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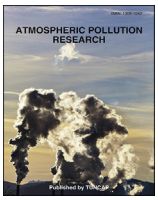

Trends in wet precipitation, particulate, and gas-phase species in New York State

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ABSTRACT

Here we characterized wet deposition National Atmospheric Deposition Program (NADP) species and Clean Air Status and Trends Network (CASTNET) dry deposited particle and gas species across New York over the last 2-3 decades. In addition measurements of NH_3 from the Ammonia Monitoring Network (AMoN) were analyzed. In general decreasing annual trends are observed for wet deposition SO_4^{2-} and NO_3^- species and dry deposited particle SO_4^{2-}, NO_3^- and NH_4^+ as well as gas phase SO_2 and HNO_3 consistent with reductions in SO_2 and NO_x emissions. Wet deposited NH_4^+ however does not show consistent trends with most sites showing little trend across the region and an indication that levels at some sites maybe increasing. NH_3 concentrations also appear to be increasing although the data record is only 8 years. Base cations, Ca^{2+} and Mg^{2+} show some decreases in the 1980s but concentrations are relatively uniform since the mid-1990s. Na^+ and K^+ show large year to year variations, by more than an order of magnitude for Na^+ due to influence of marine air at a near coastal site. In general there was a balance between the sum of cations and the sum of anions earlier in the record but the tendency has been for a cation excess in the more recent 5–10 years. Understanding the deposition of reduced nitrogen species is likely to be of concern for the foreseeable future. Such data are important in understanding acidification recovery in response to emission controls.

1. Introduction

Over the past several decades various emission controls on sulfur dioxide (SO_2) and nitrogen oxides (NO_x) have been implemented (http://www.epa.gov/airtrends) due to concerns over acidic deposition, visibility degradation and ambient particulate matter levels. Such controls include the Clean Air Act (CAA) and Clean Air Act Amendments (CAAA), NO_x State Implementation Plan (SIP) Call, Clean Air Interstate Rule (CAIR) which targeted SO_2 and NO_x emissions mainly from the energy generation sector. Trends in SO_2 and NO_x emissions since 1990 are −6.1% and −3.6%/yr, respectively (Xing et al., 2013). Long term measurements are key in understanding the response of ambient concentrations to emission reductions. Sulfate (SO_4^{2-}) and nitrate (NO_3^-) are important contributors to acidic deposition leading to negative impacts on ecosystems in certain sensitive regions (e.g. Stoddard et al., 2003; Fenn et al., 2011; Sullivan et al., 2011) including the Adirondack Park region in northern New York. The region around the Great Lakes and the Northeastern US are downwind of large coal burning Electric Generating Units (EGUs) and other major point emissions sources and experience some of the highest deposition loadings of SO_4^{2-} and NO_3^- in the US (Lehmann et al., 2005). Reduced nitrogen species ammonium (NH_4^+) and ammonia (NH_3) are important because they are regarded as nutrients and can impact plant growth and diversity (Krupa, 2003). The majority of NH_3 in the US is mainly from agricultural sources (Xing et al., 2013) which may not be adequately documented and therefore estimating NH_3 emission levels poses a challenge.

Large decreases in deposition of SO_4^{2-} and NO_3^- across much of the eastern US have been previously documented (e.g. Lynch et al., 2000; Butler et al., 2001). Decreasing trends of wet and dry deposited SO_4^{2-} and NO_3^- species concentrations have occurred over the last 2-3 decades in response to emission reductions particularly from large coal burning EGUs in the Midwestern US and Northeastern states (e.g Sickles and Shadwick, 2015 and references

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within). Driscoll et al. (2016) reported decreasing trends for SO_4^{2-} and NO_3^- at two sites in the Adirondack Park region of northern New York. Trends in NH_4^+ are not as clear for example while particle NH_4^+ shows decreasing trends (Rattigan et al., 2016), wet deposition NH_4^+ appears to be increasing (Lehmann et al., 2005). Since NH_3 is efficiently scavenged by precipitation (particularly at pH below 5, Seinfeld and Pandis, 1996) forming NH_4^+ ion in solution, measurements of NH_3 are critically important to fully comprehend the wet deposition NH_4^+ trends. The available data for NH_3 indicate concentrations are increasing across most of the US (Butler et al., 2016; Li et al., 2016; Yao and Zhang, 2016) but there is a lack of long term trends since it is not a regulatory requirement which leads to some uncertainty in reduced nitrogen trends data. Lehmann et al. (2005) explored the spatial and temporal patterns in wet deposition chemical species including base cations, Ca^{2+}, Mg^{2+} and K^+ across the US from 1985 to 2002. Base cations were also measured by Tessier et al. (2002) across northeastern US states over the period 1985–1999 and may be important in helping reduce the effect of acidic deposition. These studies highlight the need for long term monitoring of multiple species in order to fully understand acid precipitation.

Here we characterize the concentrations of National Atmospheric Deposition Program (NADP) wet precipitation chemistry and Clean Air Status and Trends Network (CASTNET) dry deposition particle and gas phase sulfur and nitrogen species from 1980 to 2015, with particular emphasis on long term trends, across New York. In addition measurements of NH_3 from the Ammonia Monitoring Network (AMoN, another NADP sub-network) were analyzed for trends. We explore patterns in species data across different locations and different seasons. Trends are determined using the Mann Kendall method and Sens slope relative to median annual concentrations and compared to emission trends (e.g. Mann, 1945).

