Watershed Budgets of
Chloride and Sulfate as Integrators of Ecosystem Processes

Josslyn B. Shapiro

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ABSTRACT

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Cl^- and SO_4^{2-} budgets were developed for the Cascade Brook watershed within Black Rock Forest, in the Hudson Highlands, NY. Additionally, temporal trends in $[H^+]$, $[NO_3^-]$ and $[NH_4^+]$ and wet deposition were examined. Patterns in Cl^- wet deposition indicated that sources in addition to sea-salt aerosols contribute ~ 24% of mean annual Cl^- wet deposition. These additional sources probably include: 1) HCl emissions from coal fired generating stations; 2) HCl emissions from waste incineration; and, 3) HCl production from sea-salt dechlorination. Cl^- export budgets for Cascade Brook yielded a Cl^- export to Cl^- wet deposition ratio of 3:1 indicating that there was at least one significant source in addition to wet deposition contributing Cl^- to Cascade Brook. We conclude that additional Cl^- sources contributing appreciable amounts to Cl^- export include dry deposition and mineralization of soil organic matter.

Decadal trends (1981-2003) in precipitation chemistry near Cascade Brook indicate that SO_4^{2-} wet deposition decreased by ~ 37% and that this decrease was consistent with decreases in SO_2 emissions upwind of Black Rock Forest. In addition, SO_4^{2-} wet deposition per unit area represented only ~ 20% of local and regional SO_2 emissions, indicating that appreciable amounts of S were probably deposited locally as dry deposition or as wet and dry deposition at sites beyond the northeastern USA. An independent estimate of S dry deposition near Cascade Brook, derived using a dry

deposition inferential technique, indicated that S dry deposition contributed 50% as much S as SO_4^{2-}-S wet deposition. Finally, temporal patterns in Cascade Brook SO_4^{2-} surface water export indicate two important trends: 1) appreciable amounts of S are probably stored temporarily within the Glycerine Hollow wetlands; and 2) the ~ 2.8 - 3.1 ratio of SO_4^{2-} export to SO_4^{2-} wet deposition indicate that sources other than wet deposition contribute significant amounts of S to the watershed. Using a watershed mass balance approach, we estimate an upper limit for S dry deposition of 14-17 kg S ha^{-1} yr^{-1}, which was ~ 3.5 - 4.3 times the amount of S dry deposition derived from the inferential technique (4.0 kg S ha^{-1} yr^{-1}).

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INTRODUCTION

Ecosystem studies using a watershed approach to biogeochemical analysis regard an entire catchment as a single unit with interacting components (Likens, Bormann, 1995). This integrated approach considers the sum of biotic and abiotic factors on the abundance and movement of water, organic matter and inorganic matter as it travels through a watershed. The watershed considered for the work presented here is the 135-hectare Cascade Brook watershed located within the Black Rock Forest, a relatively pristine 1500-hectare preserve located near the western shore of the Hudson River in the Hudson Highlands of NY ~ 70 km north of New York City. Black Rock Forest is an active research site for numerous ecological, botanical, physiological and hydrological studies (e.g. Engel, *et al.*, 2002; e.g. Shaman, *et al.*, 2002; Barringer, Clemants, 2003; Nagel, Griffin, 2004; Whitehead, *et al.*, 2004)

Concentrations and fluxes of Cl^-, SO_4^{2-}, H^+, NO_3^- and NH_4^+ within or proximal to Cascade Brook were chosen for comprehensive analysis. Chloride has been widely used as a conservative tracer in the hydrologic cycle since it is often considered not to be subject to significant influences from chemical weathering, mineral formation (absent any evaporite minerals in many catchments) or biological processes (Feth, 1981). The primary input of sea-salt ions, such as chloride, to the atmosphere is generated by wind stress on the ocean surface, which produces bubbles from air entrained by breaking waves that burst at the surface and eject sea water aerosols into the atmosphere (Woodcock, *et al.*, 1953). This process is the dominant source for Cl^- in rain and snow over both continents and the ocean (Feth, 1981), although there are several additional regional processes known to contribute significant amounts of non-marine Cl^- to total Cl^- deposition. In addition to obtaining watershed Cl^- budgets, there are other motivations for investigation of Cl^- within Cascade Brook. For example, it has become of considerable regional interest to document $[Cl^-]$ in streams that have been perturbed by anthropogenic sources of chloride salts (Hauser, 2004). Surface water chemistry of the Cascade Brook watershed within Black Rock Forest provides a valuable example of a relatively pristine forested ecosystem. A number of Hudson River tributaries have Cl^- concentrations that have been greatly affected by winter road salting and effluent from wastewater treatment plants (Godwin, *et al.*, 2003; Hauser, 2004; Nieder, 2005). Elevated $[Cl^-]$ can have significant negative impacts on the health and composition of terrestrial vegetation (Hofstra, *et al.*, 1979; Panno, *et al.*, 1999; Viskari, Karenlampi, 2000; Richburg, *et al.*, 2001) as well as industrial infrastructure and therefore it is important to establish the degree to which $[Cl^-]$ for a given stream exceeds natural background levels in pristine watersheds such as Cascade Brook.

An additional issue related to anthropogenic pollution relevant to Cascade Brook concerns the deposition of sulfuric and nitric acids in the northeastern USA, which can have had significant impacts on sensitive terrestrial and aquatic ecosystems in the region (Likens, *et al.*, 1972; Siccama, *et al.*, 1982; Likens, *et al.*, 1996; Norton, Vesely, 2003) such as acidification of soil and lake waters, discoloration of leaves or needles, tree dieback and leaching of vital nutrient cations from soils (Driscoll, *et al.*, 2001; Tomlinson, 2003). Specific to reduced tree growth, it has been shown that acid deposition increases the flux of base cations, such as Ca^{2+}, into soil solution, subsequently leading to increased Ca^{2+} outflow in streams, which decreases availability for biomass uptake (Lawrence, *et al.*, 1995; Shortle, *et al.*, 1997; Tomlinson, 2003). In an effort to reduce these and other detrimental effects, the 1990 Clean Air Act Amendments (CAAA) were designed to significantly lower emissions of SO_2 and NO_x from electricity generating stations. These reactive gases are subsequently oxidized and hydrolyzed in the atmosphere, resulting in acidic precipitation and therefore lowering large point source emissions should lessen impacts on downwind ecosystems (Holland, *et al.*, 1999; Lynch, *et al.*, 2000). For Cascade Brook, two main objectives regarding acidic precipitation are to: 1) characterize seasonal and interannual variability in precipitation concentration and wet deposition of ions associated with acidic precipitation (i.e. H^+, SO_4^{2-} and NO_3^-) and identify processes consistent with various temporal patterns; and 2) measure seasonal and interannual variability in Cascade Brook stream water [SO_4^{2-}] and SO_4^{2-} export and identify processes consistent with emergent trends.

The specific fluxes estimated in this dissertation for developing ion budgets for Cascade Brook were the atmospheric deposition and stream water export of Cl^- and SO_4^{2-} and the wet deposition of H^+, NO_3^- and NH_4^+. Atmospheric deposition occurs via two main pathways relevant to Cascade Brook; wet and dry deposition. Wet deposition refers to the process by which gases and aerosols react with water during both cloud condensation and during scavenging as precipitation (i.e. rain or snow) falls to the ground (Lovett, 1994; Berner, Berner, 1996). This process is primarily controlled by meteorological conditions and the concentration and solubility of gases and aerosols in the atmosphere (Lovett, 1994). Estimation of this flux is relatively straightforward and is currently measured using weekly composite precipitation samples by the National Atmospheric Deposition Program (NADP) at more than 200 monitoring stations across the USA (Lamb, Bowersox, 2000). Precipitation amount and composite chemistry have been measured by the NADP at the West Point Military Academy, NY from June 1979 to the present (NADP, 2004). This monitoring station is ~ 5 km SSW of Cascade Brook and for the purposes of developing watershed budgets, precipitation amount and corresponding chemistry data from this West Point monitoring station are assumed here to be spatially representative proxy data for concentration and wet deposition to the Cascade Brook catchment.

A second route for gas and aerosol deposition is via dry deposition. Aerosol dry deposition occurs by gravitational settling and wind induced impaction for particles > 5μm, and by diffusion across the boundary layer of a receptor surface for smaller particles. For gases, dry deposition occurs via boundary layer diffusion and subsequent vegetative absorption (Lovett, 1994). Key factors that influence the rate of dry deposition include: 1) concentrations of gases or aerosols of interest in the atmosphere; 2) temporal variability in local meteorology (especially turbulence in the lower atmosphere) and; 3) variation in site-specific vegetative characteristics (Ollinger, *et al.*, 1993; Lovett, 1994). Dry deposition fluxes of aerosols and gases, which can contribute at least as much as wet deposition to total deposition (Lovett, 1994) are significantly more complicated to estimate than wet-only deposition and the derived fluxes have a greater degree of uncertainty (Hicks, *et al.*, 1991; Meyers, *et al.*, 1991). Three methods often used to estimate this flux are the Dry Deposition Inferential Measurement (DDIM), the net throughfall flux and the watershed mass balance approach. Each method has inherent strengths and weaknesses and thus a particular watershed study may rely on a combination of approaches to constrain the magnitude of dry deposition (e.g. Likens, *et al.*, 2002).

Once gases and aerosols are delivered to a watershed via wet or dry deposition, export of the relevant ion of interest can be estimated by the product of a measured concentration in stream water and the corresponding water discharge amount. A mass balance approach to ion budgeting compares the atmospheric input flux with the stream water export flux. If an ion moves conservatively through a watershed, then hypothetically, a watershed budget would be balanced (i.e: wet + dry inputs = stream export). This mass balance approach was applied to Cl^- and SO_4^{2-} budgets at Cascade Brook since surface water exports of these atmospherically-derived ions are generally thought to outweigh perturbation from biological and geochemical processes within a drainage basin free of evaporite minerals. (Feth, 1981; Lovett, 1994). Results presented here for Cascade Brook suggest that sources in addition to atmospheric deposition (wet + dry) are likely to provide appreciable amounts to watershed Cl^- and SO_4^{2-} export budgets, thus indicting that Cl^- and SO_4^{2-} may not behave strictly conservatively on time-scales of a few years within Cascade Brook. Such additional sources of Cl^- and SO_4^{2-} internal to the Cascade Brook watershed include for example possible contributions from: 1) mineralization of soil organic matter formed during periods with greater deposition of Cl^- and SO_4^{2-} ions; 2) chemical weathering of Cl^- and S bearing rocks and minerals within Cascade Brook and 3) desorption of SO_4^{2-} from the mineral soil layer.

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CHAPTER 1

Precipitation chemistry near West Point, NY: summer dominance of chloride in excess of sea water Cl^-/Na^+

J. B. Shapiro[1, 2] *, H. J. Simpson[1,2], K. L. Griffin[1,2] and W. S. F. Schuster[3]

[1]Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964

[2] Department of Earth and Environmental Sciences, Columbia University, New York, NY 10027

[3] Black Rock Forest, 129 Continental Road, Cornwall, NY 12518

*Author for correspondence: Phone: 845 365 8395; Email: jbs59@ldeo.columbia.edu

Abstract

Chloride derived from the atmosphere can be a valuable tracer in ecosystem and watershed processes. For these purposes and other environmental studies, it is important to establish temporal patterns in Cl^- wet deposition. Weekly composite precipitation samples have been analyzed by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) at a monitoring station near West Point, NY for more than two decades. Chloride and sodium ion seasonal wet deposition fluxes (1980-2003) were highest in winter (4.7 ± 0.9 mEq m^{-2} and 3.5 ± 0.7 mEq m^{-2}) and lowest in summer (1.9 ± 0.2 mEq m^{-2} and 1.0 ± 0.1 mEq m^{-2}), probably as a result of more frequent marine air storms in the winter. However, the ratio of $[Cl^-]/[Na^+]$ was higher in summer and lower in winter. Higher summer $[Cl^-]/[Na^+]$ occurred consistently throughout the record, often reaching values twice the sea water ratio. Based only on the ratio of $[Cl^-]/[Na^+]$ in sea water ~ 18% of annual wet deposition of Cl^- was in excess of that for marine aerosols. Additionally, a distinct terrestrial dust Na^+ component was estimated and two systematic analytical errors in NADP/NTN data reported for Na^+ were assessed, which had the net effect of increasing excess Cl^- wet deposition to at least ~ 24% (3.30 ± 0.2 mEq m^{-2} or 1.17 ± 0.07 kg ha^{-1}) of annual wet deposition of Cl^- near West Point. Consistent with large regional sources of non-marine Cl^-, we attribute ~ 29-50% of the excess Cl^- wet deposition to HCl emission from coal fired generating stations, ~ 5-9% to HCl emissions from domestic and industrial waste incineration and ~ 40-60% to HCl formation in the atmosphere from reactions of sea-salt aerosols with acidic gases.

Key Words: NADP, HCl, coal combustion, incineration, sea-salt dechlorination

Introduction

Deposition via precipitation of dissolved ions offers a valuable opportunity to gain information about input and subsequent transport of a range of chemical species in forested ecosystems (Peters and Ratcliffe, 1998; Feng *et al*., 2004). The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) currently collects and reports weekly composite precipitation amounts and chemical compositions from more than 200 sites in the USA (Lamb and Bowersox, 2000), one of which is located on the West Point Military Reservation in New York. Wet deposition from this monitoring station can be used to estimate atmospheric inputs to forested ecosystems in this region.

Chloride has been widely used as a conservative tracer in the hydrologic cycle since it is often not subject to significant influences from chemical weathering, mineral formation or biological processes (Feth, 1981). For environments with low dissolved ion levels in groundwaters, no evaporite minerals in the soils or rocks and no significant anthropogenic sources, the input of Cl^- to surface waters should be predominantly from the atmosphere. These properties make Cl^- ideal for studies of watershed hydrological processes such as estimating evapotranspiration averaged over months to years from measurements of $[Cl^-]$ input via precipitation and $[Cl^-]$ output via stream flow (Claassen and Halm, 1996; Forti *et al*., 2000). The primary input of sea-salt ions, such as chloride, to the atmosphere is generated by wind stress on the ocean surface, which produces bubbles from air entrained by breaking waves that burst at the surface and eject sea water aerosols into the atmosphere (Woodcock *et al*., 1953). Once the water in these marine droplets evaporates, sea-salt aerosols can remain airborne for days to weeks and be transported over the land. This process is the dominant source of Cl^- in rain and snow over both continents and the ocean (Feth, 1981).

The goals of this investigation include: 1) quantify annual and seasonal wet deposition fluxes near West Point, NY of ions derived primarily from marine sources; 2) relate selected ion concentrations to seasonal atmospheric processes; and 3) identify regional sources and atmospheric processes consistent with excess Cl^- wet deposition near West Point, NY.

Methods

NADP site NY99 (41.35°N, 74.05°W, 201 m elevation) is located within the West Point Military Reservation, in Orange County, New York, approximately 100 km inland from the Atlantic coast [Fig.1]. The specific location of NY99 is at Camp Buckner, which is on the grounds of the West Point Military Reservation but ~ 8 km west of West Point proper. West Point proper extends to the edge of the Hudson River. Therefore, NY99 is closer to the border of the Black Rock Forest (< 3 km) and the towns of Highlands Falls (7 km), Fort Montgomery (6 km), Central Valley (6 km) and Highland Mills (5 km). Thus, the meteorological conditions at this monitoring station reflect much more the conditions typical of the Black Rock Forest and surrounding Hudson Highlands than they do the corridor along the Hudson River where West Point is located.

The regional climate for this area usually defined as humid continental and an average of ~ 100 mm of precipitation is received each month. Precipitation during colder months in the northeastern USA is marked by strong and frequent cyclones originating from the Atlantic coast or offshore regions (Lawrence *et al.,* 1982). Collection of precipitation samples at NY99 began on 9/13/1983 and has continued through the present.

To complement NY99 data, precipitation chemistry for the neighboring NADP site NY51 (located ~ 1 km ESE of NY99 and operated from 6/26/1979 to 10/2/1984) was examined for data quality and compatibility with that of NY99 (NADP, 2004a). Operation of NY51 was terminated in 1984 for logistical reasons (S. Dossett, 2004). Both NY99 and NY51 were active from 9/13/1983 to 10/2/1984. This period of 55 weeks of overlap presents an opportunity to compare weekly precipitation chemistry for stations in close proximity on the West Point Military Reservation.

Based on the presence of a number of anomalously high values of $[Na^+]/[Cl^-]$ in the first year of operation for NY51 [Fig. 2A], data prior to July 1, 1980 were excluded here from further consideration. Ratios of $[Na^+]/[Cl^-]$ for NY99 [Fig. 2B] did not show any periods of unusually high values. Precipitation amounts and ion concentrations from NY51 and NY99 (NADP, 2004a) were spliced here into one data set from July 1, 1980 through February 3, 2004, with data from NY99 representing the 55 weeks of the overlap period.

A modified version of the weekly data was developed to calculate amount-weighted mean concentrations for each ion. These fluxes can be used to derive wet deposition amounts for NY51/NY99. For this modified data, an infilling procedure was employed to estimate ion concentrations for all weeks in the combined NY51/NY99 data where a non-zero amount of precipitation was measured but no companion chemistry data were reported. In total, 167 or 13.6% of the 1231 weeks of the NY51/NY99 data required estimation [Table 1]. Overall, the infilling procedure increased the annual wet deposition by ~ 12% for both Cl^- and Na^+, a value that seems reasonable considering that infilling increased the number of weeks with ion chemistry by ~ 14%. The infilling procedures used were as follows:

1) During the period of data overlap at NY51 and NY99 (9/13/1983 to 10/2/1984) seasonal linear regressions forced through zero were calculated for each ion with NY99 data regressed against NY51. Throughout this study, "seasonal" refers to winter, spring, summer and fall where winter months are DJF, spring months are MAM, summer months are JJA, and fall months are SON. For weeks with no reported NY99 ion data, measured concentrations at NY51 were used to generate infill values for NY99 through the above linear regressions (2 weeks).
2) For weeks that either NY51 or NY99 required infill values outside of the period of data overlap, two other NADP stations in close proximity to NY51 or NY99, that were operational at the time, were used to calculate seasonal multiple linear regressions for each ion (28 weeks). For NY51, the two NADP stations used were NY12 and NJ99 and for NY99 the two NADP stations used were PA72 and NJ99.
3) If precipitation amounts at NY51 or NY99 for a week that required infilled chemistry values were not in reasonable agreement with precipitation amounts measured at both of the stations in close proximity, a seasonal linear regression forced through zero of data for one site close to either NY51 or NY99 that did have a similar precipitation amount, was used to calculate infill chemistry values (70 weeks). For example, precipitation amounts for the week of 8/5/1986 were 2.79 mm at NY99, 2.54 mm at PA72 and 37.08 mm at NJ99. In this case, a seasonal linear regression between NY99 and PA72 was used to calculate infill chemistry values for that week. This approach was also used for weeks where chemistry data were available from only one of the proximal locations.

