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Short Communication

A Summary of Long-Term Trends in Sulfur and Nitrogen Deposition in the United States: 1990-2013

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Abstract

The Clean Air Status and Trends Network (CASTNET) is a nationwide air quality monitoring network that began operation in 1991 under Title IX of the 1990 Clean Air Act Amendments (CAAA). Under that directive, CASTNET has collected air pollutant concentration data at rural sites across the nation to determine the effectiveness of national and regional emission control programs by evaluating air quality, atmospheric deposition, and ecological effects. CASTNET provides estimates of dry deposition fluxes across the nation using the Multi-Layer Model (MLM). Current and future work is focused on improving the measurement and modeling of deposition fluxes with the implementation of advanced sampling and modeling techniques.

ABBREVIATIONS

AMoN: Ammonia Monitoring Network; Ca^{+2}: Calcium ion; CAAA: Clean Air Act Amendments; CASTNET: Clean Air Status and Trends Network; CMAQ: Community Multiscale Air Quality; Cl^-: Chloride Ion; EPA: Environmental Protection Agency; EGU: Electrical Generating Units; HONO: Nitrous Acid; HNO_3: Nitric Acid; K^+: Potassium Ion; MARGA: Monitor for Aerosols and Gases; Mg^{2+}: Magnesium Ion; Na^+: Sodium Ion; NADP: National Atmospheric Deposition Program; NH_3: Ammonia Gas; NH_4^+: Ammonium Ion; NO_3^-: Nitrate Ion; NOx: Nitrogen Oxides (Nitric Oxide (NO) + Nitrogen Dioxide (NO_2)); NTN: National Trends Network; PRISM: Parameter-Elevation Regression on Independent Slopes Model; SEARCH: Southeastern Aerosol Research and Characterization Network; SO_2: Sulfur Dioxide; SO_4^{2-}: Sulfate ion; TDEP: Total Deposition Science Committee

INTRODUCTION

The Clean Air Status and Trends Network (CASTNET) is a nationwide air quality monitoring network that began operation in 1991 under Title IX of the 1990 Clean Air Act Amendments (CAAA). Under Title IX Congress mandated that the U.S. Environmental Protection Agency (EPA) provide consistent, long-term measurements for determining relationships between changes in emissions and subsequent changes in air quality, atmospheric deposition, and ecological effects. In response, the EPA expanded its National Dry Deposition Network, which began in 1987, to create CASTNET. CASTNET is managed by the EPA, National Park Service, Wyoming's Bureau of Land Management, and is supported by many federal, state, tribal and local partners.

The principal function of CASTNET is to provide air pollutant concentration data to evaluate the effectiveness of national and regional emission control programs (i.e., Acid Rain Program, NOx Budget Trading Program, Cross-State Air Pollution Rule). CASTNET was also designed to determine long-term trends in rural atmospheric ozone, nitrogen, and sulfur concentrations and deposition fluxes of nitrogen and sulfur pollutants. CASTNET is the only network in the US to provide dry deposition estimates. Most CASTNET sites are collocated with or nearby a National Atmospheric Deposition Program's National Trends Network (NADP/NTN) wet deposition site. There are more than 250 NTN sites throughout the US and Canada that provide wet deposition fluxes of sulfur and nitrogen pollutants. Together, CASTNET and NTN data provide estimates of total deposition.

The network is currently operating 95 monitoring stations throughout the contiguous United States, Alaska, and Canada. The locations of those sites and NADP/NTN sites operational as of the end of 2015 are depicted in Figure [1].

