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Trends in atmospheric ammonium concentrations in relation to atmospheric sulfate and local agriculture

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Relationships between NH_4^+ and SO_4^{2-} suggest that aerosol NH_4^+ may be more strongly linked to SO_2 emissions than to local agricultural NH_3 emissions.

Abstract

Ammonium (NH_4^+) concentrations in air and precipitation at the Institute of Ecosystem Studies (IES) in southeastern New York, USA declined over an 11-year period from 1988 to 1999, but increased from 1999 to 2001. These trends in particulate NH_4^+ correlated well with trends in particulate SO_4^{2-} over the 1988–2001 period. The NH_4^+ trends were not as well correlated with local cattle and milk production, which declined continuously throughout the period. This suggests that regional transport of SO_4^{2-} may have a greater impact on concentrations of NH_4^+ and subsequent deposition than local agricultural emissions of NH_3. Ammonium concentrations in precipitation correlated significantly with precipitation SO_4^{2-} concentrations for the 1984–2001 period although NH_4^+ in precipitation increased after 1999 and SO_4^{2-} in precipitation continued to decline after 1999. The correlation between NH_4^+ and SO_4^{2-} was stronger for particulates than for precipitation. Particulate NH_4^+ concentrations were also correlated with particulate SO_4^{2-} concentrations at 31 of 35 eastern U.S. CASTNet sites that had at least 10 years of data. Air concentrations of NH_4^+ and SO_4^{2-} were more strongly correlated at the sites that were located within an agricultural landscape than in forested sites. At most of the sites there was either no trend or a decrease in NH_4^+ dry deposition during the 1988–2001 period. The sites that showed an increasing trend in NH_4^+ dry deposition were generally located in the southeastern U.S. The results of this study suggest that, in the northeastern U.S., air concentrations of NH_4^+ and subsequent deposition may be more closely linked to SO_4^{2-} and thus SO_2 emissions than with NH_3 emissions. These results also suggest that reductions in S emissions have reduced NH_4^+ transport to and NH_4^+-N deposition in the Northeast.

Keywords: Ammonia emissions; Atmosphere; Ammonium; Sulfate; Particulate matter

1. Introduction

Ammonia (NH_3) and ammonium (NH_4^+) can play an important role in the fertilization of natural systems (Aneja et al., 1998; Driscoll et al., 2003a,b; Erisman et al., 2003; Fenn et al., 2003; Galloway et al., 2003; Whitall et al., 2003), the control of acidity in precipitation, aerosols and cloud water (Galloway and Likens, 1981; Galloway, 1995; Likens and Lambert, 1998; Adams et al., 1999; Rodhe et al., 2002; Anderson et al., 2003) and the formation of fine particulate matter, which can impact human health and impair visibility (McCubbin et al., 2002; Anderson et al., 2003; Battye et al., 2003; Hazi et al., 2003; USEPA, 2003). Although NH_3 can neutralize acidic species in the atmosphere, when NH_3 or NH_4^+ is deposited to ecosystems they can have an acidifying effect (Galloway, 1995; Rodhe et al., 2002). Agricultural activities are the prime source of atmospheric NH_3 (McCubbin et al., 2002), but NH_3 is

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also emitted from other sources including vehicles, waste disposal, and manufacturing (Anderson et al., 2003; Battye et al., 2003). Ammonia gas can be directly deposited to natural systems or it can react in the atmosphere with acidic species to form particulate salts such as $(NH_4)_2SO_4$, NH_4NO_3 or NH_4Cl, which can be deposited by wet or dry deposition. Ammonia in the atmosphere has a relatively short lifetime, but the particulate salts have much longer atmospheric lifetimes and thus can be transported longer distances (Aneja et al., 1998; Walker et al., 2000a). In the eastern United States, NH_4^+ aerosols are important components of fine particulate matter, (Anderson et al., 2003; USEPA, 2003). Concentrations of NH_4^+ in precipitation increased in the United States between 1995 and 2002 (NADP, 2003). This suggests that NH_3 emissions in the U.S. have increased during the same time period. About 20–40% of the NH_3 emitted is likely to be directly deposited near its source (Aneja et al., 2001) and the rest is transformed to NH_4^+, which can be deposited locally or transported long distances as aerosols or in precipitation (Walker et al., 2000a). The rate of conversion of NH_3 to NH_4^+ is controlled by factors such as relative humidity, temperature, the availability of oxides of nitrogen and sulfur (Loubet et al., 2001; Aneja et al., 2003; Gilliland et al., 2003; Mathur and Dennis, 2003; Sutton et al., 2003). The conversion rate can determine whether the NH_3 is deposited locally or transported longer distances (Walker et al., 2000a; Aneja et al., 2001).