4) If a week in NY51 or NY99 required infill values but there were no chemistry data available at either proximal location or if neither proximal location had precipitation amounts in reasonable agreement with that measured at NY51 or NY99, values from a seasonal power function of ion concentration vs. precipitation amount were generated from the complete NY51 or NY99 data set (67 weeks).

Monthly amount-weighted mean concentrations (c_w) for each ion in the infilled data set were calculated as follows:

$$c_w = \frac{\sum_{1}^{n} c_i p_i}{\sum_{1}^{n} p_i} \qquad \text{Equation (1)}$$

Where *n* is the number of weeks per month, c_i is the weekly ion concentration (μEq L^{-1}) and p_i is the weekly precipitation amount.

A second version of the combined NY51/NY99 weekly values, entitled here as "screened" data, was used to address questions regarding temporal variability in $[Cl^-]/[Na^+]$ ratios and excess $[Cl^-]$. The following screens were applied to the combined NY51/NY99 data:

1) Concentrations for all weeks designated by the NADP as being invalid were removed (147 weeks) (NADP, 2004b).

2) Concentrations for all weeks with reported ion chemistry and precipitation amounts < 2.0 mm were removed to reduce biases created by evaporation for small samples (75 weeks) (Gilliland *et al.,* 2002).

3) Concentrations were removed from all weeks where the percent charge imbalance was > 3 times the standard deviation of the mean charge imbalance for the entire data set (20 weeks). For the NY99 data, the average charge

imbalance was –5.95% and the standard deviation was 6.89%. Charge imbalances for weekly ion data were calculated as follows:

$$= \left(\left(\sum cations - \sum anions\right) / \left(\left(\sum cations + \sum anions\right) * 0.5\right)\right) * 100 \qquad \text{Equation (2)}$$

Excess ion concentrations were calculated for Cl^- and Na^+ as follows:

$$Ion\ \mathrm{A}_{\mathrm{EX}} = Ion\ \mathrm{A}_{\mathrm{OBS}} - (Ion\ \mathrm{A} \,/\, Ion\ B * Ion\ B_{\mathrm{OBS}}) \qquad \text{Equation (3)}$$

Where $Ion\ A_{\mathrm{EX}}$ is the excess concentration of the ion of interest, $Ion\ A_{\mathrm{OBS}}$ is the measured ion concentration, $Ion\ A \,/\, Ion\ B$ is an assumed ratio of ions A and B in sea water or terrestrial dust and $Ion\ B_{\mathrm{OBS}}$ is the measured ion concentration.

Systematic analytical errors for NADP measured [Na^+] have been reported for data collected during the period of analysis here. One issue concerned the method of shipping precipitation samples to the Central Analytical Lab (CAL), the lab used for all NADP chemical analysis. Prior to January 11, 1994, precipitation samples were sent from each NADP site to the CAL in a high density polyethylene (HDPE) field collection bucket sealed with a lid containing a rubber O-ring. It was subsequently established that the lid O-ring added measurable amounts of the same ions found in rainwater to site samples, thus contaminating the samples (Lynch *et al.*, 1996; NADP, 2004c). As of January 11, 1994, precipitation samples were shipped to CAL in one liter HDPE bottles with screw on caps and this systematic bias was eliminated. It has been reported that the percentage bias caused by the O-ring contamination was greatest and negative for [H^+] and relatively small and positive for other ions. The bias that the O-ring produced for [Na^+] was +9.9 ± 2.5% compared to non-contaminated samples. No significant bias due to O-ring contamination was reported for [Cl^-] (NADP, 2004c).

A second systematic analytical error reported was [Na^+] increases for precipitation samples from Millipore filters used to filter samples in the lab before proceeding with chemical analysis (Gordon *et al.,* 2003). In January of 1998 Gelman filters replaced Millipore filters, which served to minimize [Na^+] contamination (Gilliland *et al.,* 2002; Gordon *et al.,* 2003). Gilliland *et al.,* 2002, attribute a ~ 16-32% enrichment of [Na^+] in precipitation samples analyzed prior to the procedural change. In both cases of systematic analytical errors prior to the procedural changes, [Na^+] was positively biased.

Results

Ion concentrations for [Cl^-] and [Na^+] (μEq L^{-1}) at the two West Point sites during the period of overlap (9/13/1983 to 10/2/1984) were quite similar [Fig. 3], with R^2 values of 0.95 and 0.97 for linear regressions of [Cl^-] and [Na^+], respectively. Precipitation amounts (mm $week^{-1}$) at NY51 and NY99 during the overlap period were very highly correlated [Fig. 3C] with a slope of 1.0 and an R^2 value of 0.99.

Annual average [Cl^-] (μEq L^{-1}) (Fig. 4), [Na^+] (μEq L^{-1}) (data not shown) and [Cl^-]/[Na^+] (data not shown) for the infilled and screened data over the decadal record (1981-2003) indicate relatively constant absolute concentrations over the measurement period. Additionally, there is no significant statistical difference in mean annual [Cl^-] (μEq L^{-1}) (1981-2003) (Fig. 4) between the infilled and screened data. Identical conclusions can be drawn for the [Na^+] (μEq L^{-1}) infilled and screened mean annual values (data not shown).

Ions predominantly of marine origin, [Cl^-] and [Na^+], displayed a prominent seasonal pattern in monthly aggregated amount-weighted concentrations [Fig. 5] and wet deposition fluxes [Table 2]. [Cl^-] and [Na^+] both had maximum concentrations in winter months, lower values in spring and minimum summer concentrations. Fall calendar month concentrations increased progressively to values comparable to those in winter. Mean values for amount-weighted concentrations of [Cl^-] and [Na^+] were appreciably greater than median concentrations during late fall and winter [Fig. 5], probably reflecting low frequency occurrences of large marine storm events with high concentrations of sea-salt ions.

The ratio of [Cl^-]/[Na^+] had a distinctive, albeit opposite seasonal trend [Fig. 6] for monthly amount-weighted concentrations. The ratio of [Cl^-] to [Na^+] during fall and winter was relatively low and much closer to the [Cl^-]/[Na^+] sea water ratio of 1.16. In contrast, [Cl^-]/[Na^+] ratios from April through August were much higher, reaching double the sea water ratio in June, July and August.

Temporal variations over more than two decades (1980-2003) in seasonal [Cl^-]/[Na^+] ratios indicate a consistent pattern [Fig. 7]. During non summer seasons [Cl^-]/[Na^+] ratios averaged ~ 35% greater than sea water whereas summer [Cl^-]/[Na^+] ratios averaged ~ 93% greater than the sea water ratio. This seasonal pattern was particularly evident after January 1998 when both O-ring and filter [Na^+] contamination issues had been eliminated. For the first three years of the combined NY51/NY99 record, derived entirely from NY51 samples, the prominent summer peak [Cl^-]/[Na^+] ratio was absent.

Annual wet deposition of excess Cl^- was 2.6 ± 0.2 mEq m^{-2} (0.92 ± 0.07 kg ha^{-1}) or 18% of total Cl^- wet deposition measured near West Point [Table 2], assuming only a marine source of Na^+. Excess [Cl^-] wet deposition was a much higher percentage of total Cl^- wet deposition during summer (38%) and lower than the annual mean during the fall (13%) [Table 2] with excess Cl^- deposition amount at a maximum in May and a minimum in October [Fig. 8A]. Calendar month variability in excess [Cl^-] [Fig. 8A] indicates that contributions to total wet deposition from marine [Cl^-] and excess [Cl^-] were comparable during the summer whereas the marine component dominated throughout the rest of the year.

Thus far, one of our implicit assumptions has been that all [Na^+] in precipitation measured near West Point had a marine aerosol origin, with no [Na^+] contributed from terrestrial dust. To explore the validity of this assumption using NY99 screened weekly data, [Na^+] was plotted against [Ca^{2+}], with Ca^{2+} assumed to be derived primarily from terrestrial dust (Berner and Berner, 1996). The total population of weekly screened data was separated into eight subdivisions based on the ratio of [Na^+]/[Ca^{2+}] for each sample with each subdivision containing an equal number of data points. The data were segregated into eight groups to provide a large number of individual weekly samples in each group (~ 100), and also capture the large range of Na^+/Ca^{2+} ratios in separate groups. We were primarily interested in defining the Na^+ vs. Ca^{2+} trend in the group with the lowest ratio of these ions. A linear regression equation, forced through zero, was calculated for data from each of the eight groups [Fig. 9]. Companion histograms plotting the frequency with which data in each group occurred during each calendar month indicated a clear discrimination of winter vs. summer [Na^+]/[Ca^{2+}] groups [Fig. 10]. Subdivisions of data with [Na^+]/[Ca^{2+}] slopes ≥ 2.2 occurred primarily during fall and winter and very infrequently during summer months. For comparison, the [Na^+]/[Ca^{2+}] ratio for sea water is ~ 23:1. The opposite pattern was observed for subdivisions of data with [Na^+]/[Ca^{2+}] slopes ≤ 0.6, with most frequent occurrence during spring and summer months. The lowest slope (0.15) for a sample group was assumed here to approximate precipitation composition when the contribution of marine Na^+ was minimal and therefore Na^+ could be attributed to a terrestrial dust component.

Using this approach, separate contributions of Na^+ wet deposition attributed to terrestrial dust and to marine sources were estimated [Fig. 8B]. The relative magnitude of terrestrial Na^+ and marine Na^+ wet deposition sources [Fig. 8B] indicate that: 1) approximate inputs of Na^+ from dust could be estimated, although the annual sum of Na^+ dust relative to total Na^+ wet deposition was not statistically significant (0.6 ± 0.02 and 10.4 ± 0.9); and 2) marine sources dominated Na^+ wet deposition throughout the year. The annual contribution of Na^+-dust to total Na^+ wet deposition measured near West Point was ~ 5% (0.6 ± 0.02 mEq m^{-2} or 0.14 ± 0.005 kg ha^{-1}). This contribution of terrestrial Na^+ translates into an additional 0.7 ± 0.02 mEq m^{-2} (0.25 ± 0.006 kg ha^{-1}) of excess Cl^- not accounted for in our initial derivation of excess Cl^-. Therefore, annual excess Cl^- wet deposition, taking into account an adjustment for dust derived Na^+, was 3.3 ± 0.2 mEq m^{-2} (1.17 ± 0.07 kg ha^{-1}) or ~ 24% of Cl^- wet deposition measured near West Point [Table 3].

Discussion

Wet deposition of Cl^- and Na^+ both are highest during colder months [Table 2], probably as a result of higher frequencies of rain and snow events with a major component of marine aerosols (Lawrence *et al.*, 1982). Wet deposition rates of $[Cl^-]$ and $[Na^+]$ during warmer months were significantly lower, presumably because of lesser influence from major marine storms.

The relatively stable decadal trend (1981-2003) in $[Cl^-]$ (μEq L^{-1}) (Fig. 4) is consistent with the trend in $[Cl^-]$ of bulk deposition recorded at the long term ecological research site at Hubbard Brook in New Hampshire (Lovett *et al.*, 2005) over the same time period. The absolute $[Cl^-]$, however, is significantly greater at the precipitation monitoring station near West Point, on the order of twice that recorded at Hubbard Brook, likely a result of lesser influence of marine storms at Hubbard Brook than at West Point. It is interesting to note that the long term $[Cl^-]$ (1967-2000) at Hubbard Brook reveals two distinct trends. The period from 1967-1980 records relatively high $[Cl^-]$ with a decreasing secular trend, whereas the period from 1981-

2000 records relatively low annual [Cl^-] with perhaps a slight increasing trend. The high annual [Cl^-] during the period from 1967-1980 was attributed to HCl deposition likely derived from coal burning, whereas the main source for the lower [Cl^-] from 1981-2000 was attributed primarily to a marine origin (Lovett *et al*., in press).

Calendar month and seasonal [Cl^-]/[Na^+] ratios in precipitation measured near West Point indicate a significant [Fig. 6] and persistent [Fig. 7] pattern of Cl^- deposition in excess of marine ratios, particularly during summer [Table 2]. When a correction for [Na^+] derived from a terrestrial dust source was included in the calculation of excess Cl^-, the total excess increased to 1.17 kg ha^{-1} (3.30 mEq m^{-2}) [Table 3]. This finding of a significant quantity of excess Cl^- wet deposition measured near West Point is consistent with regional sources and atmospheric processes known to contribute to precipitation [Cl^-] including: 1) coal combustion emissions of HCl (Lightowlers and Cape, 1988; McCulloch *et al* 1999), 2) waste incineration emissions of HCl (Lightowlers and Cape, 1988; McCulloch *et al* 1999); and 3) sea-salt dechlorination production of HCl (Yue *et al.*, 1976; Foltescu *et al.*, 1996; Roth and Okada, 1998; Erickson *et al.,* 1999) [Table 4A]. Estimates can be made of absolute and relative contributions of these three sources to the total excess Cl^- wet deposition measured near West Point.

Emissions of gaseous HCl from electricity generating stations are predominantly attributed to those that combust coal since chlorine abundance in fuel oils is generally very low and therefore will not be considered further (Lightowlers and Cape, 1988; McCulloch *et al* 1999). Based on relative proportions of chlorine and sulfur content in coal and assumptions regarding regional SO_2 emissions and SO_4^{2-} deposition listed below, we estimate that ~ 50% (1.66 mEq m^{-2} or 0.59 kg ha^{-1})

of annual excess Cl^- in wet deposition measured near West Point can be attributed to HCl emissions from coal combustion [Table 4A]:

1) Annual wet deposition of S as SO_4^{2-} measured near West Point (1981-2003) was 8.9 kg S ha^{-1} (Shapiro *et al.,* unpublished data). Note that sea-salt contribution to SO_4^{2-} wet deposition measured near West Point is only ~ 2% of the total, based on the ratio of SO_4^{2-}/Na^+ in sea water and assuming all Na^+ deposition was derived from sea salt.
2) At least 90% of sulfate in wet deposition measured near West Point was derived from anthropogenic sources (Galloway and Whelpdale, 1980; Langner *et al*., 1992; Rodhe, 1999; Rasch *et al*., 2000).
3) Approximately 96% of total SO_2 emissions from fossil fuel combustion in NY, NJ, PA, OH and WV can be attributed to coal combustion (USEPA, 2003). The states included in the regional source emissions for West Point wet deposition were defined here by those proposed in Butler *et al*., 2001, and Butler *et al*., 2003, using the NOAA Air Resources Laboratory's Hysplit-4 model (Draxler and Rolph, 2003; Rolph, 2003). The results of these computations designate SO_2 emissions from NY, NJ, PA, OH and WV as the dominant 9-12 hour air mass back trajectories for New York State deposition.
4) The weight ratio of chlorine to sulfur in average coal combusted in the USA is 0.1% / 1.3% (McCulloch *et al*., 1999; Nimmo *et al*., 2004).
5) Mean annual wet deposition of Cl^- measured near West Point (1981-2003) was 4.8 kg ha^{-1} and mean annual total wet deposition of excess Cl^- measured near West Point (1981-2003) was 1.17 kg ha^{-1}.

No explicit correction for Flue Gas Desulfurization (FGD) has been applied here to the estimate for coal combustion derived HCl. FGD has the potential to remove ~ 70-95% of SO_2 emissions and ~ 90% of HCl emissions (McCulloch *et al*., 1999; USDOE, 2002) and on average 27% of the generating stations in the United States were using FGD technologies by the early 1990's (McCulloch *et al.,* 1999). We have assumed that the proportion of Cl^- emission removal is the same as for S emission removal using FGD.

Additionally, although some estimates of the atmospheric lifetime of HCl (~ 1-2 days) (i.e. McCulloch *et al.,* 1999) are similar to that of SO_2 (~ 1-2 days) and appreciably less than the 4-5 day lifetime of SO_4^{2-} (Rasch *et al*., 2000) no attempt has been made here to account for differential temporal and spatial deposition of these gases. This assumption adds uncertainty to our estimation of total excess Cl^- wet deposition which can be attributed to HCl emissions from coal combustion.

A second plausible source of excess Cl^- wet deposition for the West Point area is emission of HCl from the incineration of domestic and industrial waste. Estimates for the United States, adopted here, indicate that HCl emission from incineration are on the order of 19% of HCl emissions from coal combustion (McCulloch *et al.,* 1999). Applying this percentage to the annual 0.59 kg ha^{-1} (1.66 mEq m^{-2}) calculated for excess Cl^- in wet deposition attributed to coal combustion assigns 0.11 kg ha^{-1} (0.31 mEq m^{-2}) or ~ 9% of the total annual excess Cl^- in wet deposition measured near West Point to HCl emissions from incineration [Table 4A].

A third plausible source of excess Cl^- in wet deposition in the West Point area is deposition of HCl produced by the interaction between atmospheric acids, such as H_2SO_4 and HNO_3, and sea-salt aerosols (Yue *et al*., 1976; Foltescu *et al*., 1996; Roth and Okada, 1998). It has been suggested that gaseous HCl derived from such reactions has a longer atmospheric residence time than marine aerosols and thus has the potential to be deposited at appreciable distances inland (Moody *et al*., 1991;

Jourdain and Legrand, 2002; Röthlisberger *et al.,* 2003). Observations indicate Cl^- depletion in bulk deposition at a coastal site in the Netherlands (Ten Harkel, 1997) as well as in aerosol samples on the Antarctic coast where the degree of Cl^- depletion of sea-salt aerosols in the boundary layer was roughly proportional to HCl concentrations in air samples (Jourdain and Legrand, 2002). Röthlisberger *et al.* (2003) used the suggested longer residence time for gaseous HCl than marine aerosols to help explain the gradient in summer $[Cl^-]/[Na^+]$ ratios measured by Qin *et al.,* (1999) in surface snow from the Antarctic coast to locations inland. They observed that $[Cl^-]/[Na^+]$ ratios in snow at the coast had a tendency towards Cl^- depletion and sites inland on the Antarctic plateau had $[Cl^-]/[Na^+]$ more than twice the sea water ratio.