All CASTNET sites measure weekly ambient concentrations of acidic pollutants, base cations, and chloride (Cl^-) using a 3-stage

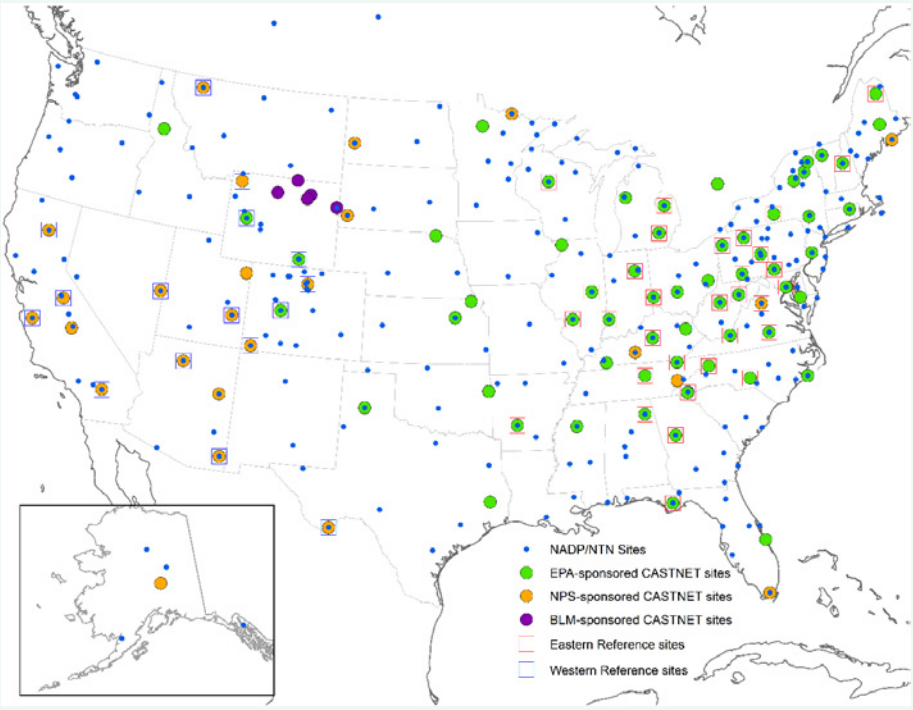

Figure 1 Map of CASTNET and NADP/NTN sites operational at the beginning of 2016.

open face filter pack with a controlled flow rate [1]. Gaseous pollutant measurements include sulfur dioxide (SO_2) and nitric acid (HNO_3). Particulate concentrations include sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+), sodium (Na^+), and Cl^-. The filter pack is exchanged each Tuesday and shipped to the analytical chemistry laboratory in Gainesville, FL where the filters are extracted and analyzed by ion chromatography (SO_4^{2-}, NO_3^-, Cl^-), by automated colorimetry (NH_4^+), and by inductively coupled plasma atomic emission spectrometry (Ca^{2+}, Na^+, Mg^{2+}, K^+) [1]. Measured meteorological parameters include 2-m temperature, wind speed and direction, standard deviation of the wind direction, solar radiation, relative humidity, precipitation, and surface wetness [1]. On site meteorological parameters were discontinued at most CASTNET sites in 2010.

CASTNET was designed to provide estimates of the dry deposition of sulfur and nitrogen pollutants across the United States. These dry deposition flux estimates are calculated with the Multi-Layer Mode l [2,3] using the method described in Bowker et al., [4]. Wet deposition fluxes are interpolated using a precipitation surface from the Parameter-Elevation Regression on Independent Slopes Model (PRISM) [5] combined with NADP/NTN pollutant concentrations and precipitation grids to develop a continuous surface of wet deposition. PRISM uses terrain elevation, slope, and aspect and climatic measurements to estimate precipitation on a 4-kilometer resolution grid. The dry and wet deposition is added to obtain estimates of total deposition in units of as kilograms per hectare per year (kg $ha^{-1}yr^{-1}$).

RESULTS AND DISCUSSION

The implementation of national and regional emission control programs has been very successful in reducing emissions of both SO_2 and NO_x from regulated sources. Annual SO_2 emissions from electric generating units (EGUs) have decreased from 15.7 million tons in 1990 to 3.2 million tons in 2013 [6], while annual NO_x emissions from EGUs and other regulated sources have decreased from 6.4 million tons in 1990 to 1.7 million tons in 2013 [7]. Ambient concentrations measured at CASTNET sites have also shown steady declines over this time period.

