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# Status and trends in atmospheric deposition and emissions near Atlanta, Georgia, 1986–99

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## Abstract

Wet and dry atmospheric deposition were investigated from weekly data, 1986–99 (1986–97 for dry deposition) at the Panola Mountain Research Watershed (PMRW), a forested research site 25 km, southeast of Atlanta, Georgia. Furthermore, the wet deposition was compared to that at three adjacent National Atmospheric Deposition Program's National Trends Network (NTN) sites (GA41, 50 km south of PMRW; AL99, 175 km northwest; NC25, 175 km north-northeast) and dry deposition was compared to that at adjacent Clean Air Status and Trends Network (CASTNET) sites, co-located at the NTN sites. The pH of precipitation is acidic and the dominant acid anion is  $\text{SO}_4$ ; the pH (derived from the volume-weighted mean H concentration) averages 4.44 for 1986–99, and varies seasonally with average lowest values in summer (4.19) and highest in winter (4.63). From 1986–99, the annual wet deposition of sulfur (S) and nitrogen (N) averaged 400 and 300  $\text{eq ha}^{-1}$  (6.4 and 4.2  $\text{kg ha}^{-1}$ ), respectively. Inferential model estimates of annual dry S and N deposition from 1986–97 averaged 130 and 150  $\text{eq ha}^{-1}$  (2.1 and 2.1  $\text{kg ha}^{-1}$ ), respectively. From 1993–99, net S deposition (dry deposition plus canopy interactions) for coniferous and deciduous throughfall (throughfall minus wet-only deposition) averaged 400 and 150  $\text{eq ha}^{-1}$  (6.4 and 2.1  $\text{kg ha}^{-1}$ ), respectively. The annual wet deposition of S and N species at PMRW was comparable to that at NTN sites, with the exception of higher N species deposition at AL99 and relatively lower H,  $\text{SO}_4$  and  $\text{NO}_3$  deposition at GA41. Dry S deposition at PMRW differed markedly from the CASTNET sites despite similarity in S concentrations for all but NC25; the differences are attributed to differences in model parameters associated with the landscape and vegetation characteristics at the sites. At PMRW, atmospheric deposition trends were not detected for the entire sampling period, but were detected for shorter periods (4–5 yr). Annual S and N deposition increased from 1986 to 1991, decreased to 1995 and then increased to 1999.  $\text{SO}_2$  emissions from seven major point sources within 120 km of PMRW decreased markedly from the late 1980s to 1995 and have remained relatively constant or increased slightly from 1995 to 1998. Annual wet and dry S deposition at PMRW significantly correlates ( $p < 0.01$ ) with  $\text{SO}_2$  emissions, and the correlation is dominated by the large  $\text{SO}_2$  emissions decreases in the early 1990s, consistent with the implementation of Phase I of Title IV of the 1990 Clean Air Act Amendments. Published by Elsevier Science Ltd.

**Keywords:** Fossil fuel emissions; Sulfur dioxide; Acid rain; Sulfate; Nitrogen; Nitrogen oxides; Dry deposition; Wet deposition

## 1. Introduction

Atmospheric deposition is a major source of chemical constituents to many ecosystems and its composition

has been affected by human activities. The transfer occurs by three major pathways: (1) precipitation scavenging, in which particles are incorporated in hydrometeors and deposited in the resulting rain, snow, sleet or hail (Hidy, 1984); (2) interception by cloudwater, fog, and mist (Schemenauer, 1986; Walmsley et al., 1996); and (3) dry deposition, in which large particles, aerosols and gases fall on or are removed by surfaces in

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the ecosystem (Wesely and Hicks, 2000). In the southeast, particularly in the Georgia piedmont, pathways (1) and (3) predominate, and temporal and spatial variations in atmospheric deposition primarily reflect variations in constituent sources, transport from source to receptor, and deposition. Human activities have had a major effect on the emission and subsequent deposition of constituents, e.g. acid deposition through combustion of fossil fuels. Consequently, it is important to assess trends in emissions and deposition and their relations, particularly as human activities change.

Emissions from large point sources have changed in response to changing technologies, operating procedures, and modifications due to regulatory requirements. Monitoring of emissions, air quality, and atmospheric deposition, however, only began when a clear problem, namely acidic deposition, was identified. Emissions from large point sources have been systematically recorded for a selected suite of compounds since the middle of the 1980s (USEPA, 1998). The National Atmospheric Deposition Program's National Trends Network (NTN) has used wet-only precipitation collectors to monitor weekly wet deposition throughout the United States beginning in 1978 (NTN, 2001). Weekly sulfur (S) and nitrogen (N) air concentrations and associated dry deposition have been monitored and modeled using micrometeorology beginning in the early 1980s (Hicks et al., 1991; Meyers et al., 1998), as part of the National Oceanic and Atmospheric Administration's (NOAA) Atmospheric Integrated Monitoring Network (AIRMoN; NOAA, 2001) and beginning in the late 1980s as part of the US Environmental Protection Agency (USEPA) and National Park Service (NPS) monitoring program, the Clean Air Status and Trends Network (CASTNET; USEPA/NPS, 2001). Also, total S deposition to a forest has been monitored at some sites using throughfall (Lovett and Lindberg, 1984; Lindberg et al., 1986), and associated dry S deposition has been determined by subtracting the wet-only deposition from the total S deposition (e.g., Lovett and Lindberg, 1984; Johnson and Lindberg, 1992; Cappellato et al., 1998).