It is plausible that a similar set of processes could influence atmospheric chloride transport to West Point, NY and thus contribute to excess Cl^- in wet deposition. In particular, the large increase during warmer months in regional atmospheric acidic gases (HNO_3, H_2SO_4) (Kelly *et al.,* 2002; Shapiro *et al*., unpublished data) provides a favorable environment for sea-salt dechlorination and thus could contribute to the consistent pattern of $[Cl^-]/[Na^+]$ ratios of approximately twice that of sea water during summer [Figs. 6 and 7]. Correlations between excess $[Cl^-]$ and $[NO_3^-]$ were relatively high during summer ($R^2 = 0.4$; $p < 0.0001$; Fig. 11) for samples collected after the bucket O-ring contamination issue had been addressed (1/1/94-2/1/04) indicating that wet deposition of excess $[Cl^-]$ correlates significantly with wet deposition of $[NO_3^-]$. This scenario is consistent with atmospheric HNO_3 interacting with sea-salt aerosols to produce HCl, which then contributes to excess $[Cl^-]$ in precipitation measured near West Point.

Additionally, measurements of atmospheric HCl concentrations in New York City, southern California, and the coastal Antarctic indicate that the highest HCl concentrations occur in summer (Eldering *et al.*, 1991; Jourdain and Legrand, 2002; Bari *et al.*, 2003; Fig. 12) and sea-salt dechlorination was specified as the primary process responsible for variability in measured HCl as a function of season. For precipitation measured near West Point, we estimate by difference that 0.47 kg ha^{-1} (1.33 mEq m^{-2}) or ~ 40% of the total excess Cl^- in wet deposition can be attributed to HCl deposition resulting from regional sea-salt dechlorination [Table 4A].

Regarding the persistent pattern in the calendar month values of the $[Cl^-]/[Na^+]$ ratio, it is plausible that because wet deposition of Cl^- during summer is significantly lower than other seasons, due to less frequent storm events with a strong marine component, the ratio of $[Cl^-]/[Na^+]$ during summer is more sensitive to small increases in non-marine Cl^- deposition. Emissions from coal combustion and incineration are less likely to have such a strong seasonal component, and thus the relative contribution of HCl from sea-salt dechlorination could be more important during summer when regional acidic gases (HNO_3, H_2SO_4) are formed at higher rates by atmospheric oxidants. Note that the calendar month pattern of summer maximum for Cl^-/Na^+ ratios in wet deposition measured near West Point is opposite to that for the flux computed for the global sea salt dechlorination production of HCl, which has a maximum during January that is about four times greater than in July (Erickson *et al.,*1999).

In conclusion, on an annual basis, ~ 24% of Cl^- deposition via precipitation measured near West Point is in excess of that predicted from ratios of $[Cl^-]/[Na^+]$ in sea water. This estimate includes an adjustment for Na^+ deposition attributed to terrestrial dust rather than sea salt. If two systematic analytical corrections for $[Na^+]$

(discussed in the Methods section) were applied to this data set the [Cl$^-$]/[Na$^+$] ratios and excess [Cl$^-$] wet deposition during the period prior to 1998 would have been further increased, perhaps by up to 34% for a significant fraction of the record. Excluding incorporation of systematic analytic errors for [Na$^+$] ~ 50% of excess Cl$^-$ is attributed to HCl emission from regional coal fired electricity generating stations, ~ 9% is attributed to emissions of HCl from incineration of domestic and industrial waste and ~ 40% is attributed to HCl produced by sea-salt dechlorination in the regional atmosphere. If we explicitly include Na$^+$ sources from two systematic analytical errors for the fraction of the record for each error (see Tables 4B and 5) the proportions of excess Cl$^-$ from coal, incineration and dechlorination of marine aerosols become, respectively: 29%, 5% and 65%. These calculations should provide a plausible upper limit for the effect of two systematic analytical errors for Na$^+$ on the allocation of excess Cl$^-$ wet deposition measured near West Point. We do not, however, find any obvious decadal trends for either [Na$^+$] (μEq L^{-1}) or [Cl$^-$]/[Na$^+$] to corroborate the combined affect of the two Na$^+$ analytical biases. Nonetheless, these budget calculations indicate that both coal combustion and dechlorination of marine aerosols are important contributors to excess Cl$^-$ deposition measured near West Point.

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Table Captions

Table 1: Description of infill methods for ion concentrations in combined NY51/NY99 data for weeks with precipitation amounts but no chemistry reported. [a]promixal NADP stations used were: PA72 and NJ99 for NY99 and NY12 and NJ99 for NY51.

Table 2: Wet deposition for combined NY51/NY99 infilled data compiled seasonally and annually. Wet deposition (mEq m^{-2}) for excess Cl^- and dust (derived from non-marine aerosols) Na^+ are also listed.

Table 3: Components and magnitude of excess Cl^- wet deposition measured near West Point calculated from: 1) comparison of measured $[Cl^-]/[Na^+]$ with sea-salt ratio (1.16) and 2) corrected for $[Na^+]$ derived from terrestrial dust.

Table 4: A) Absolute and relative contributions of sources of excess Cl^- in wet deposition measured near West Point excluding $[Na^{2+}]$ systematic analytical error corrections. B) Absolute and relative contributions of sources of excess Cl^- in wet deposition measured near West Point including $[Na^{2+}]$ systematic analytical error corrections.

Table 5: Sources of $[Na^+]$ in wet deposition analytical data measured near West Point.

Figure Captions

Figure 1: Regional map of NADP sites discussed here:

NADP site	Latitude	Longitude	Elevation (m)	Start Date	End Date	Distance from NY99 (km)
NY99	41.35	-74.05	201	9/13/1983		0
NY51	41.35	-74.04	186	6/26/1979	10/2/1984	1
PA72	41.33	-74.82	212	12/27/1983		64
NY12	42.38	-73.50	406	1/2/1980	8/6/1985	123
NJ99	40.32	-74.85	72	8/4/1981		133

Figure 2: (A): $[Na^+]/[Cl^-]$ (μEq L^{-1})/(μEq L^{-1}) raw weekly concentration ratios (i.e. not screened and not infilled) at NADP NY51 from 6/26/79 to 10/2/84. (B): $[Na^+]/[Cl^-]$ (μEq L^{-1})/(μEq L^{-1}) raw weekly concentration ratios at NADP NY99 from 9/13/83 to 2/3/04.

Figure 3: All reported weekly values for the period of data overlap 9/13/83 to 10/2/84: (A) $[Cl^-]$ (μEq L^{-1}) for NY51 (open circle/dashed line) and NY99 (solid circle/solid line), $R^2 = 0.95$. (B) $[Na^+]$ (μEq L^{-1}) for NY51 (open circle/dashed line) and NY99 (solid circle/ solid line), $R^2 = 0.97$. Note that in Figs A and B the first data point for both NY99 and NY51 are not plotted. The values were 591 and 324 μEq L^{-1} for $[Cl^-]$ and 517 and 306 for $[Na^+]$ for NY51 and NY99, respectively. The precipitation amount for that week was only 0.51 mm at both stations. (C) Precipitation amounts (mm) for NY51 (open circle/ dashed line) and NY99 (solid circle/ solid line), $R^2 = 0.99$.

Figure 4: Mean ± SEM annual (1981-2003) $[Cl^-]$ amount-weighted (μEq L^{-1}) concentrations for the combined infilled NY51/NY99 (closed circles/solid line) data and the combined screened NY51/NY99 data (open circles/dashed line).

Figure 5: (A) Mean ± SEM (solid circles/solid line) and median (open circles/dashed line) calendar month $[Cl^-]$ amount-weighted concentrations (μEq L^{-1}) for

combined infilled NY51/NY99 data (1980-2003). (B) Mean ± SEM (solid circles/solid line) and median (open circles/dashed line) calendar month $[Na^+]$ amount-weighted concentrations (μEq L^{-1}) for combined infilled NY51/NY99 data.

Figure 6: Mean ± SEM (solid circles) and median (open circles) calendar month $[Cl^-]/[Na^+]$ amount-weighted concentration ratios (μEq L^{-1})/ (μEq L^{-1}) for: A) infilled NY51/NY99 data; and B) screened NY51/NY99 data. Sea water $[Cl^-]/[Na^+]$ ratio (1.16) is indicated by a dashed line.

Figure 7: $[Cl^-]/[Na^+]$ (μEq L^{-1})/(μEq L^{-1}) amount-weighted concentration ratios. Infilled combined NY51/NY99 data compiled seasonally (JJA = June, July, August). Arrows indicate, from left to right: 1) transition from NY51 data to NY99 data; 2) protocol change eliminating contamination of $[Na^+]$ from sample collector O-ring; 3) filter protocol change. The solid line at $[Cl^-]/[Na^+]$ = 1.16 indicates the sea water ratio.

Figure 8: (A) Infilled combined NY51/NY99 calendar month means: total (open circles), marine (solid circles), and excess (solid triangles) Cl^- wet deposition. (B) Infilled combined NY51/NY99 calendar month means: total (open circles), marine (solid circles), and excess (solid triangles) Na^+ wet deposition (estimated from Na^+/Ca^{2+} ratios).

Figure 9: $[Na^+]$ vs. $[Ca^{2+}]$ for screened NY99 weekly concentrations divided into eight subdivisions (A-H) with equal sample numbers, based on Na^+/Ca^{2+} ratios. Regressions, forced through zero, for each of the eight groups have the following slopes (m) and R^2 values: A) m=9.62, R^2=0.72; B) m=3.41, R^2=0.96; C) m= 2.18, R^2=0.97; D) 1.34, R^2=0.94; E) m=0.93, R^2=0.99; F) m=0.62, R^2=0.97; G) m=0.36, R^2=0.91, H) m=0.15, R^2=0.88.

Figure 10: Frequency (percentage) of occurrence per calendar month for data in each of eight [Na^+] vs. [Ca^{2+}] subdivisions (see Fig. 8, A-H). Divisions with the highest slopes (A-C) occur predominantly in colder months; those with the lowest slopes (F-H) occur predominantly in warmer months.

Figure 11: Excess [Cl^-] (μEq L^{-1}) vs. [NO_3^-] (μEq L^{-1}) in screened NY99 data for summer weekly values after the change in protocol to eliminate sample collector O-ring contamination (1/1/94 to 2/1/04). Linear regression forced through zero, $m = 0.07$, $R^2 = 0.4$, $p < 0.0001$.

Figure 12: HCl (ppb) concentration in summer and winter air samples for NYC (gray bars) and a coastal Antarctic site (white bars) (data from Bari *et al.,* 2003 and Jourdain and Legrand, 2002, respectively). Summer in Bari *et al.,* 2003 was defined as July, August and September.

Table 1

Infill Method	Number of weeks	Percentage of total weeks
NY99 data regressed against NY51 data	2	0.2
Multiple linear regression with data from 2 proximal stations[a]	28	2.3
Linear regression with data from one proximal station	70	5.7
Seasonal power function for station with missing data	67	5.4
Total number of weeks that were infilled	167	13.6
Number of weeks with zero precipitation amount	57	4.6
Number of weeks with reported chemistry	1007	81.8
Total number of weeks in the NY51/NY99 data set	1231	100.0

Table 2

Mean ± sem	Cl^- ($mEq\ m^{-2}$)	Cl^- ($kg\ ha^{-1}$)	Na^+ ($mEq\ m^{-2}$)	Na^+ ($kg\ ha^{-1}$)
winter	4.7 ± 0.9	1.7 ± 0.3	3.5 ± 0.7	0.8 ± 0.2
spring	3.8 ± 0.4	1.4 ± 0.2	2.7 ± 0.4	0.6 ± 0.1
summer	1.9 ± 0.2	0.7 ± 0.1	1.0 ± 0.1	0.2 ± 0.02
fall	4.2 ± 0.5	1.5 ± 0.2	3.2 ± 0.4	0.7 ± 0.1
annual	14.7 ± 1.1	5.2 ± 0.4	10.4 ± 0.9	2.4 ± 0.2

Median	Cl^- ($mEq\ m^{-2}$)	Cl^- ($kg\ ha^{-1}$)	Na^+ ($mEq\ m^{-2}$)	Na^+ ($kg\ ha^{-1}$)
winter	2.5	1.2	1.6	0.4
spring	2.8	1.0	1.8	0.4
summer	1.6	0.6	0.8	0.2
fall	3.1	1.1	2.1	0.5
annual	10.1	3.9	6.3	1.5

Mean	Excess Cl^- ($mEq\ m^{-2}$)	Excess Cl^-/ Cl^- total	Dust Na^+ ($mEq\ m^{-2}$)	Dust Na^+/ Na^+ total
winter	0.6 ± 0.1	14%	0.1 ± 0.01	2.1%
spring	0.7 ± 0.1	19%	0.2 ± 0.01	7.5%
summer	0.7 ± 0.1	38%	0.2 ± 0.01	17.3%
fall	0.5 ± 0.1	13%	0.1 ± 0.01	3.0%
annual	2.6 ± 0.2	18%	0.6 ± 0.02	5.2%

Table 3

	% of total excess Cl- in wet deposition at West Point	Excess Cl- in wet deposition at West Point (mEq m-2)	Excess Cl- in wet deposition at West Point (kg ha-1)
Annual excess Cl- in wet deposition	79	2.6	0.92
Contribution to excess Cl- from Na+ dust correction	21	0.7	0.25
Total excess Cl- in wet deposition	100	3.3	1.17

Table 4

A. Excluding [Na^+] systematic analytical error corrections

Sources of excess Cl^- wet deposition at West Point	% of total excess Cl^- in wet deposition at West Point	Excess Cl^- in wet deposition at West Point (mEq m^{-2})	Excess Cl^- in wet deposition at West Point (kg ha^{-1})
Coal combustion	50.4	1.66	0.59
Incineration	9.4	0.31	0.11
Sea-salt dechlorination	40.2	1.33	0.47
Total excess Cl^-	100	3.30	1.17

B. Including [Na^+] systematic analytical error corrections

Sources of excess Cl^- wet deposition at West Point	% of total excess Cl^- in wet deposition at West Point	Excess Cl^- in wet deposition at West Point (mEq m^{-2})	Excess Cl^- in wet deposition at West Point (kg ha^{-1})
Coal combustion	29.1	1.66	0.59
Incineration	5.4	0.31	0.11
Sea-salt dechlorination	65.4	3.73	1.32
Total excess Cl^-	100	5.70	2.02

Table 5

	Interval	Years	Time Fraction	mEq m^{-2}	(Time fraction) * (mEq m^{-2})
Dust (from Na^+/Ca^{2+})	1981-2003	23	1.00	0.6	0.6
O-ring (+ 9.9%)	1981-1993	13	0.57	0.94	0.54
Filter (+ 24 ± 8%)	1981-1997	17	0.74	2.01	1.49
Marine (by difference)	1981-2003	23	1.00	-	7.77
Total (measured)	1981-2003	23	1.00	10.4	10.4

Figure 1

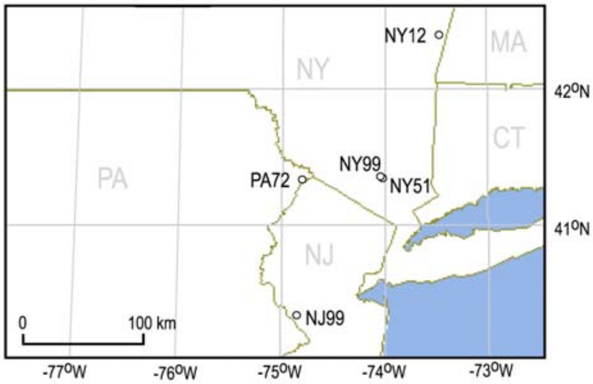
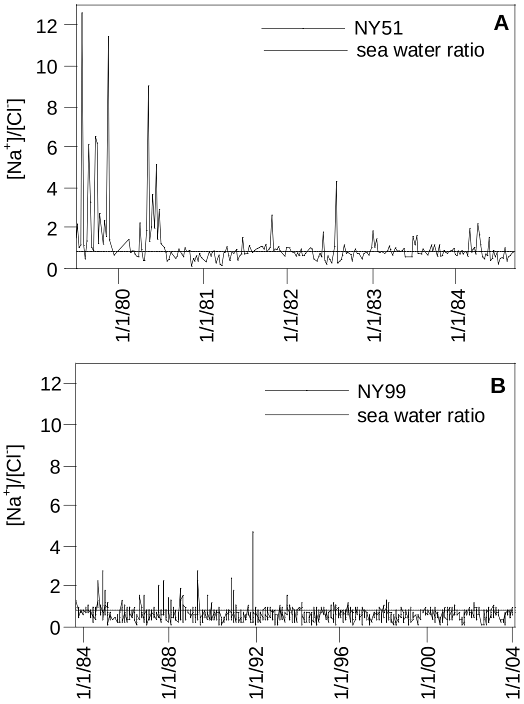


Figure 2



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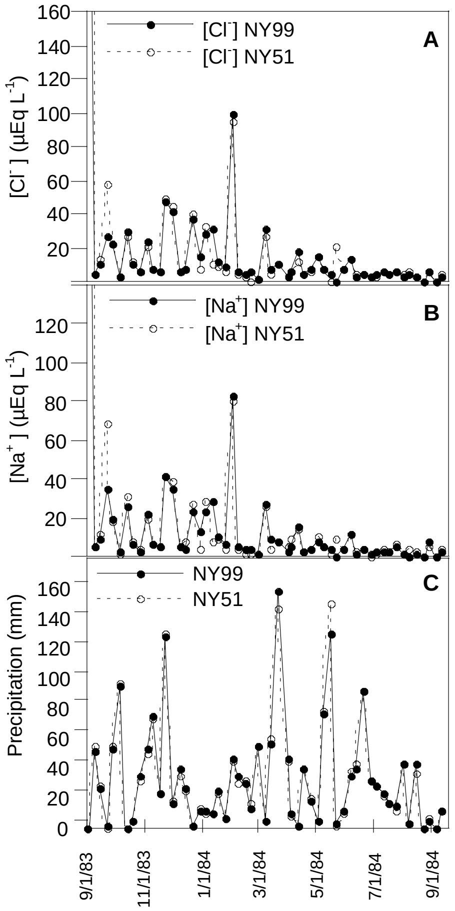
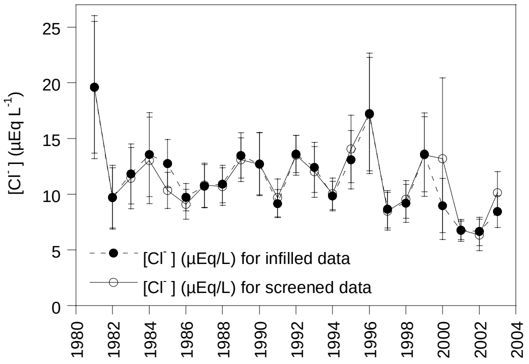