The CASTNET data presented in this report runs through 2013. Table (1) shows three-year mean measured concentrations of SO_2, SO_4^{2-}, total NO_3^-, and NH_4^+ from the 34 CASTNET eastern reference sites that operated over the period from 1990 through 2013 and from the 17 western reference sites operating from 1996 through 2013. The reference site locations are shown in Figure (1). Three-year mean concentrations for all species have decreased significantly over these periods for both eastern and western sites. Sampling and quantification uncertainties for the three-year mean concentrations are small compared to variance from geo-spatial and temporal fluctuations from year to year. To assess the uncertainties of the aggregate annual averages, three-year averages were calculated for each three year period in the data record and compared against one another using a two-tailed t-test (α =0.05). For the eastern reference sites (N=34), a < 2% difference in the annual aggregate average was considered significant, and for the western reference sites (N=17), a < 5% difference was considered significant. The percent changes shown in Table 1 are all well above these thresholds and should be considered significant changes.

Three-year mean SO_2 concentrations for the eastern reference sites for 1990-1992 and 2011–2013 were 8.9 µg/m^3 and 1.7 µg/m^3, respectively. This change constitutes an 80 percent reduction

in 3-year mean SO_2 concentrations between the two periods. The 2013 mean level of 1.4 µg/m^3 was the lowest mean value measured by the eastern reference sites in the history of the network.

The trend in SO_2 emissions from regulated EGUs from 1990 - 2013 aggregated over six states (Illinois, Indiana, Kentucky, Ohio, West Virginia, and Pennsylvania) was an 84 percent reduction [8]. This suggests an approximately linear relationship between SO_2 concentrations and emissions.

Ambient pollutant concentrations were much lower at the western reference sites than the eastern sites. This owes to the greater density of EGUs, other anthropogenic pollution sources, and overall population in the eastern US. A direct comparison of three-year mean SO_2 concentrations at eastern reference sites from 1996 through 1998 shows a 74% decrease from 6.4 µg m^{-3} to the 2011-2013 level of 1.7 µg m^{-3} whereas SO_2 concentrations at the western sites decrease 54% from 0.6 µg m^{-3} in 1996-1998 to 0.3 µg m^{-3}over 2011-2013.

Nitrate concentrations are presented as "total nitrate", which is the sum of HNO_3 and particulate NO_3^- to account for volatilization effects that can occur in the filter pack [9,10]. Three-year mean concentration levels declined from 3.0 µg/m^3 in 1990-1992 to 1.8 µg/m^3 in 2011–2013, producing a 41 percent reduction in total NO_3^-.

Figures (2,3) are box plots that show the trends in estimates of total *(*dry + wet)sulfur (as S) and nitrogen (as N) deposition for the western (left panel) and eastern (right panel) reference sites. These box plots were based on the same concentration data as described in Table (1) with the modeled deposition fluxes factored in to calculate total deposition as described in

Table 1: *Trends in Aggregated Western and Eastern Sulfur and Nitrogen Pollutant Concentrations.*

Pollutant (µg/m3)	***Western Sites***		***Eastern Sites***			***Percent Changes***		
	1996-98	*2011-13*	*1990-92*	*1996-98*	*2011-13*	*West*	*East 1990-92*	*East 1996-98*
SO_2	*0.6*	*0.3*	*8.9*	*6.4*	*1.7*	*-54*	*-80*	*-74*
SO_4^{2-}	*0.8*	*0.6*	*5.4*	*4.6*	*2.2*	*-20*	*-59*	*-53*
Total NO_3^-	*1.0*	*0.7*	*3.0*	*3.0*	*1.8*	*-27*	*-41*	*-41*
NH_4^+	*0.3*	*0.2*	*1.8*	*1.6*	*0.9*	*-17*	*-50*	*-45*

Abbreviations: *µg/m^3*: Micrograms per cubic meter; *SO_2*: Sulfur dioxide; *SO_4^{2-}*: Sulfate ion; *Total NO_3^-*: Total Nitrate is the sum of nitric acid and particulate nitrate ion; NH_4^+: Ammonium ion

