part of the specific charges for the Total Deposition Science Committee (TDEP), which was officially established in October 2011 as part of the NADP. The committee was formed by a group of interested scientists in order to discuss scientific and other issues related to estimating total deposition across North America. The mission of TDEP is to improve estimates of atmospheric deposition by advancing the science of measuring and modeling atmospheric wet, dry, and total deposition of pollutant species, such as sulfur, nitrogen, and mercury, by providing a forum for exchange of information on current and emerging issues within a broad multi-organization context, including atmospheric and ecosystem scientists, resource managers, and policy makers. TDEP coordinates its efforts with the Critical Loads of Atmospheric Deposition Science Committee (CLAD) and other groups to advocate use of the most scientifically defensible deposition estimates for critical loads and other environmental assessments.

The TDEP committee's first effort involved a needs assessment that categorized work and research currently being conducted, described projects and project status, and listed partner organizations. Compiling these types of information served the primary purpose of prioritizing early actions for TDEP including the generation of total sulfur and nitrogen deposition estimates as a grid-based product.

The hybrid modeling approach summarized here has been submitted for publication in a scientific journal. For more information on the approach, see the Total Deposition Project (EPA, 2013d). In the meantime, the MLM/Bowker method for dry deposition estimates was used in this report and will continue to be used until the hybrid approach becomes operational in the CASTNET program.

The hybrid approach uses a combination of actual air pollutant measurements and multi-year average Community Multiscale Air Quality Modeling System (CMAQ; Byun and Schere, 2006) modeled results. Developers of the hybrid approach methodology (EPA, 2013d) determined this to be the most practical method for producing relatively near-term total deposition estimates while avoiding the limitations (e.g., three- to five-year time lag and use of historical data) of constructing the emission inventories and meteorological databases required for atmospheric chemistry and transport models, such as CMAQ. Although actual field measurements are more accurate than modeled results for specific locations, it is beneficial to fill in spatial and chemical gaps in the measurements with modeled results in order to improve coverage for the continental United States. CMAQ is currently the most accessible modeling system for use by CASTNET and TDEP and was, therefore, selected for the hybrid approach. CMAQ output for 2002 through 2009 was used during the development of the methodology and initial releases.

The monitoring data used to support the dry deposition estimates included CASTNET air pollutant concentrations of HNO_3 , SO_2 , NO_3^- , NH_4^+ , SO_4^{2-} ; AMoN NH_3 data; and the Southeastern Aerosol Research and Characterization Network (SEARCH) rural concentrations of HNO_3 , SO_2 , and NH_3 . SEARCH measurements are collected in Alabama, Florida, Georgia, and Mississippi. The CMAQ Centers for Disease Control (CDC) Public Health Air Surveillance Evaluation (PHASE; CDC, 2013) runs were used for generating the modeling data for CMAQ v4.7 for 2002 through 2006. These runs utilized Pennsylvania State University/National Center for Atmospheric Research MM5 mesoscale model meteorological data and 2002 National Emissions Inventory (NEI) emissions with year-specific major point sources, mobile sources, fires, biogenic and agricultural activities. CMAQ v4.7.1 was used for 2007 through 2009 with Weather Research and Forecasting (WRF) Model meteorological data, National Land Cover Database (NLCD) 2001 land use, and the NEI 2005 emissions for 2007, and NEI 2008 emissions for years 2008 and 2009. Year-specific emissions from major point sources,

mobile sources, fires, and biogenic and agricultural sources were utilized in the modeling. For wet deposition estimates, NADP/NTN concentrations in precipitation, including SO_4^{2-} , NO_3^- , and NH_4^+ , were combined with precipitation measurements from NADP sites and the PRISM precipitation product using the method previously developed and described in the 2010 CASTNET Annual Report (AMEC, 2012a). Modeled air pollutant concentrations were adjusted for bias where sufficient monitoring data were available.

The specific hybrid approach involved calculation of hourly mean, minimum, maximum, and standard deviation of V_d , concentration, and flux values of nitrogen and sulfur species from the CMAQ runs for eight years, 2002 through 2009. Hourly data were then aggregated to the standard Tuesday to Tuesday CASTNET week. Weekly ambient air concentrations were estimated using data from the networks listed previously using inverse-distance weighting applied to 12 km grids. Estimations of the weekly dry deposition fluxes were calculated by multiplying the air concentration grids by the CMAQ V_d values to create deposition product grids for measured species. The grid resolution for the CMAQ V_d values was 36 km for 2002–2006 and 12 km for 2007–2009. The 2002–2006 data were regridded to a 12-km resolution. For the years 2002–2008, the year-specific weekly average concentration was multiplied by the weekly average V_d for the specific year. For 2000–2001 and 2010–2012, the concentrations were multiplied by weekly average V_d determined from the years 2002 and 2009 data, respectively.

The final steps consisted of summing the weekly dry deposition values into annual aggregations for all measured species and the addition of the CMAQ-modeled deposition of unmeasured species [nitrous acid (HNO_2), dinitrogen pentoxide, NO, nitrogen dioxide (NO_2), peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PAN_x), and organic nitrates (NTR)] to obtain annual dry deposition fluxes. The sum of dry deposition and wet deposition estimates resulted in total deposition fluxes across the United States. For more information view <ftp://ftp.epa.gov/castnet/tdep>.

Figures 3a through 3d show example maps for 2012 of total sulfur (S) deposition as kilograms per hectare per year (kg/ha/yr); percentage of total S deposition due to dry S deposition; total nitrogen (N) deposition as kg/ha/yr; and percentage of total N deposition due to dry N deposition. CASTNET, AMoN, and rural SEARCH sites are shown on the four maps. The shading in the figures indicates the magnitude of the fluxes and the percentages of dry deposition. Maps of 2012 dry and total deposition of sulfur and nitrogen based on the MLM/Bowker and the NADP/PRISM approaches are presented later in this chapter in Figures 3-1 through 3-10.



Cranberry, NC (PNF126)

The TDEP map in Figure 3a shows the highest total S deposition fluxes as kilograms per hectare (kg/ha) were observed along the Ohio River Valley from southern Illinois to New Jersey and from Tennessee south to Louisiana and west to Texas. High S fluxes were also observed in North Dakota. Figure 3b shows the percentages of total S deposition attributed to dry deposition.

As shown in Table 3a, the five highest total S fluxes in 2012 were modeled using TDEP and MLM/NTN/PRISM for the indicated CASTNET sites.

Table 3a Highest Total Sulfur Fluxes for 2012

Site	TDEP		MLM/NTN/PRISM	
	Flux (kg/ha)	Percent Dry Deposition	Flux (kg/ha)	Percent Dry Deposition
VPI120, VA	17.0	84	4.6	42
QAK172, OH	14.1	70	8.1	40
LRL117, PA	12.8	70	3.6	26
KEF112, PA	12.5	70	4.8	20
PSU106, PA	11.6	73	5.6	37

Figure 3c (TDEP) shows several areas in the eastern United States with total N fluxes greater than or equal to 10.0 kg/ha/yr. Regions with noticeably high N fluxes were modeled in Iowa, eastern North Carolina, the San Joaquin Valley in CA, and a few other areas. Figure 3d shows the percentages of total N deposition attributed to dry deposition.

Table 3b shows the CASTNET sites with the five highest total 2012 N fluxes.

Table 3b Highest Total Nitrogen Fluxes for 2012

Site	TDEP		MLM/NTN/PRISM	
	Flux (kg/ha)	Percent Dry Deposition	Flux (kg/ha)	Percent Dry Deposition
SND152, AL	18.2	77	5.4	24
STK138, IL	17.2	72	5.5	27
ARE128, PA	17.2	57	9.3	21
CDZ171, KY	14.8	73	5.2	31
ALH157, IL	13.9	65	6.0	20

Comparing Figure 3a with Figure 3-2 and Figure 3c with Figure 3-7 provides insights into the hybrid TDEP modeling system versus the MLM/Bowker/NTN/PRISM system. The big difference between the two approaches is that the TDEP maps show significantly higher percentages of dry deposition for both S and N than the MLM-based maps. Dry S deposition for 2012 contributes more than half the total S deposition for about half of the United States. TDEP total S fluxes (Figure 3a) are significantly higher than those shown in Figure 3-2. Dry N deposition constitutes more than half total N deposition for 90 percent of United States. TDEP total N fluxes (Figure 3c) are significantly higher than those shown in Figure 3-7.

Some possible explanations of the differences between TDEP/CMAQ and MLM/NTN/PRISM results include:

- Different algorithms are used in CMAQ to simulate dry deposition than in MLM;
- Different meteorological conditions are used to drive the two sets of model calculations;
- Differences in land use in the grid and at the site affect the model results;
- Higher N deposition is in TDEP because of the addition of deposition of NH_3 and NO_y ;

- More extensive monitoring data, e.g., AMoN and SEARCH data, are used in the TDEP hybrid simulations;
- CMAQ modeling includes estimates of N deposition where monitoring results were unavailable, e.g., North Dakota, San Joaquin Valley in California, Iowa, and eastern North Carolina.

Figure 3a TDEP Total Sulfur Deposition for 2012

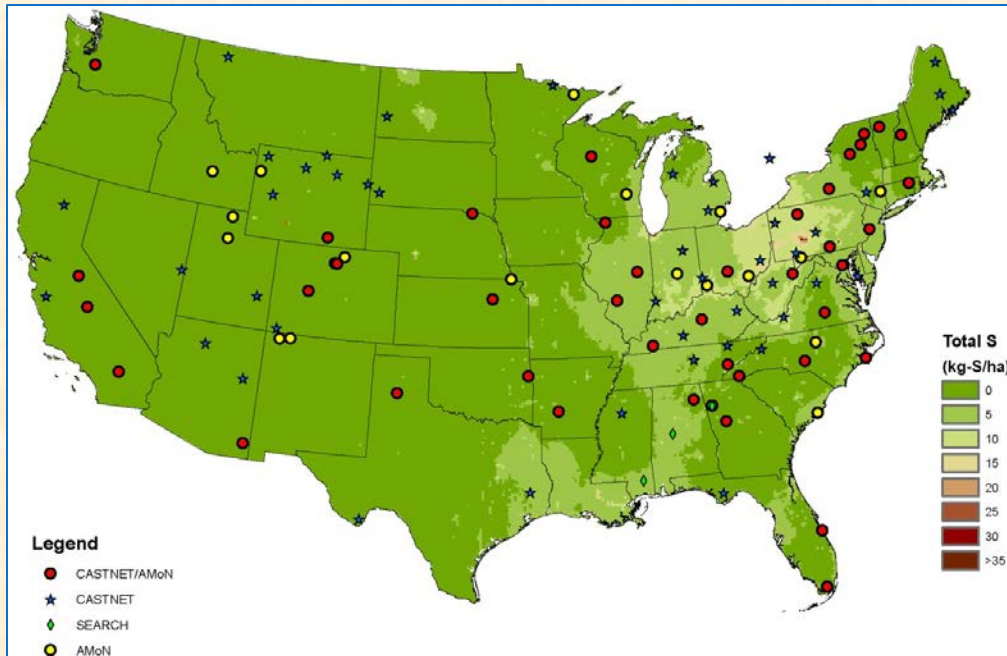


Figure 3b TDEP Percent Dry Sulfur Deposition for 2012

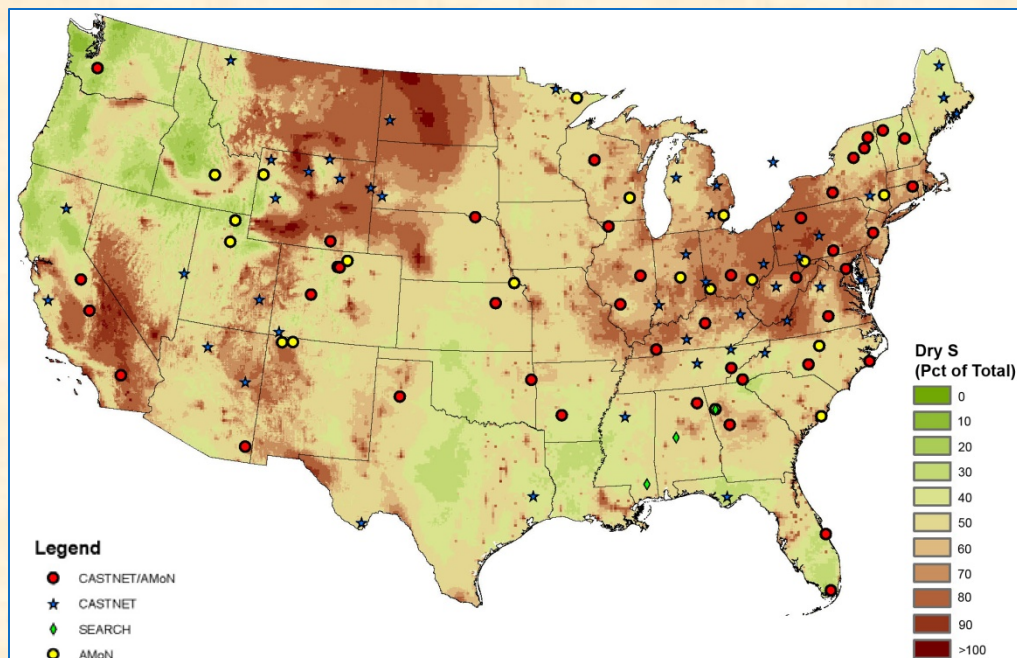


Figure 3c TDEP Total Nitrogen Deposition for 2012

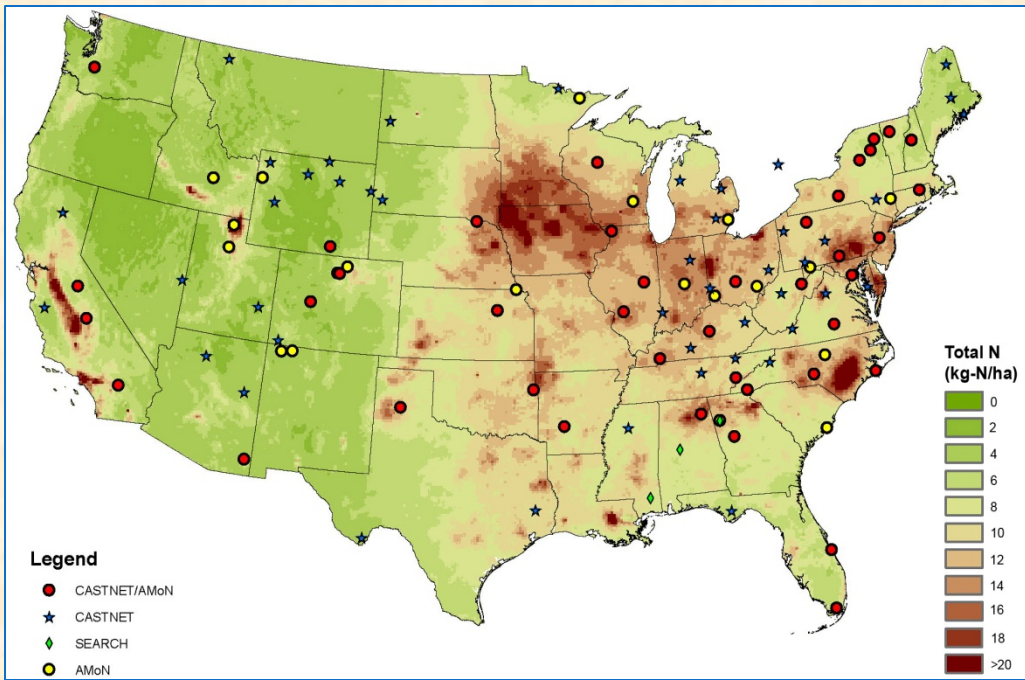
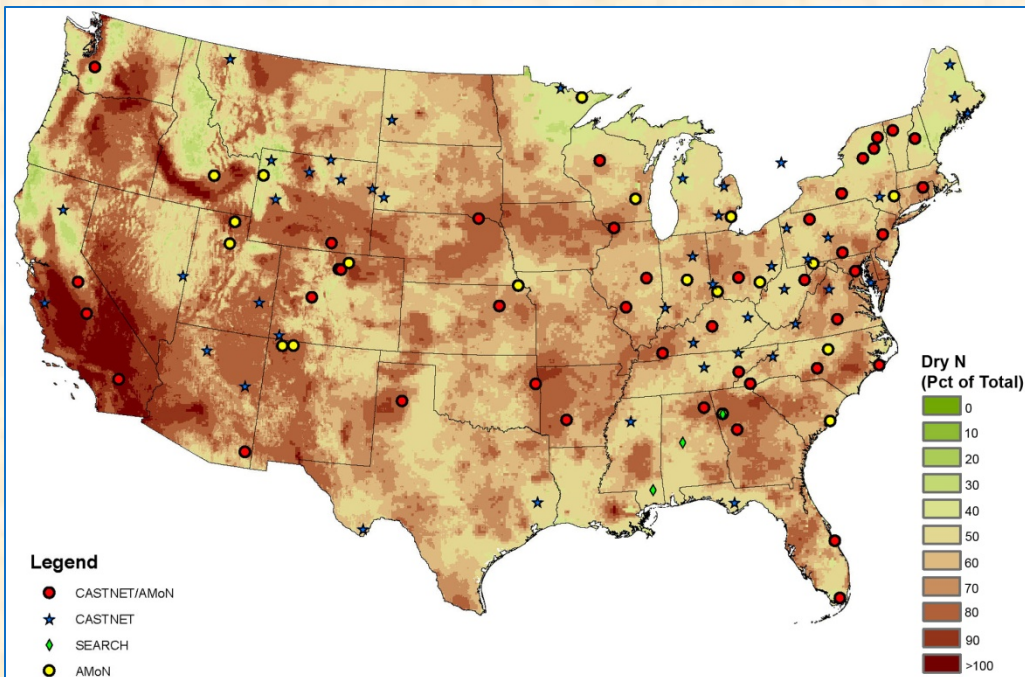


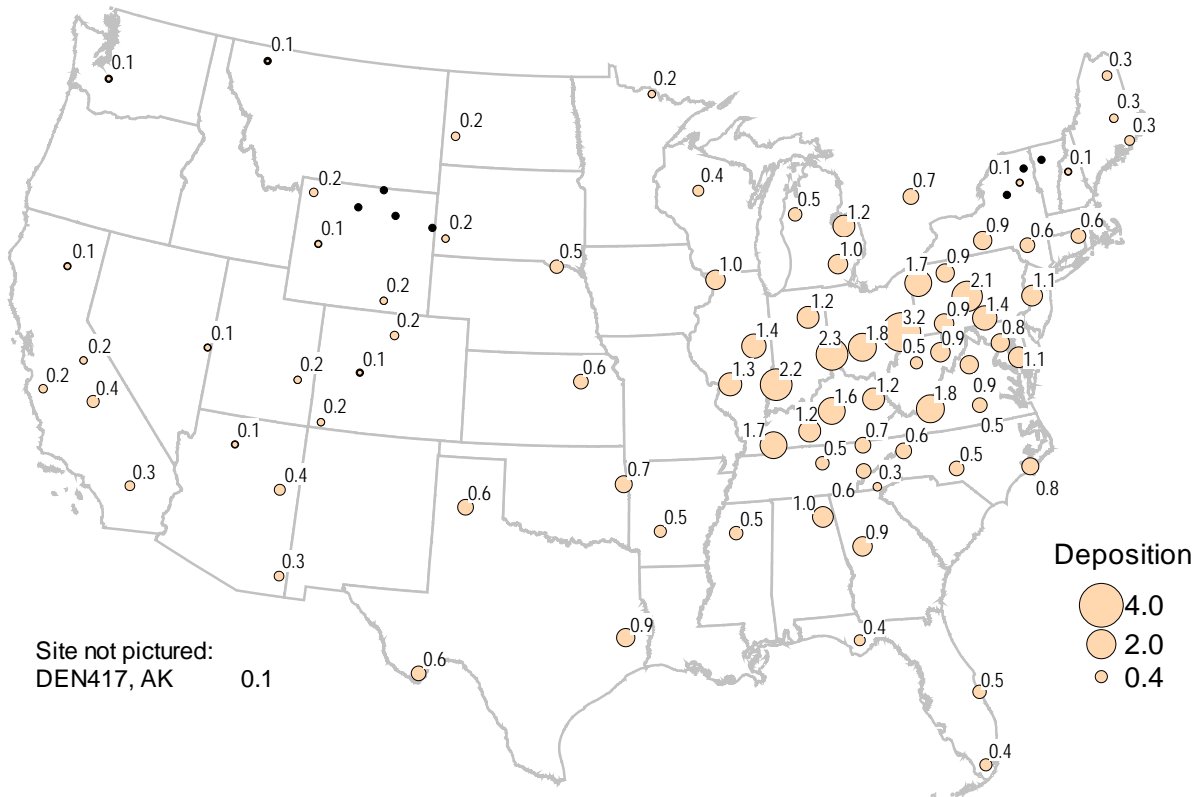
Figure 3d TDEP Percent Dry Nitrogen Deposition for 2012



Sulfur Deposition

The MLM/Bowker approach was utilized to produce separate products for SO₂ and SO₄²⁻. The calculations of SO₂ and SO₄²⁻ dry deposition were summed to obtain the 2012 estimates of dry sulfur deposition (as S). Figure 3-1 shows a map of the modeled dry sulfur fluxes. The magnitude of deposition is illustrated by the size of the circle. The map shows only one CASTNET site in Ohio (QAK172) with an estimated flux greater than 3.0 kg/ha/yr. This site had the highest estimated deposition rate for 2012 with a flux of 3.2 kg/ha/yr, which is a marked decrease from 5.2 kg/ha/yr in 2011 and 5.5 kg/ha/yr in 2010. The highest estimated dry sulfur deposition rates occurred along the Ohio River Valley and coincided with the major SO₂ source region (Figures 1-3 and 2-1). The deposition rates declined with distance from the Ohio River 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 (SO₂ + SO₄²⁻) Deposition (kg/ha/yr) for 2012



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 blue shading signifies the percent of wet deposition, and the tan shading shows the percent of dry deposition. The values estimated for 2012 were lower than 2011 and 2010 values (Figure 3-3) continuing the overall trend of declining sulfur deposition and represent the lowest

historic values. Six CASTNET sites in the states of Indiana, Ohio, and Pennsylvania and the Canadian province of Ontario had total (dry + wet) sulfur deposition fluxes greater than 5.0 kg/ha/yr in 2012. The highest total sulfur deposition rate was estimated for QAK172, OH with a value of 7.4 kg/ha/yr. The total sulfur deposition values for QAK172 were 13.0 kg/ha/yr in 2011 and 9.8 kg/ha/yr in 2010. Total sulfur deposition at western sites was less than or equal to 2.1 kg/ha/yr, which was the estimate for PAL190, TX in 2012. PAL190 began operating in the spring of 2007 and started reporting annual deposition values in 2008. Except for 2010, PAL190 has had the highest annual total sulfur deposition values among the western sites.