2. Experimental methods

Data from 12 of the longest operating NADP's National Trends Network (NTN) sites (http://nadp.sws.uiuc.edu/ntn) across New York considered in this paper are listed in Table 1 and shown in Fig. 1. Since not all sites have a continuous record extending back to 1980 measurements at sites with at least 10 years of data are considered here. Note that Connecticut Hill, NY67, is not part of the NTN, but rather the Atmospheric Integrated Research Monitoring Network (AIRMoN, another sub-network run by the National Oceanic Atmospheric Administration (NOAA) with the aim of obtaining information on daily or event-based deposition). The NTN was established to track changes in energy generation, purposely avoiding urban and major motor vehicle emission areas as far as possible. Fig. 1 shows the geographical location of the long term monitoring sites. They are distributed with a group to the north in Adirondack Park, a group to the west around the Great Lakes and Finger Lake regions and a group towards the south in the Catskills, with one site at a coastal location on Long Island. Sites are mainly at rural locations with the intention of capturing long term pollutant concentrations across large ecosystem sensitive areas rather than monitoring specific local sources. The NTN is considered the nation's primary source of wet deposition data and provides weekly wet deposition fluxes at more than 200 sites across the US, Canada, Argentina, Puerto Rico and the US Virgin Islands. Each site has an automated collector and gage. This ensures the sample is exposed only during precipitation (wet-only sampling). Samples are collected weekly following standard operational procedures to ensure data comparability and representativeness. Samples are weighed at the site and transferred into a shipping bottle. Quality Assurance is provided by the Central Analytical Laboratory (CAL), Illinois State Water Survey. A list of documents is provided on the site (www.nadp.isws.illinois.edu/CAL/CAl_publications.html). CAL provides the analysis, data entry, verification and screening. Samples that are mishandled, had collection failures or contaminated are flagged. Organophosphate, PO_4^{3-}, is measured only as an indicator of sample contamination. We observed that measured conductivity was in good agreement with that calculated based on the measured ions (slope of 0.96 and an R^2 of 0.98).

CASTNET is a long-term environmental monitoring network with over 90 sites located throughout the US and Canada (https://www.epa.gov/castnet). CASTNET is managed and operated by EPAs Clean Air Markets Division (CAMD) in cooperation with the National Park Service (NPS) and other federal, state and local partners. The network was established under the 1991 CAAA to assess the trends in acidic deposition due to emission reduction programs. CASTNET samples ambient SO_2, HNO_3 and particle SO_4^{2-}, NO_3^- and NH_4^+ species over a weekly integrated period using a 3-stage filter pack. Three New York sites discussed here are listed in Table 2a, two of which, Connecticut Hill, CTH110 and Claryville, CAT175, have more than 20 years of data. One site Huntington Wildlife Forest HWF187 is located in the Adirondack Park while CTH110 and CAT175 lie towards the western and southern part of the state, respectively. Notice that these sites are paired with wet deposition sites. For example, CAT175 is paired with NY68 although these sites lie approximately 7 KM apart. The Ammonia Monitoring Network (AMoN) within the NADP started operation in fall 2007 (http://nadp.sws.uiuc.edu/amon). Measurements of NH_3 are made using Radiello® passive diffusion samplers, where ammonia adsorbs to a phosphoric acid-coated surface. The resulting NH_4^+ is removed via sonication and measured with flow injection analysis (Puchalski et al., 2011). Triplicate samples are deployed randomly at each station every 6 months. Normally a single sample is deployed. Travel blanks are performed but not for each bi-weekly period. The passive sampler measurements used by AMoN have a 2 sigma uncertainty of 6.5% (www.radiello.com). Gas phase NH_3 data at Connecticut Hill, Table 2b, are used here as it is the only site with a reasonable time period (8 years since 2008) of measurements.

3. Results and discussion

3.1. Trends in precipitation chemistry

Volume weighted statewide median annual concentrations of various ions, SO_4^{2-}, NO_3^-, NH_4^+, Cl and sum of base cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+), pH and H^+ as well as precipitation volume for the longest operating sites listed in Table 1 are shown in Fig. 2. Clearly SO_4^{2-} is the dominant anion while H^+ is the dominant cation. The bars denote the spatial variation across sites which is typically a factor of 2–3 is discussed in section 3.2. In the early 1980s median SO_4^{2-} was around 50–70 μeq/l, NO_3^- was approximately 25–30 μeq/l and NH_4^+ was 15–20 μeq/l. Concentrations of all 3 species have merged in the past few years to 10–15 μeq/l, approaching the range at remote sites elsewhere (Galloway et al., 1982). Notice the marked difference between species SO_4^{2-} and NO_3^- which shows decreases of 80 and 60%, respectively versus NH_4^+ which shows no clear trend.

Trends were determined using the Mann Kendall method and Sens slope normalized to median values for the time period with significance at the 0.05 level. These calculations were based on annual averages (volume-weighted for NADP and arithmetic for CASTNET and AMoN). SO_4^{2-} shows statistically decreasing trends across all sites with a statewide median value of −3.8%/yr ($p < 0.05$) and range from −2 to −8.6%/yr. Statically decreasing annual trends for NO_3^- were also observed, at 11 of the 13 sites, Table 3, varying from −1.1% to −8.1%/yr. Annual trends were not significant for 2

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