Following the 1 January 1995 implementation of Phase I of Title IV of the 1990 Clean Air Act Amendments (Public Law 101-549, 1990), atmospheric S deposition was expected to decrease in response to SO<sub>2</sub> emission reductions. An assessment of changes in weekly wet sulfate (SO<sub>4</sub>) deposition at NTN sites for the 3 yr following implementation (1995–97) indicates a substantial annual decrease of 2.4–4.0 kg ha<sup>-1</sup> or 10–25% for stations primarily in the mid-Appalachian and northeastern regions (Lynch et al., 2000). Although Phase I of Title IV of the 1990 Clean Air Act Amendments was to be implemented in 1995, substantial emission reductions and associated air concentration decreases also were reported in the eastern US for the

period from 1989 to 1995 (Holland et al., 1999). For many sites in the eastern US, wet SO<sub>4</sub> deposition decreases reported for the post-Phase I implementation, however, exceeded the extrapolated decreases from the 1983–94 deposition trends and are consistent with the changes in emissions during 1995–97 (Lynch et al., 2000). Wet SO<sub>4</sub> deposition, however, increased at several sites, whereas precipitation SO<sub>4</sub> concentrations decreased. This underscores the importance of concurrently assessing the effects of changes in precipitation quantity, particularly when considering the combined effects of acid precipitation inputs on sensitive ecosystems (Lynch et al., 2000). Butler et al. (2001) assessed the linkages between SO<sub>2</sub> emissions and precipitation SO<sub>4</sub> concentrations by assessing the percentage changes in each from 1991–94 to 1995–97. Butler et al. (2001) concluded that for most regions in the eastern US the relation is 1:1, but the relations for Georgia were not assessed. Although the regional deposition response to changing emissions is consistent in the Northeast, it is not clear how changes in point-source emissions and rapid urban development have affected atmospheric deposition in the Southeast, and in particular, in the Atlanta region, where the population increased rapidly, from 2.2 to 4.1 million from 1985 to 2000 (Atlanta Regional Commission, 2001).

This paper investigates atmospheric deposition at the Panola Mountain Research Watershed (PMRW) near Atlanta to assess temporal changes in wet and dry deposition and the relative contributions to total atmospheric deposition from 1986 to 1999. Wet and dry atmospheric deposition at PMRW were compared with nearby and more rural NTN and CASTNET sites in Georgia, Alabama, and North Carolina to determine the status and spatial trends in the region for 1985–99. The atmospheric deposition of S and N were compared with the 1987–98 SO<sub>2</sub> and NO<sub>x</sub> emissions for the seven largest point sources within 120 km of PMRW.

## 2. Methods

PMRW is a 41-ha forested watershed, 25 km southeast of Atlanta, Georgia, in the Georgia Department of Natural Resources' Panola Mountain State Conservation Park near Stockbridge (Fig. 1). Biogeochemical and hydrological processes research at PMRW is being conducted as part of the US Geological Survey (USGS) Water, Energy, and Biogeochemical Budgets Project and Atmospheric Deposition Program (USGS, 2001a,b). The site is in the northern part of one of the 10 counties that constitute the "Atlanta Region". Deciduous and coniferous throughfall (1993–99) and wet-only deposition (1985–99) were monitored weekly using an

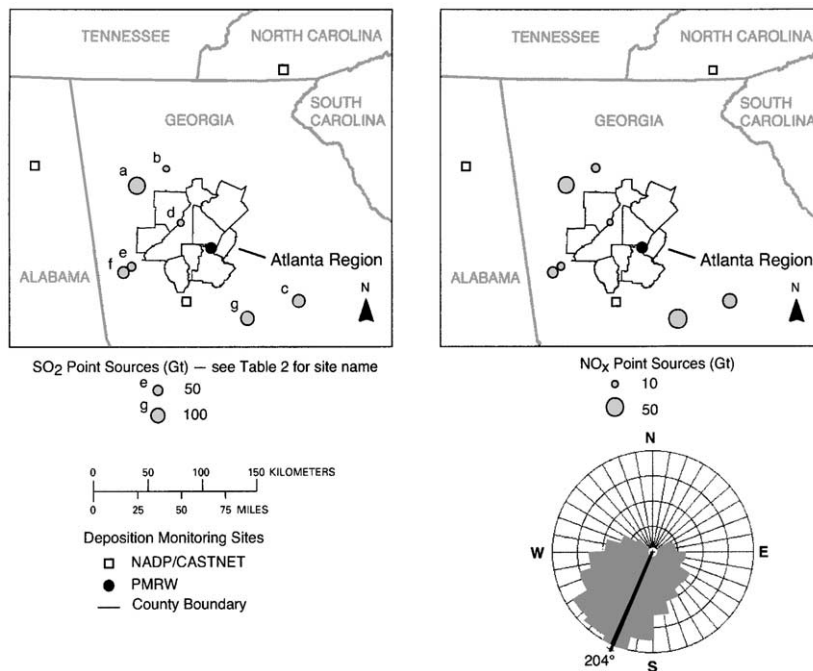


Fig. 1. Maps of atmospheric deposition monitoring sites of the National Atmospheric Deposition Program/National Trends Network (NTN) and the Panola Mountain Research Watershed (PMRW) near Atlanta, Georgia, and major SO<sub>2</sub> and NO<sub>x</sub> emission point sources within 120 km of PMRW, and a wind rose of the prevailing daily wind direction at PMRW (1985–99).

Aerochem Metrics Model 301<sup>1</sup> wetfall/dryfall collector, following NTN protocols (Dossett and Bowersox, 1999). Wet-only deposition also was monitored weekly during the same period at three adjacent NTN sites (NTN, 2001): the Coweeta site in North Carolina (NC25) 175 km north-northeast of PMRW, Sand Mountain Experiment Station in Alabama (AL99) 175 km northwest, and the Georgia Station (GA41) 50 km south (Fig. 1). From August 1985 through November 1997, dry S and N deposition were monitored weekly by combining air concentrations from a filter-pack with micrometeorological data in a canopy resistance model (Hicks et al., 1991; Meyers et al., 1991). The site at PMRW is part of the AIRMoN-dry network. CASTNET dry deposition was monitored using similar protocols developed by NOAA for the AIRMoN-dry sites. The CASTNET sites are co-located at the NTN sites. The CASTNET site identifiers are COW137 for Coweeta, SND152 for Sand Mountain Experimental Station, and GAS153 for the Georgia Station (USEPA/NPS, 2001); the CASTNET air

concentration and dry deposition are referred to herein by the associated NTN site identifiers.