Figure 3-2 Total (Dry + Wet) Sulfur Deposition (kg/ha/yr) for 2012

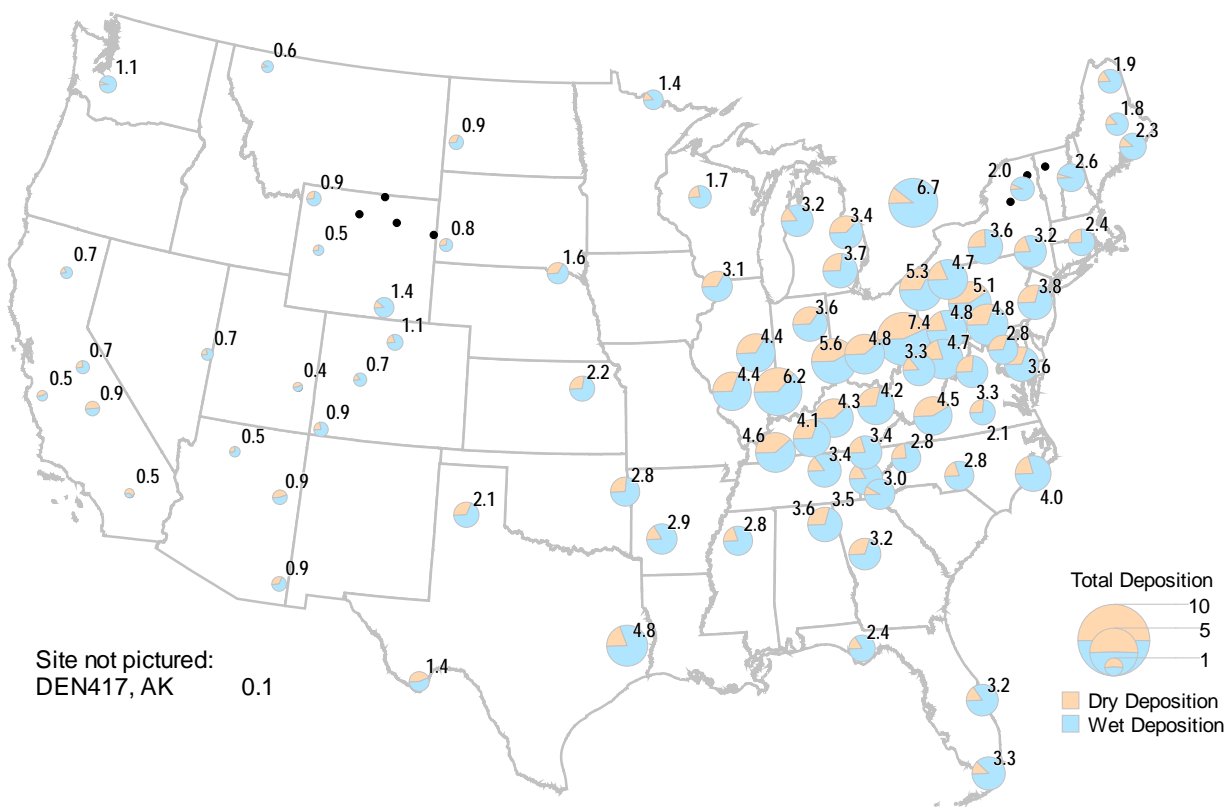


Figure 3-3 presents box plots that show the trend in dry sulfur deposition (as S) for the eastern (right side) and western (left side) reference sites. The box plots were based on data obtained from the 34 CASTNET eastern reference sites for the period 1990 through 2012 and from the 17 western reference sites for 1996 through 2012. 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 2010–2012 mean of 1.4 kg/ha/yr, a 73 percent reduction. Dry sulfur deposition declined at the western reference sites from a 1996–1998 mean of 0.3 kg/ha/yr to a 2010–2012 mean of 0.2 kg/ha/yr, a 40 percent reduction.

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

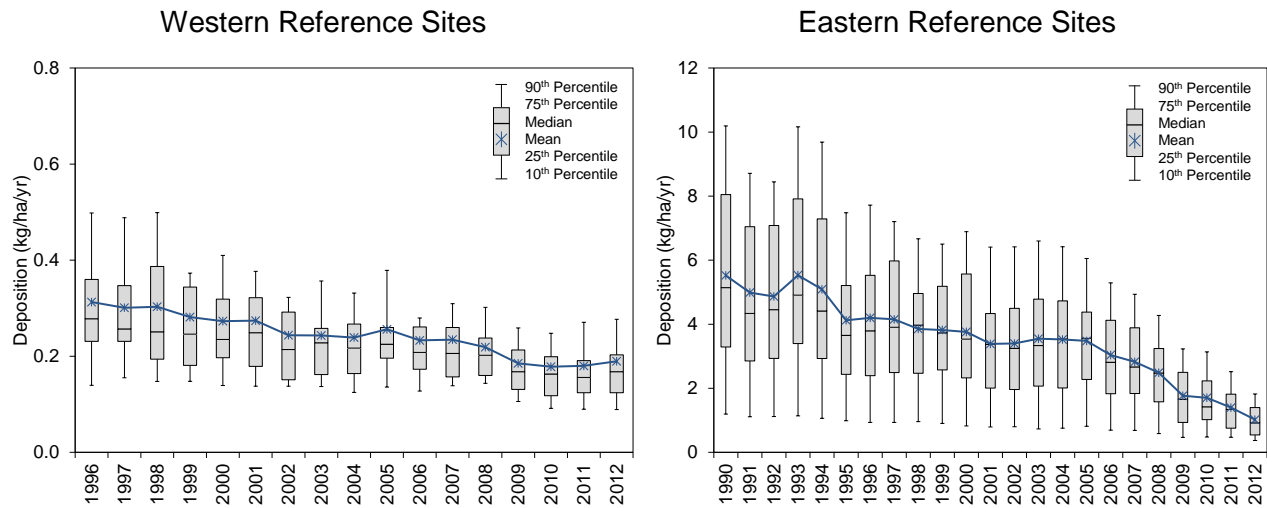


Figure 3-4 shows the trend in annual total (dry + wet) sulfur deposition (as S) at the CASTNET reference sites. Aggregated sulfur deposition declined considerably at the eastern and western reference sites over their respective periods. Overall, total sulfur deposition declined at the eastern reference sites from a 1990–1992 mean of 12.9 kg/ha/yr to a 2010–2012 mean of 4.6 kg/ha/yr, a 64 percent reduction. Total sulfur deposition declined at the western reference sites from a 1996–1998 mean of 1.3 kg/ha/yr to a 2010–2012 mean of 0.8 kg/ha/yr, a 36 percent reduction. The 2012 total sulfur deposition values for eastern and western sites were the lowest in the history of the network. Wet deposition in 2012 was a major component of sulfur flux with a contribution of 74 percent, which is approximately the same as the contribution from wet deposition in 2011 (75 percent). The average contribution from wet deposition from 1990 through 2010 was 62 percent. The 74 percent and 75 percent contributions from wet flux for the past two years were the highest in the history of the project.

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, precipitation



Quaker City, OH (QAK172)

amounts and dry deposition. The dotted line shows concentrations in precipitation, which are independent of precipitation amount. The figure shows that wet, dry, and total sulfur deposition have declined substantially for the eastern sites. The aggregated total sulfur deposition (3.7 kg/ha/yr) for 2012 estimated for the eastern sites decreased after the upswing in 2011 (5.5 kg/ha/yr) to below 2010 levels (4.8 kg/ha/yr). Both the total sulfur deposition and sulfur concentrations in precipitation at the western sites show slight declines from 2011 values while the dry deposition value has been steady.

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

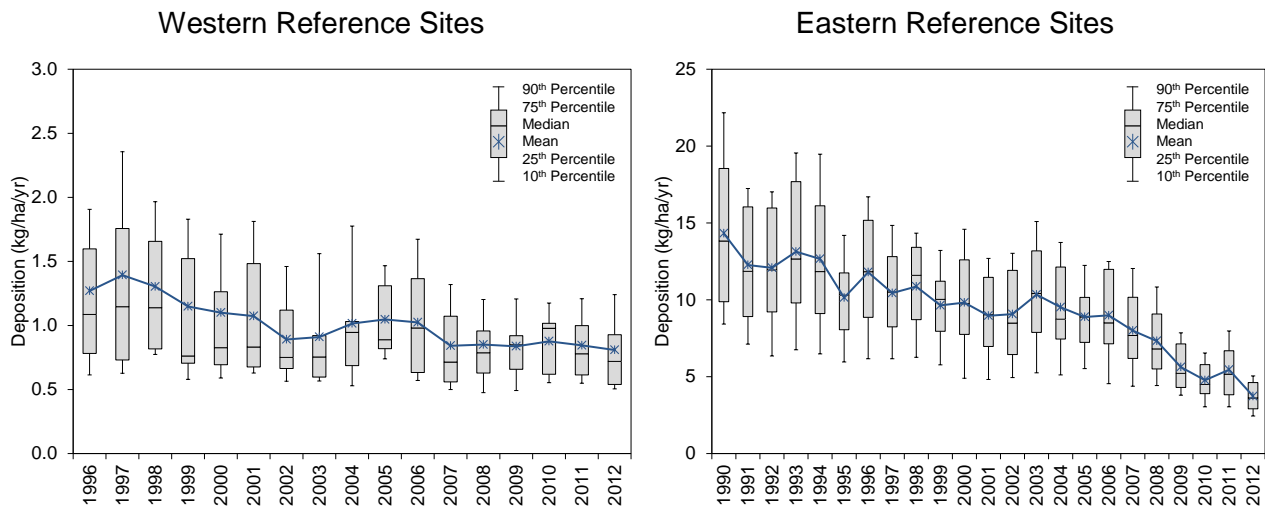
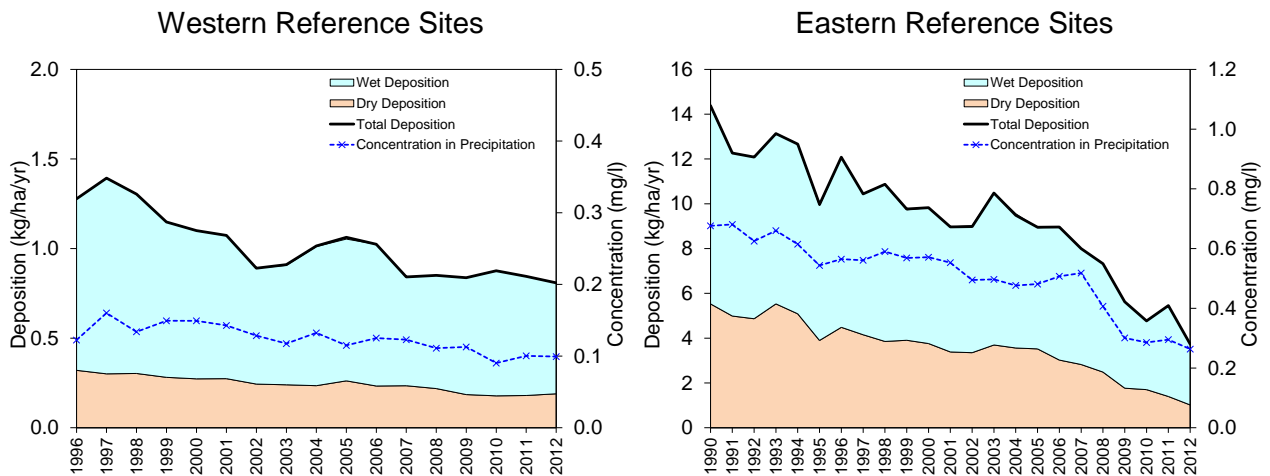


Figure 3-5 Trend in Sulfur Deposition (kg/ha/yr) with Concentrations in Precipitation [milligrams per liter (mg/l)]



Total Reactive Oxides of Nitrogen Measurements at Beaufort, NC

In addition to the NH_3 sampling discussed in Chapter 2, another measurement study was conducted at the CASTNET BFT142, NC site (Figure 1-1). The study focused on continuous measurement of NO_y , which is defined as NO_x plus NO_z (HNO_3 , HNO_2 , PAN, NTR, and nitrite). NO_y measurements began in February 2012 and were completed in April 2013. Trace-level NO_y measurements were obtained using a Thermo Scientific Model 42i-Y NO_y analyzer, which is a chemiluminescent trace-level gas analyzer that measures all reactive oxides of nitrogen in the ambient air. A second converter that permitted the measurement of NO_x in addition to NO_y and NO was used for the BFT142 NO_y study. The first converter was located at 10 m to measure NO_y , and the second was situated in the shelter at the instrument to measure NO_x . A program was written for the data logger to switch between the converters. Thus, NO_2 could be calculated using differences ($\text{NO}_x - \text{NO}$). For every minute of data collection, 20 seconds were dedicated to the NO measurement, 20 seconds to a pre-reactor measurement, and 10 seconds each to NO_y and NO_x measurements. Performance of the data logger program was verified at the AMEC field equipment calibration laboratory before deployment to BFT142. The sampling configuration produced hourly concentrations of NO_y , NO_x , NO, and calculated NO_2 and NO_z .

Figures 3e through 3g illustrate results from the NO_y monitoring study. The data cover the entire measurement period from February 2012 through May 2013. Figure 3e shows six plots of composite NO_y , NO_x , NO_2 , NO_z , NO, and O_3 concentrations. The curves were constructed by averaging all hours for each hour of the day for each parameter for the entire measurement period. The results show typical diurnal distributions with NO values at 0.0 for much of the night due to oxidation by O_3 and conversion to NO_2 . NO_z levels showed little variation during the day. NO_y , NO_x , and NO_2 levels increased after sunrise with fresh NO emissions produced by vehicular traffic and other sources. O_3 concentrations peaked around 1500 local time. The growth of the convective boundary layer, photochemical transformations, and dry deposition decreased nitrogen concentrations during the day as O_3 levels increased.

Figure 3f provides a time series of weekly average concentrations of NO_y , NO_x , calculated NO_2 , calculated NO_z , and NO concentrations collected over the entire measurement period. The results show reasonable relationships between the measurements.

Time series of weekly average concentrations of continuous NO_y and weekly concentrations of total nitrate ($\text{HNO}_3 + \text{particulate NO}_3^-$) measured by the CASTNET filter pack deployed at the BFT142 site are shown in Figure 3g. To evaluate the components of NO_y measurements NO_y concentrations were compared with total NO_3^- concentrations. Since NO_y species include HNO_3 and particulate NO_3^- , the ratio of total NO_3^- to NO_y should always be less than or equal to 1.0. Other than for two weeks, the NO_y concentrations were consistently higher than the total NO_3^- levels, as expected.



Beaufort, NC (BFT142)

Figure 3e Composite NO_y , NO_x , NO_2 , NO_z , NO , and O_3 Concentrations (ppb)

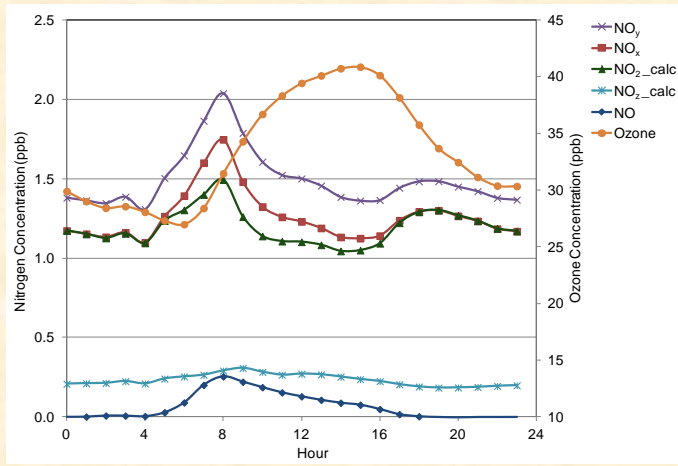


Figure 3f Weekly NO_y , NO_x , NO_2 , NO_z , and NO Concentrations (ppb)

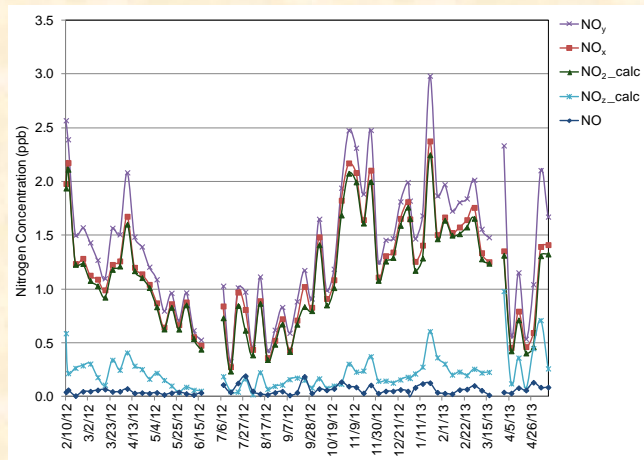
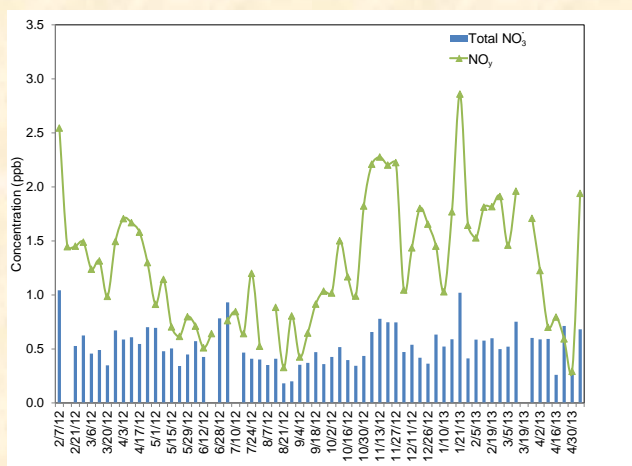


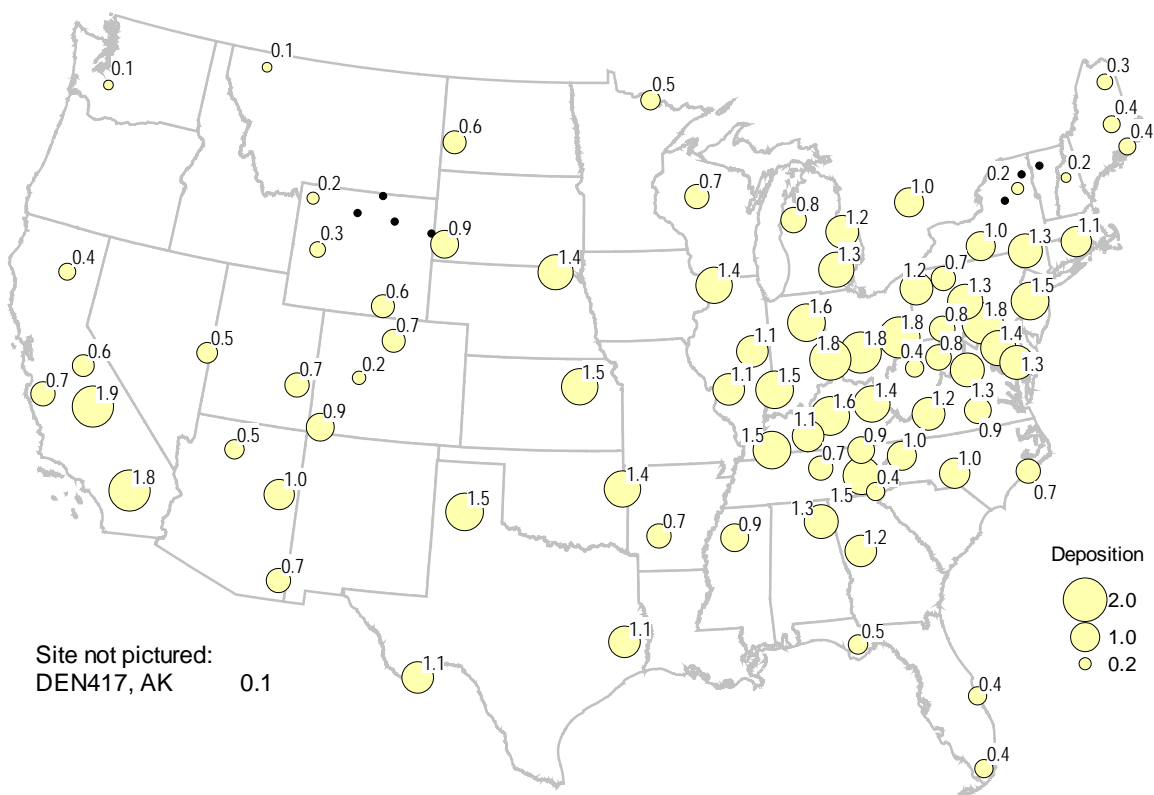
Figure 3g Weekly Total Filter Pack NO_3^- and Weekly Average Continuous NO_y Concentrations (ppb)



Nitrogen Deposition

Figure 3-6 illustrates estimates of dry fluxes of nitrogen (as N) for 2012. The year 2012 was the first year with dry nitrogen deposition values less than 2.0 kg/ha/yr at all sites in the network. The dry nitrogen deposition depicted in Figure 3-6 represents the sum of dry deposition estimates of $\text{HNO}_3 + \text{NO}_3^- + \text{NH}_4^+$. A majority of CASTNET sites in the eastern United States had estimated dry nitrogen deposition rates greater than 1.0 kg/ha/yr. Four eastern sites had deposition rates equal to 1.8 kg/ha/yr. The highest value for all sites was calculated for the western CASTNET site SEK430, CA with a dry nitrogen flux of 1.9 kg/ha/yr.