Figure 4



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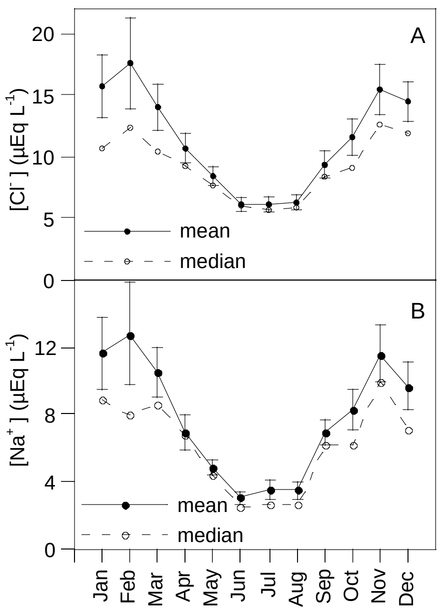

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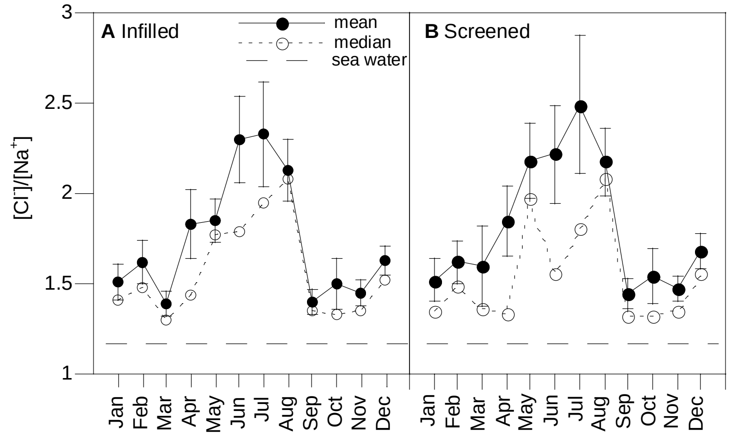

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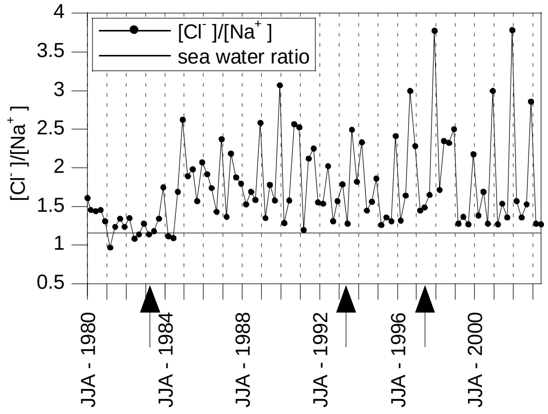

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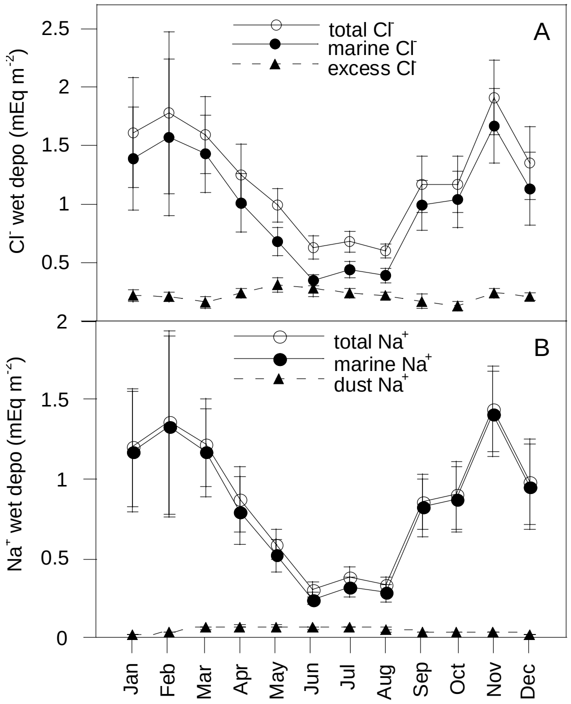


Figure 9

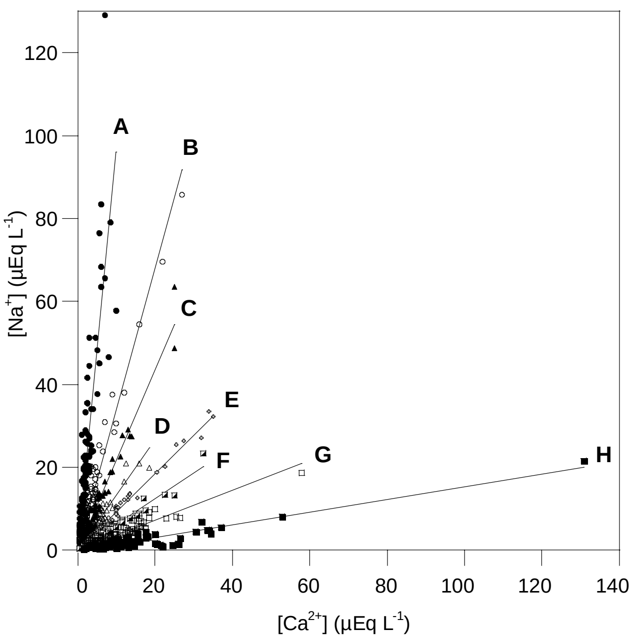


Figure 10

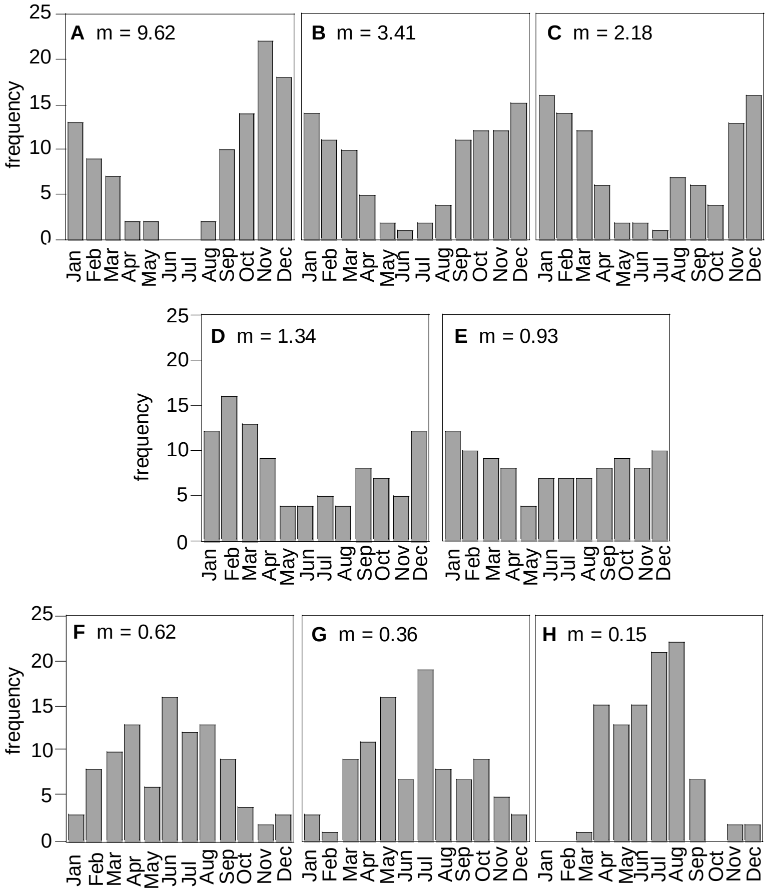


Figure 11

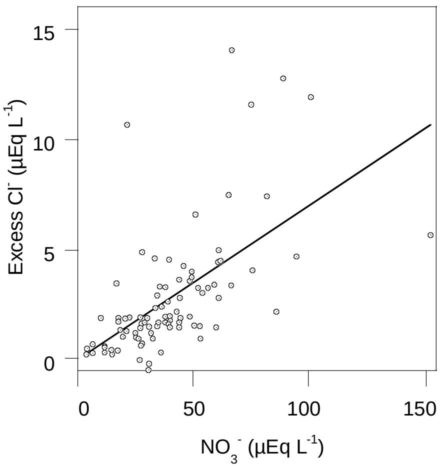
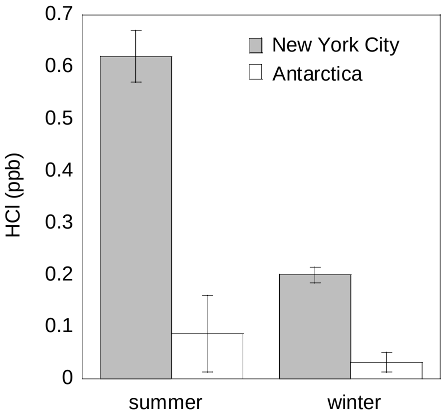


Figure 12



CHAPTER 2

Chloride influxes to a pristine deciduous forest watershed: the importance of dry deposition

J. B. Shapiro[1, 2] *, H. J. Simpson[1,2], K. L. Griffin[1,2], M. Stute[1,3] and W. S. F. Schuster[4]

[1]Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964

[2] Department of Earth and Environmental Sciences, Columbia University, New York, NY 10027

[3] Department of Environmental Science, Barnard College, New York, NY 10027.

[4] Black Rock Forest, 129 Continental Road, Cornwall, NY 12518

*Author for correspondence: Phone: 845 365 8395; Email: jbs59@ldeo.columbia.edu

Abstract

Chloride concentrations in precipitation and stream water can provide valuable insights into a range of watershed processes. For example, Cl^- delivered from the atmosphere can in some watersheds be considered as a conservative tracer in soils and surface water runoff when averaged over a period of years. With this assumption, a first-order estimate of Cl^- influx from dry deposition can be derived from the difference between stream Cl^- discharge and precipitation Cl^- influx. Stream water $[Cl^-]$ from the Cascade Brook watershed (1994-2005) within Black Rock Forest in the Hudson Highlands, NY, and precipitation $[Cl^-]$ from a nearby National Atmospheric Deposition Program (NADP) station were examined for these purposes. Comparison of temporal patterns in monthly stream water and coincident precipitation $[Cl^-]$ indicate significant dampening of seasonal variations in stream water $[Cl^-]$ compared to that of precipitation. Furthermore, Cl^- and water budgets for three water years demonstrate that stream Cl^- export was consistently and substantially greater than Cl^- derived from wet-only deposition, indicating at least one major source of Cl^- to the watershed in addition to wet deposition via rain and snow. The magnitude of annual Cl^- export was highly correlated with annual stream water discharge amount ($R^2 = 0.83$). The ratio of stream Cl^- export to Cl^- wet deposition was ~ 3:1, indicating contributions from additional sources comparable to or greater than from precipitation. If all additional stream Cl^- were attributed to dry deposition, this flux would provide an average of 22 ± 6 mEq Cl^- m^{-2} yr^{-1} compared to the 12 ± 0.8 mEq Cl^- m^{-2} yr^{-1} average annual wet deposition. However, in addition to dry deposition, it is possible that Cl^- in stream export was also a result of input from mineralization of organic material formed in prior decades during periods of higher atmospheric $[Cl^-]$. We estimate minimum fluxes of 5.8 and 4.0 mEq Cl^- m^{-2} yr^{-1} for dry deposition and mineralization of organic matter, respectively. Contributions of Cl^- from chemical weathering of rocks and minerals were also considered here and estimated to be on the order of ~ 0.2 - 0.3 mEq Cl^- m^{-2} yr^{-1}. The average flux-weighted monthly [Cl^-] for Cascade Brook stream samples (44 ± 1.6 μEq l^{-1}) was much lower than that of several nearby Hudson River tributaries (560 - 6300 μEq l^{-1}), consistent with Cascade Brook being unaffected by anthropogenic perturbation from winter road salting or contamination from waste water effluent.

Key words: wet deposition, mineralization, conservative tracer, mass balance, NADP, Black Rock Forest

Introduction

Watershed budgets can provide a sensitive approach to examine the behavior of an ion, such as chloride, which in some watersheds can be considered as a conservative tracer when averaged over a number of years. The most widespread source of Cl^- deposition from the atmosphere to the earth's surface is from oceanic sea-salt injected into the atmosphere from bursting bubbles at the sea-surface (Woodcock et al. 1953; Graedel and Keene 1996). Once deposited on land via either wet or dry deposition, Cl^- has relatively little involvement in terrestrial biological processes and can be considered to move passively though most ecosystems (Feth 1981; Neal and Rosier 1990; Lovett et al. 2005). Numerous studies have exploited the first order conservative behavior of Cl^- to elucidate important ecosystem processes such as: 1) deriving relative contributions of precipitation and groundwater to stream water (Peters and Ratcliffe 1998); 2) estimating time-scales and pathways by which precipitation and soluble environmental tracers travel through a catchment and enter surface runoff (Kirchner et al. 2000); and 3) estimating watershed-scale retardation factors for Na^+, which is considered more reactive than Cl^- in most ecosystems (Feng et al. 2004).

One further advantage in consideration of data for $[Cl^-]$ in precipitation and stream water is the opportunity to derive estimates of cumulative magnitudes of Cl^- dry deposition and other possible Cl^- inputs. Although Cl^- is generally considered to be a conservative tracer in terrestrial ecosystems, some additional sources have been proposed to provide appreciable contributions to watershed Cl^- export via stream discharge (Lovett et al. 2005). Dry deposition of Cl^--bearing aerosols and gases onto soils and vegetative surfaces is very difficult to measure directly (Appelo and Postma 1996; Lovett et al.

2005). Therefore a watershed mass balance approach can offer important constraints on this flux, although dry deposition derived by this method probably should be considered as an upper limit. The magnitude of Cl^- dry deposition to land areas is sometimes presented as comparable to that of Cl^- wet deposition in first order global approximations. Assuming an ice free land area of 1.26×10^{18} cm^2, estimates calculated from Cl^- fluxes presented in Graedel and Keene (1996), which assign equal amounts of total Cl^- deposition to wet and dry fluxes, approximate a total global average flux of 7.6 mEq Cl^- m^{-2} yr^{-1}. For comparison, an independent global estimate indicates that wet plus dry sea-salt Cl^- deposited onto ice-free land, which is subsequently exported into natural rivers, amounts to a total of 5.9 mEq Cl^- m^{-2} yr^{-1} (Berner and Berner 1996).

The watershed examined here is within Black Rock Forest (BRF), a 1500-hectare preserve in the Hudson Highlands of southern New York, where a number of ecological, botanical and hydrological studies have been conducted (e.g. Shaman et al. 2002; Barringer and Clemants 2003; Nagel and Griffin 2004). Calendar month compilations of precipitation $[Cl^-]$ and Cl^- wet deposition collected near West Point, NY, in close proximity to BRF (~ 5km) (1980-2003) indicate that during fall and winter months, precipitation $[Cl^-]$ and Cl^- wet deposition were significantly greater than during spring and summer months; this seasonal trend can be attributed to the greater influence of regional marine air storms during cold seasons (Shapiro et al. 2005b). Additionally, summer ratios of precipitation $[Cl^-]/[Na+]$, which average approximately twice the sea-water ratio, indicate that ~ 24% of the mean annual Cl^- wet deposition was in excess of that expected from the sea-salt $[Cl^-]/[Na+]$ ratio (1.16 in equivalent units). This "excess" Cl^- wet deposition is consistent with sources in addition to sea-salt aerosols contributing significantly to total Cl^- wet deposition. Processes which probably contribute to excess Cl^- wet deposition in this area are: 1) HCl emissions from regional coal combustion; 2) HCl emissions from domestic and industrial waste incineration; and 3) HCl production from the reaction of sea-salt aerosols with acidic gases in the atmosphere such as H_2SO_4 and HNO_3 (Shapiro et al. 2005b).

In addition to establishing a watershed Cl^- budget for BRF, there were other motivations for investigation of stream Cl^- at this site. For example, it has become of considerable regional interest to document $[Cl^-]$ in streams that have been perturbed by anthropogenic sources of salt (Hauser 2004). Surface water chemistry of the Cascade Brook (CB) watershed within BRF provides a valuable example of a pristine forested ecosystem. A number of Hudson River tributaries have Cl^- concentrations that have been greatly perturbed by winter road salting and effluent from wastewater treatment plants (Godwin et al. 2003; Hauser 2004; Nieder 2005). Elevated $[Cl^-]$ can have significant negative impacts on the health and composition of terrestrial vegetation (Hofstra et al. 1979; Panno et al. 1999; Viskari and Karenlampi 2000; Richburg et al. 2001) as well as industrial infrastructure and therefore it is important to establish the degree to which surface water $[Cl^-]$ exceeds natural background levels in pristine watersheds such as CB.

The goals of the research outlined here include: 1) establish seasonal and interannual trends in $[Cl^-]$ for the CB watershed of BRF and compare them with corresponding temporal trends in precipitation $[Cl^-]$; 2) compare the magnitude of Cl^- export in stream water with Cl^- input from wet deposition; 3) quantify imbalances in the Cl^- input-export budget and, if appropriate, to identify plausible sources and/or sinks; and 4) compare $[Cl^-]$ in CB to that of other streams in the region.

Methods

Site description

BRF (41°23 N, 73°59W - location of the CB weir) is a pristine ~1500 ha forested preserve on the west side of the Hudson River in the Hudson Highlands of NY ~ 70 km north of New York City (Fig. 1A). The bedrock of the Hudson Highlands consists of highly resistant Precambrian gneiss derived from sedimentary rocks, which accumulated on the order of 1.3 billion years ago, originally deposited as sandstones, shales and limestones and subsequently metamorphosed during the Grenville Orogeny (0.95 billion years ago) (Schuberth 1968; Isachsen and Gates 1991; Press and Siever 1998). Areas of exposed bedrock occur throughout the forest. Mean precipitation amount during the period with precipitation chemistry data available (1980-2003) was ~ 106 ± 3 mm month^{-1} and 1290 ± 50 mm year^{-1} (Shapiro et al. 2005a). Temperature has large seasonal variability with an average monthly maximum of 23 °C in July and minimum of -3 °C in January (Engel et al. 2002). The range in elevation at BRF is from 110 to 450 m above mean sea level (Engel et al. 2002).

CB watershed (Fig. 1C) drains to the south and is located in the southeastern section of BRF. Vegetation is predominantly deciduous with a composition of ~ 80% *Quercus* (oak) species. Soils within the watershed are mostly medium texture loams and excluding exposed bedrock, soil depths are somewhat thinner in upland areas > 400m elevation (28 cm) than down slope areas (32 cm) near the weir gauging station where soils are more organic (Engel et al. 2002; Nagel et al. 2002; Pederson 2005). There are two stream sites from which water samples have been systematically collected along CB: 1) North Bridge (NB), which drains in the upstream half of CB catchment (65 hectares) and is immediately upstream of Glycerine Hollow; and 2) Old West Point Road (OWPR) (Fig. 1B), which is downstream of Gylcerine Hollow (~ 8 ha wetland), and includes the entire catchment upstream of the discharge gauge (135 hectares). The latter site (OWPR) includes a 120° V-notch weir and a discharge gauging station (268 m elevation) where hourly stage heights have been recorded since 1999. The maximum elevation within the watershed is 427 m.