At PMRW, precipitation and throughfall were analyzed for major ion concentrations at the USGS laboratory in Atlanta (Fishman and Friedman, 1989). Amounts of precipitation and throughfall were determined by the volume collected and the collector area. Prior to 1991, the major ions (Na, K, Ca, Mg, NH<sub>4</sub>, Cl, NO<sub>3</sub>, and SO<sub>4</sub>) were determined by ion chromatography (IC). For 1991–99, the cations—Na, K, Ca, and Mg—were determined by direct current plasma on a filtered (0.45 μm) acidified aliquot, and NH<sub>4</sub> was determined colorimetrically using salicylate hypochlorite. Individual solute deposition was computed by multiplying the solute concentration by the rainfall or throughfall amount. The weekly solute deposition was summed by month and monthly concentrations were determined by dividing the deposition by the monthly precipitation (or throughfall) depth. Annual solute deposition and concentrations were calculated similarly.

The weekly average air quality for the CASTNET and AIRMoN-dry sites was determined for N and S species only using a filterpack (Hicks et al., 1991; USEPA/NPS, 2001). At the CASTNET sites, weekly air concentrations are monitored with an open-faced, 3-stage filterpack assembly. At PMRW, the atmospheric concentration

<sup>1</sup>The use of brand names in this report is for information purposes and does not indicate endorsement by the US Geological Survey.

data were monitored with a closed-faced, heated inlet, 3-stage filterpack assembly. The filterpack at each site (CASTNET and PMRW) contains a Teflon filter for collection of particulate species ( $\text{SO}_4$ ,  $\text{NO}_3$ , and  $\text{NH}_4$ ), a nylon filter primarily for nitric acid (from measured  $\text{NO}_3$ ), but also some  $\text{SO}_2$  (from measured  $\text{SO}_4$ ), and a potassium carbonate-impregnated cellulose (Whatman) filter for  $\text{SO}_2$  (from measured  $\text{SO}_4$ ), but also some  $\text{NO}_3$ . The filterpacks are exposed for 1 week, i.e., Tuesday to Tuesday, at a constant flow rate of  $1.51 \text{ min}^{-1}$ , and sent to the USEPA contract laboratory in Gainesville, Florida, for chemical analysis. The Teflon filter is extracted in deionized water with sonication and shaking. Nylon filters are extracted in IC eluent ( $0.5 \text{ M Na}_2\text{CO}_3$ ) with 0.05% hydrogen peroxide. The Whatman filter is extracted in deionized water with 0.05% hydrogen peroxide. Atmospheric concentrations are then calculated based on the analyte mass per filter and the volume of air sampled, which is recorded at the site. The individual filter totals were combined in a micrometeorological model to produce the deposition of individual species, e.g.,  $\text{SO}_2$  and  $\text{SO}_4$ . The individual species deposition was combined by element to give estimates of total S and N dry deposition. Monthly and annual dry-deposition were computed by summing the weekly deposition.

The USEPA maintains a database for air quality and emissions from major stationary (point) sources (Bryan Bloomer, USEPA, written communication, 2001). For the monthly emissions for individual point sources, monthly consumption by fuel type is multiplied by an appropriate emission factor, summed for all fuels reported, and post-combustion control is applied to the sum using the annual average control efficiency following the procedures described by USEPA (1998). Trends in the monthly and annual emissions of  $\text{SO}_2$  and  $\text{NO}_x$  from the seven major point sources within 120 km of PMRW were evaluated for 1987–98 and with respect to annual deposition at PMRW.

Finally, the deposition at PMRW was evaluated with respect to major emission sources within 120 km of the site and to the dominant weather patterns. The Kendall test (Gilbert, 1987), a nonparametric test, was used to evaluate trends in annual solute concentrations and the Seasonal Kendall test (Hirsch and Slack, 1984) was used to evaluate trends in the monthly volume-weighted mean (VWM) concentration and deposition.

### 3. Results and discussion

#### 3.1. Status of precipitation and wet deposition

For calendar years 1986–99, annual precipitation at PMRW averaged 1160 mm and ranged from 840 mm in 1987 to 1530 mm in 1994. Monthly precipitation ranged

from 5 mm in June 1990 to 455 mm in July 1994, a result of Tropical Storm *Alberto*. The cation composition (Na, K, Ca, Mg,  $\text{NH}_4$ , and H) of precipitation is dominated by H (~50%) and  $\text{NH}_4^+$  (~20%), and the anion composition (Cl,  $\text{NO}_3$ , and  $\text{SO}_4$ ) is dominated by  $\text{SO}_4$  (>50%) and  $\text{NO}_3$  (~25%).

Precipitation is acidic, with the annual pH (from VWM H concentration) averaging 4.44 and ranging from 4.21 to 4.66; the pH of weekly samples, however, was more variable ranging from 3.29 to 6.37 with the lowest pH in the lowest-volume samples. Precipitation pH is controlled primarily by the concentrations of the strong-acid anions,  $\text{SO}_4$  and  $\text{NO}_3$ ; the  $r^2$  of a linear regression of H concentration of weekly samples on  $\text{SO}_4$  was higher than on  $\text{NO}_3$  (0.91 and 0.73, respectively). The stronger association with  $\text{SO}_4$  compared to  $\text{NO}_3$  concentrations primarily reflects the dominance of  $\text{SO}_4$ ; concentrations of  $\text{SO}_4$  exceeded  $\text{NO}_3$  by more than a factor of two and the average annual concentrations for the entire period were 36 and  $16 \mu\text{eq l}^{-1}$ , respectively. Individual solute concentrations were highest in the lowest-volume samples, reflecting the concentrating effect of atmospheric washout (Durana et al., 1992; Peters, 1994; Peters and Ratcliffe, 1998). Relations between solute concentration and rainfall are not statistically significant ( $p < 0.05$ ), however, and display considerable heteroscedasticity, having the largest concentration variance during weeks with the lowest rainfall.