Figure 3-6 Dry Nitrogen ($\text{HNO}_3 + \text{NO}_3^- + \text{NH}_4^+$) Deposition (kg/ha/yr) for 2012



A map of total nitrogen deposition (as N) for 2012 is given in Figure 3-7. The map was constructed by summing the estimates of dry (yellow shading) and wet (blue 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 (9.2 kg/ha/yr). Most of the western sites had estimated total nitrogen deposition rates below 3.0 kg/ha/yr. The CASTNET site at PAL190, TX had the highest total nitrogen flux for the western sites with an estimated flux of 5.6 kg/ha/yr. Three other western sites in California, South Dakota, and Wyoming 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. Dry nitrogen deposition did contribute more than half of total nitrogen deposition at three of the five monitors in California. These three California sites are in a region with limited rainfall. Dry nitrogen deposition contributed about 75 percent of the total nitrogen deposition at JOT403 and about 65 percent at Pinnacles National Monument (PIN414) and SEK430.

Figure 3-7 Total (Dry + Wet) Nitrogen Deposition (kg/ha/yr) for 2012

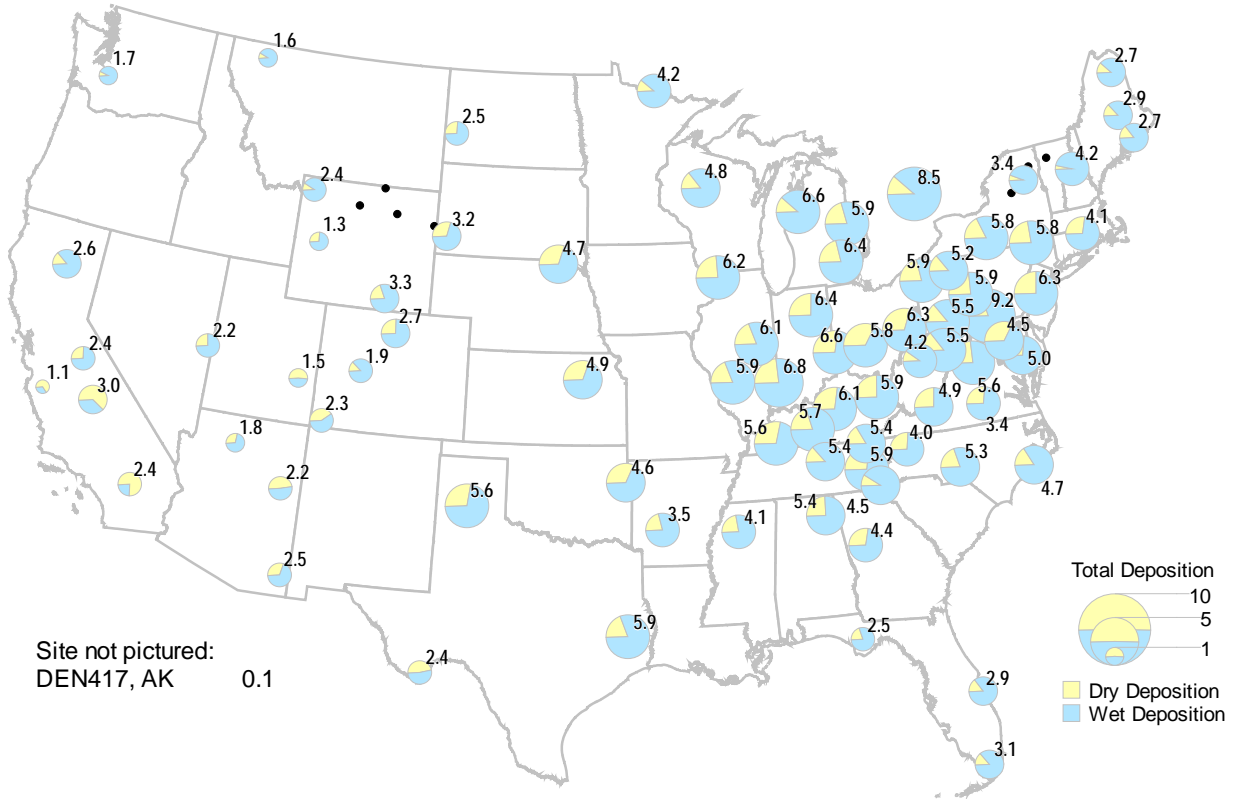


Figure 3-8 presents box plots that were constructed using data from the 34 eastern reference sites over the period 1990 through 2012 (right side) and 17 western reference sites for 1996 through 2012 (left side). The box plots show the trends in dry nitrogen deposition (as N). The box plots for the eastern sites in Figure 3-8 show a reduction in dry nitrogen deposition beginning in 2000. Three-year mean fluxes declined from 2.2 kg/ha/yr for 1990–1992 to 1.2 kg/ha/yr for 2010–2012, a 46 percent reduction over the 23 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 2010–2012.

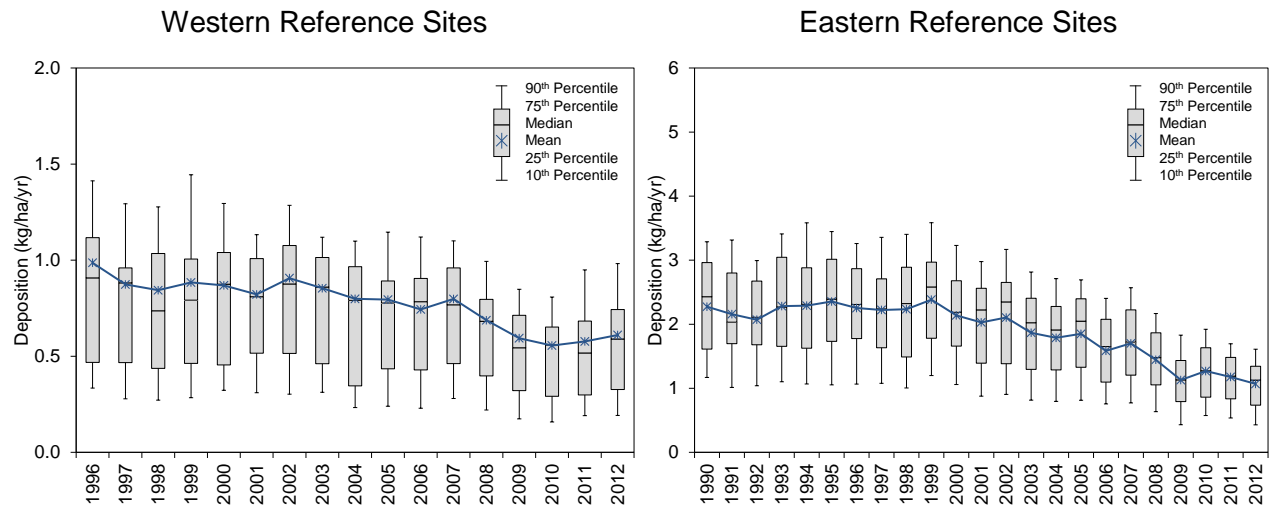
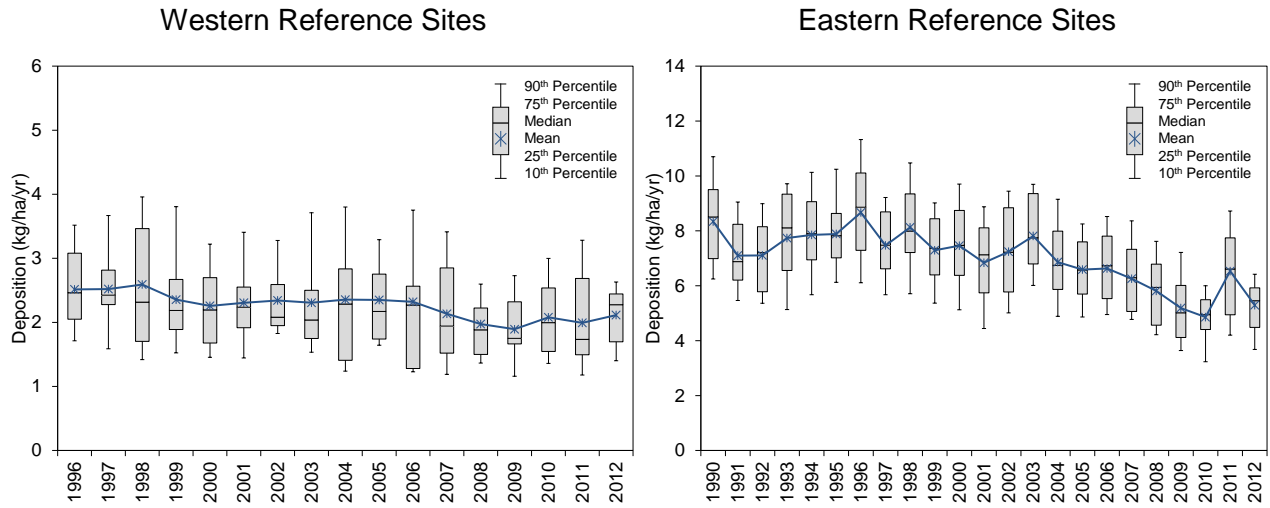
Figure 3-8 Trend in Dry Nitrogen Deposition (kg/ha/yr)

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. The trend in total nitrogen flux for the eastern sites has fluctuated since 2009. Total nitrogen deposition for the eastern sites was reduced from a 1990–1992 mean of 7.5 kg/ha/yr to a 2010–2012 mean of 2.1 kg/ha/yr, a 72 percent reduction. Total nitrogen deposition for the western sites shows a relatively flat trend from a 1996–1998 mean of 2.5 kg/ha/yr to a 2010–2012 mean of 2.1 kg/ha/yr, which constitutes a 19 percent decline.

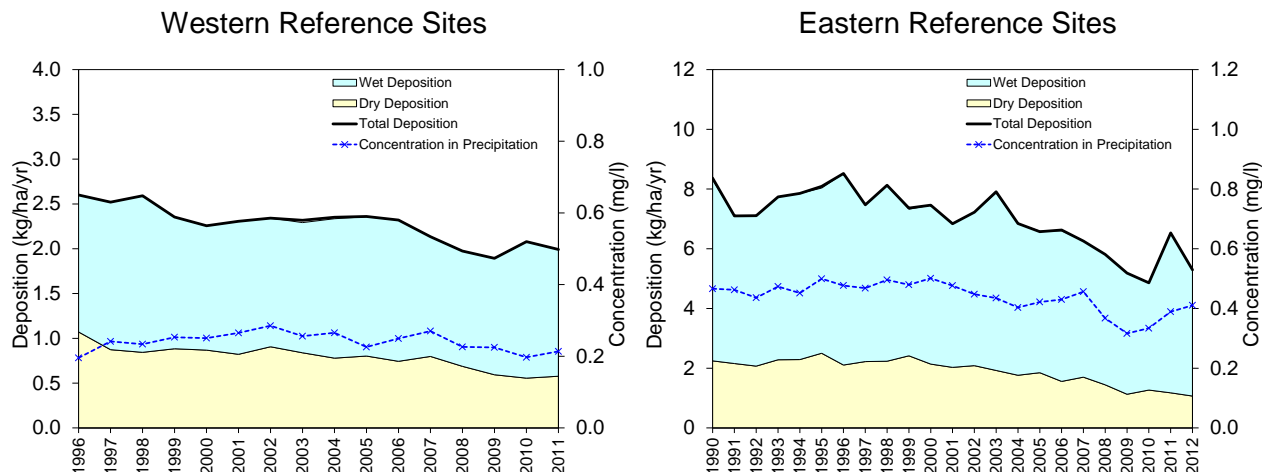
Estimates of trends in wet, dry, and total deposition of atmospheric nitrogen (as N) are presented in Figure 3-10 for both eastern and western reference sites. The trend line (dotted) for precipitation-weighted mean nitrogen concentrations in precipitation measured at eastern sites shows an overall slow downward trend from 2000 through 2009. However, precipitation-weighted mean nitrogen concentrations in precipitation have increased since 2009. This trend is reasonably representative of the effect of changes in NO_x emissions because it does not depend on precipitation amounts. Although total N deposition (solid top line) at eastern sites increased by 34 percent from 2010 to 2011, this increase can be explained by an increase in N concentration in precipitation coinciding with the highest average annual rainfall rate (138 centimeters) at eastern sites over the 23-year period. A 19 percent decrease in total nitrogen deposition was observed from 2011 to 2012.

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



Everglades National Park, FL (EVE419)

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



An Analysis of Critical Loads of Streams near Seven CASTNET Sites in Eastern United States

Air pollutant emission reduction programs have been successful in reducing the extent of lakes and streams impacted by acidic deposition in acid sensitive regions of the United States (Burns *et al.*, 2011). In recent years, emissions of SO₂ and NO_x from power generating plants have continued to decline sharply, likely providing greater protection of forest and aquatic resources. 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 can be used as an assessment tool that provides a benchmark against which to assess whether a water body is 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 exceeding its critical load. A critical load exceedance is the measure of pollutant exposure above the critical load and is higher than, or “exceeds,” the critical load, which exposes water bodies to damaging levels of S and N deposition.

In this case study, wet and dry S and N deposition at selected streams were estimated and compared with available surface water critical loads estimates. Two periods, 2000–2002 and 2010–2012, were compared in order to investigate how wet and dry S and N deposition and their proportional contributions to critical loads have changed. Wet and dry S and N deposition were obtained from the new TDEP maps (EPA, 2013d) for each year. Critical loads for each stream in this case study represent the amount of acidic deposition of total S and N that a stream’s watershed could receive and still allow the surface water chemistry to maintain an acid neutralizing capacity (ANC) of 50 microequivalents per liter (µeq/L) or higher. Fifty µeq/L is the threshold above which healthy aquatic ecosystem are supported (Henriksen *et al.*, 2002). Critical loads were obtained from the National

Critical Load Database (NCLD) (<http://nadp.isws.illinois.edu/committees/clad/db/>) and are expressed in terms of ionic charge balance as milliequivalents per square meter per year ($\text{meq}/\text{m}^2/\text{yr}$).

In addition, critical loads were summarized for streams in the NCLD located near seven CASTNET sites: Parsons, WV (PAR107); Kane Experimental Forest, PA (KEF112); Beltsville, MD (BEL116); Shenandoah National Park, VA (SHN418); Horton Station, VA (VPI120); Cranberry, NC (PNF126); and Coweeta, NC (COW137). Critical Loads were summarized for the selected streams near each of the seven CASTNET monitoring locations as the 15th percentile critical load value (Figure 3h). The 15th percentile is the critical load value below which 15 percent of the observations were summarized for a given CASTNET site. These are the streams with the lowest critical load values and are most vulnerable to acidic deposition. The selection of the 15th percentile critical load value is just one choice among many options that could be selected. It is also important to note while the NCLD is extensive in its coverage of water bodies, the water bodies analyzed herein are not intended to represent all water bodies that are within 25 km of CASTNET locations.

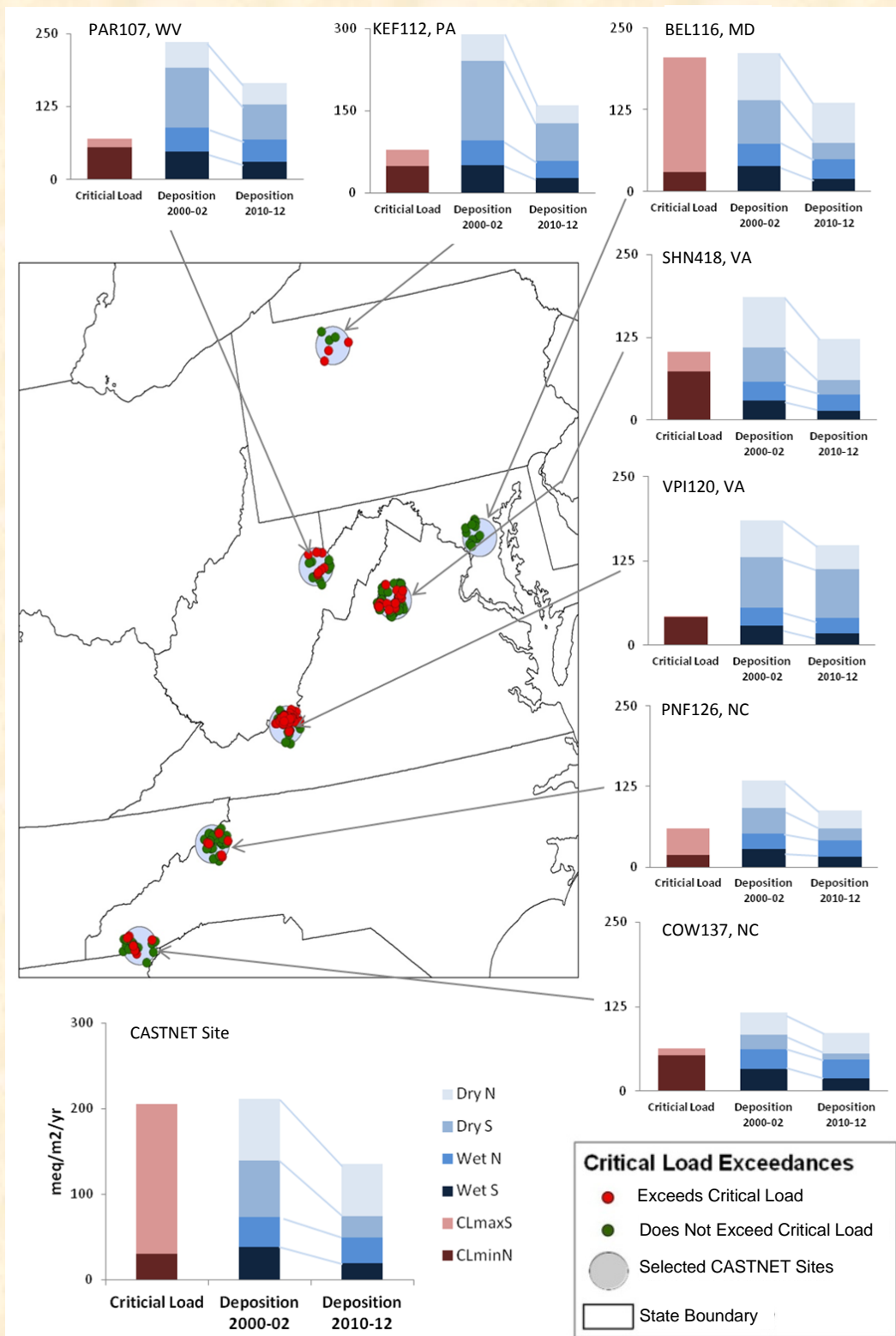
This analysis examined over 250 streams within 25 km of the seven CASTNET monitoring locations in the eastern United States (Figure 3h). Gray circles indicate CASTNET monitoring sites while red and green symbols represent lakes or streams that exceed or do not exceed, respectively, their critical load for an ANC of $50 \mu\text{eq}/\text{L}$. Graphs represent the 15th percentile critical load and total sulfur and nitrogen deposition for years from 2010–2012 at CASTNET locations. On the graphs, light and dark red bars represent the maximum critical load for S (CLmaxS) and the amount of N that is removed by the ecosystem (CLminN), respectively. Dark to light blue represents inorganic and organic wet sulfur, wet nitrogen, dry sulfur, and dry nitrogen deposition, respectively.

Figure 3h shows comparisons of the 15th percentile critical load value with total average N and S deposition from 2000–2002 and 2010–2012. For all the CASTNET locations, total acid deposition decreased on average by $56 \text{ meq}/\text{m}^2/\text{yr}$ or 32 percent between 2000–2002 and 2010–2012, indicating an important reduction in the acidic loading to these aquatic ecosystems. KEF112, PA had the largest decline of $129 \text{ meq}/\text{m}^2/\text{yr}$ or 45 percent during this period. The contributions of wet and dry deposition varied among the seven CASTNET locations. On average, total dry deposition ($43.18 \text{ meq}/\text{m}^2/\text{yr}$) decreased twice as much as wet deposition ($21.87 \text{ meq}/\text{m}^2/\text{yr}$), and total dry deposition was on average about 32 percent higher than total wet deposition, making dry depositional loading the largest contributor to the critical load exceedances.

The contribution of N versus S deposition also varied at the seven CASTNET locations for both time periods. Three CASTNET locations had on average more total N deposition, compared with four sites that had higher total S deposition relative to N. For 2010–2012, N total deposition was on average only slightly higher ($9.54 \text{ meq}/\text{m}^2/\text{yr}$) than total S deposition among the CASTNET locations. However, total S deposition on average declined three times more than total N deposition over the period of comparison, making declining S the largest contributor to the declining acid loading.

For all but the BEL116, MD site, the 15th percentile critical load is less than current total N and S deposition, indicating that acidification critical loads are being exceeded and that some vulnerable streams surrounding CASTNET monitoring locations are still being affected by acid deposition today despite significant reductions in deposition in recent years.

Figure 3h Critical Load Estimates (2000–2002 and 2010–2012) for Selected Streams with 25 km of Seven Eastern CASTNET Sites



CHAPTER 4: OZONE CONCENTRATIONS

CASTNET is the primary air quality network for monitoring rural, ground-level O₃ concentrations in the United States and for providing critical information on geographic patterns in rural O₃ levels. CASTNET was not originally designed to operate as a regulatory network; however, NPS-sponsored CASTNET sites have complied with regulatory monitoring requirements from site inception, and during 2010 and 2011, EPA-sponsored CASTNET O₃ monitoring systems were upgraded in order to comply with regulatory monitoring requirements. Data collected from the NPS-sponsored sites and data collected from EPA-sponsored sites for 2011 and 2012 were submitted to EPA's AQS. In this report, O₃ measurements collected during 2010–2012 were evaluated with respect to the current NAAQS (EPA, 2008a) of 0.075 parts per million (ppm). For the 2010–2012 period, three California, one other western, and eight eastern sites recorded concentrations above the 0.075 ppm standard. The geographic extent of O₃ levels above 0.075 ppm was greater in 2012 than in the previous four years.

Most CASTNET sites operate an O₃ analyzer that measures hourly average concentrations, which are archived in the CASTNET database and delivered to AQS. At the end of 2012, 83 O₃ analyzers were operated throughout the network. Data from these sites, with the exception of YOS204, CA; ROM206, CO; and HOW191, ME, which are designated as non-regulatory, can be used to calculate design values as three years of Title 40 CFR-compliant data become available. CASTNET's geographic coverage of the United States provides data that are essential for evaluating rural O₃ concentrations in the context of the O₃ NAAQS and in terms of presenting information on trends and geographic patterns in regional O₃. The analyses presented in this chapter provide maps and examine trends in the annual fourth highest daily maximum 8-hour average (DM8A) O₃ concentrations measured at CASTNET sites. A map of 2012 W126 values is also presented and discussed on pp. 55-56. Vertical gradient profile O₃ data within a forest canopy collected at the HOW191, ME AmeriFlux site are analyzed and summarized. Additional maps of O₃ concentrations from the NPS Air Atlas can be viewed at <http://nature.nps.gov/air/maps/airatlas/index.cfm>.