Deicing salts are not applied to any roads within the CB watershed. Outside of the forest there are three paved roads that receive winter road salting which are proximal to CB. However, these roads are ~ 500 m to 750 m away from the watershed boundary and at least 30 m to 80 m lower in elevation than the stream gauging station. Thus, we conclude it is very unlikely that Cl^- contamination from winter road salting affects surface water $[Cl^-]$ within the CB watershed.

Stream discharge

Stage height data were used to derive discharge estimates using an empirical equation for a 120° V-notch weir (Hertzler 1938) converted to metric units:

$$Q = 2.302 * H^{2.449} \qquad \text{(equation 1)}$$

where Q is discharge ($m^3\ s^{-1}$), and H is stage height (m) measured as the vertical distance upward from the bottom of the V-notch. Discharge derived from this equation have been compared with stream velocities within ~ 30 meters of the weir and were consistent by both methods. Once converted from stage heights, discharge was normalized to total watershed area and reported here in mm wk^{-1} to facilitate comparison with precipitation amounts for the same period.

A compound weir approach (Grant and Dawson 1997) was used to calculate stream discharge during 19 days from the 1999-2004 record during which stage height exceeded the maximum height of the V-notch weir (0.61 m). During these high runoff episodes, total discharge was assumed to equal the sum of: 1) discharge calculated for a 120° V-notch weir (equation 1) for stage height of 0.61 m, plus 2) discharge calculated using an equation for a rectangular weir for the portion of stage height that exceeds 0.61 m. We assumed that the width of the rectangular portion of the weir was equivalent to the width of the stream channel upon approach and that the weir face slope was vertical. The equation used to calculate the portion of discharge attributed to the rectangular portion of the weir was:

$$Q = 0.55*C_d*L*H^{1.5} \qquad \text{(equation 2)}$$

where Q is discharge ($m^{-3}\ s^{-1}$), C_d is the coefficient of discharge (dimensionless), L is total length across the weir (2.83 m) and H is stage height above the top of the V-notch (m). C_d was approximated specifically for this data set to be 3.3 from a C_d vs. H/P diagram where the average value for stage height within the rectangular portion of the weir (H), divided by the height of the cutoff wall (P) equaled 0.09.

The maximum daily discharge among the 19 days requiring the compound weir approach occurred during 3/22/1999, when a total of 56.1 mm of water was estimated to leave the watershed during a 24-hour period. The amount of water attributed to the v-notch and rectangular portions of the “compound weir” were 36.3 and 19.8 mm, respectively. During this discharge event, the average height of the water that exceeded the top of the v-notch portion of the weir was 21.3 cm or, comparatively, 7.5% of the total length across the weir. This compound weir approach has not been independently calibrated at CB and thus represents only a first order approximation for total discharge during extreme high flow episodes.

Large gaps in recorded stage height data make it difficult for water budget analysis of two of the five water years during the period 1999-2004. We have defined the water year for our annual budgets to include October 1st through September 31st although these dates were not exact since corresponding composite precipitation data were compiled terminating each Tuesday morning. Stage height data gaps were as follows: 17 days in water year 1999-2000; 95 days in water year 2000-2001; and 64 days in water year 2001-2002. Missing discharge values during water year 1999-2000 were infilled using previously derived daily discharge data for CB based on TOPMODEL hydrologic model calculations (Shaman et al. 2002). The slope from a linear regression forced through zero of daily TOPMODEL output and daily measured discharge at CB was 0.89 over the period from 5/22/1998 - 10/15/2000 ($R^2 = 0.86$). For the following analyses, water year 1999-2000 includes 17 days of TOPMODEL values, which accounted for ~ 3% of the total discharge for the 1999-2000 water year. In addition, several minor data gaps for stage height exist for water years 2002-2003 and 2003-2004 and linear interpolation was used to infill these missing data. In total, linear interpolations were used to infill single missing hours during 34 days and two or more consecutive missing hours during 16 days during the 2002-2003 and 2003-2004 water years. For this study, water years 1999-2000, 2002-2003 and 2003-2004 have the most complete data and were used to derive water and Cl^- budgets for the CB watershed.

Stream chemistry

Weekly CB samples were collected at the NB and OWPR sampling sites from January 1997 to June 2005 (Fig. 1). Samples were stored in HDPE bottles (250 ml) and all samples were refrigerated prior to analysis, with the exception of 9 weeks of samples collected during 1997 and 36 weeks of samples collected during 2002, which were stored at room temperature for one or more months. All stream water analyses were done by ion chromatograph (Dionex, DX-100; Dionex Corporation, Sunnyvale, CA) where the relative standard deviation (RSD) (standard deviation/mean*100) of eight samples with a [Cl^-] of 42.3 μEq l^{-1} was 2-3%. The RSD gives an indication of variability within the data with respect to the mean value. Stream samples taken between January 1997 and November 2004 were analyzed during the period from November 2004 to February 2005. Although it is possible that the range of storage times could affect [Cl^-] in these samples we conclude that this was unlikely. We have conducted a sample storage experiment to address this issue. On January 4, 2005 five stream samples were collected in 250 ml HDPE bottles from the OWPR site at the same time, filtered through 0.4 μm Whatman® nuclepore® polycarbonate membranes, analyzed using ion chromatography (mean ± sem of five samples = [Cl^-] of 37.3 ± 0.41 μEq l^{-1}) and stored in the dark at 3-4°C. During 27 subsequent weeks of measuring water from these five bottles, we did not find systematic changes in [Cl^-] (mean [Cl^-] ± sem of 140 measurements = 35.8 ± 0.12 μEq l^{-1}; RSD = 4.1%) (Fig. 2). Additionally, we estimate that evaporative water loss from a full 250 ml HDPE bottle would be minor, with a maximum water loss of ~ 2.1 ml over 8 years (1997-2005) if stored at 22-24ºC (Kennan 1991). It is likely that evaporative losses from HDPE bottles would be considerably less for refrigerated samples. A similar storage experiment using soil water from a hemlock stand in Ulster County, NY reported no significant change in a range of initial [Cl^-] (~ 7 to 18 μEq l^{-1}) when analyzed over a period of 16 weeks (Yorks and McHale 2000). Stream water samples collected after November 2004 were analyzed within a few weeks of each sampling date.

Samples from 1994, were collected only at the OWPR site and were analyzed by both coulometric titration using a silver electrode and by ion chromatography. Regression analysis of results from the two methods indicates a slope of 0.80 and an R^2 value of 0.70 for these samples. Departure from a slope closer to unity was mainly attributed to a single outlier. There was not any systematic bias between concentrations derived from the two analytical methods and results from coulometric titrations were used to represent the 1994 [Cl^-] discussed here.

As occurred for water discharge rates, there were gaps in weekly stream chemistry data (1994-2005). In particular, there were weekly data available for 1994, no data for 1995-1996, discontinuous data for 1997, no data for 1998 and relatively complete weekly data for 1999-2005. Despite these gaps, the record of stream water [Cl^-] at the OWPR site provides valuable information on long-term trends in [Cl^-] in the CB watershed. However, annual budgets here primarily utilize [Cl^-] data from the OWPR site for water years 1999-2000, 2002-2003 and 2003-2004, which have relatively complete data for both [Cl^-] and water discharge. Cl^- export fluxes reported here were calculated as the product of discharge measured from 10AM Tuesday until 9AM the following Tuesday multiplied by the weekly [Cl^-] corresponding to the stream sample taken at 9AM on the second Tuesday of the measurement period. For comparison, Cl^- export was also calculated as the product of discharge measured from 10AM Tuesday until 9AM the following Tuesday multiplied by the average [Cl^-] from stream samples taken on the first and following Tuesdays during the measurement period. Comparison of these two approaches indicates no statistically significant difference between the means ± sem Cl^- export fluxes or ratios of Cl^- export/Cl^- wet deposition for the water years analyzed here.

The OWPR site was selected for Cl^- budget estimates rather than the NB site for the CB watershed for the following reasons: 1) 1994 $[Cl^-]$ was only reported for samples taken at OWPR; 2) the weir and stage height recorder are located at the OWPR site; 3) there was no statistically significant difference between $[Cl^-]$ measured at the two sites ($P = 0.64$); and 4) the OWPR site is further downstream and thus includes a larger catchment area. A linear regression, forced through zero, of $[Cl^-]$ at NB vs. OWPR yields a slope of 0.98 and an R^2 of 0.69 (Fig. 3). In analyzing the residuals from a linear regression between $[Cl^-]$ at NB and OWPR, five points with residuals values greater than 3σ of the mean of all residuals were removed. For comparison, a linear regression forced through zero of $[Cl^-]$ at NB vs. OWPR with the five outliers removed yielded a slope of 1.0 and an R^2 of 0.87.

Although relatively complete, there were a number of weeks during the 1999-2000, 2002-2003 and 2003-2004 water years that lacked $[Cl^-]$ data at the OWPR site when a non-zero discharge rate was measured. These weeks had $[Cl^-]$ infilled using one of the following methods applied in the hierarchy presented:

1) If $[Cl^-]$ was measured at NB during a week when $[Cl^-]$ was not measured at OWPR, NB $[Cl^-]$ was used to infill the OWPR value. This method was used to infill five weeks during the 2003-2004 water year.

2) If [Cl$^-$] was missing for a single week and [Cl$^-$] was measured the prior and subsequent week, an infill value was estimated for the missing week by linear interpolation. This method was used to infill one week in the 1999-2000 water year and five weeks in the 2003-2004 water year.

3) If [Cl$^-$] was missing during consecutive weeks, [Cl$^-$] was infilled with a calendar month average value. Monthly average values used to infill these missing weeks were calculated from weekly [Cl$^-$] at OWPR during 1999-2005. This method was used for 20 weeks in the 2002-2003 water year and two weeks in the 2003-2004 water year

An important caveat with respect to analysis of Cl$^-$ concentrations measured at OWPR concerns the use of monthly means to represent calendar month means and long-term trends in [Cl$^-$] rather than using flux-weighted mean concentrations. Flux weighted concentrations (c_w) were calculated as follows:

$$c_w = \frac{\sum_1^n c_i q_i}{\sum_1^n q_i}$$

where n is the number of weeks per month, c_i is the weekly ion concentration (µEq l^{-1}) and q_i is the weekly stream discharge amount. Comparison of monthly means vs. flux-weighted mean Cl$^-$ concentrations (1999-2005) indicates no statistically significant difference between these two data sets ($P = 0.91$) (Fig. 4) and a linear regression of these two sets of [Cl$^-$], forced through zero, yields a slope of 1.0 and an R^2 value of 0.94. We would have preferred to use flux-weighted mean concentrations to represent calendar month means and long term trends in [Cl^-], however, we have chosen to use monthly mean [Cl^-] to maximize the availability of CB [Cl^-] data to derive these trends. The number of available years for discharge data (1999-2004) was considerably less than for stream chemistry and precipitation [Cl^-] data (1994-2004).

Precipitation

Four precipitation collection stations in the vicinity of the Cascade Brook watershed (≤ 5km distance) (Fig. 1B), active during years of weir operation, were examined for data quality. A linear regression, forced through zero, of weekly precipitation amount (1996-2004) from two collocated precipitation collectors (Open Lowland (OL) and Old Forest Headquarters (OFHQ)) yields a slope of 0.83 and an R^2 of 0.84 (Fig. 5A). The OL collector is not equipped to accurately convert incident snow to equivalent rain amount and thus the data for the two nearby collectors differ appreciably. Snow that accumulates at the OL collector may be lost due to wind without being recorded, or it may melt at a time subsequent to the snowfall event and thus erroneously contribute to precipitation amount reported for a later date. In contrast, snow accumulation at the OFHQ collector is melted and recorded as corresponding precipitation amount on an event basis and therefore should more accurately represent weekly precipitation amounts throughout the year. For these reasons, precipitation measured at the OL site was not used to estimate precipitation for CB. The temporal resolution for the OFHQ data is daily and during water years 1999-2004, ~ 17 % of the total annual precipitation measured at the OFHQ was attributed to snow. The OFHQ precipitation collector is ~ 3 km NNW of the CB watershed.

The same shortcomings for the OL also pertain to snow events for the Ridge Top (RT) collector, and these data were also excluded. A linear regression, forced through zero, of weekly precipitation amount (1996-2004) for the RT vs. the OFHQ collectors yielded a slope of 0.77 and an R^2 of 0.75 (data not shown). Despite these shortcomings of snowfall amount measurements at the OL and RT collectors, the data from these collectors provide valuable high resolution temporal (hourly) rainfall data, which are useful for documenting the responsiveness of catchment runoff to individual rainfall events.

A fourth set of proximal precipitation data were available from the National Atmospheric Deposition Program (NADP) station NY99 (NADP 2004), located on the West Point Military Reservation ~ 4 km SW of CB and ~ 5 km SSW of the OFHQ collector (Fig. 1) (NADP 2004). A linear regression, forced through zero, of weekly precipitation amount at OFHQ vs. NY99 (1996-2004) yields a slope of 1.0 and an R^2 value of 0.85 (Fig. 5B). We have chosen to estimate precipitation input to the CB watershed by an unweighted average of weekly precipitation amounts from the OFHQ and the NADP, NY99 station at the West Point Military Reservation.

Precipitation amount-weighted mean [Cl^-] and Cl^- wet deposition were derived from precipitation chemistry measured as weekly composite samples at NADP NY99 (NADP 2004). Infilling procedures were used for all weeks reporting non-zero amounts of precipitation but that lacked corresponding [Cl^-], providing infill values for 167 of the total 1231 weeks considered. In brief, infilled data were derived from: 1) seasonal linear regressions between [Cl^-] at NY99 and [Cl^-] at proximal NADP sites; or, 2) seasonal power functions between [Cl^-] and precipitation amount at NY99. Additionally, a screened version of the NADP data was derived to eliminate weeks with, for example, invalid ion chemistry as reported by the NADP; the screened version removed 242 of 1231 weeks of data. Detailed descriptions of screening and infilling procedures used here for the NADP NY99 data have been documented elsewhere (Shapiro et al. 2005b). There were no statistically significant differences between annual infilled mean [Cl^-] (1981-2003) and annual screened mean [Cl^-] (Shapiro et al. 2005b), confirming that infilling procedures did not significantly bias the mean annual values of the NADP [Cl^-] data.

Results

A multi-year hydrograph for CB (Fig. 6) (1999-2004) illustrates the large variability in weekly discharge reflecting the influence of thin soils and steep topography in this small catchment. Differences between precipitation and discharge for the same week were caused by evapotranspiration (ET) losses and antecedent soil moisture conditions as a function of seasonal cycles. ET (mm wk^{-1}), estimated as the difference between precipitation and discharge, for each calendar month for individual water years 1999-2000, 2002-2003 and 2003-2004 as well as the mean ET ± sem for these three water years indicates appreciable seasonal variability (Figs. 7 A and B). Given that ET was simply estimated as precipitation - discharge, changes in net storage of soil moisture and snow are affectively ignored and therefore this estimation may more accurately be designated as an "apparent" ET. On average (Fig. 7B), during the warmest months, apparent ET is at a maximum whereas apparent ET is at an annual minimum during colder months of the year. Apparent ET indicates negative values (i.e. excess of discharge relative to precipitation) during months that typically experience pulses of spring snow melt, such as appears to have occurred during February, March and April of at least one year (Fig. 7A).

Hourly precipitation data, combined with corresponding stream discharge data provide evidence of the responsiveness of the CB watershed to large rainfall inputs (Fig. 8). For example, during a substantial winter rain event on January 17-18, 1999, a total of 34.3 mm of precipitation was measured at the OL collector over the course of ~ 16 hours (Fig. 8A). Maximum stream discharge occurred 14 hours after the beginning of the rainfall event and ~ 3 hours after the highest hourly precipitation. Total stream discharge (40.6 mm) was ~ 18% greater than precipitation input. Prior to this rain event, 14.2 mm of rain (January 16 - 17, 1999) and 35.0 mm of equivalent rain attributed to snow (January 13 - 15, 1999) were delivered to the watershed. In contrast, during a major summer rain event occurring from June 5, 2002 through June 8, 2002 (Fig. 8B), a total of 53.2 mm of rain was measured at the OL collector over the course of 36 hours with corresponding stream discharge (25.9 mm) equal to about half of precipitation input. Maximum stream discharge occurred ~ 9 hours after the peak in precipitation. Two prior rain events had occurred: 1) earlier in the day on June 5, 2002 (7.9 mm); and 2) during May 27 – 29, 2002 (26.6 mm). These two rain events (January 1999, June 2002) illustrate the temporally responsive nature of stream discharge in this small watershed.

[Cl^-] (μEq l^{-1}) in weekly CB samples were plotted against weekly stream discharge (mm wk^{-1}) (1999-2004) (Fig. 9), which indicates little systematic relationship. Similar results were found using [Cl^-] vs. discharge segregated by season (spring, summer, winter, fall) as well as [Cl^-] vs. discharge for the day of stream sampling, the day prior to sampling and the sum of discharge for the day of and prior to stream sampling (data not shown). Average [Cl^-] in stream water aggregated by calendar month (January 1994 - March 2005) (Fig. 10) indicates only minor systematic seasonal variability, with [Cl^-] ~ 20-30% greater in January compared to spring and summer months. January [Cl^-] average was ~ 1.3 times that of the minimum [Cl^-] (May). It should be noted that because there are gaps in [Cl^-] data during 1994-2005 due to either zero weekly discharge or failure to obtain stream samples, monthly averages reported here represent an estimation using available data. An average of 26 measurements were used to calculate each calendar month mean [Cl^-] at OWPR. Calendar month averages of precipitation amount-weighted [Cl^-] (January 1994 - November 2004) (note that there were four fewer months available for precipitation data than for stream chemistry data) show much larger systematic seasonal variation, with late fall and winter values averaging much greater than those in spring and summer. Maximum precipitation amount-weighted [Cl^-] occurred during November and was ~ 3.2 times minimum concentrations during July and August.