Deposition, and cation and anion composition varied seasonally—the seasons were divided into sequential 3-month periods with March–May for spring, June–August for summer, September–November for fall, and December–February for winter (Fig. 2). The highest H (lowest pH) and  $\text{SO}_4$  deposition typically occurs during the summer and the lowest occurs in winter. The summer pH averaged 4.19 (from weekly H deposition) and winter pH averaged 4.63. Summer  $\text{SO}_4$  deposition was more than three times the winter deposition; winter was the season having the lowest deposition for each solute. Na and Cl deposition varied the least among seasons, but even for these solutes, summer deposition was 2.0 and 1.3 times the winter deposition, respectively. The  $\text{SO}_4$  concentration of wet precipitation varied seasonally similar to and probably related to the atmospheric  $\text{SO}_4$  concentrations through aerosol washout during rainstorms.

The annual wet deposition of each major solute for 1985–99 at PMRW generally is similar to adjacent NTN sites (Fig. 3). The annual precipitation, on average, was similar at the Georgia sites and increased to 1330 mm in Alabama and 1750 mm in North Carolina (Fig. 3). The wet-only S and N deposition among sites are consistent with the NTN annual deposition maps showing a general decrease in S and N deposition from north to south (e.g., NADP, 2000). An exception is the high N

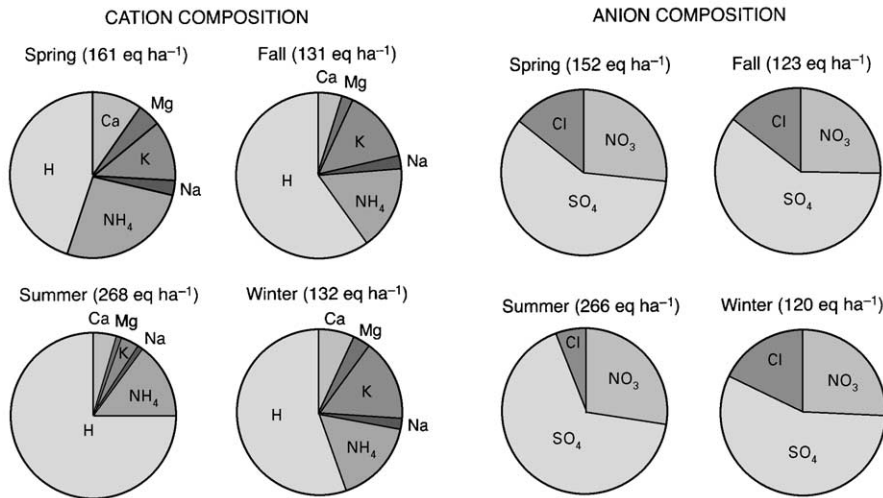


Fig. 2. Seasonal cation and anion composition of wet atmospheric deposition at the Panola Mountain Research Watershed (PMRW) near Atlanta, Georgia, 1986–99. The average seasonal cation and anion deposition is given in parentheses.

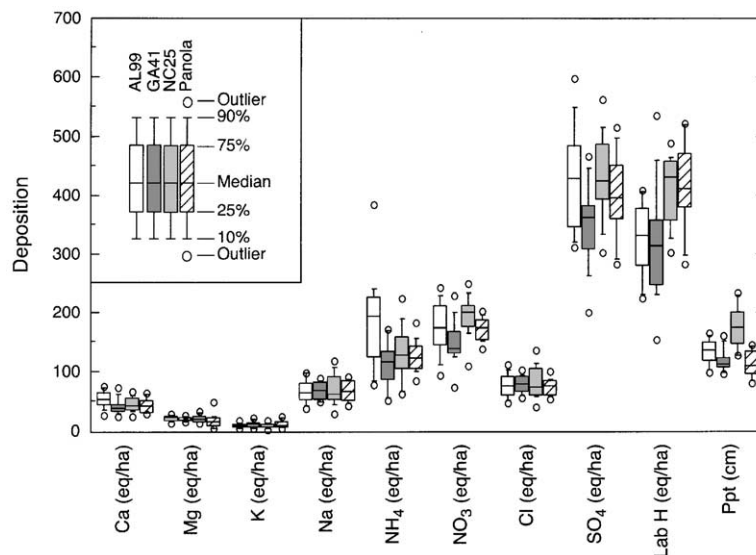


Fig. 3. Box plots of the wet deposition of major solutes at the Panola Mountain Research Watershed (PMRW), Georgia, and adjacent National Atmospheric Deposition Program/National Trends Network sites in Alabama (AL99), Georgia (GA41), and North Carolina (NC25).

species deposition, particularly  $\text{NH}_4$ , at AL99 (Fig. 3). The relatively higher  $\text{NH}_4$  deposition (and concentration) is associated with lower H deposition (and concentration, i.e., higher pH) compared to the other sites. This effect also is consistent with a lower slope and lower percentage of the variance explained by a linear regression of annual H deposition on  $\text{SO}_4$  at AL99 compared to the other sites; the slope and  $r^2$  of the linear regression for AL99 was 0.66 and 0.45,

respectively compared to slopes ranging from 0.83 to 1.1 and  $r^2 \geq 0.8$  for the other sites. Also, the deposition of N species,  $\text{SO}_4$ , Ca, and H at GA41 are relatively lower than the other NTN sites and PMRW (Fig. 3). The lower deposition relative to PMRW is puzzling given the similarity in annual precipitation, but may be related to proximity to sources, i.e., that PMRW is closer to sources of these constituents.