Ground-level O₃ is a criteria pollutant and a component of smog that can affect the human respiratory system, cause damage to vegetation and ecosystems, and reduce crop yield and quality. O₃ is formed in the lower atmosphere when NO_x and volatile organic compounds (VOC) react in the presence of sunlight. Emissions from motor vehicles, industrial facilities, chemical solvents, surface coatings, gasoline, and power plants are the major anthropogenic sources of NO_x and VOCs. Also, biogenic VOC emissions from trees and other vegetation may contribute to O₃ formation in rural areas. Meteorological conditions play a significant role in O₃ formation. O₃ concentrations are generally higher in the warmer months because sunlight and hot weather accelerate its formation, but episodes of high O₃ concentrations vary by geographical region and

can occur in any season. O₃ concentrations typically increase during daylight and peak in the late afternoon after temperature and sunlight intensity peak. Different diurnal patterns of O₃ can be observed across sites depending on site elevation, complexity of terrain, and latitude. See the discussion of O₃ levels in the Upper Green River Basin, WY in the CASTNET 2010 Annual Report (AMEC, 2012a). Also, view the figures of diurnal distributions of O₃ and NO_y levels at four sites in the recent CASTNET Quarterly Data Reports for the second and third quarters of 2013 (AMEC, 2013d; 2014).

The DM8A O₃ standard can be used to assess the status and trends in rural O₃ levels in order to gauge the success of EPA emission reduction programs such as the ARP, NO_x SIP Call/NBP, and CAIR. On May 1, 2009, the CAIR NO_x O₃ 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 CAIR and NO_x emission reductions that were mandated by the ARP and other NO_x emission control programs have contributed to reductions in O₃ concentrations, especially in rural areas with elevated DM8A levels, because regional transport of pollutants contributes to O₃ formation. VOC emission reduction strategies also have been successful in reducing higher, short-term O₃ concentrations in and downwind of urban areas.

National Ambient Air Quality Standards for Ozone

Ozone ¹	Primary Standard		Secondary Standard	
	Level	Averaging Time	Level	Averaging Time
	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 O₃ 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). O₃ concentrations are commonly presented in units of ppb.

EPA and other federal, tribal, state, and local agencies perform O₃ measurements on an hourly basis through national and local monitoring programs. AMEC followed EPA procedures (1998) to estimate O₃ design values and 2012 fourth highest DM8A O₃ concentrations at CASTNET sites. O₃ data from EPA-sponsored CASTNET sites will not be used to gauge compliance with NAAQS until 40 CFR-compliant data are available for three years. O₃ data from NPS-sponsored sites can be used to gauge compliance with NAAQS since these sites have met regulatory quality assurance criteria since site inception. The primary O₃ NAAQS standard is designed to protect public health. The secondary standard is designed to protect public welfare and the environment. Both O₃ NAAQS are set at a level of 0.075 ppm averaged over eight hours.

W126 Index

O₃ concentrations can also be analyzed in terms of W126, a measure of exposure that can indicate damage to vegetation. W126 is a cumulative metric that sums weighted hourly O₃ concentrations during the O₃ season. For this report (see pp. 55-56), W126 was calculated for CASTNET sites for the months of May through September. The highest of the rolling 3-month sums during the five months is the W126 value for 2012.

Eight-Hour Ozone Concentrations

Figure 4-1 presents 3-year averages of the fourth highest DM8A O₃ concentrations for 2010–2012. O₃ concentrations were not included on the maps in this chapter if the 3-year average was not available because of incomplete data; these sites are shown as dots with no value. During this period, 3-year averages of the fourth highest DM8A O₃ concentrations were greater than 75 ppb at eight eastern sites, three sites in California, and the site at ROM406, CO. The eastern sites include Washington Crossing, NJ (WSP144); Blackwater National Wildlife Refuge, MD (BWR139); BEL116, MD; Great Smoky Mountains National Park, TN (GRS420); Oxford, OH (OXF122); Vincennes, IN (VIN140); Alhambra, IL (ALH157); and Cherokee Nation, OK (CHE185). The three California sites include Yosemite National Park (YOS404), SEK430, and JOT403. Three-year average concentrations were generally higher in 2010–2012 than in 2009–2011.

The 3-year averages of fourth highest DM8A O₃ concentrations for 2010–2012, which are shown on Figure 4-1, provide examples of the design values for CASTNET sites used to determine compliance with the O₃ NAAQS if all CASTNET O₃ data for 2010 through 2012 were regulatory 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 O₃ 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, if it is assumed that the 3-year averages of 2010–2012 fourth highest DM8A O₃ concentrations are design values, then any value higher than 75 ppb will have to be reduced to this level to achieve the current O₃ NAAQS.



Great Smoky Mountains National Park, TN (GRS420)

Figure 4-1 Three-year Average of Fourth Highest DM8A O₃ Concentrations (ppb) for 2010–2012

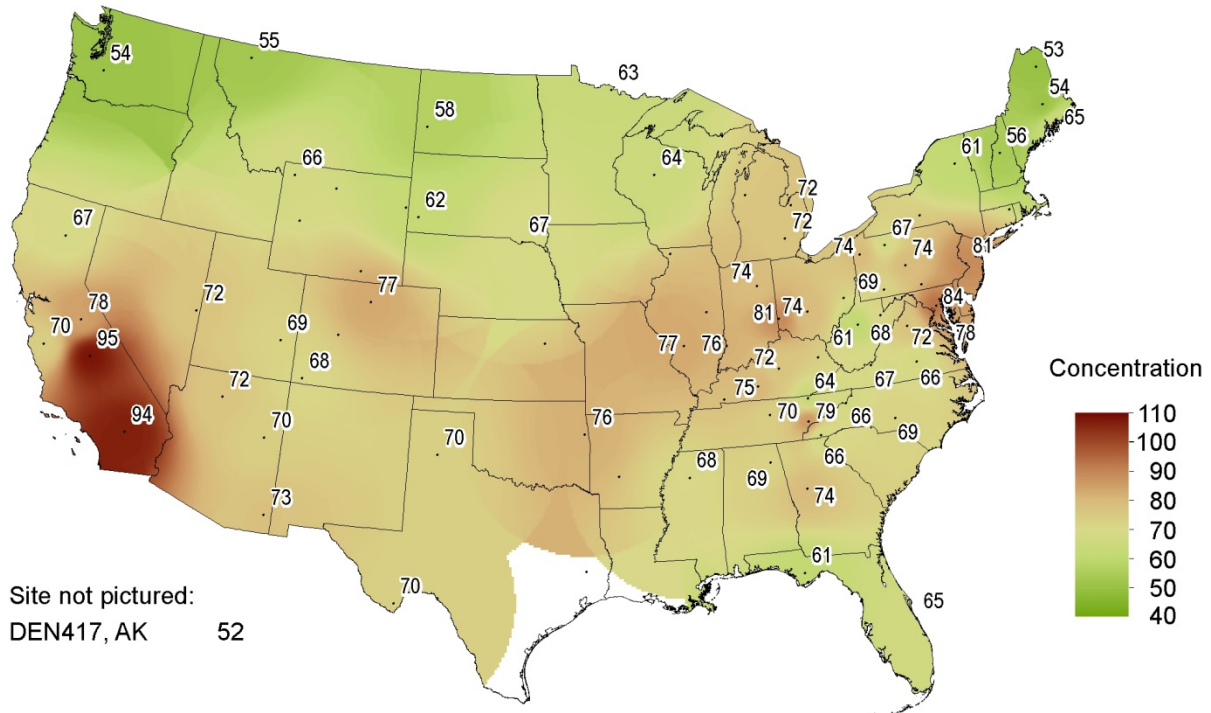
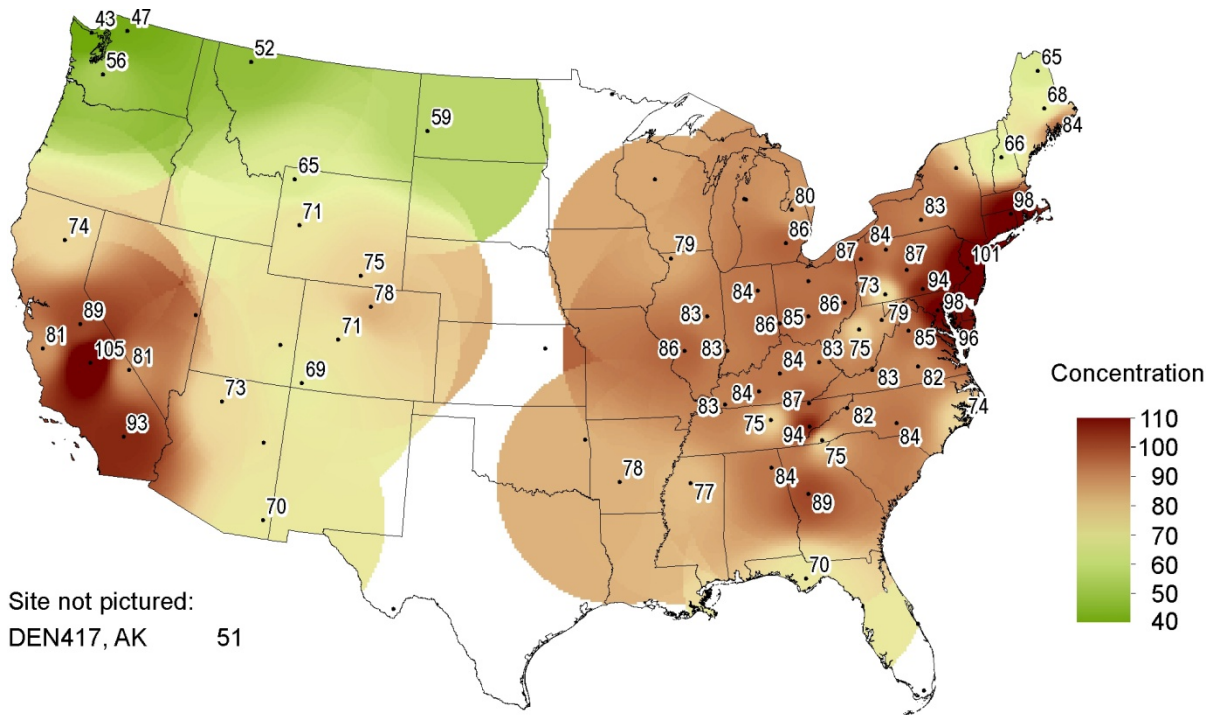


Figure 4-2 Three-year Average of Fourth Highest DM8A O₃ Concentrations (ppb) for 2000–2002



Three-year averages of the fourth highest DM8A O₃ concentrations for 2000–2002 are presented in Figure 4-2 for comparison with the 2010–2012 values shown in Figure 4-1. The period 2000–2002 was selected because it shows O₃ concentrations prior to reductions in NO_x emissions under the NO_x SIP Call/NBP, which began in 2003 for the eastern United States. The changes in O₃ concentrations from 2000–2002 to 2010–2012 illustrate the effectiveness of the emission reduction programs. Approximately 70 percent of the 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. During 2010–2012, relatively low DM8A O₃ concentrations in the East were monitored in northern New England and in the Florida panhandle, and only 12 monitors nationwide measured concentrations greater than 75 ppb.

O₃ concentrations for 2012 are shown in Figure 4-3. These data comply with regulatory requirements. All valid data are included; exceptional events have not been analyzed and, therefore, are not excluded on the map. “Exceptional events are unusual or naturally occurring events that can affect air quality but are not reasonably controllable using techniques that state, tribal, or local air agencies may implement in order to attain and maintain the NAAQS” (EPA, 2013e). Twenty eastern, three California, and two other western CASTNET sites measured fourth highest DM8A O₃ concentrations greater than 75 ppb. The geographic extent of measured fourth highest DM8A O₃ concentrations above 75 ppb was greater in 2012 than in the previous four years for the eastern sites and greater than the previous three years for the western sites. The highest eastern concentration of 85 ppb was measured at OXF122, OH, and the highest western level of 95 ppb was observed at two sites in California, JOT403 and SEK430.

The CASTNET 2011 Annual Report (AMEC, 2013a) reported that CASTNET sites at BBE401, TX; PAL190, TX; and CHE185, OK each measured a fourth highest DM8A O₃ concentration greater than 75 ppb during 2011, which was likely influenced by frequent wildfires in Texas and Arizona during the summer and fall fire season. Moderately high fourth highest DM8A O₃ concentrations persisted at these sites during 2012, again because of an active wildfire season.



Quaker City, OH (QAK172)

Figure 4-4 Trend in Fourth Highest DM8A O₃ Concentrations (ppb)

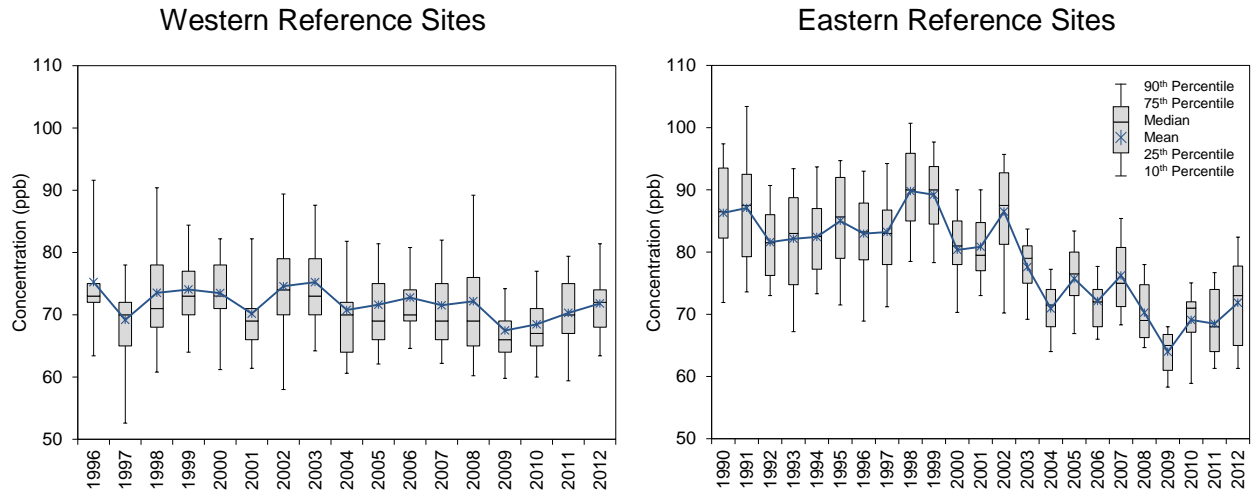
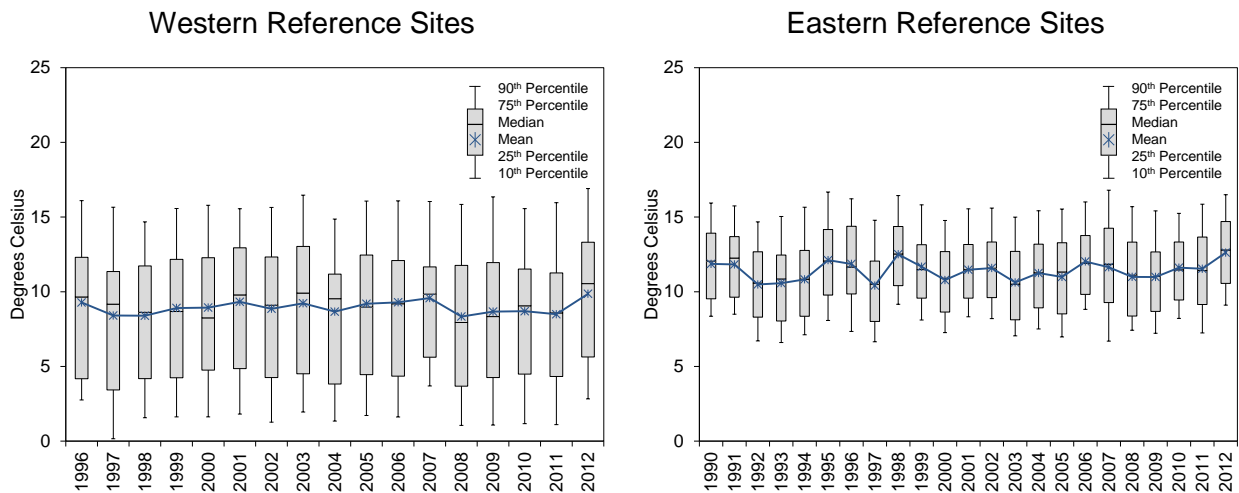


Figure 4-5 Trend in Hourly Temperature Values (degrees Celsius)



Sand Mountain, AL (SND152)

In-Canopy Measurements of Ozone and Other Gases and Particles at Howland Research Forest, ME

Ozone Concentrations

CASTNET began collecting O₃ and filter pack measurements at the Howland Research Forest AmeriFlux site (designated HOW191) in Maine in September 2011. The study ended in April 2013. This study represented the first collaboration between the two long-standing national networks. The primary goal of AmeriFlux is to measure ecosystem level exchanges of carbon dioxide, water, energy, and momentum.

The design of the O₃ system (AMEC, 2013a; Rogers *et al.*, 2012) centered on the use of a single O₃ analyzer and site transfer standard in conjunction with a solenoid system to allow for all eight levels to be measured using the same analyzer. O₃ concentrations were 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. Levels were sampled in succession for three minutes each. All eight inlets were sampled within a 24-minute period at least twice per hour. Two sampling periods were required each hour to calculate an hourly value.

Figure 4a depicts three plots of aggregated O₃ 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 period of record. These data show a decrease in concentrations with decreasing elevation throughout the 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, dry deposition and other depletion mechanisms (Talbot *et al.*, 2005). 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 O₃ production and atmospheric mixing of O₃ from aloft.

Figure 4a Aggregated O₃ Concentrations for Entire Database (September 2011 through April 2013) for Specific Hours at HOW191, ME

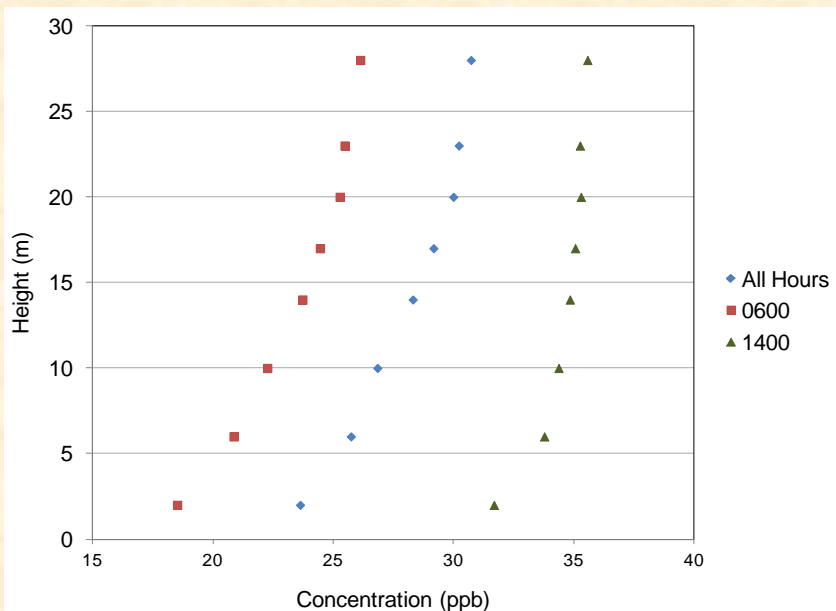
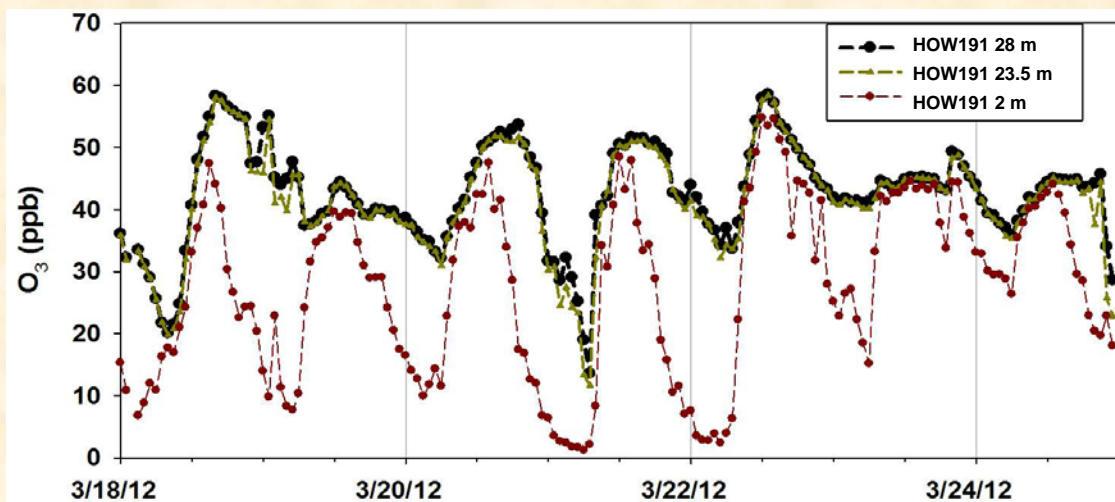


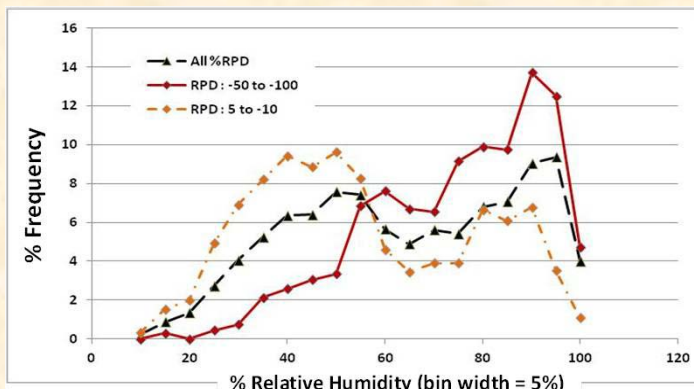
Figure 4b Time Series of O₃ Concentrations at the Highest Inlet above the Canopy (28 m), the Inlet Just above the Forest Canopy (23.5 m), and the Lowest Inlet below the Canopy (2 m)



The HOW191 O₃ concentration data were analyzed in order to understand nighttime depletion/loss mechanisms that produce lower O₃ concentrations at 2 m relative to values measured near the canopy top. Figure 4b shows a time series of O₃ concentrations (the 1-week period chosen at random) at the highest inlet (28 m), the inlet just above the forest canopy (23.5 m), and the lowest inlet (2 m). The plot shows that there is little difference between measurements taken above the canopy, but losses were observed between the above canopy and below canopy measurements. These O₃ losses in the lower canopy occurred during the nighttime but did not occur every night. The analyses can be summarized as follows:

- Non-loss events were defined as relative percent difference (RPD) from 5 to -10 percent O₃ concentration values measured at 28 m. They occurred more frequently than loss events (RPD from -50 to -100 percent) with ~25 to 55 percent relative humidity (RH), and loss events occurred more frequently than non-loss events with RH from ~60 to 100 percent (Figure 4c).
- Loss events did not occur at high wind speeds and were only observed when wind speeds were less than 3.5 meters per second.
- Loss events were more frequent during hours with lower sigma theta values.
- Loss events were more frequent in stable conditions when temperature difference (ΔT) from 2 m to 23.5 m was positive. The ratio of loss to non-loss events increased with increasing ΔT until no non-loss events occurred when ΔT was greater than 1.5 °C.