During 1999-2005 the mean ± sem of weekly stream [Cl^-] was 44.4 ± 0.8 μEq l^{-1} with a relative standard deviation (RSD) of 27%. The RSD gives an indication of variability within the data with respect to the mean value. In contrast, the mean ± sem for weekly precipitation [Cl^-], which is not an amount-weighted average, was 14.2 ± 0.9 μEq l^{-1} and had a RSD of 219%; ~ 8 times the RSD for stream water. On a monthly basis, the mean ± sem of monthly flux-weighted [Cl^-] for stream water was 44.1 ± 1.6 μEq l^{-1} with a corresponding RSD of 26% and the monthly mean ± sem of precipitation amount-weighted [Cl^-] was 8.5 ± 0.84 μEq l^{-1} with a RSD of 82%.

The weekly and monthly means and RSD's for [Cl$^-$] indicate the much lower temporal variability in stream samples compared to that for precipitation (Figs. 11A & B). Additionally, monthly mean ± sem [Cl$^-$] (Fig. 11D) as a function of time indicates a decreasing trend in stream [Cl$^-$] (1994-2005) ($R^2 = 0.55$; slope = -0.21 mEq l^{-1} month^{-1}). The annual mean [Cl$^-$] for 1994 was almost twice that for 2004 (61.2 ±1.4 μEq l^{-1} vs. 35.8 ±1.4 μEq l^{-1}, respectively). Using monthly mean [Cl$^-$] during 1994-2004, a -43.6% decrease in [Cl$^-$] was derived from the linear regression equation. The decreasing temporal trend in monthly stream water [Cl$^-$] appears generally consistent with the decadal record in annual precipitation [Cl$^-$] (Fig. 11C), which also shows a decreasing trend from 1981-2003 ($R^2 = 0.23$; slope = -0.22 mEq l^{-1} yr^{-1}) (Shapiro et al. 2005b). The percentage decrease in precipitation [Cl$^-$] for values derived from the linear regression equation indicate a -34.8% change in annual precipitation [Cl$^-$] during 1981-2004. For comparison, the percentage change for stream water and precipitation [Cl$^-$] estimated using values derived from respective linear regression equations during the time period with overlapping data (1994-2003) indicate that stream water and precipitation [Cl$^-$] decreased by 4.0 % and 2.0 % per year respectively.

Water year hydrologic budgets for 1999-2000, 2002-2003 and 2003-2004 were used to estimate, by difference, water loss via ET. The mean ET loss percentage for these three years was ~ 47% of precipitation (37% - 58%) (Table 1). Chloride budgets for the watershed during these three water years indicate that export consistently exceeded input from wet deposition by approximately a factor of three, indicating that there were significant additional sources contributing Cl$^-$ to the watershed or from within the watershed. On average, these additional sources accounted for twice as much Cl^- as the amount delivered by wet deposition during the same years.

As previously discussed, water discharge data for 2000-2001 and 2001-2002 have large data gaps and therefore have not been included in detailed hydrological or chemical budgets thus far. However, we estimated values for missing discharge and stream [Cl^-] data during these years to facilitate first order comparisons of Cl^- export during these two years with Cl^- export during 1999-2000, 2002-2003 and 2003-2004 water years. Missing water discharge data were estimated using linear regression equations between weekly stream discharge and weekly precipitation specific for each calendar month. Missing [Cl^-] data were infilled using [Cl^-] measured at NB for one week during 2000-2001, calendar month averages for 13 weeks during 2000-2001 and calendar month averages for 3 weeks during 2001-2002. Using these approximations, first-order estimates of Cl^- budgets were made for two additional water years. For 2000-2001 and 2001-2002, the ratio of Cl^- export to Cl^- wet deposition was 2.1:1 and 3.5:1 respectively, which fall within the range of ratios derived here for water years 1999-2000, 2002-2003 and 2003-2004 (Table 1).

A linear regression forced through zero of Cl^- export for all five water years plotted against annual water discharge (mm yr^{-1}) indicates a positive linear relationship ($R^2 = 0.83$) for CB (Fig. 12). This trend had some general similarities to that for the Hubbard Brook Experimental Forest (HBEF) in NH (Lovett et al. 2005), but the slope of Cl^- export vs. annual stream discharge was much steeper at BRF than for HBEF.

Discussion

Comparison of calendar month mean [Cl^-] in CB with [Cl^-] of precipitation measured near West Point (Fig. 10) indicates two clear trends: 1) [Cl^-] in stream water shows much less variability in calendar month averages compared with precipitation, and 2) [Cl$^-$] in stream water was greater than [Cl$^-$] in precipitation by about a factor of five. The Cl$^-$ variability expressed in terms of the ratio of maximum to minimum calendar month concentrations was only ~ 1.3 in stream water compared with ~ 3.2 for precipitation. The RSD of the mean values for weekly and monthly flux-weighted [Cl$^-$] for CB (27% and 26%, respectively) were much lower than for weekly and monthly precipitation amount-weighted [Cl$^-$] (219% and 82%, respectively); these differences in the degree of relative variability are also illustrated in Figures 11A and B. The relatively low temporal variability in stream water [Cl$^-$] results from mixing of [Cl$^-$] from precipitation events occurring over extended periods, [Cl$^-$] of soil water and subsequent mixing of soil water and surface runoff as water travels down the hillslopes through the watershed (Reynolds and Pomeroy 1988; Kirchner et al. 2001). The dampening of stream water [Cl$^-$] variability with respect to precipitation [Cl$^-$] in watershed studies has been reported elsewhere (Reynolds and Pomeroy 1988; Neal and Rosier 1990; Neal and Kirchner 2000). For example, Neal and Kirchner (2000) report a ~ 15 - 22% RSD of [Cl$^-$] in stream water samples within the Plynlimon catchment in Wales compared to a 114% RSD for [Cl$^-$] in the incident precipitation during corresponding time periods.

A second feature of the comparison of calendar month [Cl$^-$] for CB and precipitation illustrates the combined effects of ET water losses and additional Cl$^-$ sources to stream water [Cl$^-$]. ET was ~ 50% of precipitation for the three water years examined at BRF. If this were the only factor to affect [Cl$^-$] in stream water, based on the average monthly amount-weighted [Cl$^-$] in precipitation measured near West Point of 8.5 μEq l^{-1}, the expected mean [Cl$^-$] in CB would be 17 μEq l^{-1}. However, the average monthly flux-weighted stream water [Cl$^-$] was 44.1 μEq l^{-1}, or ~ 2.6 times the expected concentration based only on ET water losses, indicating that at least one additional source other than precipitation contributes significant amounts of Cl$^-$ to stream water [Cl$^-$]. Peters and Ratcliffe (1998) also report a ~ five-fold difference between weekly median [Cl$^-$] in stream water and precipitation [Cl$^-$] during a one-year period at a catchment in the Panola Mountain Research Watershed (PMRW) in Georgia. Combined with collocated throughfall [Cl$^-$] measurements, which were ~ 2.5 times that of precipitation [Cl$^-$], the authors attribute these large differences in concentration primarily to input of Cl$^-$ from dry deposition (Peters and Ratcliffe 1998).

Watershed mass balance data for CB for each of three water years indicate that Cl$^-$ export was consistently greater than input from wet deposition, corroborating that there was at least one major source of Cl$^-$ in addition to wet deposition. On average, the ratio of additional Cl$^-$ sources to Cl$^-$ input from wet deposition appears to be ~ 2:1 although the range in Cl$^-$ export indicates a relatively high degree of interannual variability. One key factor influencing Cl$^-$ export from CB was annual water discharge amount, a relationship also reported elsewhere, including at the HBEF (Fig. 12) (Neal and Rosier 1990; Lovett et al. 2005). The steeper slope for the relationship between Cl$^-$ export and water discharge at BRF probably reflects the greater average amount-weighted [Cl$^-$] in precipitation at BRF [8.5 μEq l^{-1}] compared to that at the HBEF [~ 4-6 μEq l^{-1}) (Lovett et al. 2005).

Watershed Cl$^-$ budgets at other locations have reported both additional sources and sinks of Cl$^-$ compared to wet deposition influxes (Reynolds and Pomeroy 1988; Neal and Rosier 1990; Peters and Ratcliffe 1998; Lovett et al. 2005). Neal and Rosier (1990) reported net accumulation of Cl^- during one year for a watershed in Scotland and concluded this was probably a result of low temporal resolution stream sampling, combined with high variability in precipitation influxes. Conversely, a five-year average Cl^- budget for a watershed in Wales (Reynolds and Pomeroy 1988) indicated that a source of Cl^- in addition to bulk precipitation was consistently exported in stream water. The additional Cl^- source was attributed to unmeasured inputs of Cl^- bearing aerosols. Interannual variability in the magnitude of this flux was suggested to be related to variability in hydrological conditions (Reynolds and Pomeroy 1988). Likewise, the Cl^- budget at the PMRW in Georgia during May 1994 to April 1995 reported a stream Cl^- export to Cl^- wet deposition ratio of 3.7:1 (Peters and Ratcliffe 1998) with excess Cl^- export attributed to unmeasured Cl^- dry deposition. The average decadal ratio at the PMRW (1985-1995) was 2.3:1 with the range in the export:input ratio attributed to interannual variability in hydrological conditions, which can result in Cl^- retention during dry years compared with apparent excess Cl^- export during relatively wet years (Peters and Ratcliffe 1998). At the HBEF, annual Cl^- input-export balance (1966-2000) reported eight years of a net Cl^- sink, two years with a zero balance and 24 years exhibiting an apparent additional Cl^- source to or within the watershed (Lovett et al. 2005). In general, the long-term trend in watershed Cl^- at HBEF has transitioned from a net sink prior to 1980 to a net source subsequent to 1980, coincident with a decline in net biomass accumulation (Lovett et al. 2005).

Several plausible sources that could contribute to stream water [Cl^-] and watershed Cl^- export at CB are: 1) Cl^- inputs derived from dry deposition of marine aerosols and chlorine-containing gases, 2) Cl^- input from ongoing mineralization of organic material formed prior to the 1980's when precipitation [Cl^-] was probably significantly greater (Lovett et al. 2005) and 3) additional Cl^- derived from chemical weathering of Cl^- bearing rocks and minerals.

Based on first-order assumptions, it is likely that dry deposition of Cl^- bearing aerosols and gases are significant contributors of Cl^- to CB. The dominant source of Cl^- in wet deposition to CB can be attributed to sea-salt aerosols, although annually ~24% of Cl^- wet deposition appears consistent with HCl derived from regional coal combustion, domestic and industrial waste incineration and sea-salt dechlorination via acidic gases (Shapiro et al. 2005b). Analogously, Cl^- dry deposition to CB could have contributions from these four identified Cl^- sources. Cl^- dry deposition could have significant seasonal variation because: 1) sea-salt aerosol abundance is higher during fall and winter months, associated with marine storms; 2) vegetation interception of Cl^- containing aerosols and gases should be at a maximum during seasons when deciduous trees have leaves; and 3) HCl produced from reactions of sea-salt aerosols and regional acidic gases is at a maximum during summer, corresponding to months with the highest concentrations of regional acidic gases (Stein and Lamb 2003; Shapiro et al. 2005b).

Another potential source of Cl^- within CB is from mineralization of organic material formed during previous decades when Cl^- from wet and dry deposition may have been greater. Bulk deposition of Cl^- measured at HBEF (Lovett et al. 2005) has been reported as being relatively high during the 1960's and 1970's. This mechanism (Lovett et al. 2005) is based on two concepts: 1) organic material formed during periods of relatively high Cl^- atmospheric deposition contains more Cl^-, and 2) there can be significant delay between incorporation of Cl^- into organic material and subsequent release of Cl^- via mineralization into soil and stream water. If such fluxes involving organic material were appreciable, Cl^- cannot be considered as a conservative tracer of atmospheric influxes in watersheds on relatively short time scales (a few years) since a significant fraction of Cl^- deposition could be stored in vegetation during periods of high influx and then released subsequently.

A multi-decadal time series (1967-2000) of $[Cl^-]$ in bulk deposition at the HBEF indicates a pronounced decrease in $[Cl^-]$ during 1967-1982, attributed to decreased influence on precipitation $[Cl^-]$ from coal combustion (Lovett et al. 2005). Data for precipitation $[Cl^-]$ for the site near West Point were not available prior to 1979 (Fig. 11A), although the existing data do indicate a slight decrease in mean annual precipitation $[Cl^-]$ from 1981 to 2004. This was a period of decreasing regional and local SO_2 emissions, as well as decreasing $[SO_4^{2-}]$ and SO_4^{2-} wet deposition measured near West Point (Shapiro et al. 2005a), lending support to the possible connection between declining rates of both coal combustion and local precipitation $[Cl^-]$. However, precipitation $[Na^+]$ measured near West Point over the same period (1981-2004) decreased at a rate similar to that for $[Cl^-]$, consistent with a decline in marine aerosol input rather than a decreasing contribution of Cl^- from coal combustion. Nevertheless, if we assume that $[Cl^-]$ in wet and dry deposition at BRF during the 1960's and 1970's was elevated compared to the 1980's and 1990's, as occurred in NH at the HBEF, it is plausible that organic material formed at BRF during those earlier decades contains Cl^- in amounts greater that it currently does. Subsequent mineralization of this relatively high Cl^- organic material could currently contribute additional Cl^- to CB.

A third potential source of Cl^- concerns a key assumption in developing our watershed Cl^-budget, which is that the magnitude of Cl^- input from chemical weathering of rocks and minerals is minor compared to that of atmospheric inputs (Lovett et al. 2005). However, it has been documented that gneiss in BRF has Cl^- bearing biotite and amphibole (Leger et al. 1996) and therefore the possibility of a significant contribution from chemical weathering should be examined. This flux cannot be estimated with much confidence since there have not been systematic studies of Cl^- or Na^+ weathering rates at BRF. Nevertheless, stream water samples taken along the axis of the stream from the headwaters of CB downstream to the discharge gauging station do not reveal any significant changes in $[Cl^-]$ along this transect (Fig. 13) despite a 11-15% increase in dissolved silica (data not shown). If Cl^- input from weathering of Cl^- bearing minerals were a significant source within the watershed, one might expect that $[Cl^-]$ would also increase along the stream axis. Estimates of Cl^- contribution from chemical weathering of rocks and minerals at the HBEF are approximately 2-3 mol ha^{-1} yr^{-1} (0.2 - 0.3 mEq m^{-2} yr^{-1}). This order of magnitude Cl^- contribution would account for less than 1% of average CB Cl^- export reported here (Table 1). Additionally, Neal and Kirchner, (2000), concluded that the lack of correlation between stream water $[Cl^-]$ and water discharge in a watershed in Wales indicated that weathering was not a significant source of Cl^-. CB also does not demonstrate appreciable correlation between $[Cl^-]$ and discharge rate (Fig. 9).

We therefore conclude that Cl^- from both dry deposition and mineralization of organic material formed during periods of relatively high $[Cl^-]$ provide mechanisms consistent with the magnitude and temporal trends of: 1) the large difference between $[Cl^-]$ in precipitation and stream water and 2) the excess of Cl^- export over corresponding Cl^-

input via wet deposition. Note that the magnitude of Cl^- export for CB (Table 1) is on the order of ~ 5-6 times a global estimate for unpolluted rivers of 5.9 mEq Cl^- m^{-2} yr^{-1} (Berner and Berner 1996). This could be explained by a combination of local and regional factors contributing to non-marine Cl^- previously discussed as well as the close proximity of CB to sources of sea-salt aerosols originating from marine storms off the Atlantic coast.

Direct assessment of relative contributions of these three "excess" Cl^- fluxes from CB are not feasible at this time since there are no independent measurements of Cl^- dry deposition, Cl^- from soil organic matter (SOM) mineralization or Cl^- from chemical weathering at or proximal to BRF. At HBEF, Lovett *et al*., (2005) attribute one-third to one-half of "excess" Cl^- export relative to Cl^- input via bulk deposition to dry deposition with the remainder of Cl^- excess primarily attributed to Cl^- from SOM mineralization. Dry deposition at HBEF was estimated independently, by measuring the Cl^- net throughfall flux (NTF) (throughfall – bulk deposition) of mature northern hardwoods during the growing season (June through September). Using the relationship between Cl^- dry deposition measured by this method at HBEF (12.5 mol Cl^- ha^{-1}) (1989-1992) and the corresponding bulk deposition at HBEF during NTF measurements (25.1 mol Cl^- ha^{-1}) (1989-1992) (Lovett et al. 1996), a growing season Cl^- dry deposition flux for CB of 15.4 mol Cl^- ha^{-1} was estimated based on the mean growing season Cl^- wet deposition flux of 31 mol Cl^- ha^{-1} for water years 1999-2000, 2002-2003 and 2003-2004. This approach assumes that the ratio of dry deposition to bulk deposition at the HBEF could be applied linearly to the ratio of dry deposition to wet deposition at CB. Although the growing season flux for Cl^- dry deposition measured at HBEF is used to represent the total annual

Cl$^-$ dry deposition flux at HBEF, we conclude the Cl$^-$ dry deposition flux estimated for CB (15.4 mol ha^{-1} or 1.54 mEq m^{-2}) represents a minimum value for annual Cl$^-$ dry deposition for the following reasons: 1) the HBEF Cl$^-$ dry deposition flux was reported to be an underestimate since it was based on the NTF and did not include stemflow Cl$^-$ contributions, which would have the effect of increasing Cl$^-$ dry deposition estimate by 5-10% (Johnson and Lindberg 1992; Lovett et al. 2005), and; 2) the HBEF Cl$^-$ NTF flux only approximates dry deposition during the growing season and excludes aerosol and gas contributions of Cl$^-$ to dry deposition during the remainder of the year (October through May). Mean Cl$^-$ wet deposition at CB during the growing season (31 mol ha^{-1}) represents 26% of the mean annual Cl$^-$ wet deposition reported here for water years 1999-2000, 2002-2003 and 2003-2004. If linearly scaled to represent an annual flux (15.4/31 = x/117 in mol ha^{-1} yr^{-1}), Cl$^-$ dry deposition to CB would be 58.1 mol ha^{-1} yr^{-1} (5.8 mEq m^{-2} yr^{-1}), or ~ 17% of the average Cl$^-$ export during water years 1999-2000, 2002-2203 and 2003-2004. However, temporal patterns in precipitation [Cl$^-$] and Cl$^-$ wet deposition for CB indicate large seasonal variability with minimum values occurring during summer and maximum values occurring during winter (Fig. 10) (Shapiro et al. 2005b). For example, mean Cl$^-$ wet deposition during three winter months (1980-2003) was approximate twice that measured during three summer months (Shapiro et al. 2005b). It is possible that utilizing a growing season Cl$^-$ dry deposition flux scaled to an annual flux may accurately represent the fraction of total dry deposition attributed to summer dry deposition at CB but inaccurately represent winter deposition of marine aerosols. We therefore conclude that this estimate of 58.1 mol Cl$^-$ ha^{-1} yr^{-1} (5.8 mEq Cl$^-$ m^{-2} yr^{-1}) may represent a lower limit for Cl$^-$ dry deposition with a second estimate derived from a watershed mass balance approach (mean Cl^- export – mean Cl^- wet deposition) of ~ 218 mol Cl^- ha^{-1} yr^{-1} (~ 21.8 mEq Cl^- m^{-2} yr^{-1}) for water years 1999-2000, 2002-2003 and 2003-2004 representing an upper limit for CB Cl^- dry deposition.