3.2. Status of air quality and dry S and N deposition

Air concentrations of S and N species, measured with the filterpack, were positively skewed, i.e., with most of the weekly values less than the mean. Consequently, median concentrations are reported to represent the populations. SO<sub>2</sub> concentrations varied seasonally, with high concentrations in winter and low concentrations in summer. The highest median weekly SO<sub>2</sub> concentration (8.2 μg m<sup>-3</sup>) was in February and the lowest (3.2 μg m<sup>-3</sup>) was in August. In contrast, SO<sub>4</sub> concentrations are low in winter and high in summer; lowest median weekly SO<sub>4</sub> concentration (2.8 μg m<sup>-3</sup>) was in December and highest (8.8 μg m<sup>-3</sup>) was in July. The total S air concentrations also were seasonal following the pattern of SO<sub>2</sub> concentrations with highest concentrations during winter and lowest during summer. The seasonal SO<sub>2</sub> and SO<sub>4</sub> concentration variations probably reflect a more rapid conversion of SO<sub>2</sub> to SO<sub>4</sub> under warmer conditions in summer (Calvert et al., 1985; Liu et al.,

1987); during the study period, mean-monthly air temperatures at PMRW ranged from 5.9°C in January to 25.6°C in July. In contrast to SO<sub>4</sub>, aerosol NO<sub>3</sub> concentrations were low, and varied seasonally with highest median weekly concentrations in spring (0.24 μg m<sup>-3</sup>) and lowest in summer (0.08 μg m<sup>-3</sup>). The weekly HNO<sub>3</sub> concentrations were higher than aerosol NO<sub>3</sub> and were less variable seasonally than the other N and S species; the highest median weekly concentration was 1.6 μg m<sup>-3</sup> in March and the lowest was 1.2 μg m<sup>-3</sup> in November.

During 1986–97 at PMRW, the annual dry S (SO<sub>2</sub> plus SO<sub>4</sub>) and N (HNO<sub>3</sub> plus NO<sub>3</sub>) deposition averaged 126 and 152 eq ha<sup>-1</sup> (2.1 and 2.1 kg ha<sup>-1</sup>), respectively (Fig. 4A). The annual dry N deposition was highly correlated with S deposition (*r*<sup>2</sup> = 0.77). Weekly dry SO<sub>4</sub> deposition varied seasonally having the same pattern as the air concentrations, i.e., highest deposition in summer. The SO<sub>2</sub> deposition was more variable throughout the year than the SO<sub>4</sub>, but generally was

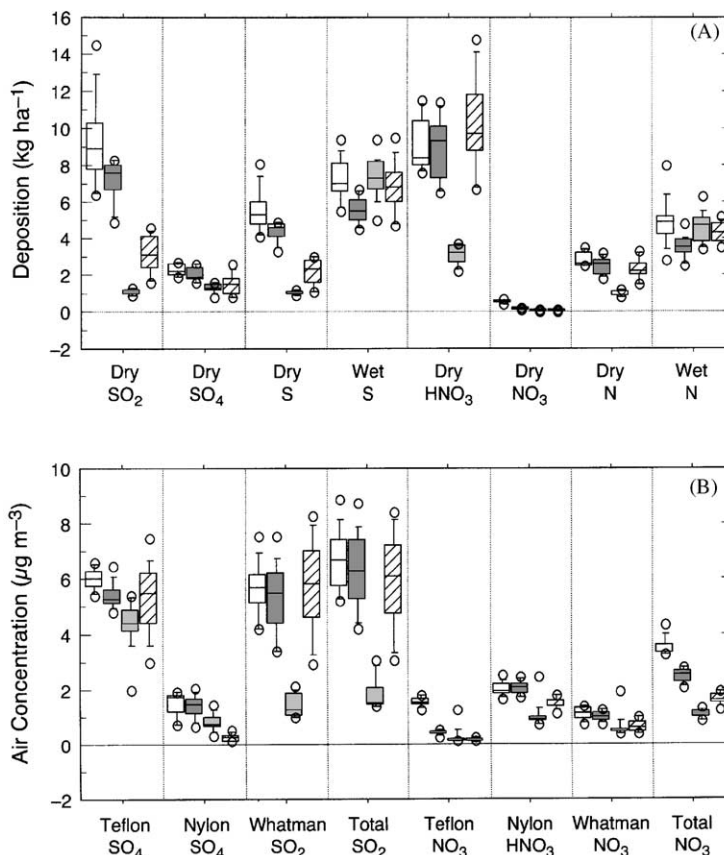


Fig. 4. (A) Box plot of the annual dry atmospheric deposition of S and N species and wet deposition of S and N at the Panola Mountain Research Watershed (PMRW), Georgia, and at adjacent Clean Air Status and Trends Network (CASTNET) and National Atmospheric Deposition/National Trends Network sites; and (B) box plot of the annual average air concentrations of S and N species from the weekly filterpack at the Panola Mountain Research Watershed (PMRW), Georgia (1986–99) and adjacent CASTNET sites.

higher than  $\text{SO}_4$  deposition with seasonally high deposition occurring in summer. The modeled  $\text{SO}_2$  deposition is sensitive to vegetation type and age (stomatal resistance), surface wetness, and temperature; surface wetness varies markedly throughout the year, which partly explains the high variability in the modeled  $\text{SO}_2$  deposition (Shreffler, 1978; Meyers et al., 1998). Seasonal variations in N species deposition were not as pronounced as those for the  $\text{SO}_4$ . The highest modeled deposition for both  $\text{HNO}_3$  and  $\text{NO}_3$  occurs in spring and the lowest in late summer.

The annual dry S deposition at PMRW differed markedly from the CASTNET sites (Fig. 4A). The air concentrations, however, were similar among AL99 and Georgia sites despite the large (3-fold) differences in deposition (Fig. 4B). The dissimilarities in deposition, therefore, are attributed to differences in the multilayer model parameters used to characterize the landscapes at each site (Meyers et al., 1998). The model parameters include type and height of vegetation and the associated leaf area index (LAI, leaf surface area per unit land surface area), information on the plant reactivity to light and temperature, and a minimum stomatal resistance (Clarke et al., 1997; Meyers et al., 1998). The difference in vegetation types probably is a more important control on deposition than LAI, reflected by only small differences in modeled dry S deposition at PMRW with modest changes ( $\pm 25\%$ ) in LAI for white oak and loblolly pine, the dominant species at PMRW (Cappellato et al., 1998). The North Carolina CASTNET site and PMRW are forested and simulated dry S and N deposition is low. The forest is less efficient in removing S and N than the grassland and agricultural lands at AL99 and GA41 sites (Meyers et al., 1998). The much lower air S and N concentrations and modeled dry deposition at the NC25 site is puzzling, but consistent with results of the Integrated Forest Study, for which dry S deposition estimates to a white pine forest at Coweeta were more comparable to sites in Florida and upstate New York than adjacent sites in Georgia or Tennessee (Johnson and Lindberg, 1992).