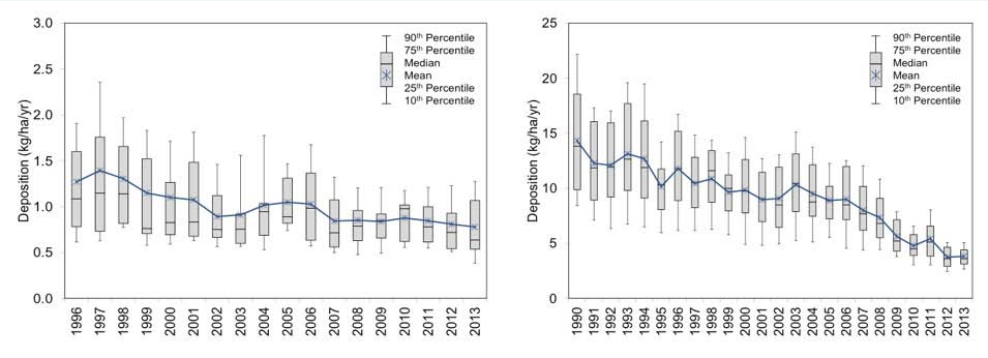

Figure 2 Trends in Total S deposition for Western (left panel) and Eastern (right panel) reference sites.

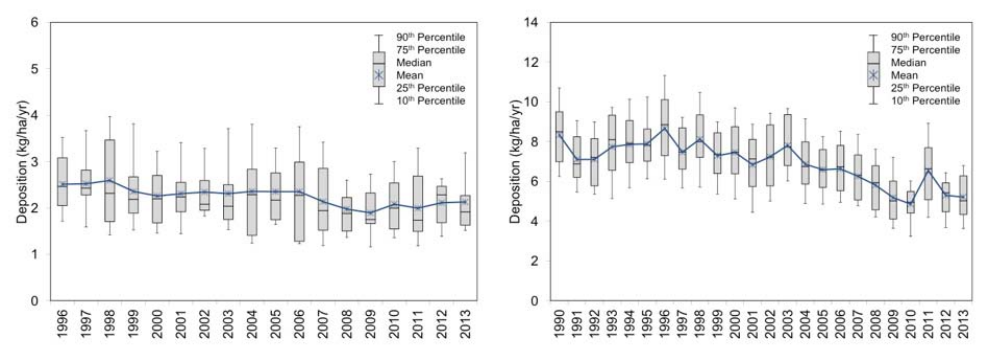

Figure 3 Trends in Total N deposition for Western (left panel) and Eastern (right panel) reference sites.