With regard to the contribution of Cl^- export attributed to SOM mineralization reported at HBEF, the maximum annual contribution was 23.8 mol ha^{-1} yr^{-1} (1982-2000), or 34% of Cl^- bulk deposition at HBEF reported during the period from 1979-1996 (Lovett et al. 2005). If this ratio (34%) were linearly applied to the amount of Cl^- SOM relative to Cl^- wet deposition at CB during 1999-2000, 2002-2003 and 2003-2004, Cl^- from SOM mineralization would account for an annual flux of 39.8 mol Cl^- ha^{-1} yr^{-1} (4.0 mEq m^{-2} yr^{-1}). Overall, estimates presented here indicate that mean Cl^- export at CB (33.5 mEq m^{-2} yr^{-1}) likely reflects contributions from Cl^- wet deposition (11.7 mEq m^{-2} yr^{-1}), Cl^- dry deposition (5.8 - 21.8 mEq m^{-2} yr^{-1}), Cl^- from the mineralization of SOM (4.0 mEq m^{-2} yr^{-1}) and Cl^- from chemical weathering (~ 0.3 mEq m^{-2} yr^{-1}).

Comparison of temporal trends for annual precipitation [Cl^-] (1981-2003) and monthly average stream [Cl^-] (1994-2005) (Fig. 11) indicate that stream concentrations have generally reflected temporal changes in mean annual precipitation concentration. It would be preferable to compare annual values for both data sets but the relatively short and discontinuous record for stream [Cl^-] discourages such an approach. Using values derived from linear regression equations representing each data set, annual stream [Cl^-] appears to be decreasing at twice the rate as precipitation [Cl^-] (4% vs. 2%) for years with overlapping data (1994-2003). This indicates that generally, stream [Cl^-] appears to be responsive to temporal variability in factors in addition to changes in [Cl^-] input via precipitation. The record of stream [Cl^-] (1964-2000) for HBEF indicates that long-term variability in stream [Cl^-] probably reflects changes in precipitation [Cl^-] with an additional perturbation from organic matter mineralization (Lovett et al. 2005). The temporal trends in CB [Cl^-] at BRF are similar to general trends observed at the HBEF.

Finally, with respect to current [Cl^-] in CB compared to that of other Hudson River tributaries, average flux-weighted Cl^- concentrations at CB (44.1 μEq l^{-1} or 1.56 mg l^{-1}) were much less than those reported for Sparkill Creek in Rockland County (40-100 mg l^{-1}), Saw Kill Creek in Dutchess county (20-40 mg l^{-1}), Patroon Creek in Albany County (224 mg l^{-1}), and the Mohawk River basin for 14 central New York counties (20 mg l^{-1}) (Godwin et al. 2003; Hauser 2004; Nieder 2005). It appears that CB is much more pristine than these other tributaries to the Hudson River and unaffected, to the first approximation, by anthropogenic contamination. Additionally, concentrations of [Cl^-] for CB appear to have decreased in recent years, opposite to temporal trends for several Hudson River tributaries with much higher [Cl^-] (Godwin et al. 2003; Hauser 2004; Nieder 2005).

There are several other sources of uncertainty in hydrologic and Cl^- budgets discussed here for CB. One is the assumption that there is negligible net water loss through deep seepage through bedrock fractures. There has not been direct measurement of the permeability of bedrock at BRF and thus it is possible that ET losses estimated by difference (P-Q) (~ 50%) also include a small component of deep seepage loses. However, permeability for crystalline metamorphic rocks, which dominate the Hudson Highlands, are generally quite low, with water seepage mainly occurring in highly fractured areas. As bedrock in the Hudson Highlands is know to contain faults (Isachsen and Gates 1991), we recognize that loss via deep seepage in bedrock probably occurs to some extent but conclude that it is quite small compared to water export via stream discharge.

With regard to uncertainties introduced from estimating missing [Cl^-] and stream discharge data, it is unlikely that procedures used to infill [Cl^-] caused significant bias since on a calendar month basis there was low variability in [Cl^-] with the average relative standard error for monthly [Cl^-] at ± 6.0%. Additionally, gaps in discharge for the three water years presented here with the most confidence (1999-2000, 2002-2003 and 2003-2004) were only approximated for the 17 days during 1999. These days were infilled using previously derived TOPMODEL output calculations which were considered to be our best option for infilling missing stream discharge data. Conversely, water years 2000-2001 and 2001-2002, which have been presented separately, utilized infilled discharge data derived from monthly relationships between precipitation and discharge and should therefore be viewed with greater caution.

As a result of these uncertainties, values presented here for hydrologic and Cl^- budgets should be considered an attempt to establish general temporal trends and plausible sources. The following conclusions are consistent with the data described here:

1) The average [Cl^-] of stream water is substantially greater than average precipitation [Cl^-] even after the concentration effect of ET losses (~ 50%) are included. Temporal variability for weekly intervals in [Cl^-] in stream water is much less than that of precipitation.

2) Cl^- budgets indicate that Cl^- export exceeds Cl^- input from wet deposition by an average of ~ 3:1. If all "excess" Cl^- in stream discharge were attributed to dry deposition, the average dry deposition would be ~ 22 mEq m^{-2} yr^{-1} compared with

wet deposition of ~ 12 mEq m^{-2} yr^{-1}. However, we conclude that in addition to contributions from dry deposition, Cl^- from mineralization of organic material with relatively high Cl^- abundance is also a plausible significant contributor.

3) Measured [Cl^-] in Cascade Brook since 1994 indicates a significant decrease over time, generally consistent with observed decreases in mean annual precipitation [Cl^-] since 1981.

4) The very low [Cl^-] in Cascade Brook, compared to other Hudson River tributaries in the region, indicates that it can be described as pristine and not significantly affected by anthropogenic contamination such as winter road salting and waste water effluent.

Acknowledgements

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Table Captions

Table 1: Hydrologic and Cl^- budget components for water years 1999-2000, 2002-2003 and 2003-2004. Evapotranspiration was calculated by difference of precipitation - discharge. Hydrologic and Cl^- budget components for water years 2000-2001 and 2001-2002, which are of lesser quality, are included separately (below) for comparison.

Table 2: Measured and estimated dry, wet and bulk deposition fluxes for the Hubbard Brook Experimental Forest (HBEF) and Cascade Brook (Cascade Brook) for: A) the June through September growing season, and; B) annual fluxes. [a]measured average dry (NTF) and bulk deposition fluxes for June through Sept (1989-1992) (Lovett et al. 1996; Lovett et al. 2005); [b]estimated dry deposition flux for CB during June through September utilizing the relationship between dry and bulk deposition at HBEF and wet deposition to CB; [c]measured average Cl^- wet deposition flux to CB during June through September for water years 1999-2000, 2002-2003 and 2003-2004; [d]estimated annual dry deposition flux for CB during water years 1999-2000, 2002-2003 and 2003-2004; [e]measured annual average Cl^- wet deposition flux to CB for water years 1999-2000, 2002-2003 and 2003-2004.

Table 3: Measured and estimated Cl^- budget components for the Cascade Brook watershed during water years 1999-2000, 2002-2003 and 2003-2004 as discussed in the text. [a]measured mean values for three water years; [b]estimated values.

Table 1

Water Year	Precipitation (mm)	Discharge (mm)	Evapotranspiration (mm)	Evapotranspiration (% of precipitation)	Cl^- wet deposition (mEq m^{-2} yr^{-1})	Cl^- export (mEq m^{-2} yr^{-1})	Cl^- export (mole ha^{-1})	Cl^- export/ Cl^- wet deposition
1999-2000	1371	744	627	45.7	11.1	35.5	355	3.2
2002-2003	1704	1071	633	37.1	10.7	43.3	433	4.0
2003-2004	1537	644	893	58.1	13.3	21.9	219	1.7
average	1537	820	717	47.0	11.7	33.5	335	3.0
± SEM	96	129	88	6.1	0.8	6.3	63	0.7
2000-2001	1016	466	550	54.1	7.9	16.6	166	2.1
2001-2002	884	415	469	53.1	6.2	21.4	214	3.5

Table 2

A	Growing Season Flux	mEq Cl$^-$ m^{-2} (Jun. through Sept.)	mol Cl$^-$ ha^{-1} (Jun. through Sept.)
	HBEF dry deposition[a]	1.25	12.5
	HBEF bulk deposition[a]	2.51	25.1
	CB dry deposition[b]	1.54	15.4
	CB wet deposition[c]	3.1	31.0

B	Annual Flux	mEq Cl$^-$ m^{-2} yr^{-1}	moles Cl$^-$ ha^{-1} yr^{-1}
	CB dry deposition[d]	5.8	58.1
	CB wet deposition[e]	11.7	117

Table 3

	mEq Cl$^-$ m^{-2} yr^{-1}
Cl$^-$ wet deposition[a]	11.7
Cl$^-$ dry deposition[b]	5.8 - 21.8
Cl$^-$ from mineralization of SOM[b]	4.0
Cl$^-$ from chemical weathering[b]	0.2 - 0.3
Cl$^-$ export[a]	33.5

Figure Captions

Figure 1: A) New York State map with locations of Black Rock Forest, the Hudson River and Mohawk River, which is the largest tributary to the Hudson River. B) Black Rock Forest boundary map, indicating the Old Forest Headquarters (OFHQ), the Open Lowland (OL) and the Ridge Top (RT) precipitation collectors, as well as the site of the National Atmospheric Deposition Program (NADP NY99) composite precipitation amount and chemistry collector. The boundary for the Cascade Brook watershed (CB) is also indicated, C) Contour map (intervals of 10 m of elevation) of the Cascade Brook watershed within BRF. Two stream sampling sites, North Bridge (NB) and Old West Point Road (OWPR), are identified (open squares) as is the Glycerine Hollow (GH) wetlands.

Figure 2: Cl^- storage experiment results for 28 weeks. Five stream water samples (250 ml each) from Old West Point Road were collected and filtered on January 5th 2005 and were subsequently analyzed on a weekly basis for 28 weeks (mean $[Cl^-]$ ± sem of 140 measurements = 35.8 ± 0.12 μEq l^{-1}; RSD = 4.1%). Samples were stored refrigerated (3-4ºC) in high-density polyethylene bottles in the dark. Values shown are the mean ± sem for 5 samples.

Figure 3: $[Cl^-]$ (μEq l^{-1}) at the North Bridge (NB) vs. the Old West Point Road (OWPR) sites in Cascade Brook for samples taken on the same day for a total of 256 days or 512 individual samples. The slope of the linear regression for all data points (forced through zero) is 0.98 (R^2 = 0.69). There was no statically significant difference between these two data sets (NB, OWPR) (P = 0.64). When five outliers (circled) are removed, the slope becomes 1.0 (R^2 = 0.87).

Figure 4: Flux-weighted (open circles) and monthly means ± sem (filled circles) for [Cl^-] (μEq l^{-1}) in Cascade Brook at the Old West Point Road sampling site from January 1999 to March 2005. There was no statistically significant difference between the two data sets ($P = 0.91$), and a linear regression forced through zero yields a slope of 1.0 and an R^2 value of 0.94.

Figure 5: Linear regressions, forced through zero, for precipitation (mm wk^{-1}) (1996-2004) measured at: A) collocated Open Lowland (OL) and Old Forest HeadQuarters (OFHQ) collectors (slope = 0.83; $R^2 = 0.84$); B) the OFHQ and National Atmospheric Deposition Program (NADP) NY99 collectors (slope = 1.0; $R^2 = 0.85$). Note that in Fig. 5B, one extremely high data point is not shown (226, 282) but was included in the linear regression slope.

Figure 6: Hydrograph of weekly stream water discharge (mm wk-1) (black line) and precipitation (mm) (gray line) during 1999-2004.

Figure 7: Calendar month evapotranspiration (ET in mm): A) for individual water years 1999-2000 (open bars), 2002-2003 (filled bars) and 2003-2004 (cross-hatched bars) and; B) as the mean ± sem of water years 1999-2000, 2002-2003 and 2003-2004. ET was calculated as precipitation (P) - discharge (Q) for observations during each month. This ignores changes in net storage of soil moisture or snow.

Figure 8: Hydrographs for hourly stream discharge (black line) and precipitation (gray dashed line) during discrete rain storms occurring: A) from 1/17/1999 17:00 through 1/20/1999 11:00. Total precipitation was 34.3 mm and total stream water discharge was 40.6 mm; B) from 6/5/2002 22:00 through 6/8/2002 16:00. Precipitation during the event was a total of 53.2 mm and total water discharge

was 25.9 mm. Note for both graphs that x-axis intervals are 8 hours per tick mark and cover a total of 66 hours.

Figure 9: [Cl] (μEq l^{-1}) at weekly intervals for the Old West Point Road site vs. stream water discharge (mm) for the preceding week from Cascade Brook (1999-2004) for 189 individual dates shown by season. Symbols: fall (solid triangles), spring (open triangles), summer (open circles) winter (solid circles).

Figure 10: Mean ± sem (solid circles) calendar month Cascade Brook (CB) [Cl^-] (μEq l^{-1}) (January 1994 - March 2005) for the Old West Point Road site and mean ± sem (open circles) calendar month West Point precipitation (WP) [Cl^-] (μEq l^{-1}) (January 1994 - November 2004). Note the additional months for stream chemistry and that the y-axis scale for Cascade Brook stream water [Cl^-] is five times that for West Point precipitation [Cl^-], corresponding to the average difference in [Cl^-] for these two data sets.

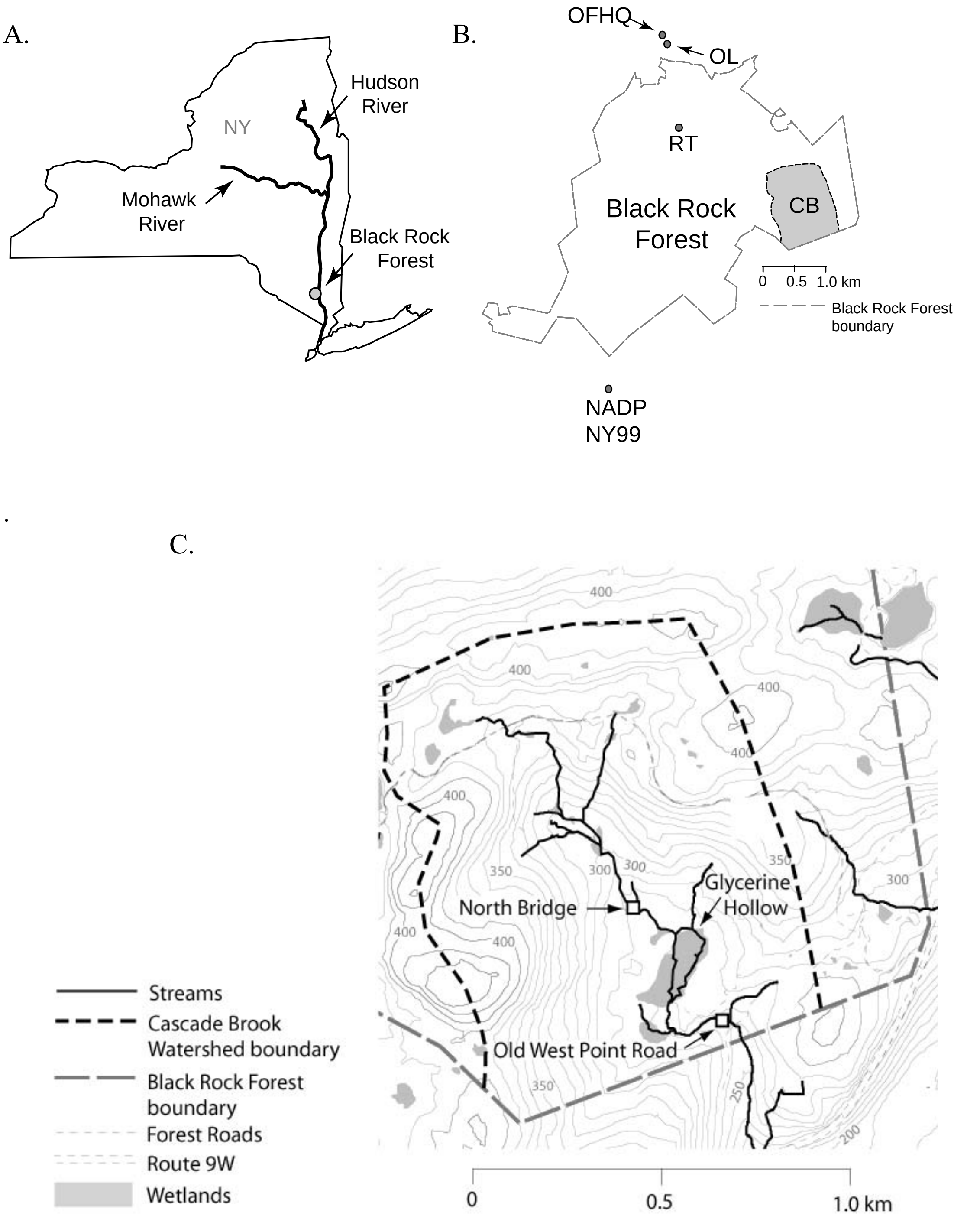
Figure 11: A) Weekly precipitation [Cl^-] (μEq l^{-1}) during 1994-2004 (open gray circles), and weekly stream [Cl^-] (μEq l^{-1}) during 1994-2005 (filled black circles); B) Note different time scales for Figs. B, C and D: Monthly precipitation amount-weighted mean [Cl^-] (μEq l^{-1}) during 1980-2004 (open gray circles), monthly mean ± sem Cascade Brook [Cl-] (μEq l^{-1}) during 1994-2005 (filled black circles) and monthly flux-weighted [Cl^-] at Cascade Brook during 1999-2005 (open blue triangles). Dates and corresponding values for six precipitation amount-weighted mean [Cl^-] > 40 μEq l^{-1} (i.e. beyond the y-axis) were as follows: (1/27/81, 51), (2/24/81, 70), (2/21/84, 46), (1/23/96, 48), (2/20/6, 60) and (3/23/99, 41). C) Annual mean ± sem (open gray circles) precipitation amount-weighted [Cl-] (μEq

l^{-1}) during 1981-2003 (Shapiro, *et al.,* 2005a) ($R^2 = 0.23$; slope = -0.22; P = 0.02); D) Monthly mean ± sem (solid black circles) Cascade Brook [Cl-] (μEq l^{-1}) during 1994-2005. ($R^2 = 0.55$; slope = -0.21). Note the scale for stream water [Cl^-] is generally five times that for precipitation [Cl^-], corresponding to the average difference in [Cl^-] for these two fluxes.