### 3.3. Estimates of S deposition from throughfall

During 1993–99 at PMRW, net throughfall S deposition (dry deposition plus canopy interactions) for coniferous and deciduous sites (throughfall minus wet-only precipitation) averaged 400 and 150  $\text{eq ha}^{-1}$  (6.4 and 2.3  $\text{kg ha}^{-1}$ ), respectively. The differences are attributed to variations in the LAI above the collectors, the type of vegetation, and the representativeness of the throughfall collectors for each canopy type. Wet-only S deposition averaged 350  $\text{eq ha}^{-1}$  (6.0  $\text{kg ha}^{-1}$ ) during the same collection period as that of the throughfall. The dry S deposition estimated from the throughfall S mass balance, therefore, ranges from 28% to 52% of

the total S deposition depending on vegetation type. In a mass-balance study of dry S deposition for a 500- $\text{m}^2$  lichen and moss covered bedrock outcrop at PMRW, Peters (1989) reported that 30% of the total atmospheric S deposition to the outcrop was dry deposition, which is similar to the results herein. The lower estimate for the outcrop (Peters, 1989) and for the deciduous throughfall, probably reflects a lower LAI and minimum canopy resistance, and hence a lower filtering of atmospheric constituents of the respective canopies. From a rainstorm-based S cycling study at PMRW conducted from October 1987 to November 1989, Cappellato et al. (1998) estimated dry S deposition to be 42% of the total S deposition to the deciduous and coniferous forests.

Despite the removal/conversion of the inorganic N species by the coniferous canopy, throughfall is acidic. The excess  $\text{SO}_4$  (and presumably N species deposition) in coniferous throughfall over precipitation, which is primarily derived from dry deposition to the canopy, is associated with a lower pH. The pH (from H deposition) of average weekly coniferous throughfall was 4.43 whereas for the same collection period, the precipitation pH was 4.51 and deciduous throughfall was 5.0. The coniferous throughfall generally is more acidic during winter and spring and less acidic from late spring through early fall. Also, although deciduous throughfall is less acidic than precipitation, the pH of weekly samples is most similar to the precipitation during spring and winter.

### 3.4. Temporal trends in atmospheric deposition

At PMRW, there are no statistically significant trends ( $p < 0.05$ ) in the annual wet deposition of H,  $\text{NH}_4$ ,  $\text{SO}_4$ , and  $\text{NO}_3$  from 1986 to 1999 (see Fig. 5 for  $\text{SO}_4$  and  $\text{NO}_3$  plus  $\text{NH}_4$ ). At the adjacent NTN sites, however, annual deposition significantly increased ( $p < 0.05$ ) during 1986–99 for  $\text{NH}_4$  at GA41 and AL99, and  $\text{NO}_3$  at AL99. Although trends in annual or monthly precipitation quantity were not statistically significant at  $p < 0.05$ , monthly concentration trends were detected for some solutes, several of which did not have comparably significant trends in deposition (Table 1). In particular, monthly  $\text{SO}_4$  concentrations significantly ( $p < 0.05$ ) decreased at AL99 and Georgia sites, but no trend was detected in deposition. At the two Georgia sites, GA41 and PMRW, decreasing trends in monthly H concentrations also were detected, consistent with the trends in the dominant acid anion. No trend was detected for monthly H concentration at AL99, probably due to increases in N species. Finally, trends were not statistically significant for monthly Cl deposition or concentration at any site supporting the hypothesis that the either the climate or Cl source did not change

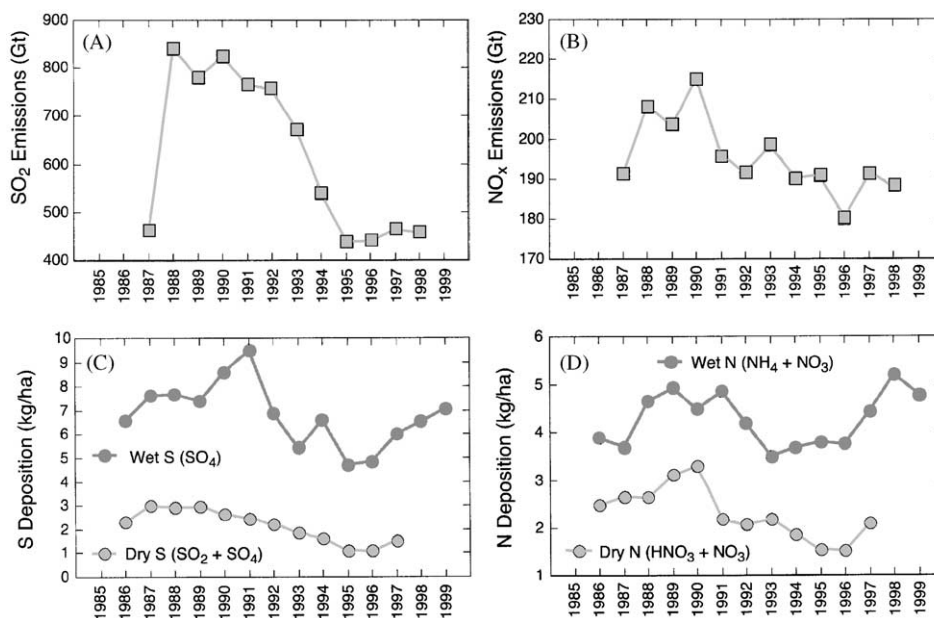


Fig. 5. Temporal trends in annual sum of (A)  $\text{SO}_2$  and (B)  $\text{NO}_x$  emissions from the seven major point sources within 120 km of the Panola Mountain Research Watershed, 1987–98, and associated annual wet and dry deposition of (C) S and (D) N 1986–99.