Figure 4c Percent Frequency of Non-loss Events (RPD = 5 to -10 percent; orange) and Loss Events (RPD = -50 to -100 percent; red) Binned to Percent Relative Humidity



Note: RPD = relative percent difference

Filter Pack and Ozone Concentrations

CASTNET filter pack sampling systems were operated at 2 m and 23.5 m. Weekly ambient concentrations measured with filter packs support the O₃ concentration observations. The below-canopy concentrations were approximately 62 percent and 64 percent of above-canopy concentrations for SO₂ and HNO₃, respectively. Above and below-canopy concentrations of particulate matter components (i.e., SO₄²⁻, NO₃⁻, and NH₄⁺) show much less difference, which is indicative of slower deposition rates compared with those of the gaseous species.

Hourly O₃ and weekly filter pack concentration data were collected at the nearby HOW132, ME CASTNET monitoring site, where measurements occurred in a clearing at a height of 10 m. For the first 10 months of measurements, November 2011 through August 2012, concentrations of SO₂ (4 percent higher) and SO₄²⁻ (5 percent lower), HNO₃ (3 percent lower), and NO₃⁻ (3 percent lower) at HOW132 were very similar to the above canopy concentrations measured at HOW191. NH₄⁺ concentrations showed the greatest difference and were 13 percent lower at HOW132. Hourly O₃ concentrations at HOW132 were about 9 percent lower than the HOW191 above-canopy (28 m) measurements (R² = 0.93).



Howland, ME (HOW191) AmeriFlux site

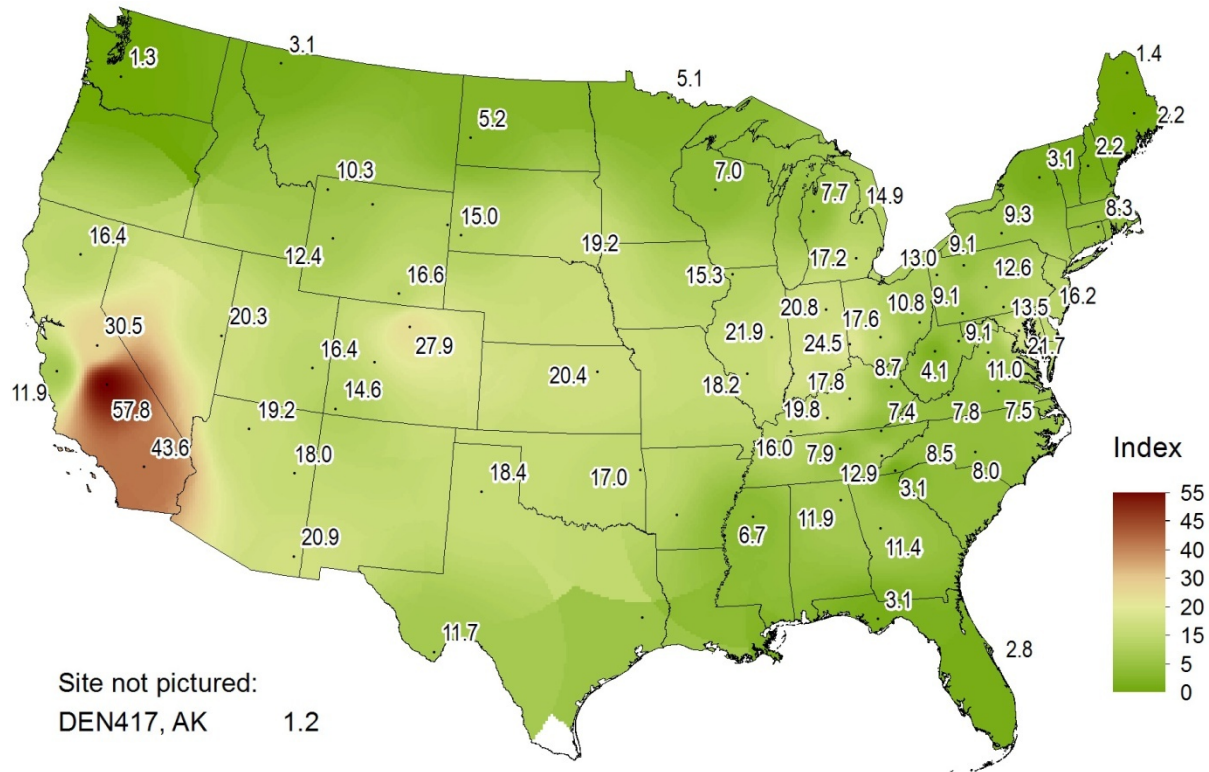
W126 Values for 2012

The W126 O₃ exposure index is a cumulative peak-weighted exposure index (Lefohn and Runeckles, 1987; EPA, 1996; 2006) for relating reduced vegetation yields to O₃ exposure. W126 was developed as a seasonal measure from the sum of weighted hourly values measured during the approximately 12-hour daylight period during the O₃ season with the higher hourly concentrations being weighted more heavily than lower concentrations (EPA, 2010). In this report, W126 is used to characterize high O₃ concentrations over a seasonal, 3-month exposure period. The highest rolling 3-month W126 value for each site is presented in Figure 4-6.

W126 exposures (ppm-hours) were calculated using O₃ values measured during the 12 hours from 8:00 a.m. to 8:00 p.m. in the months of May through September 2012. 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. For reference, a W126 index value of 21 ppm-hours is associated with a level of crop protection of approximately no more than 10 percent yield loss in 50 percent of crop cases studied in the National Crop Loss Assessment Network (NCLAN) experiments (2013). A W126 index value of 13 ppm-hours is associated with a level of crop protection of approximately no more than 10 percent yield loss in 75 percent of NCLAN cases. In addition, vegetative sensitivity to O₃ varies between and within species.

W126 levels for 2012 are presented for CASTNET sites in Figure 4-6. The higher W126 values were measured in California, at western sites in high terrain, and at a few eastern sites with relatively high DM8A O₃ concentrations. The highest W126 value (57.8 ppm-hour) was measured at SEK430, CA. O₃ concentrations measured at high elevation sites (AMEC, 2003; Talbot *et al.*, 2005) typically persist during the night because dry deposition and scavenging of O₃ by nitric oxide are low at night. Nighttime dry deposition is low because shallow boundary layers typically do not form at elevated sites, and scavenging is low because little fresh nitric oxide is available to react with the existing O₃. The persistence of moderate O₃ concentrations at night produces steady exposure and high W126 levels. The 2012 W126 values were higher than values in 2011, reflecting higher ambient concentrations in 2012. For example, OXF122, OH measured a W126 value of 24.5 ppm-hour in 2012 versus a value of 14.6 ppm-hour in 2011.

Figure 4-6 W126 Values (ppm-hour) for 2012



Sequoia National Park, CA (SEK430) south view

Ozone Monitoring System Performance Audits

CASTNET Ozone Monitoring

CASTNET measures ground-level O₃ concentrations at 83 sites nationwide. Measurements are made via ultraviolet absorbance using Thermo Scientific 49i O₃ analyzers. CASTNET O₃ monitoring systems comply with the regulatory monitoring requirements described in 40 CFR Parts 50, 53, and 58 and Appendix A to Part 58 (EPA, 2011; 2012a). CASTNET is the primary source of rural O₃ monitoring data for the United States. The data collected are used to calculate design values for all sites where data completeness requirements are met and are also used to assess the effectiveness of CAIR and other EPA NO_x emission reduction programs. Additionally, CASTNET data are used to support the development of primary and secondary air quality standards.

CASTNET O₃ data are collected as hourly averages and submitted in near real-time to the EPA AIRNow system. Hourly concentration data for all sites are also submitted to EPA's AQS each month.

Regulatory Auditing Requirements

Federal air monitoring regulations require application of a specified program of internal, independent, and external (i.e., regulatory agency) audits of technical systems and instrument performance. These required audits are summarized in Table 4a. Audit criteria are listed in Table 4b.

Table 4a Summary of 40 CFR Regulatory Audit Requirements

Required Audits	Performed By	Administrator	Audit Frequency	Results Submitted
Recertification of site transfer standard*	Program contractor**	Program contractors	Once every 6 months	EPA/NPS/BLM program contractors
Certification to Level 1 standard for Level 2 standards	NIST and EPA regional laboratories	Program contractors	Annually	EPA/NPS/BLM program contractors
Annual performance evaluation	Independent auditor	EPA	Annually (all sites)	AQS EPA
National Performance Audit Program (NPAP)	EPA (Regional office coordination)	EPA	20% of sites each year	AQS
Technical systems facilities audit	Third party auditor	EPA/NPS	Each facility every 3 years	EPA/NPS AQS program contractors

Note: *CASTNET site transfer standards generally carry Level 3 authority in the EPA traceability hierarchy (please refer to Figure 4d on page 60).

**AMEC (EPA contractor), Air Resource Specialists (NPS and BLM contractor). Managed subcontractors may perform on-site work.

NIST = National Institute of Standards and Technology

Table 4b Operational Criteria for O₃ Audits

Requirement / Type of Audit	Frequency	Acceptance Criteria	Information /Action
Annual performance evaluation of single analyzer	Every site once per year within period of monitor operation, 25% of sites quarterly	Percent difference of audit levels 3-10 $\leq \pm 15\%$ Audit levels 1 and 2 ± 1.5 ppb difference or $\pm 15\%$	^{1,2} 40 CFR Part 58, App A, Section 3.2.2 ³ Recommendation: Three audit concentrations not including zero. AMTIC guidance 2/17/2011 http://www.epa.gov/ttn/amtic/cpreldoc.html
Federal audits (NPAP)	Once per year at selected sites, 20% of sites audited per year	Audit levels 1 and 2 ± 1.5 ppb difference All other levels percent difference $\pm 10\%$	¹ 40 CFR Part 58, App A, Section 2.4 ² NPAP adequacy requirements on AMTIC, ³ NPAP QAPP/SOP
Ozone Transfer Standard – Level 2			
Certification/ recertification to SRP (Level 1)	Once per year	Single point difference $\leq \pm 3\%$	¹ 40 CFR Part 50, App D, Section 5.4 ^{2,3} Transfer Standard Guidance, EPA-454/B-10-001
Level 2 and greater transfer standard precision	Once per year	Standard deviation less than 0.005 ppm or 3%, whichever is greater	¹ 40 CFR Part 50, App D, Section 3.1 ² Recommendation: part of re-verification ³ 40 CFR Part 50, App D, Section 3.1
If recertified via a transfer standard	Once per year	Regression slopes = 1.00 ± 0.03 and two intercepts are 0 ± 3 ppb	^{1,2,3} Transfer Standard Guidance, EPA-545/B-10-001
Ozone Transfer Standard – Level 3 and Level 4			
Certification	After qualification and upon receipt/ adjustment/repair	RSD of six slopes $\leq 3.7\%$ Standard deviation of 6 intercepts ≤ 1.5 ppb	^{1,2,3} Transfer Standard Guidance, EPA-545/B-10-001 1
Technical systems audit of monitoring organization program and facilities	Once per 3 years	Compliance with established regulations	^{1,2} 40 CFR Part 58, App A, Section 2.5, ³ QA Handbook, Volume 2, Section 15.3

Note: AMTIC = Ambient Monitoring Technology Information Center

App = appendix

NPAP = National Performance Audit Program

QAPP = quality assurance project plan

SOP = standard operating procedures

SRP = standard reference photometer

RSD = relative standard deviation

¹ Audit requirement citation

² Frequency requirement citation

³ Acceptance criteria citation

Semiannual Recertification for Site Transfer Standards

Each site utilizes a second in-station photometer as a transfer standard to verify site analyzer performance each day. To perform the semiannual recertifications of these transfer standards, the concentration of a calibration gas is introduced to the system, and the concentration detected by the site transfer standard is compared with the concentration detected by a traveling transfer standard with Level 2 authority using the statistical criteria listed in Table 4b. During the semiannual recertification at EPA-sponsored sites, the internal O₃ generation system of the on-site transfer standard is used to generate specific concentrations of O₃ as the calibration gas. At NPS-sponsored sites, the site analyzer generates the calibration gas.

Semiannual Verification for Level 2 Transfer Standards

The bench standards that are used in the CASTNET instrumentation laboratories and the traveling transfer standards that are used for the recertification of site transfer standards are defined as Level 2 transfer standards in the EPA traceability hierarchy depicted in Figure 4d. Level 2 standards are verified annually by a National Institute of Standards and Technology (NIST) standard reference photometer (SRP) or EPA Regional SRP. Additionally, traveling transfer standards are audited approximately twice per calendar quarter against the Level 2 laboratory bench standards. Failing standards are removed from service until they are repaired and recertified.

Annual Performance Evaluation

Using a technical process similar to that used for recertification of site transfer standards, an independent auditor brings a Level 2 traveling transfer standard to each site on an annual basis to verify site analyzer performance. The auditor compares the results reported by the site analyzer with the Level 2 traveling transfer standard as described in Table 4b.

National Performance Audit Program

The National Performance Audit Program (NPAP) audits follow a technical process similar to that utilized by auditors performing the annual performance evaluation but are managed directly by the EPA Office of Air Quality Planning and Standards. NPAP audit acceptance criteria are tighter than criteria used for the annual performance evaluation while audits may be performed less frequently (Table 4b), depending on the site. However, all sites will be audited at least once every five years.

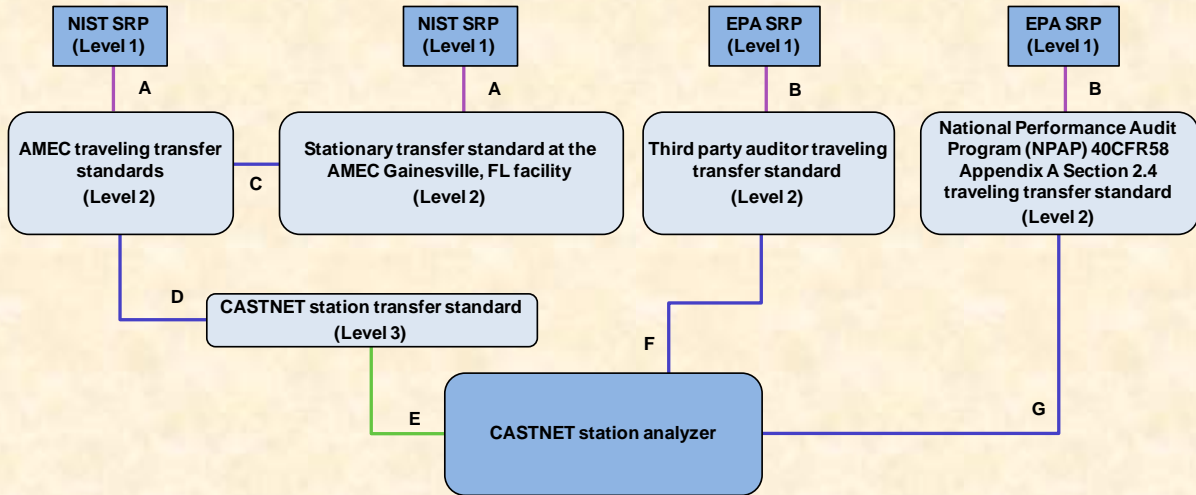
State Audit Programs

Monitoring programs in states where CASTNET monitors are located may require additional audits. State, tribal, or local monitoring organizations are welcome to perform audits at CASTNET sites as needed for their individual programs with advance notice provided to EPA, NPS, or BLM.

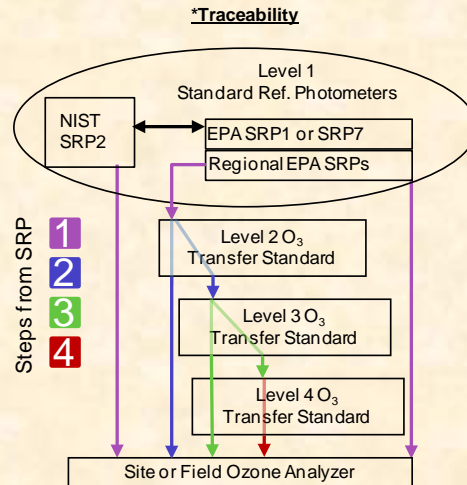


Coweeta, NC (COW137)

Figure 4d Ozone Standard Verification and Traceability* Hierarchy



- Legend**
- A = Annual reverification
 - B = Quarterly reverification
 - C = Audited ~once/6 weeks
 - D = reverification once/6 months
 - E = Zero, span and single point QC check daily
 - F = Audited annually
 - G = Audited once/5 years



Audit Summary for 2012

Table 4c summarizes audits performed for 2012. Since this was the first complete year of regulatory protocol network operation for EPA-sponsored sites, some portions of the audit program were initiated in the third calendar quarter. The audit procedures used by NPS and the audit results through 2011 are provided on the web site: <http://www.nature.nps.gov/air/monitoring/network.cfm>.



Speedwell, TN (SPD111)

Table 4c 2012 Audit Summary

Sites* or Equipment Audited	Audit/Certification Performed	Results
All sites	Recertification of site transfer standard	All sites passed
All Level 2 standards utilized during the year	Certification to Level 1 standard for Level 2 standards	All standards passed
All sites	Annual performance evaluation	All sites passed
BEL116, MD BWR139, MD HOW132, ME HWF187, NY KEF112, PA LAV410, CA SEK430, CA	National Performance Audit Program	All sites passed
BFT142, NC CND125, NC AMEC field instrumentation laboratory, FL	Technical systems facilities audit	Minor findings related to documentation.**
BEL116, MD BWR139, MD	State of Maryland technical systems and performance audit	All sites passed
GTH161, CO ROM206, CO ROM406, CO	State of Colorado technical systems and performance audit	All sites passed

Note: *Please refer to site locations table in Appendix A for detailed information.

**The complete audit report and AMEC response are posted to the EPA CASTNET website - <http://epa.gov/castnet/javaweb/ozone.html>



Rocky Mountain National Park, CO (ROM206)

CHAPTER 5: DATA QUALITY

Data quality indicators (DQI), such as precision, accuracy, and completeness, are used to assess CASTNET measurements and supporting activities. Routine assessment and analysis help guarantee the production of high-quality data and information to meet project objectives. Measurements taken during 2012 and historical data collected over the period 1990–2011 were analyzed relative to DQI and their associated metrics. These analyses demonstrate that CASTNET data can be used with confidence and that CASTNET continues to produce information of the highest quality.

The CASTNET Quality Assurance (QA) program was designed to ensure that all reported data are of known and documented quality in order to meet CASTNET objectives. The QA program was developed to deliver data that are reproducible and comparable with data from other monitoring networks and laboratories. The 2012 QA program elements are documented in the CASTNET Quality Assurance Project Plan (QAPP), Revision 8.0 (AMEC, 2012d). The QAPP includes standards and policies for all components of project operation from site selection through final data reporting. The QAPP is comprised of a project overview and sections on field measurements, chemical analysis of field samples, data management, and 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 2012 data were analyzed and compared with historical data collected during the period 1990 through 2011. Comparability is supported by the use of conventional and standard units for reporting results and participation in laboratory intercomparison studies. The information in this report is supplemented by analyses that are discussed in quarterly QA reports (AMEC, 2012c; 2012f; 2012g; 2013c). 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 (ROM406/206) during 2012. The MCK131/231 sites are operated by EPA. The ROM406/206 monitors are operated independently by NPS and EPA, respectively, and ensure consistency between NPS and EPA monitoring activities. At the MCK131/231 site pair, both O₃ monitors are regulatory. At the ROM406/206 site pair, ROM406 is the regulatory O₃ monitoring site. NPS began operating a collocated O₃ monitoring site at YOS204, CA in June 2012. At the YOS404/204 site pair, YOS404 is the regulatory O₃ monitoring site. Beginning with 2012 measurements, precision of

O₃ measurements was estimated based on requirements in 40 CFR and the EPA QA Handbook for Air Pollution Measurement Systems, Volume II, Appendix D (2008b). In other words, precision of O₃ measurements was assessed based on comparisons with a transfer standard.

In addition to precision of O₃ measurements, precision of other measurement parameters based on collocated data is also presented in this report. Meteorological measurements were performed at 6 EPA, 25 NPS, and 4 BLM sites in 2012. Precision was calculated for 2012 filter pack flow and temperature data, which are two measurements that are continuing at all CASTNET sites. Accuracy was estimated for all parameters.

Summary of Data Quality Results

DQI results demonstrate that CASTNET field and laboratory processes were sufficiently monitored through QA/quality control (QC) procedures and were free of systemic bias during 2012.

Historical and 2012 precision data for filter pack parameters are considered acceptable. An analysis of filter pack bias revealed no convincing pattern of bias at either ROM406/206 or MCK131/231. O₃ precision was estimated based on requirements in 40 CFR and the EPA QA Handbook for Air Pollution Measurement Systems, Volume II, Appendix D (2008b). O₃ precision was acceptable at all but two sites. The precision of quarterly and annual flow and temperature measurements for 2012 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 2012. Completeness results for 2012 are considered excellent. Results from Environment Canada (ECAN) proficiency test studies (0100 and 0101) showed that the CASTNET laboratory performed well for the interlaboratory chemical analyses (ECAN, 2013).