In this study, we asked the question: are NH_4^+ concentrations in air and precipitation at our research site in southeastern New York State controlled by local agricultural activities (and thus local NH_3 emissions), by regional SO_2 emissions or by both? To answer this question, we examined trends in NH_4^+ and SO_4^{2-} concentrations (in air and precipitation) as well as correlations between NH_4^+ and SO_4^{2-} and between NH_4^+ and local agriculture. We compared the results from our site with data from sites within the CASTNet network to look for patterns of controls on fine particulate NH_4^+.

2. Methods

Our research site is at the Institute of Ecosystem Studies (IES) and is located in eastern Dutchess County, in rural southeastern New York State (41.78560° North and 73.74140° West). The county is a rectangular area about 32 by 48 km and IES is roughly in the center of the county. The county is about 60% forested, 15% urban and residential, and 20% agricultural land. The chief agricultural activity is dairy farms.

Aerosol concentrations were measured using a Teflon filter, which is the first filter exposed to air in three-stage, low-volume filter packs. The methods were similar to the sampling procedures used by the U.S. Environmental Protection Agency CASTNet program (Clarke et al., 1997). The 47-mm diameter Teflon filters (Zefluor, 1-μm pore size, Gelman Sciences, Inc.) were placed in Teflon filter packs. The filter packs were deployed in a rain shield on a tower approximately 10 m above a mowed grass surface. A continuous flow of air was drawn through the filter pack at 3.00 lpm using a vacuum pump, which was regulated using a mass flow controller (Tylan General Inc.). When the mass flow controller was off line for calibration or repair (approximately 2–3 weeks per year), flow was regulated using a needle valve and flow measurements were corrected for instantaneous temperature and pressure. Exposed filter packs were exchanged for clean ones every Tuesday.

The Teflon filters were extracted in 50 ml of double deionized water for 24 h in the dark at 2 °C after sonication for 15 min. The solution was then decanted into sample bottles, preserved with two drops of chloroform, and analyzed for SO_4^{2-} by ion chromatography (Dionex 500 DX Ion Chromatograph, AS4A and AG4A columns, micro-membrane suppressor) and NH_4^+ by continuous flow analysis (Alpkem Flow Solution III, phenate method). Before 1993 samples were not preserved, but all samples were stored in the dark at 4 °C until analysis. The change in procedures to preserve samples with chloroform from 1993 onward did not result in a step function change in sample chemistry. Using the total amount of time that each filter was exposed and the average flow rate during that time, weekly concentrations were calculated. All concentration values that were below analytical detection limits were set to equal one half of that limit. Hourly deposition velocities were estimated using a multi-layer dry deposition model (Meyers et al., 1998). This model was parameterized with hourly meteorological data from a tower adjacent to the air sampling tower, and canopy structure and leaf area data from a forest that is within 200 m of the towers. Weekly average deposition velocities were combined with weekly concentrations to estimate weekly fluxes. From these data, total annual deposition of sulfur and nitrogen species was calculated. The data record used in this paper includes the years 1988–2001. In addition to the aerosol data collected at IES, we examined data collected at 35 Clean Air Status and Trends network (CASTNet) sites located in the eastern United States with at least a continuous 10-year record.

Precipitation samples were collected using an Aerochem Metrics wet–dry collector (wet side only). Precipitation samples were collected after each event, and chemically analyzed at IES. Volume weighted mean concentrations were estimated based on precipitation volume using a universal recording rain gauge (Belfort Instrument Co. Series 5-780). The data record for wet deposition in this paper includes the years 1984–2002.

Ammonia emissions data were taken from the United States Environmental Protection Agency