Table 1

Statistically significant ( $p < 0.05$ ) results of a seasonal trend analysis (Hirsch and Slack, 1984) of monthly volume-weighted mean concentration and deposition of select solutes in precipitation at the Panola Mountain Research Watershed, Georgia, and three adjacent NADP/NTN sites in Alabama (AL99), Georgia (GA41), and North Carolina (NC25). The analysis period is in parentheses for each site. For site locations, see Fig. 1

Parameter <sup>a</sup>		AL99 (01/1985–02/2000)		GA41 (01/1985–02/2000)		NC25 (01/1985–02/1999)		PMRW (04/1985–02/2000)	
		<i>p</i> level	Slope	<i>p</i> level	Slope	<i>p</i> level	Slope	<i>p</i> level	Slope
NH <sub>4</sub>	Concentration	0.003	0.29	0.009	0.24			0.05	0.15
	Deposition	0.003	0.44	0.003	0.32	0.02	0.23		
NO <sub>3</sub>	Concentration	0.004	0.22						
	Deposition	0.003	0.38						
Ca	Concentration								
	Deposition								
H	Concentration			0.02	−0.48			0.003	−0.74
	Deposition								
SO <sub>4</sub>	Concentration	0.04	−0.51	0.007	−0.47			0.003	−0.71
	Deposition								
Cl	Concentration								
	Deposition								

<sup>a</sup>Concentrations are in  $\mu\text{eq l}^{-1}$  and fluxes are in  $\text{eq ha}^{-1} \text{yr}^{-1}$ .



significantly at each site during the study period, i.e., Cl is primarily derived from a marine source.

At PMRW, annual wet deposition trends for acid anions and H are statistically significant for shorter periods (Fig. 5); SO<sub>4</sub> and NO<sub>3</sub> increased from 1986 to 1991 ( $p < 0.01$ ), and H, SO<sub>4</sub>, and NO<sub>3</sub> decreased from 1991 to 1995 ( $p < 0.05$ ) and increased from 1999 ( $p < 0.01$  for SO<sub>4</sub>, and NO<sub>3</sub> and  $p < 0.05$  for H). From 1986 to 1999, annual concentrations and deposition of H, SO<sub>4</sub>, and NO<sub>3</sub> were lowest in 1994. The increasing trends in solute deposition, particularly SO<sub>4</sub>, since 1995 are of interest because atmospheric S deposition was expected to decrease beginning in 1995 due to SO<sub>2</sub> emission reductions associated with the 1 January 1995 implementation of Phase I of Title IV of the 1990 Clean Air Act Amendments. Wet deposition is controlled in part by precipitation amount (Lynch et al., 2000), but no trends were detected in precipitation and the relations between annual VWM solute concentration and annual precipitation were not statistically significant ( $p < 0.1$ ). The trends in wet deposition at PMRW, therefore, were not directly affected by precipitation amount, and therefore, must be controlled by changes in sources.

Because of the potential additional errors/variability introduced to the dry deposition by the micrometeorological model, trends in air concentrations were evaluated as a surrogate for trends in dry deposition. Significant ( $p < 0.05$ ) decreasing trends were detected in SO<sub>2</sub> concentrations at PMRW and each CASTNET site for 1988–97, a comparable collection period at all sites. A significant decreasing trend in the SO<sub>4</sub> concentration from the Teflon filter was detected for PMRW, but not the other sites; this probably is a result of the slight design difference in filterpack for PMRW compared to the CASTNET sites. The PMRW filterpack has a 50-cm-long, heated inlet, whereas the CASTNET filterpack has an open inlet. The heated inlet might partly affect the accumulation of S and N species on the filters, but more likely affects the form of the species and therefore the filter on which S accumulates than on the total accumulation. No trends were detected for any of the air N species concentrations.

The annual total deposition, as measured by weekly throughfall, increased significantly after 1993 to the coniferous forest for SO<sub>4</sub> and H ( $p < 0.05$ ), and to the deciduous canopy for H ( $p < 0.01$ ). A significant ( $p < 0.05$ ) increasing trend in monthly dry deposition (throughfall minus wet deposition) was detected in coniferous throughfall for H and SO<sub>4</sub>, but statistically significant deposition trends were not detected in deciduous throughfall for these solutes. The absence of a significant trend in the deciduous canopy probably reflects the combination of the imprecision of this method for estimating dry deposition and the generally lower total deposition in the deciduous canopy compared to the coniferous canopy, which results in more

Table 2

Results of a seasonal trend analysis (Hirsch and Slack, 1984) of monthly NO<sub>x</sub> and SO<sub>2</sub> emissions in Gt for major point sources within 120 km of the Panola Mountain Research Watershed. For site locations noted in parentheses, see Fig. 1

Site	NO <sub>x</sub>		SO <sub>2</sub>	
	<i>p</i> value	Slope	<i>p</i> value	Slope
Bowen (a)	0.003	−0.13	0.003	−1.0
Hammond (b)	0.003	−0.05	0.003	−0.32
Harlee Branch (c)	0.003	−0.06	0.003	−0.14
McDonough (d)	0.003	−0.01	0.003	−0.32
Yates (e)	0.003	−0.06	0.003	−0.46
Wansley (f)	0.003	−0.11	0.003	−1.2
Scherer (g)	0.003	0.32	0.003	0.55
Total	0.003	−0.17	0.003	−3.3

noise in the computed dry deposition (throughfall minus wet deposition).

### 3.5. Relation between atmospheric deposition and emissions

The total annual SO<sub>2</sub> emissions from seven major point sources within 120 km of PMRW decreased markedly from 1988 to 1995 (Fig. 5A and Table 2). The pattern was similar for individual point sources as well, except for plant Scherer (g on Fig. 1). The annual SO<sub>2</sub> emissions were highly correlated among the power plants ( $p < 0.01$ ), but the correlation for the emissions of plant Scherer, to the southeast of PMRW was negative with the other plants. Since 1995, the SO<sub>2</sub> emissions have remained relatively constant or increased slightly for most of the individual sources. The annual wet and dry S deposition at PMRW were significantly correlated ( $p < 0.01$ ) with each other ( $r^2 = 0.65$ ) and with the total annual SO<sub>2</sub> emissions ( $r^2 = 0.85$ ) and with the emissions of individual sources ( $r^2$  range from 0.71 to 0.95), with the highest positive correlation for plants closest to PMRW to the southwest (Yates:  $r^2 = 0.94$ ) and northeast (McDonough:  $r^2 = 0.94$ ). None of the major point sources, however, were located directly upwind of PMRW, according to the predominant daily SSE wind direction (204°) (Fig. 1). Nevertheless, large variations in air circulation occur rapidly and the related mixing can alter the S sources on the short term. Also, the regional analysis by Holland et al. (1999) shows marked decreases in SO<sub>2</sub> emissions regionally from 1989 to 1995, particularly for Georgia and major sources to the west of PMRW in Alabama.