Precision

Exposed Filter Concentrations

Historical (1990 through 2011) mean absolute relative percent difference (MARPD) data for filter pack concentrations for all 11 collocated site pairs operated over the history of the network and the 2012 data for the current collocated sites at MCK131/231 and ROM406/206 are provided in Figure 5-1. Precision estimates for base 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 2012 Precision Data for Atmospheric Concentrations

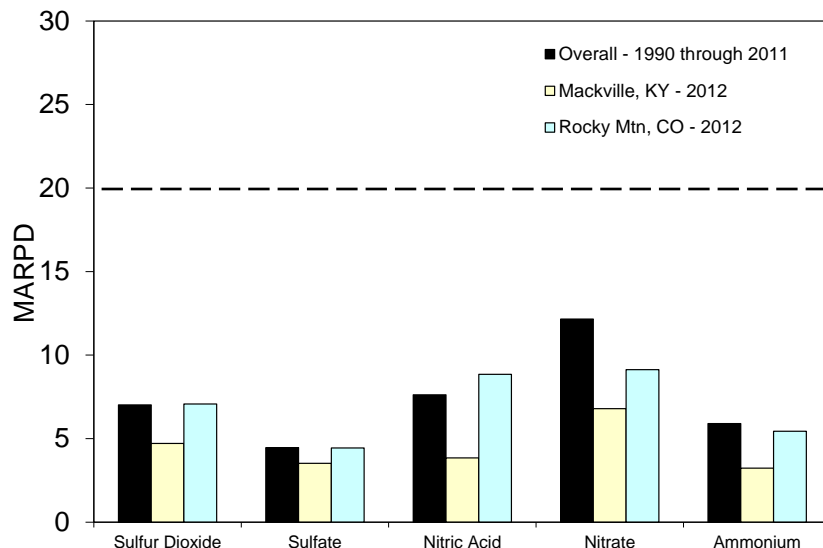


Table 5-1 Data Quality Indicator Criteria for CASTNET Laboratory Measurements

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
- ICP-AES = inductively coupled plasma-atomic emission spectrometry
- IC = ion chromatography
- mg/l = milligrams per liter
- µg/Filter = micrograms per filter
- * = as nitrogen

Values are rounded according to American Society for Testing and Materials (2008).

For more information on analytical methods and associated precision and accuracy criteria, see the CASTNET QAPP, Revision 8.0 (AMEC, 2012d)

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 2012 were within the 20 percent criterion (dashed line in Figure 5-1) for the CASTNET filter pack measurements shown in Table 5-1. The precision of historical and 2012 NO_3^- measurements was worse than for the other analytes, largely because NO_3^- concentrations include sampling artifacts.

The precision results for all parameters shown in Figure 5-1 indicate that the MARPD data for MCK131/231 were lower in 2012 (i.e., more precise) than the historical results. The 2012 results for ROM406/206 showed better precision than historical precision for NO_3^- and NH_4^+ and were about the same as historical precision for the other three parameters. 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 2012 as in 2011. The precision values for ROM406/206 showed some improvement in 2012.

Historical and 2012 precision statistics for four base cations and Cl^- are summarized in Figure 5-2. The historical and 2012 MARPD statistics for both MCK131/231 and ROM406/206 met the DQI criterion of 20 percent (dashed line). The 2012 precision results for the four base cations and Cl^- were about the same as 2011 at both collocated sites.

Table 5-2 summarizes 2012 precision results by quarter for the two sets of collocated sites. See the 2012 Quarterly Data Reports (AMEC, 2012b; 2012e; 2013b; 2013e) and Quarterly QA Reports (AMEC, 2012c; 2012f; 2012g; 2013c) for discussions of quarterly precision data.

Figure 5-2 Historical and 2012 Precision Data for Cation and Cl^- Concentrations

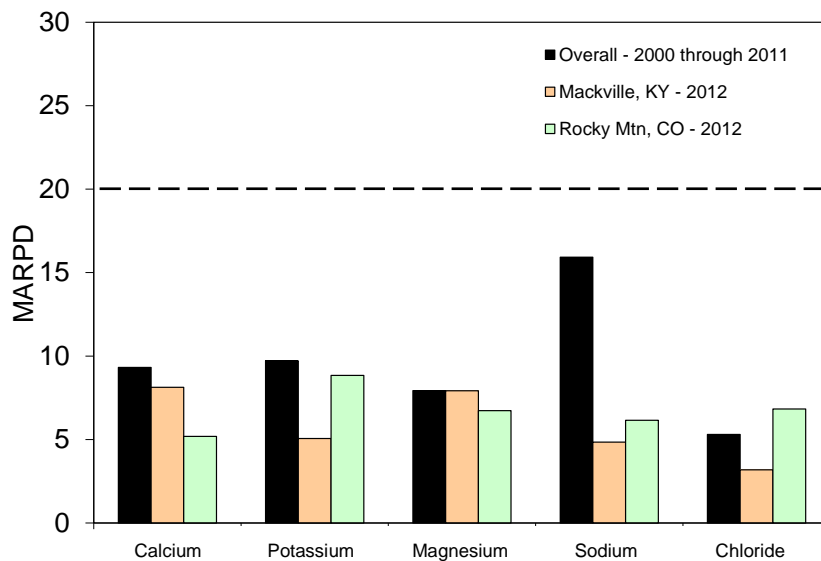


Table 5-2 Collocated Precision Results (MARPD) for 2012 Filter Pack Data by Quarter

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											
Quarter 1	3.25	5.80	2.88	9.68	8.52	5.26	4.86	3.82	3.63	3.35	4.70
Quarter 2	3.44	8.02	3.67	7.60	7.76	4.41	5.36	3.14	3.86	3.76	0.99
Quarter 3	3.05	7.77	2.59	6.11	5.98	4.15	4.84	5.08	6.81	4.67	1.98
Quarter 4	4.36	5.61	3.81	9.13	9.43	5.58	5.20	3.34	4.56	4.26	5.09
2012	3.53	6.80	3.24	8.13	7.92	4.85	5.07	3.85	4.72	4.01	3.19
ROM406/206											
Quarter 1	5.95	6.73	4.73	6.05	8.12	8.03	5.88	10.16	5.38	7.85	9.67
Quarter 2	3.84	5.73	4.25	4.43	6.05	3.87	6.94	8.23	4.06	6.15	7.73
Quarter 3	4.42	10.19	5.25	4.70	5.21	5.26	8.03	7.65	6.68	7.13	6.25
Quarter 4	3.56	13.87	7.53	5.56	7.54	7.45	14.52	9.36	12.17	7.66	3.66
2012	4.45	9.13	5.44	5.19	6.73	6.15	8.84	8.85	7.07	7.20	6.83

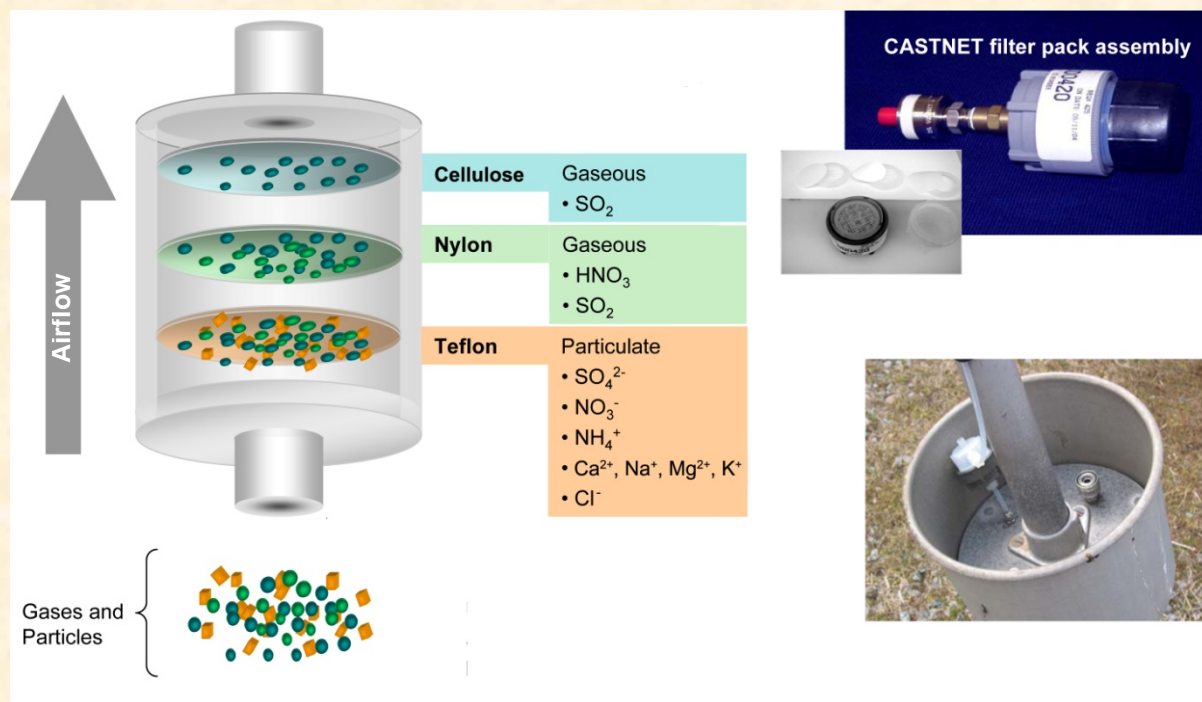


Towers at Mackville, KY (MCK131/231) and Rocky Mountain National Park, CO (ROM406/206)

Filter Pack Bias Comparison

CASTNET was designed primarily to measure trends in seasonal and annual average concentrations and to model depositions over many years. Consequently, measurement of weekly average concentrations was selected as the basic sampling strategy. Over the course of seven days, air is drawn at a controlled flow rate through an open-face, 3-stage filter pack (Figure 5a) mounted atop a 10-m tower to collect air pollutants in the form of gases and particles. CASTNET's principal measurements are SO_2 , SO_4^{2-} , HNO_3 , NO_3^- , and NH_4^+ . In addition to measurements of sulfur and nitrogen pollutants, each CASTNET site also includes measurements of base cations and Cl^- . The first stage of the filter pack encloses a Teflon filter to collect particles; the second, a nylon filter to collect gaseous HNO_3 and SO_2 ; and the third holds two potassium carbonate-impregnated cellulose filters to collect gaseous SO_2 . The filter pack is changed out each Tuesday and shipped to the analytical chemistry laboratory for analysis.

Figure 5a Three-Stage Filter Pack



Two CASTNET sites include collocated sampling systems for determining network precision. Both of the monitors at the collocated site pair in Kentucky, MCK131 and MCK231, are sponsored by EPA and have the same site operator. Each of the monitors at the collocated site pair in Colorado, ROM406 and ROM206, has a different sponsor and site operator. ROM406 is sponsored by NPS, and ROM206 is sponsored by EPA. Historical concentration data from these collocated sites were analyzed for potential bias. A result exceeding the collocated filter pack sample precision criterion listed in Table 5-1 may indicate that equipment, procedures, or site configuration have not been sufficient to prevent the introduction of bias. If such a result had been obtained, further investigation including, but not limited to, equipment, field and laboratory procedures, and site configuration would have been initiated to determine the cause and appropriate corrective action. All results from the comparison presented here were well within the listed criterion.

Two methods of data analysis were chosen for this investigation: 1) standard correlation analysis and 2) a bias calculation from 40 CFR Part 58 Appendix A, Section 4.1.3 (EPA, 2012a), based on the upper bound on the mean absolute value of the percent differences (%D) of each collocated pair as described in Equation 5a.

Equation 5a

$$|AB| = AB + t_{0.95, n-1} * \frac{AS}{\sqrt{n}}$$

where n is the number of single point checks being aggregated; $t_{0.95, n-1}$ is the 95th quantile of a t-distribution with $n - 1$ degrees of freedom; the quantity AB is the mean of the absolute values of the d_i and is calculated using Equation 5b.

Equation 5b

$$AB = \frac{1}{n} * \sum_{i=1}^n |d_i|$$

where $d_i = (\text{measured concentration} - \text{audit concentration})/\text{audit concentration}$, and the audit concentrations were measured at MCK131 or ROM406 (i.e., the primary of the collected pair), and the quantity AS is the standard deviation of the absolute value of the d_i and is calculated using Equation 5c.

Equation 5c

$$AS = \sqrt{\frac{n \sum_{i=1}^n |d_i|^2 - \left(\sum_{i=1}^n |d_i| \right)^2}{n(n-1)}}$$

Since the bias statistic calculated in Equation 5a uses absolute values, it does not have a negative or positive bias associated with it. A sign is designated by rank ordering the percent differences of the collocated pair. The 75th and 25th percentiles are calculated, and the absolute bias upper bound is flagged as positive if both percentiles are positive and flagged as negative if both percentiles are negative. The absolute bias upper bound is not flagged if the percentiles are different signs.

The bias of particulate SO_4^{2-} and NO_3^- was investigated, along with gaseous HNO_3 , due to their importance to the project. However, because SO_4^{2-} concentrations differ by an order of magnitude at the two monitoring locations, Ca^{2+} was selected to provide a stable on-filter particulate that showed similar concentrations at both locations. Data analyses were performed for data collected from July 2001 through December 2012 using only valid reported values above their established reporting limits.

Summary

Particulate SO₄²⁻ correlation (Figure 5b) at MCK131/231 showed an R² of 0.991 and slope of 1.012 compared with R² and slope of 0.930 and 0.923, respectively, for ROM406/206. The intercepts were similar at 0.029 and 0.021, respectively. Both sites showed signed biases (Figure 5c) with MCK131/231 at -3.39 percent and ROM406/206 at +7.28 percent.

Figure 5b Correlation Analysis for SO₄²⁻

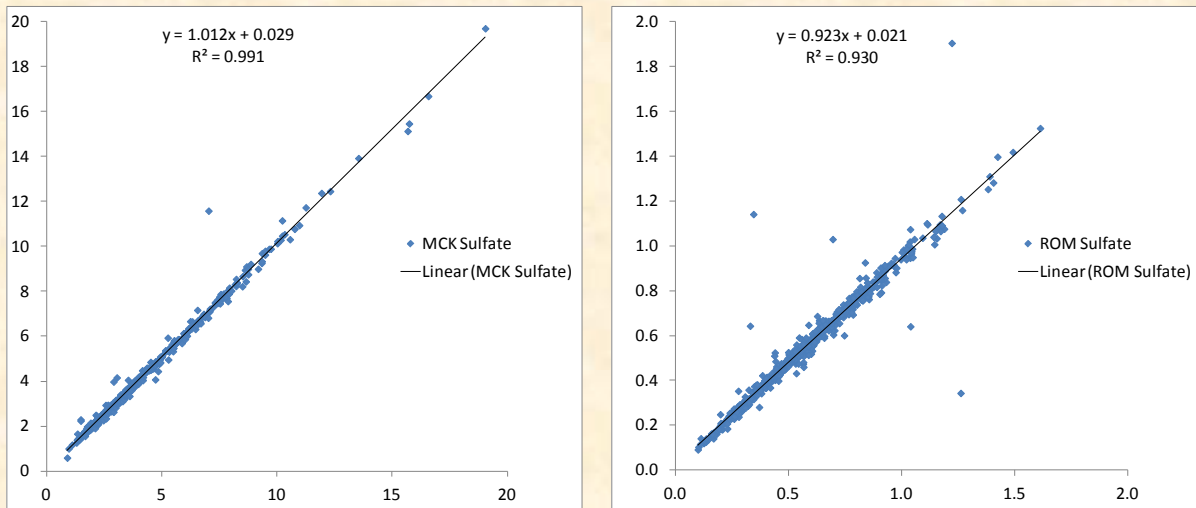
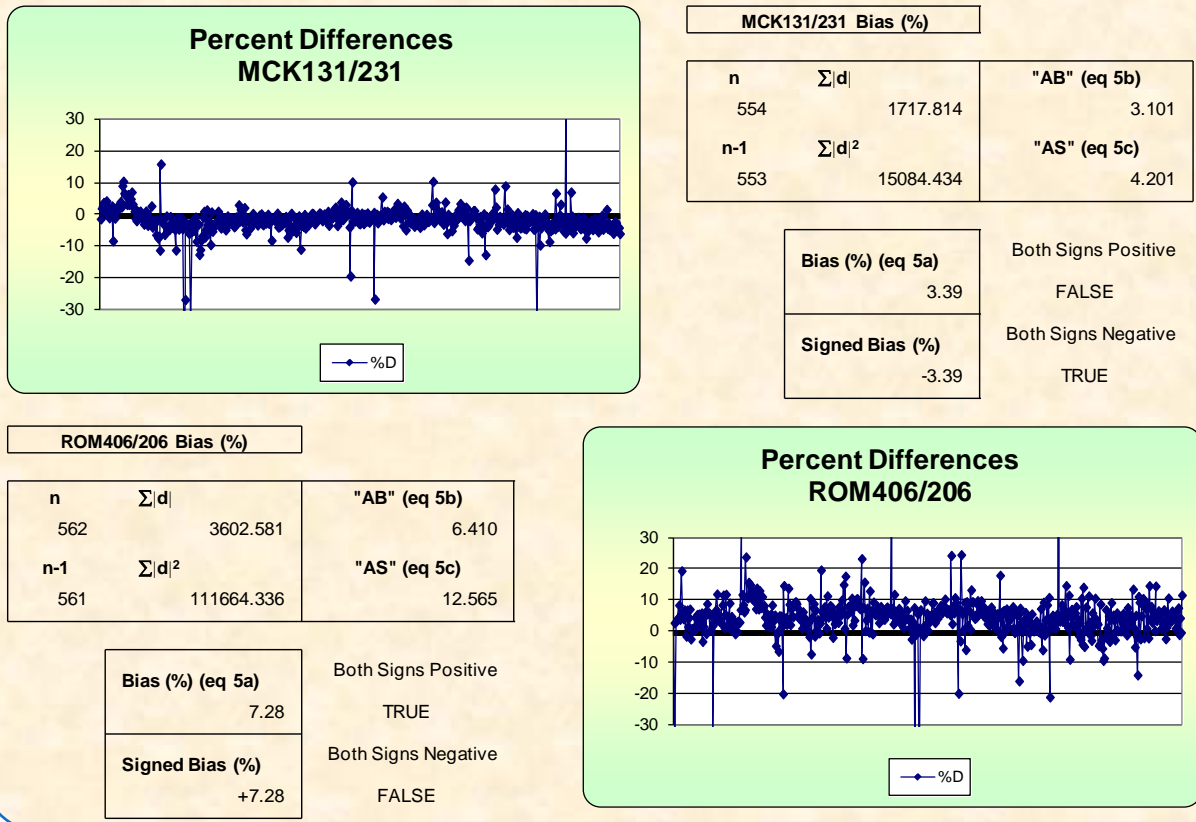


Figure 5c Bias Analysis for SO₄²⁻



Particulate NO₃ correlation (Figure 5d) at MCK131/231 showed an R² of 0.983 and slope of 1.030 while R² for ROM406/206 was 0.947 and the slope 0.915. Intercepts were again similar at 0.014 and 0.010, respectively. There was no signed bias (Figure 5e) at either site with MCK131/231 showing 11.06 percent and ROM406/206 showing 12.49 percent.

Figure 5d Correlation Analysis for NO₃

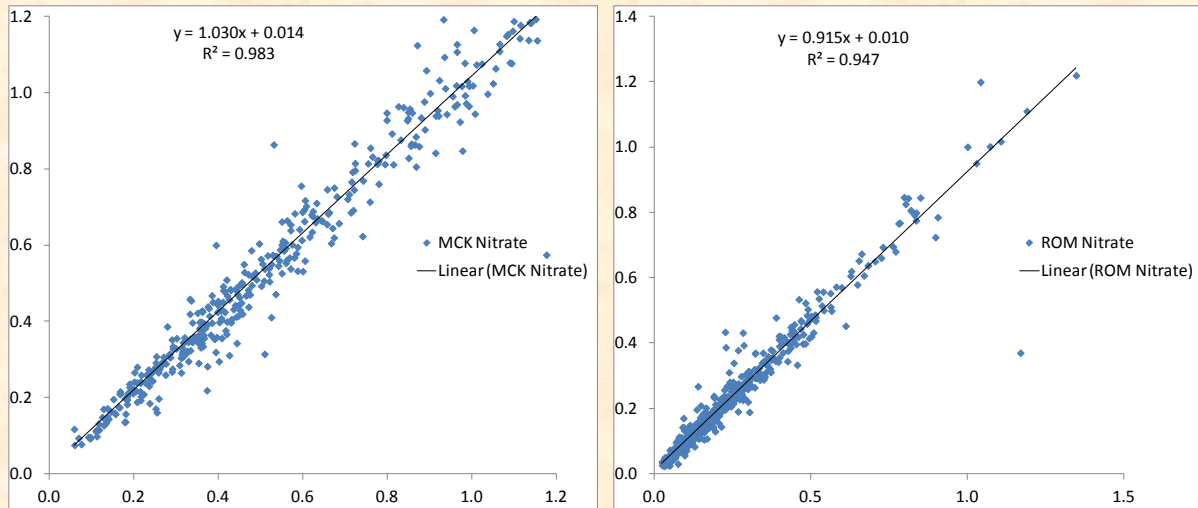
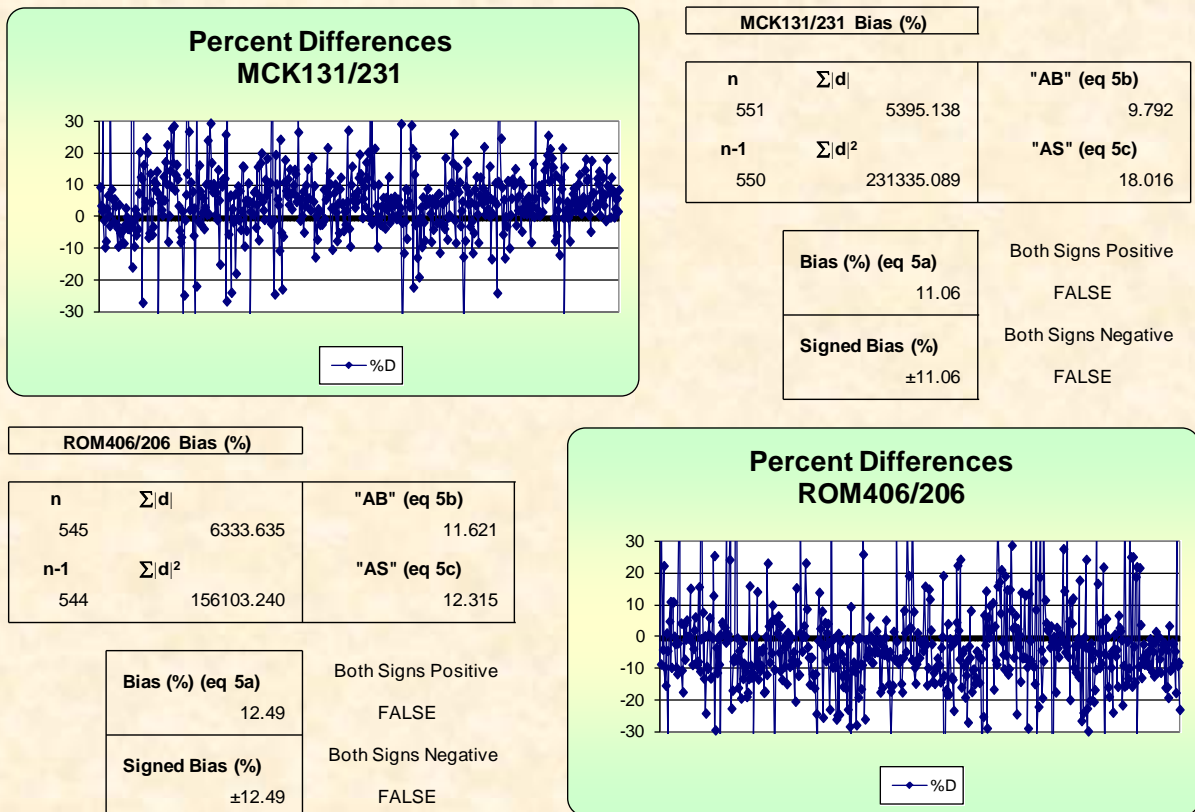


Figure 5e Bias Analysis for NO₃



The R^2 , slope, and intercept values for particulate Ca^{2+} (Figure 5f) were 0.957, 1.058, and 0.001 for MCK131/231 and 0.969, 0.938, and 0.002 for ROM406/206. There was no signed bias (Figure 5g) for ROM406/206 at 15.46 percent, but MCK131/231 showed a signed bias at -8.94 percent.