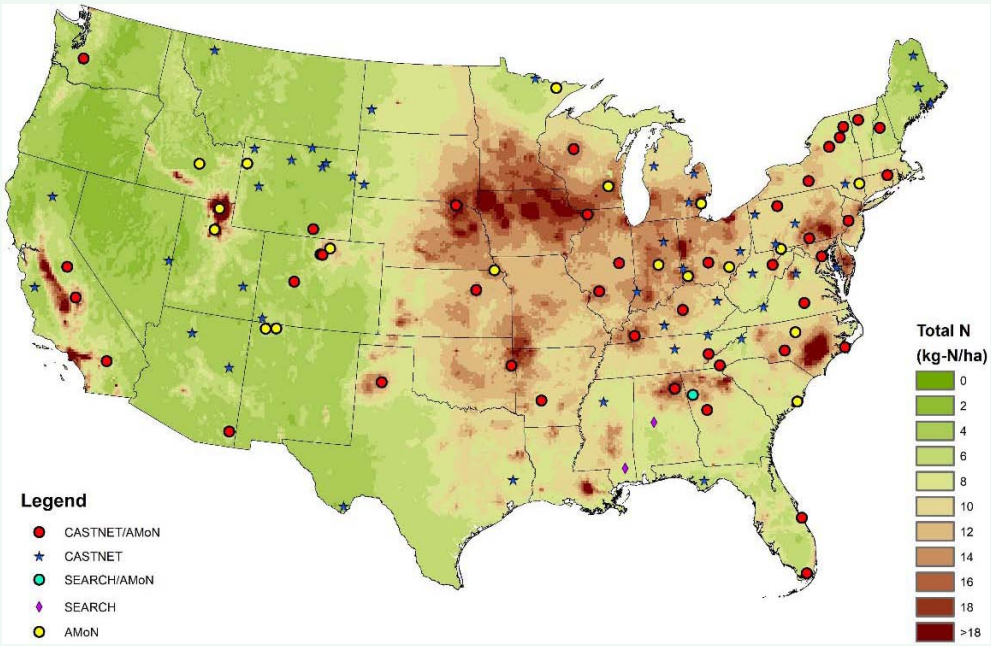

Figure 4 TDEP map of Total N Deposition Flux Estimates (kg-N ha-1 yr-1) for 2013 [13].

the Methods section. The y axes on the two panels have different scales to account for higher estimated deposition levels in the eastern sites.

Aggregated S deposition declined considerably at the eastern and western reference sites over their respective periods. Overall, total S deposition declined at the eastern sites by 66 percent. Total S deposition at the western reference sites was reduced 39 percent. The 2013 total S deposition estimates for eastern and western sites were the lowest in history of network.

The total nitrogen flux estimated for the eastern United States has decreased since 1996 with a substantial decline from 2002 through 2010, a brief increase in 2011, followed by a subsequent decline through 2013. The median total nitrogen flux (5.2 kg $ha^{-1}yr^{-1}$) estimated for 2013 was the lowest ever measured. Total nitrogen deposition estimated for the eastern sites over the period 1990–1992 to 2011-2013 was reduced by 24 percent. Total nitrogen deposition estimated for the western sites shows a relatively flat trend from 1996–1998 to 2011-2013 with an 18 percent decline.

FUTURE PROJECTS

CASTNET continues to measure consistent, long-term trends in acidic pollutant concentrations and deposition fluxes, however it has become increasingly important to improve measurement and model estimates of dry and total deposition. For example, most CASTNET sites are now collocated with NADP's Ammonia Monitoring Network (AMoN) to capture ambient concentrations of ammonia (NH_3). AMoN measures bi-weekly concentrations of ambient NH_3 at more than 90 sites. It has been shown that NH_3 deposition can contribute more than 50% of the dry N budget [11]. Field measurement studies are needed to improve model estimates of bi-directional NH_3fluxes using the AMoN measured concentrations. Soil and vegetation characteristics used as input to the bi-directional flux model will be measured at several sites to parameterize the model.

A new dynamic modeling method has been developed by NADP's Total Deposition science committee (TDEP) [12] that combines monitoring data with output from the Community Multi scale Air Quality (CMAQ) modeling system [13]. The model runs are updated as new monitoring and modeling data become available [14]. Air quality measurements are obtained from CASTNET, AMoN, and the Southeastern Aerosol Research and Characterization (SEARCH) Network. The TDEP method gives priority to measurement data from air quality monitoring sites when available and to CMAQ output in areas where monitoring data are not available. In addition, CMAQ provides modeled data for species that are not routinely measured. An example map of total Nitrogen deposition is shown in Figure (4).

Hourly direct deposition flux measurements for aerosols and gaseous nitrogen and sulfur species (HNO_3, SO_2, HONO, NH_3, NO_3^-, SO_4^{2-}, NH_4^+) have been made over a grass field in Durham, NC using a commercially available Monitor for AeRosols and GAses (MARGA) analyzer modified for field deployment [15]. The systems are currently being deployed in different locations representing different ecosystems (currently deployed in a forested canopy site and at a coastal plains site) to accumulate a database of hourly concentrations and fluxes in order to observe diurnal patterns and any chemistry owing to speciation between gas and aerosol phases, or during pollution or meteorological events. The observations and conclusions will be used to develop and improve algorithms to include in future CMAQ versions.

Shifts in the composition of nitrogen deposition to sensitive ecosystems due to changes in climate factors (temperature, precipitation, emissions sources) will continue to be monitored and evaluated. CASTNET will play a role in providing data to

assess impacts to vegetation, fresh water bodies, and high elevation ecosystems.

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