During 1986–99 at PMRW, weekly wet SO<sub>4</sub> concentration and deposition are highly correlated with wet NO<sub>3</sub> ( $r^2 \geq 0.81$ ). The regression of SO<sub>4</sub> concentration on NO<sub>3</sub> for the shorter periods during which trends were

detected, i.e., 1985–90, 1991–94, and 1995–99, also were high ( $r^2 > 0.78$ ), but the relative importance of  $\text{SO}_4$  decreases in that the slope of the linear regression decreases from 2.3 to 1.9 to 1.6 for each of the shorter periods, respectively. The decrease is consistent with and probably controlled by the pronounced decrease in  $\text{SO}_2$  emissions from the major point sources and related wet and dry  $\text{SO}_4$  deposition.

A decreasing trend in total annual  $\text{NO}_x$  emissions was detected for most of major point sources although the variance in annual emissions was small compared to  $\text{SO}_2$  (Table 2 and Fig. 5). The county-level analysis of  $\text{NO}_x$  emissions trends by Holland et al. (1999) shows a mixture of increases and decreases in the vicinity of PMRW and a general increase over most of southern Alabama, the upwind direction from PMRW. The increasing N emissions in Alabama also are consistent with the increasing N species wet deposition and concentrations at the AL99 site (Table 1).

#### 4. Summary

Trends in wet and dry deposition were investigated using data from a weekly sampling network to evaluate deposition processes at the Panola Mountain Research Watershed (PMRW), a forested research site 25 km, southeast of Atlanta, Georgia. Atmospheric deposition has been monitored using various methods at PMRW since 1985, including weekly sampling for both the National Oceanic and Atmospheric Administration's Atmospheric Integrated Monitoring Network (AIR-MoN-dry) and the National Atmospheric Deposition Program's National Trends Network (NTN). Trends in concentration and deposition were analyzed and compared to wet deposition at adjacent NTN sites and dry deposition from Clean Air Status and Trends Network (CASTNET) sites, which were co-located at the NTN sites. The pH of precipitation at PMRW is acidic; the mean pH (derived from the volume-weighted mean (VWM) H concentration) is 4.44 for 1986–99, and varies seasonally with the average lowest pH (from H deposition) in summer (4.19) and average highest in winter (4.63). The H (and pH) is highly correlated with  $\text{SO}_4$  and  $\text{SO}_4$  plus  $\text{NO}_3$ .  $\text{SO}_4$  dominates the acid anions and typically is more than two times the  $\text{NO}_3$  concentration. Coniferous throughfall also is acidic having an average annual pH (from VWM H) of 4.42 from 1993–99, but deciduous throughfall is less acidic than either precipitation (4.51) or coniferous throughfall (5.0) for the same collection period.

The 1986–99 annual wet S and N deposition averaged 400 and 300 eq ha<sup>-1</sup> (6.4 and 4.2 kg ha<sup>-1</sup>), respectively. Inferential model estimates of annual dry S and N deposition from 1986–97 averaged 130 and 150 eq ha<sup>-1</sup> (2.1 and 2.1 kg ha<sup>-1</sup>), respectively. From 1993–99, net S

deposition (dry deposition plus canopy interactions) for coniferous and deciduous throughfall (throughfall minus wet-only precipitation) averaged 400 and 150 eq ha<sup>-1</sup> (6.4 and 2.1 kg ha<sup>-1</sup>), respectively. The inferential model estimates are similar to the net S deposition of the deciduous forest.

Temporal variations of precipitation  $\text{SO}_4$  concentrations are similar to those of atmospheric  $\text{SO}_4$  concentrations, and are highest in summer and lowest in winter. In contrast, atmospheric  $\text{SO}_2$  concentrations are much higher than and negatively correlated with atmospheric  $\text{SO}_4$  concentrations. Furthermore, the highest dry S deposition ( $\text{SO}_2$  plus  $\text{SO}_4$ ) and wet  $\text{SO}_4$  deposition occurs during summer.

The annual wet deposition of S and N species at PMRW was comparable to that at NTN sites, with the exception of higher N species deposition at AL99 and relatively lower H,  $\text{SO}_4$  and  $\text{NO}_3$  deposition at GA41. Dry S and N deposition at PMRW differed markedly from the CASTNET sites, and the differences are attributed to differences in model parameters associated with the landscape and vegetation characteristics of the sites. In particular, model CASTNET dry deposition was highest at GA41 and AL99 sites, which are dominated by grassland and agriculture. Despite differences in deposition, air concentrations, however, were comparable at these sites.

At PMRW, wet deposition trends were not detected for the entire sampling period, but were detected for shorter periods (4–5 yr). Annual wet S and N deposition increased from 1986 to 1991, decreased to 1995, and then increased to 1999. Meanwhile,  $\text{SO}_2$  emissions from seven major point sources within 120 km of PMRW decreased markedly from the late 1980s to 1995 and have remained relatively constant or increased slightly from 1995 to 1998. In addition, a significant decreasing trend ( $p < 0.05$ ) was detected for  $\text{SO}_2$  concentrations from the weekly filterpacks at each site for 1988–97. Following the 1 January 1995 implementation of Phase I of Title IV of the 1990 Clean Air Act Amendments, atmospheric S deposition was expected to decrease in response to  $\text{SO}_2$  emission reductions in 1995, but the emission decrease occurred prior to 1995. The annual wet and dry S deposition at PMRW significantly correlate ( $p < 0.01$ ) with the local  $\text{SO}_2$  emissions.

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