Figure 5f Correlation Analysis for Ca^{2+}

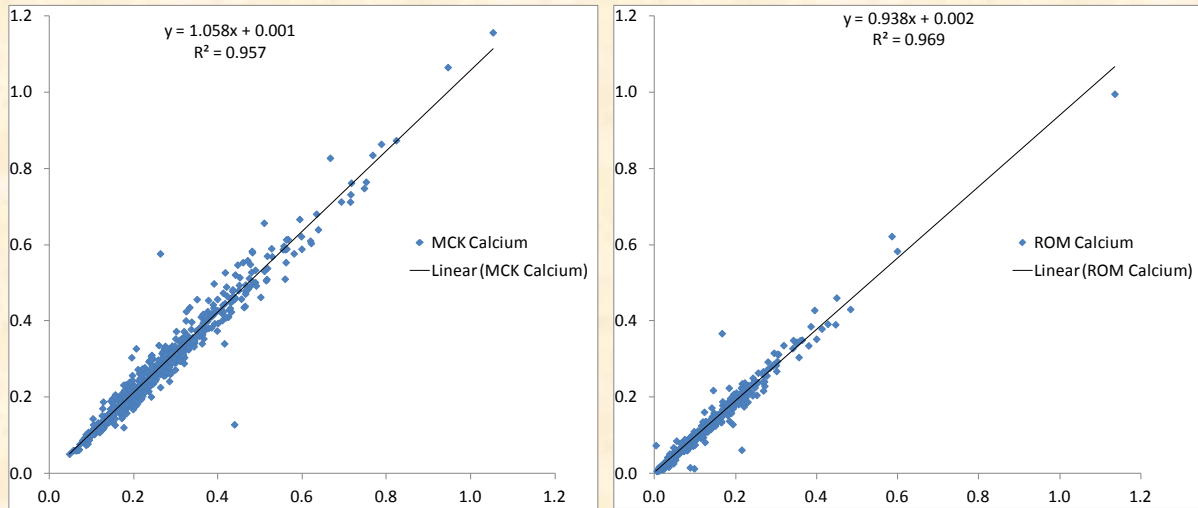
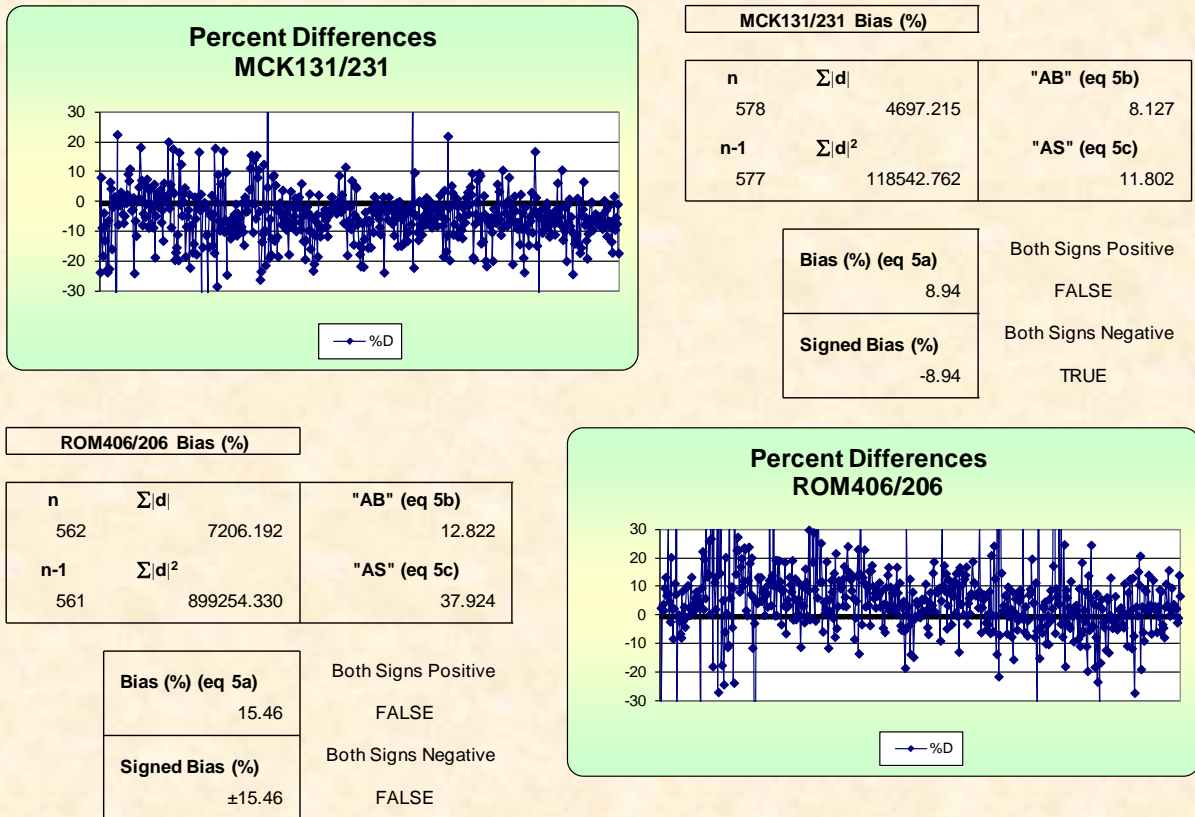


Figure 5g Bias Analysis for Ca^{2+}



Finally, results for gaseous HNO₃ (Figure 5h) for R², slope, and intercept at MCK131/231 were 0.980, 0.994, and 0.030 while ROM406/206 showed 0.950, 0.969, and 0.001. Neither site showed a signed bias (Figure 5i) with unsigned values of 4.82 percent and 8.22 percent, respectively. Overall, these analyses reveal no convincing pattern showing filter pack sampling bias at either site.

Figure 5h Correlation Analysis for HNO₃

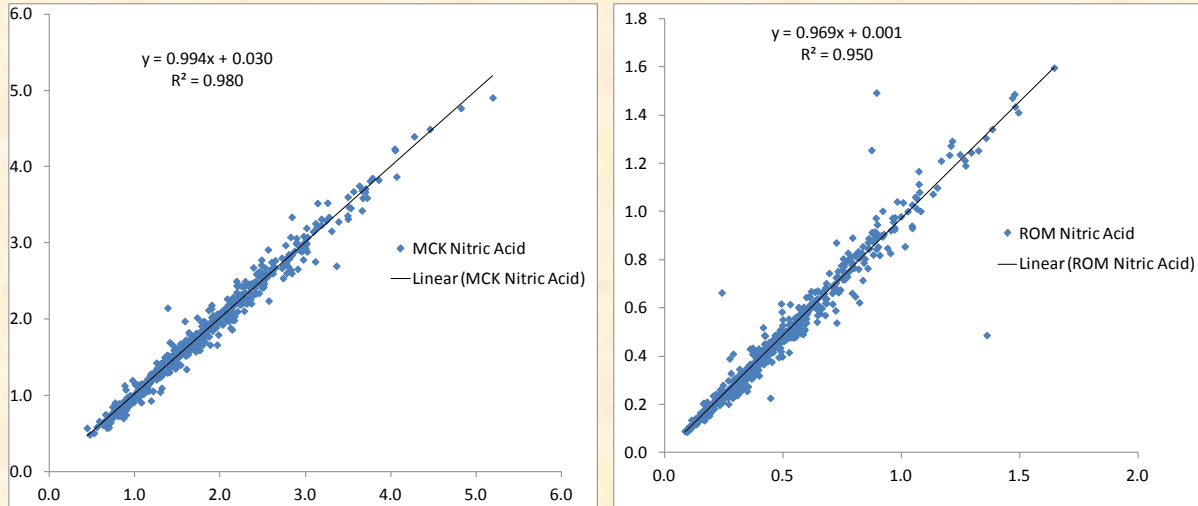
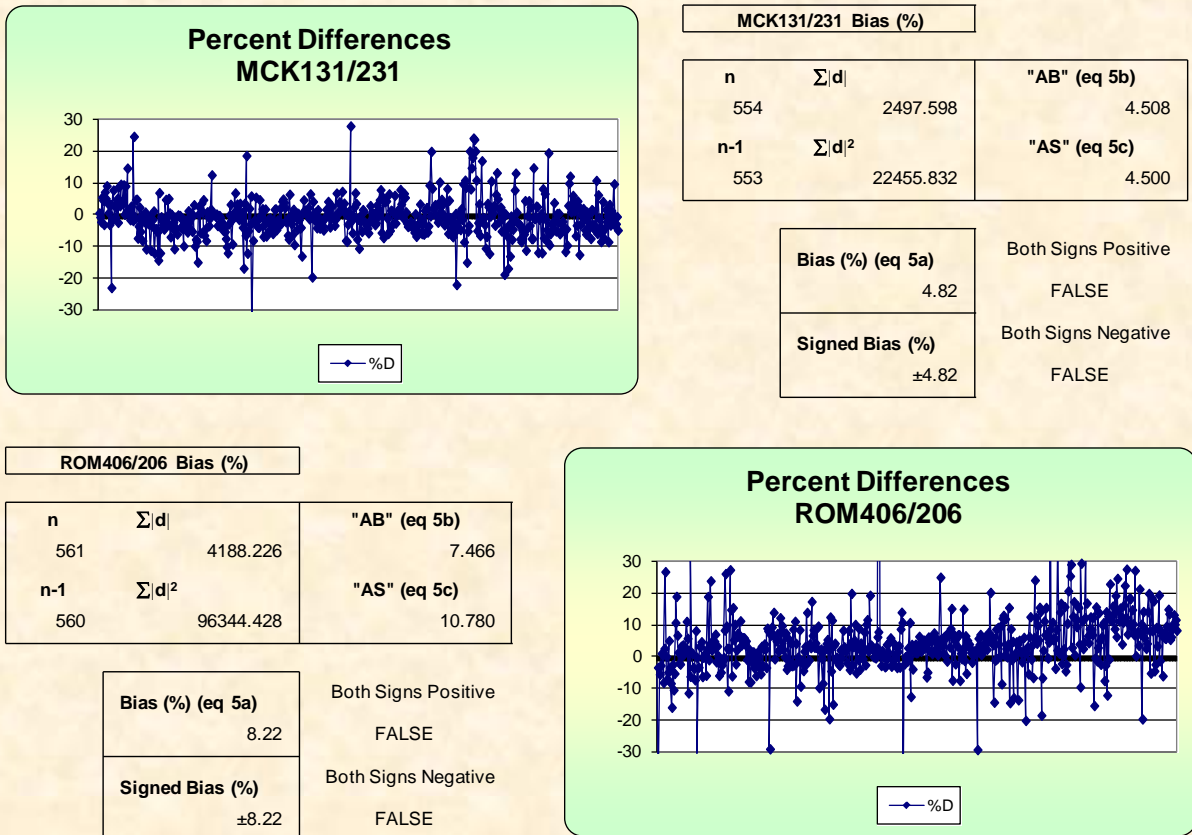
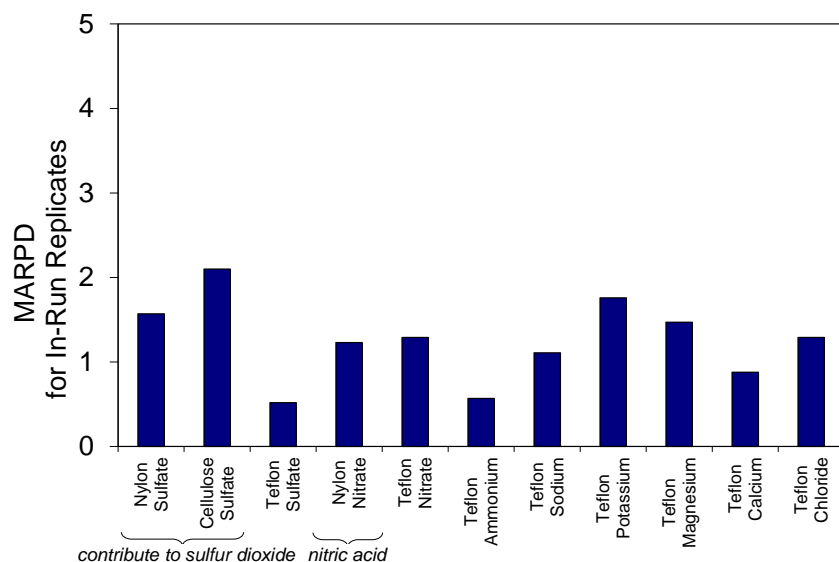


Figure 5i Bias Analysis for HNO₃



The 2012 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 criteria listed in Table 5-1.

Figure 5-3 Precision Results for Laboratory Replicate Samples (2012)



Ozone Concentrations

O₃ data quality was evaluated in terms of AQS protocol O₃ QC criteria (i.e., precision per 40 CFR Part 58). AQS protocol O₃ precision was estimated based on the acceptance criteria set forth in 40 CFR Part 58 Appendix A (EPA, 2012a). The O₃ instrument was challenged daily with a known O₃ concentration of 90 ppb. The acceptance criterion is an upper 90 percent confidence limit (CL) for the coefficient variation (CV) of 7 percent, i.e., 90 percent CL CV ≤ 7 percent. The 2012 results for EPA-sponsored sites are presented in Table 5-3, which provides the 90 percent CL and the number of values used to calculate it. O₃ precision data collected at only two EPA-sponsored sites, ALC188, TX and SUM156, FL, did not meet the criterion. Ambient data were not affected in either case. Both problems were isolated to the pneumatic system used to introduce known O₃ concentrations.

Table 5-3 Single Point Precision for 2012 O₃ Measurements at EPA-Sponsored Sites

Site	Precision		Site	Precision		Site	Precision	
	Single Point QC Count	Single Point QC CL		Single Point QC Count	Single Point QC CL		Single Point QC Count	Single Point QC CL
ABT147, CT	358	0.06	CVL151, MS	357	0.17	PED108, VA	367	0.05
ALC188, TX	353	41.83 ^a	DCP114, OH	370	3.99	PND165, WY	304	0.06
ALH157, IL	341	0.04	ESP127, TN	372	0.37	PNF126, NC	366	0.03
ANA115, MI	365	0.54	GAS153, GA	363	0.46	PRK134, WI	338	0.27
ARE128, PA	356	1.88	GTH161, CO	309	0.57	PSU106, PA	362	0.04
ASH135, ME	366	0.11	HOW132, ME	294	0.09	OAK172, OH	335	0.73
BEL116, MD	324	1.06	HOX148, MI	350	0.12	ROM206, CO	364	0.23
BFT142, NC	313	0.60	HWF187, NY	368	0.18	SAL133, IN	367	0.07
BVL130, IL	376	1.16	IRL141, FL	369	0.10	SAN189, NE	366	1.17
BWR139, MD	368	4.64	KEF112, PA	368	0.05	SND152, AL	365	0.04
CAD150, AR	371	0.52	KNZ184, KS	368	0.27	SPD111, TN	368	0.14
CDR119, WV	355	0.06	LRL117, PA	318	0.89	STK138, IL	338	0.47
CDZ171, KY	364	0.67	MCK131, KY	368	0.08	SUM156, FL	343	21.14 ^b
CKT136, KY	349	0.06	MCK231, KY	371	0.16	UVL124, MI	359	0.09
CND125, NC	364	1.10	MKG113, PA	356	0.93	VIN140, IN	371	4.14
CNT169, WY	343	2.28	OXF122, OH	351	0.11	VPI120, VA	330	0.37
COW137, NC	360	0.09	PAL190, TX	364	6.14	WSP144, NJ	353	0.09
CTH110, NY	343	0.05	PAR107, WV	293	0.08	WST109, NH	363	0.48

Note: a There were problems with the zero air system.
 b Transfer standard tubing was improperly connected.



Basin, WY (BAS601)

Table 5-4 Data Quality Indicator Criteria for CASTNET Field Measurements

Measurement		Criteria ¹	
Parameter ²	Method	Precision	Accuracy
Filter pack flow	Mass flow controller	± 10%	± 5%
Ozone ³	UV absorbance	All points within ± 2% of full scale of best fit straight line Linearity error < 5%	
Wind speed	Anemometer	± 0.5 m/s	The greater of ± 0.5 m/s for winds < 5 m/s or ± 5% for winds ≥ 5 m/s
Wind direction	Wind vane	± 5°	± 5°
Sigma theta	Wind vane	Undefined	Undefined
Ambient temperature	Platinum RTD	± 1.0°C	± 0.5°C
Delta temperature	Platinum RTD	± 0.5°C	± 0.5°C
Relative humidity	Thin film capacitor	± 10% (of full scale)	± 10%
Precipitation	Tipping bucket rain gauge	± 10% (of reading)	± 0.05 inch ⁴
Solar radiation	Pyranometer	± 10% (of reading taken at local noon)	± 10%
Surface wetness	Conductivity bridge	Undefined	Undefined

Note: °C = degrees Celsius
m/s = meters per second
RTD = resistance-temperature device
UV = ultraviolet

¹ Precision criteria apply to collocated instruments, and accuracy criteria apply to calibration of instruments. Collocated precision criteria do not apply to AQS-protocol ozone measurements.

² As of the end of 2012, meteorological parameters were only measured at 6 EPA-sponsored sites, 25 NPS-sponsored sites, and 4 BLM-sponsored sites.

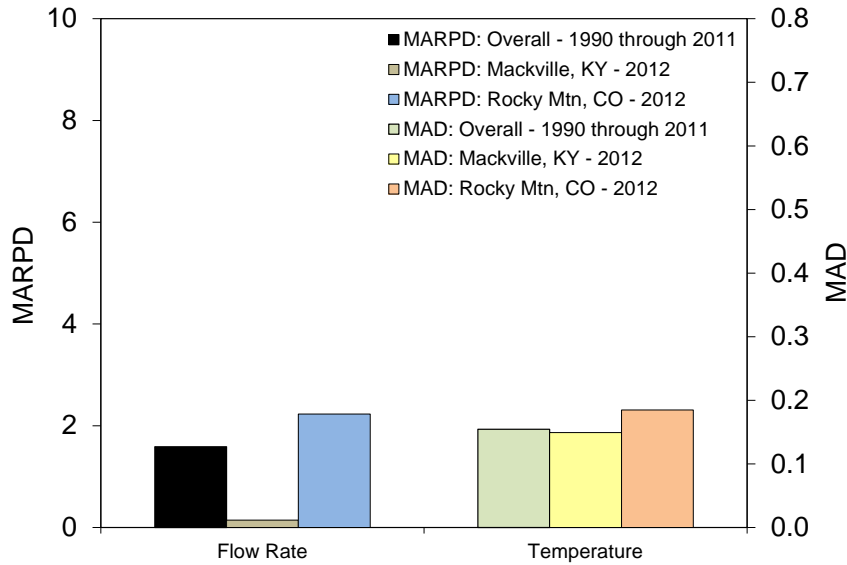
³ Ozone is measured at 83 CASTNET sites.

⁴ For target value of 0.50 inch

Continuous Measurements

Precision criteria for the continuous measurements are listed in Table 5-4. Because continuous measurements, excluding O₃, flow, and temperature, were discontinued at most EPA-sponsored sites at the end of 2010, including MCK131, MCK231, and ROM206, precision estimates were made only for flow and temperature data. Figure 5-4 provides precision results for flow and temperature for historical data (1990 through 2011) at all collocated site pairs and 2012 precision statistics at the two current collocated site pairs. Precision was calculated in terms of the MARPD for flow and mean absolute difference (MAD) for temperature. All historical and 2012 precision results met the DQI criteria. Table 5-5 gives precision data by quarter for 2012 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 5-4 Historical and 2012 Precision Data for Flow and Temperature Measurements



Note: The left y-axis indicates MARPD for flow (Table 5-5), and the right y-axis indicates MAD for temperature (Table 5-5).

Table 5-5 Collocated Precision Results for 2012 Continuous Measurements by Quarter

Sampling Period	MARPD	MAD
	Flow Rate	Temperature
MCK131/231, KY		
Quarter 1	0.17	0.15
Quarter 2	0.14	0.13
Quarter 3	0.13	0.14
Quarter 4	0.13	0.17
2012	0.14	0.15
ROM406/206, CO		
Quarter 1	1.09	0.19
Quarter 2	3.88	0.16
Quarter 3	3.85	0.22
Quarter 4	0.11	0.17
2012	2.23	0.18

Accuracy

Laboratory Filter Concentrations

Accuracy of laboratory measurements is assessed through the analysis of reference and continuing calibration verification (CCV) samples. Reference samples and CCV are procured from independent suppliers and are traceable to NIST. Reference samples are analyzed at the beginning and end of each analytical batch to verify the accuracy and stability of the calibration curve. The target value of the CCV solution is set to the midrange of the calibration curve. The CCV 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 2012. The table shows that the DQI goals (see Table 5-1) were met in 2012.

Table 5-6 Filter Pack Quality Control Summary for 2012

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⁻	99.07	1.48	129	100.80	1.38	644	0.52	0.69	276
	NO ₃ ⁻	101.09	1.43	129	100.75	1.32	644	1.29	1.51	306
	NH ₄ ⁺	101.92	1.75	128	100.30	1.42	642	0.57	0.64	338
	Ca ²⁺	99.13	1.97	129	100.57	0.93	647	0.88	0.88	300
	Mg ²⁺	102.91	1.52	129	100.01	0.84	647	1.47	1.52	300
	Na ⁺	100.32	1.29	129	100.01	0.81	647	1.11	1.21	300
	K ⁺	100.77	2.03	129	100.00	0.66	647	1.76	2.12	300
	Cl ⁻	102.09	1.56	129	101.90	1.30	644	1.29	1.41	270
Nylon	SO ₄ ²⁻	99.48	1.25	122	100.65	1.42	609	1.57	1.65	259
	NO ₃ ⁻	101.13	1.25	122	100.42	1.25	609	1.23	1.20	293
Cellulose	SO ₄ ²⁻	98.18	1.19	144	98.85	1.42	623	2.10	2.90	305

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

CASTNET sites are calibrated every six months with NIST-traceable standards. Table 5-7 presents field accuracy results for 2012 based on instrument challenges performed at EPA-sponsored sites during site calibration visits. The calibration results were evaluated using the accuracy criteria listed in Table 5-4. Each parameter was within its criterion with at least 90 percent frequency with the exception of wind speed less than 5 meters per second (m/s) at 87.5 percent, wind speed greater than or equal to 5 m/s at 87.5 percent, wind direction south at 88.9 percent, and solar radiation at 88.9 percent. However, these results did not adversely affect data collection because data are not considered invalid unless the calibration criterion is exceeded by more than two times the criterion. Using the two times standard, the four parameters passed with 100.0 percent frequency. The 2012 results for flow rate accuracy were better than for 2011.

Table 5-7 Accuracy Results for 2012 Field Measurements

Parameter*	Percent Within Criterion	Parameter	Percent Within Criterion
Flow Rate	97.3 percent	Delta Temperature (0°C)	100.0 percent
*Wind Speed < 5 m/s	87.5 percent	Delta Temperature (ambient)	100.0 percent
*Wind Speed ≥ 5 m/s	87.5 percent	Relative Humidity	100.0 percent
Wind Direction North	100.0 percent	Precipitation	100.0 percent
*Wind Direction South	88.9 percent	*Solar Radiation	88.9 percent
Temperature (0°C)	99.1 percent	Wetness (w/in 0.5 volts)	100.0 percent
Temperature (ambient)	99.1 percent		

Note: °C = degrees Celsius

m/s= meters per second

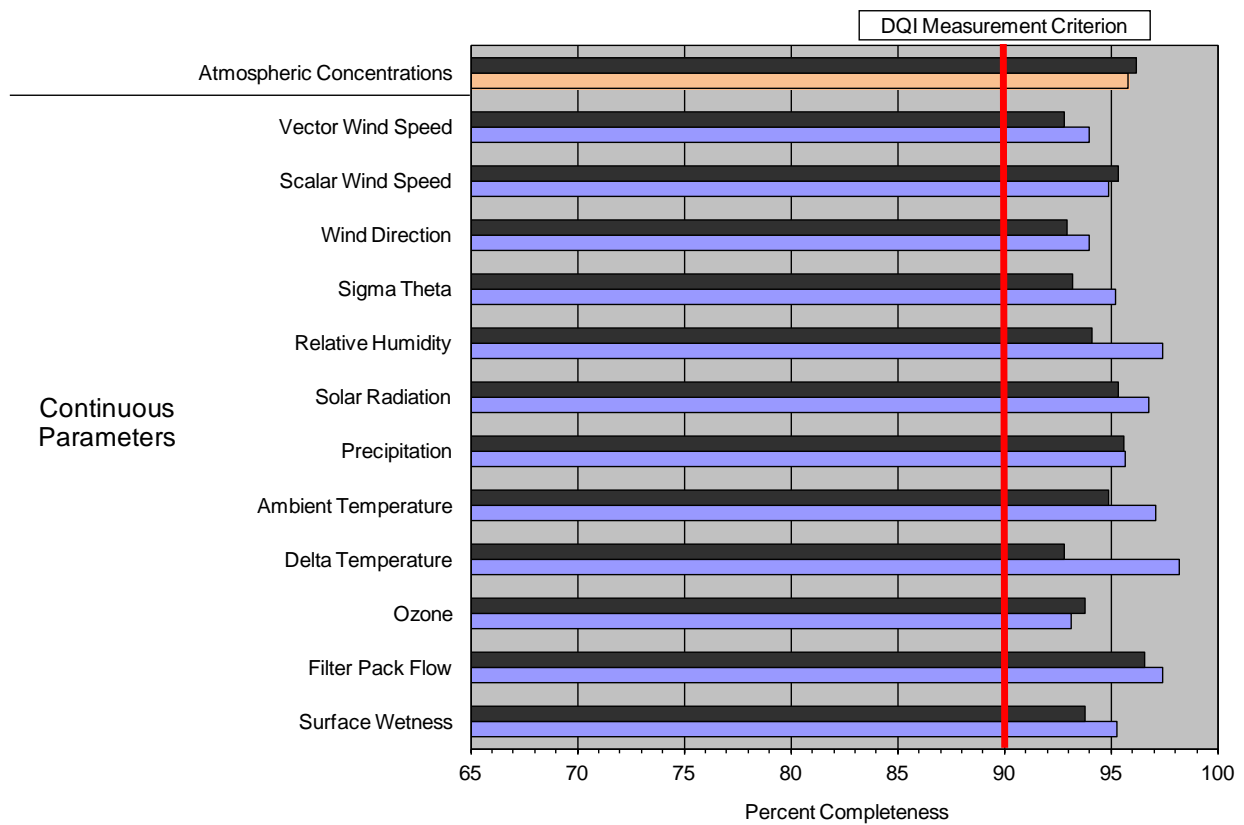
* = Results are based on all EPA-sponsored sites for flow rate and temperature. Results for all other parameters, including delta temperature, are based on the six EPA-sponsored sites that measured meteorological parameters during 2012.

† = Per CASTNET project protocols, data are flagged as “suspect” (S) but still considered valid if the calibration criterion is not exceeded by more than its magnitude (i.e., if within 2x the criterion). All calibration failures reported in 2012 for the indicated parameters were within 2x the criterion.

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 2012, all the parameters listed in Figure 5-5, except delta temperature and wetness, were measured at the NPS-sponsored sites, BLM-sponsored sites, and the six EPA-sponsored sites with ongoing meteorological measurements. Ozone concentrations were measured at 83 of 91 monitoring sites. Atmospheric concentrations, filter pack flow, and ambient temperature were measured at all sites. Delta temperature was measured at five out of six EPA sites plus the NPS sites at Acadia, ME (ACA416); GRS420, TN; and ROM406, CO. Surface wetness was measured at the six EPA sites plus ACA416, ME. Figure 5-5 presents historical (black) and 2012 completeness data for all sites for measured filter concentrations and continuous measurements. The figure shows that the 2012 direct measurements met the 90 percent completeness goal, and seven meteorological measurements plus filter pack flow exceeded 95 percent. Atmospheric concentrations also exceeded 95 percent.

Figure 5-5 Historical and 2012 Percent Completeness of Measurements (black bars are 1990–2011)



Palo Duro Canyon State Park, TX (PAL190)

Results for 2012 Environment Canada Proficiency Testing

During 2012, the AMEC CASTNET laboratory participated in the ECAN Proficiency Testing Program for Inorganic Environmental Substances (<http://www.ec.gc.ca/inre-nwri/default.asp?lang=En&n=7A20877C-1>). Specifically, the CASTNET laboratory is one of 35 laboratories that participated in the 2012 Rain and Soft Waters round robin studies, which consist of natural waters supplied by the National Laboratory for Environmental Testing. The CASTNET laboratory receives 10 samples of mixed rain and Canadian Shield waters for chemical analysis from ECAN every six months. The laboratory reported the eight CASTNET parameters for samples in two studies (study codes 0100 and 0101) during 2012.

The results reported by the 35 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 ($R-\sigma$) obtained from the ISO 13528 computation (ISO, 2005). Samples within 2 standard deviations of the assigned (median laboratory) value are not flagged; samples between 2 and 3 standard deviations are given a warning flag; and samples greater than 3 standard deviations from the assigned value are flagged as above the action limit (remedial action is required). Laboratory results are considered systematically biased when individual parameters are ranked by the Youden analysis to be consistently and significantly higher or lower than the assigned value without regard to flagged results.

The CASTNET laboratory's 2012 ECAN results for the eight CASTNET parameters are presented in Table 5a. All eight parameters received the highest possible rating of "Ideal" indicating an unbiased score in study 0100. One of the 10 individual results for ammonia was flagged "warning high" for study 0101, indicating that the flagged result was between 2 and 3 $R-\sigma$ from its assigned value. Investigation by the laboratory revealed the root cause to be incorrect significant figures used in reporting laboratory results. The laboratory had been reporting results to two significant figures when three significant figures were required, resulting in inappropriate rounding of the final result. If three significant figures had been used, the data would have passed with no bias flags. Corrective action was implemented to correct this on the forms used to report ECAN study data.

Table 5a AMEC Results for Studies 0100 and 0101

Test Parameter	Analytical Method	Reference Method	Laboratory Performance Rating	
			Study 0100 Summer 2012	Study 0101 Winter 2012
Ammonia	AC	EPA Method 350.1	Ideal	Biased High
Calcium	ICP-AES	EPA Method 6010	Ideal	Ideal
Chloride	IC	EPA Method 300.0	Ideal	Ideal
Magnesium	ICP-AES	EPA Method 6010	Ideal	Ideal
Nitrate + Nitrite	IC	EPA Method 300.0	Ideal	Ideal
Potassium	ICP-AES	EPA Method 6010	Ideal	Ideal
Sodium	ICP-AES	EPA Method 6010	Ideal	Ideal
Sulfate	IC	EPA Method 300.0	Ideal	Ideal

Note: AC = automated colorimetry
 ICP-AES = inductively coupled plasma-atomic emission spectrometry
 IC = ion chromatography

Source: Environment Canada (2013)

The overall laboratory performance rating was “Very Good” for both studies. The overall laboratory rating indicates a percent score as described in Table 5b. The 5-year historical laboratory rating is listed by ECAN as “Very Good.”

Table 5b Laboratory Performance Rating

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

*Sum of Parameters Biased & Results Flagged

Source: Environment Canada (2013)



Egbert, Ontario, Canada (EGB181)

References

- AMEC Environment & Infrastructure, Inc. (AMEC). 2014. Clean Air Status and Trends Network (CASTNET) Third Quarter 2013 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). 2013a. Clean Air Status and Trends Network (CASTNET) 2011 Annual 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). 2013b. Clean Air Status and Trends Network (CASTNET) Fourth Quarter 2012 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). 2013c. Clean Air Status and Trends Network (CASTNET) Fourth Quarter 2012 Quality Assurance Report with 2012 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). 2013d. Clean Air Status and Trends Network (CASTNET) Second Quarter 2013 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). 2013e. Clean Air Status and Trends Network (CASTNET) Third Quarter 2012 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). 2012a. Clean Air Status and Trends Network (CASTNET) 2010 Annual 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.

References continued

AMEC Environment & Infrastructure, Inc. (AMEC). 2012b. Clean Air Status and Trends Network (CASTNET) First Quarter 2012 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). 2012c. Clean Air Status and Trends Network (CASTNET) First Quarter 2012 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). 2012d. Clean Air Status and Trends Network (CASTNET) Quality Assurance Project Plan (QAPP) Revision 8.0. 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). 2012e. Clean Air Status and Trends Network (CASTNET) Second Quarter 2012 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). 2012f. Clean Air Status and Trends Network (CASTNET) Second Quarter 2012 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). 2012g. Clean Air Status and Trends Network (CASTNET) Third Quarter 2012 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.

References continued

- American Society for Testing and Materials (ASTM). 2008. Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications E 29-08.
- 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.
- 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/>
- Byun, D. and Schere, K.L., 2006. Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system. *Applied Mechanics Reviews*, 59: 51-77.
- Centers for Disease Control and Prevention (CDC). 2013. Public Health Air Surveillance Evaluation (PHASE) Project. EPA/NOAA Community Multiscale Air Quality Model. <http://www.cdc.gov/nceh/tracking/pdfs/phase.pdf> (accessed July 2013).
- Environment Canada (ECAN) Water Science and Technology Directorate. 2013. Rain and Soft Waters PT Studies 0100 and 0101 Report. Proficiency Testing Program, Burlington, Ontario, Canada. Prepared for AMEC Environment & Infrastructure, Inc.
- 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).
- Lefohn, A.S. and Runeckles, V.C. 1987. Establishing a Standard to Protect Vegetation - Ozone Exposure/Dose Considerations. *Atmos. Environ.*, 21:561-568.
- National Climatic Data Center. 2012. State of the Climate, Wildfires, September 2011. <http://www.ncdc.noaa.gov/sotc/fire/2011/9> (accessed January 2012).

References continued

- National Crop Loss Assessment Network (NCLAN). 2013. Ozone and Crop Plants, <http://people.oregonstate.edu/~muirp/ozeffect.htm> (accessed December 2013)
- National Oceanic and Atmospheric Administration. 2012. Texas, New Mexico, Arizona Wildfires, Spring-Fall 2011. <http://www.noaa.gov/extreme2011/wildfire.html> (accessed January 2012).
- 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.
- Pitchford, M.L., Tombach, I., Barna, M., Gebhart, K.A., Green, M.C., Knipping, E., Kumar, N., Malm, W.C., Pun, B., Schitel, B.A., and Seigneur, C. 2004. Big Bend Regional Aerosol and Visibility Observational Study. Final Report. <http://vista.cira.colostate.edu/improve/studies/BRAVO/reports/FinalReport/BRAVO/Cover.pdf>
- Rogers, C. M., Beachley, G., and Mishoe, K.P. 2012. In-Canopy Measurements of Ozone and Other Gases and Particles at Maine's Howland Research Forest. Presentations from the 2012 NADP Annual Meeting & Symposia. <http://nadp.sws.uiuc.edu/conf/2012/>.
- Talbot, R., Mao, H., and Sive, B. 2005. Diurnal Characteristics of Surface Level O₃ and other Important Trace Gases in New England, *J. Geophys. Res.*, 110, D09307, doi:10.1029/2004JD005449.
- U.S. Environmental Protection Agency (EPA). 2013a. 2011 National Emissions Inventory System (NEI) Version 1. <http://www.epa.gov/ttn/chief/net/2011inventory.html>. Accessed February 2014.
- U.S. Environmental Protection Agency (EPA). 2013b. Clean Air Interstate Rule, Acid Rain Program and Former NO_x Budget Trading Program, 2012 Progress Reports: SO₂ and NO_x Emissions, Compliance, and Market Analyses Report <http://www.epa.gov/airmarkets/progress/ARPCAIR12.html>
- U.S. Environmental Protection Agency (EPA). 2013c. Clean Air Interstate Rule, Acid Rain Program and Former NO_x Budget Trading Program, 2011 Progress Reports: Environmental and Health Results. http://www.epa.gov/airmarkets/progress/ARPCAIR11_02.html (accessed June 2013).

References continued

- U.S. Environmental Protection Agency (EPA). 2013d. Total Deposition Estimates Using a Hybrid Approach, Total Deposition Project, v. 2013.02. <ftp://ftp.epa.gov/castnet/tdep>. Accessed December 2013.
- U.S. Environmental Protection Agency (EPA). 2013e. Treatment of Data Influenced by Exceptional Events, <http://www.epa.gov/ttn/analysis/exevents.htm> (accessed December 2013)
- U.S. Environmental Protection Agency (EPA). 2012a. 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). 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. United States-Mexico Border 2020 Environmental Program. <http://www2.epa.gov/border2020>. (accessed March 2013).
- U.S. Environmental Protection Agency (EPA). 2011. Policy Guidance and Technical Memoranda. <http://www.epa.gov/ttn/amtic/cpreldoc.html>. (accessed March 2013).
- U.S. Environmental Protection Agency (EPA). 2010. 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

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
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 MLJ 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
NIC001	Nicks Lake	11/20/12	43.6806	74.98917	525	•	+4	NY29	Forested	Rolling	N	NYSDEC
WFM105	Whiteface Mountain	11/20/12	44.39	73.86	570	•	+4	NY98	Forested	Complex	N	NYSERDA

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 MLJs 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

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 MLJ ³	Sponsor
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
Vermont												
UND002	Underhill	11/13/12	44.52839	72.8688	399	•	• ⁴	VT99	Forested	Complex	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

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 MLJ 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
BAS601	Basin	11/06/12	44.28	108.0411	1242	•	•	MT00	Prairie	Rolling	M	BLM
NEC602	Newcastle	11/07/12	43.87306	104.1919	1468	•	•	WY99	Prairie	Rolling	M	BLM
BUF603	Buffalo	11/06/12	44.1442	106.1089	1324	•	• ⁴	WY99	Prairie	Rolling	M	BLM
SHE604	Sheridan	11/06/12	44.93	106.85	1115	•	• ⁴	MT00	Prairie	Rolling	M	BLM

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

- Teflon = SO₄²⁻, NO₃⁻, NH₄⁺, Cl⁻, K⁺, Na⁺, Mg²⁺, Ca²⁺
- Nylon = SO₄²⁻, NO₃⁻ (reported as HNO₃)
- Cellulose = SO₄²⁻ (reported as SO₂)

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. O₃ not measured.

5. Solar-powered site.

- Indicates current monitoring.

- BLM = Bureau of Land Management
- EPA = U.S. Environmental Protection Agency
- NPS = National Park Service
- NYSDEC = New York State Development of Environmental Conservation
- NYSERDA = New York State Energy Research and Development Authority

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
BART	Best Available Retrofit Technology
BBNP	Big Bend National Park, TX
BLM	Bureau of Land Management
BRAVO	Big Bend Regional Aerosol and Visibility Observational Study
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
CDC	Centers for Disease Control
CL	confidence limit
Cl ⁻	particulate chloride ion
CLAD	Critical Loads of Atmospheric Deposition science committee
CLmaxS	maximum critical load of sulfur
CMAQ	Community Multiscale Air Quality Modeling System
CLminN	nitrogen removed by an ecosystem
CO	carbon monoxide
CSN	Chemical Speciation Network
CV	coefficient variation
%D	percent difference
DM8A	daily maximum 8-hour average
DQI	data quality indicator
ECAN	Environment Canada
EGU	electric generating unit
EPA	U.S. Environmental Protection Agency
H ₂ SO ₄	sulfuric acid
HNO ₂	nitrous acid
HNO ₃	nitric acid
IMPROVE	Interagency Monitoring of Protected Visual Environments

List of Acronyms and Abbreviations (continued)

ISO	International Organization for Standardization
K ⁺	particulate potassium ion
kg/ha	kilograms per hectare
kg/ha/yr	kilograms per hectare per year
km	kilometer
lpm	liters per minute
m	meter
m/s	meters per second
MAD	mean absolute difference
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
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
NCLAN	National Crop Loss Assessment Network
NCLD	National Critical Load Database
NCORE	EPA's National Core Monitoring
NEI	National Emissions Inventory
NH ₃	ammonia
NH ₄ ⁺	particulate ammonium
NH ₄ NO ₃	ammonium nitrate
(NH ₄) ₂ SO ₄	ammonium sulfate
NIST	National Institute of Standards and Technology
NLCD	National Land Cover Database
NO	nitrogen oxide
NO ₂	nitrogen dioxide
NO ₃ ⁻	particulate nitrate
NO _x	nitrogen oxides [nitrogen oxide (NO) + nitrogen dioxide (NO ₂)]
NO _y	total reactive oxides of nitrogen
NO _z	HNO ₃ , HNO ₂ , PAN, NTR, and nitrite
NPAP	National Performance Audit Program
NPS	National Park Service

List of Acronyms and Abbreviations (continued)

NTN	National Trends Network
NTR	organic nitrates
NYSDEC	New York State Department of Environmental Conservation
NYSERDA	New York State Energy Research and Development Authority
O ₃	ozone
OTC	Ozone Transport Commission
PAN	peroxyacetyl nitrate
PAN _x	peroxypropionyl nitrate
PHASE	Public Health Air Surveillance Evaluation
PM	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
RH	relative humidity
RPD	relative percent difference
S	sulfur (SO ₂ + SO ₄ ²⁻)
SEARCH	Southeastern Aerosol Research and Characterization Network
SIP	State Implementation Plan
SO ₂	sulfur dioxide
SO ₄ ²⁻	particulate sulfate
SRP	standard reference photometer
ΔT	temperature difference
TDEP	NADP's Total Deposition Science Committee
TCEQ	Texas Commission on Environmental Quality
TERP	Texas Emission Reduction Plan
total NO ₃ ⁻	gaseous nitric acid (HNO ₃) + particulate nitrate (NO ₃ ⁻)
μeq/L	microequivalents per liter
μm	micrometer
μg/m ³	micrograms per cubic meter
V _d	deposition velocity
VOC	volatile organic compounds
WARMS	Wyoming Air Resources Monitoring System
WRF	Weather Research and Forecasting Model



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:

www.epa.gov/castnet

**Clean Air Markets
Division Home Page:**

www.epa.gov/airmarkets

EPA Home Page:

www.epa.gov