Figure 12: Linear regression forced through zero of Cl^- export (mole ha^{-1} yr^{-1}) vs. stream discharge (mm yr^{-1}) for three water years of highest quality (filled squares) and two years of lesser quality (includes estimated discharge for gaps in the discharge record) (open squares) at Cascade Brook (CB) (slope = 0.4; $R^2 = 0.83$) and a linear regression forced through zero for the Hubbard Brook Experimental Forest (HBEF) (open circles) for Cl^- export (mole ha^{-1} yr^{-1}) vs. stream discharge (mm yr^{-1}) for 37 years of data (slope = 0.13; $R^2 = 0.53$) (Lovett et al. 2005). Note that water years for HBEF were defined as June 1st to May 31st.

Figure 13: Stream water samples along transects along the axis of Cascade Brook from the headwaters downstream to the weir gauging station (0 km). Filled circles were collected 2/11/05, open circles were tributary samples on the same date, filled squares were collected 3/29/05, open squares were tributary samples on the same date. Distance (km) was calculated from the latitude and longitude at each sampling site with respect to the latitude and longitude at the weir gauging station. Distances measured along the axis of the stream would be appreciably greater. Discharges at the weir during these two dates equaled 3.7 mm day^{-1} (2/11/05) and 33.5 mm day^{-1} (3/29/05), respectively.

Figure 1


A.
NY
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Mohawk River
Black Rock Forest
B.
OFHQ
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RT
Black Rock Forest
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Black Rock Forest boundary
NADP NY99
C.
400
350
300
250
200
North Bridge
Glycerine Hollow
Old West Point Road
Streams
Cascade Brook Watershed boundary
Black Rock Forest boundary
Forest Roads
Route 9W
Wetlands
0
0.5
1.0 km

Figure 2

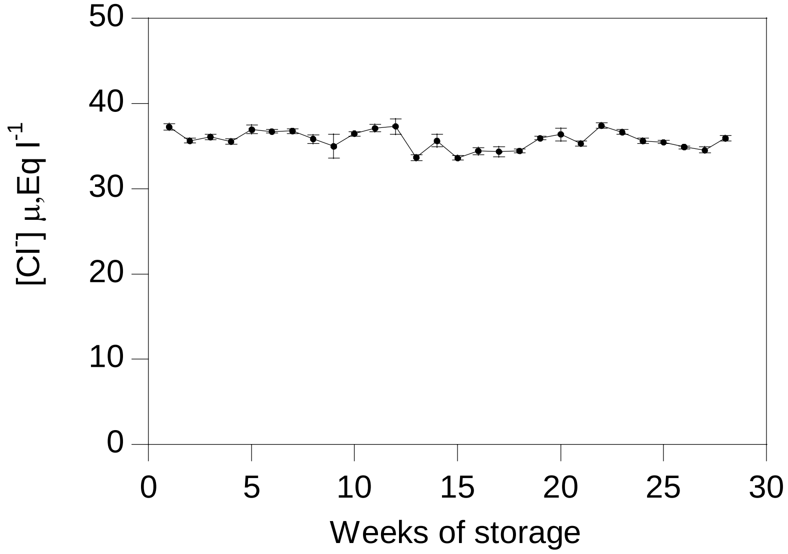


Figure 3

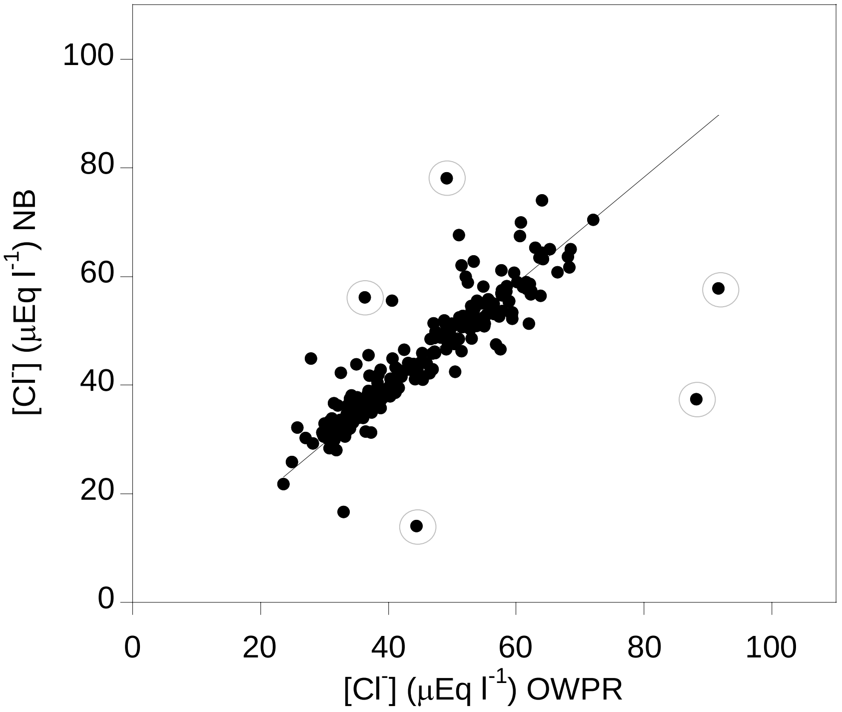


Figure 4

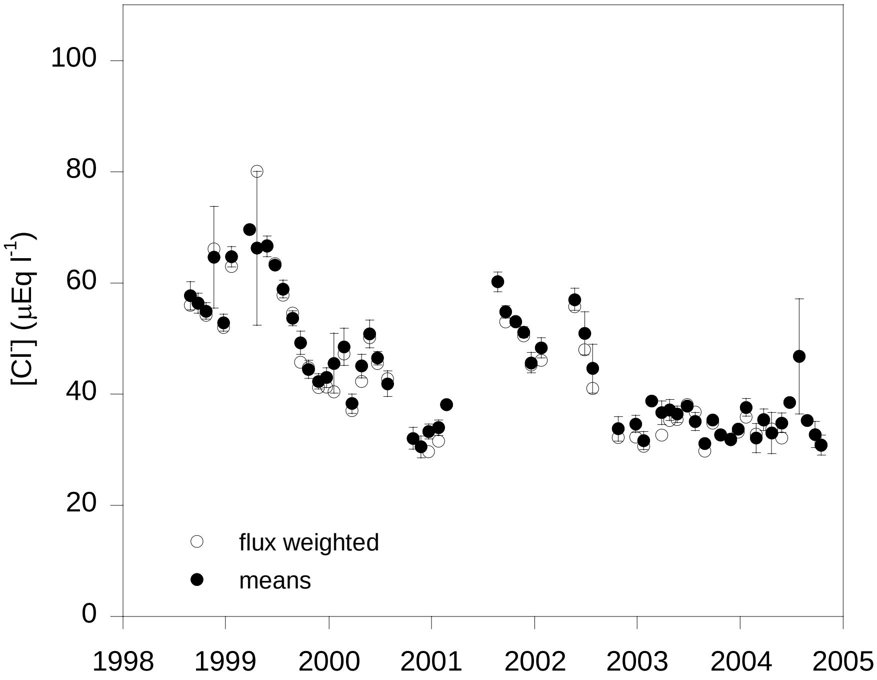
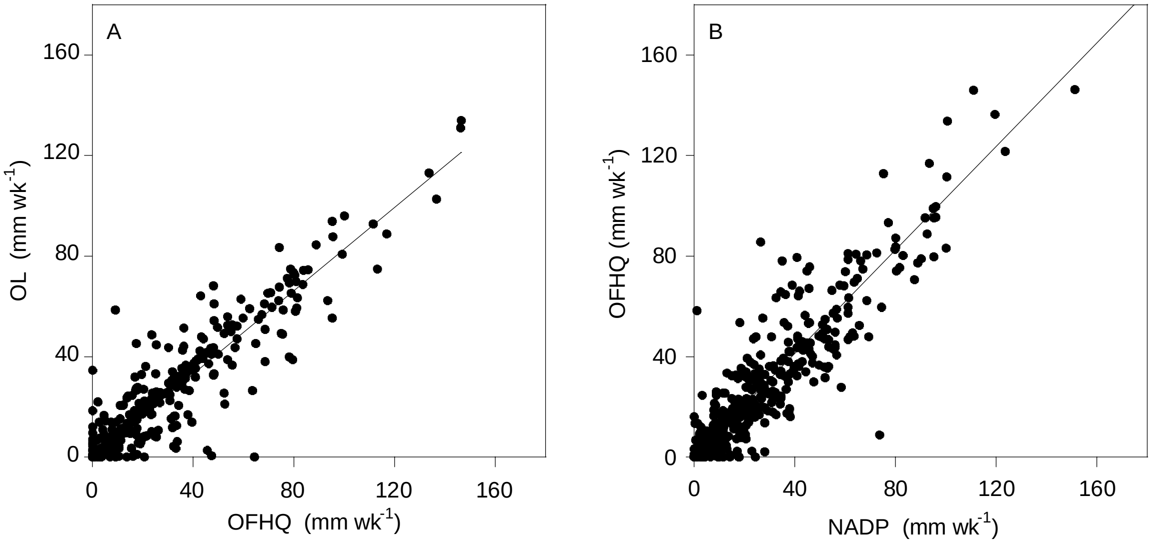


Figure 5



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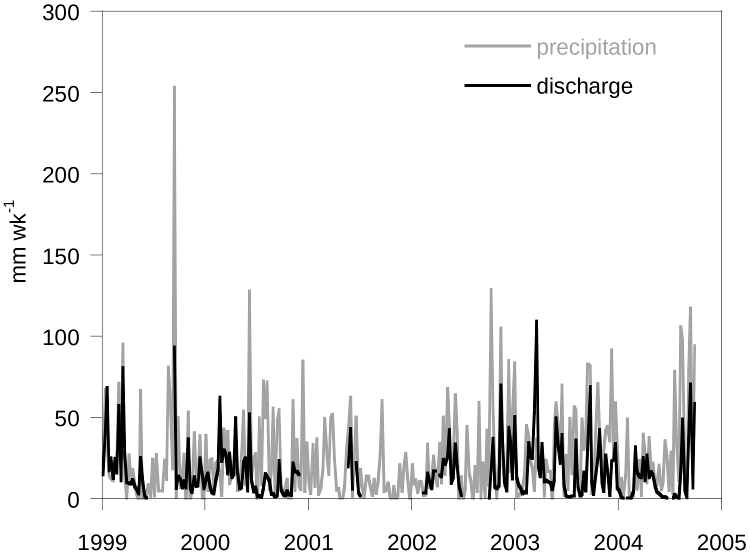


Figure 7

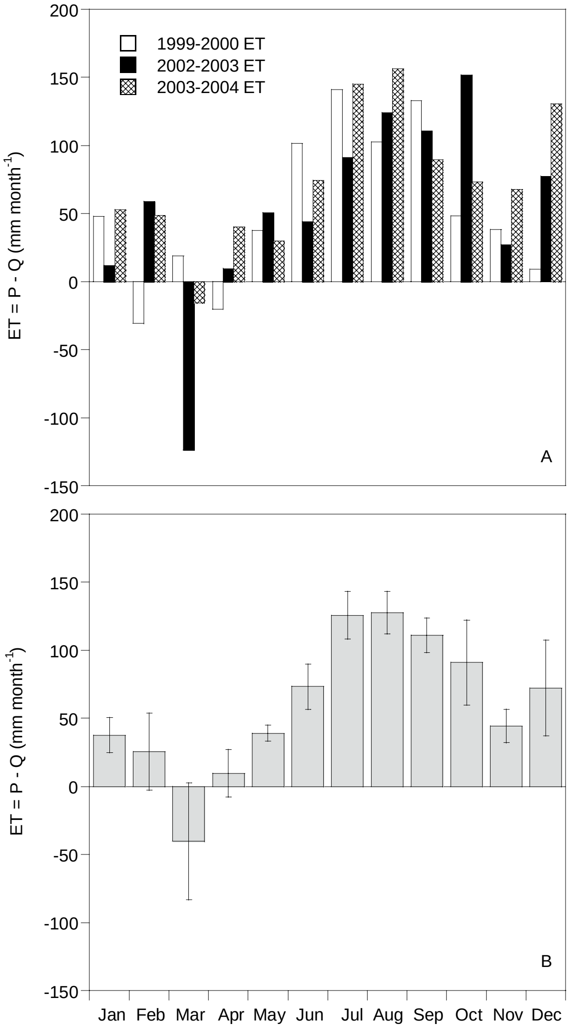


Figure 8

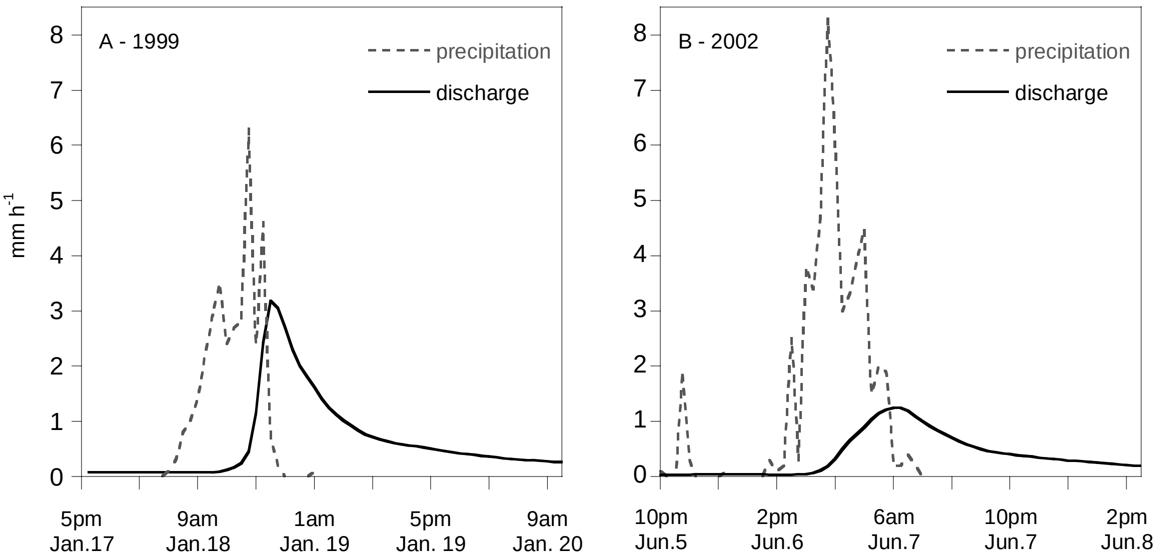


Figure 9

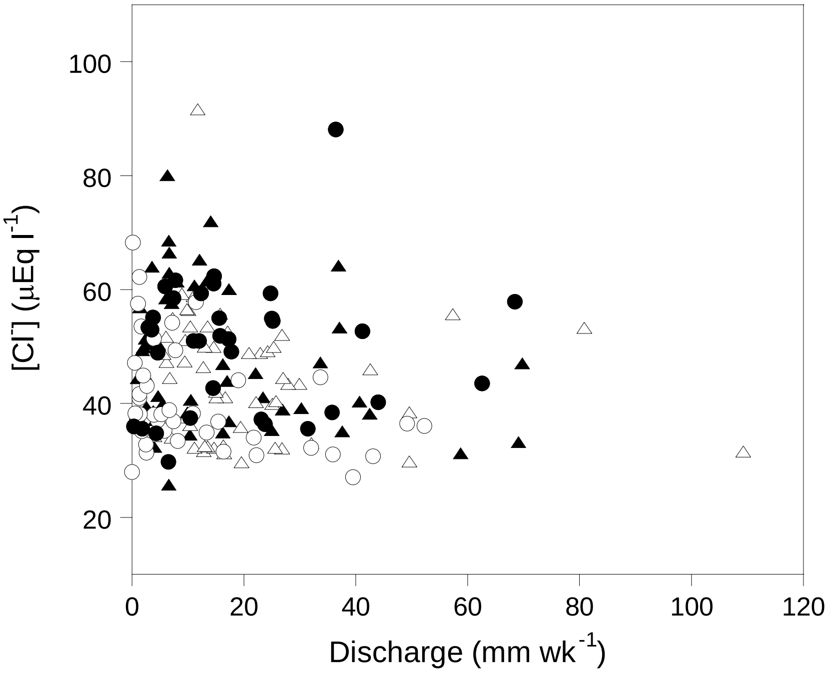
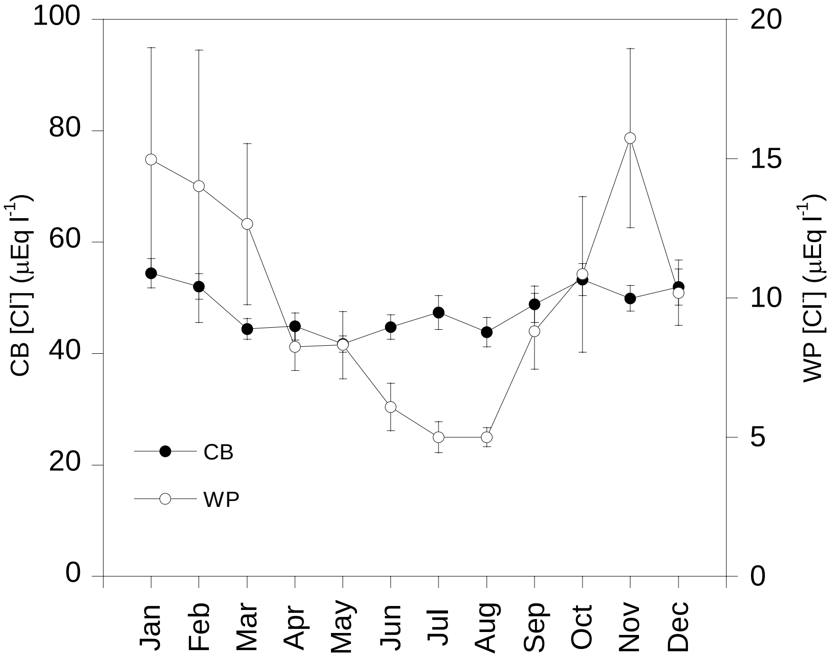


Figure 10


100
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CB [Cl$^-$] (μEq l^{-1})
WP [Cl$^-$] (μEq l^{-1})
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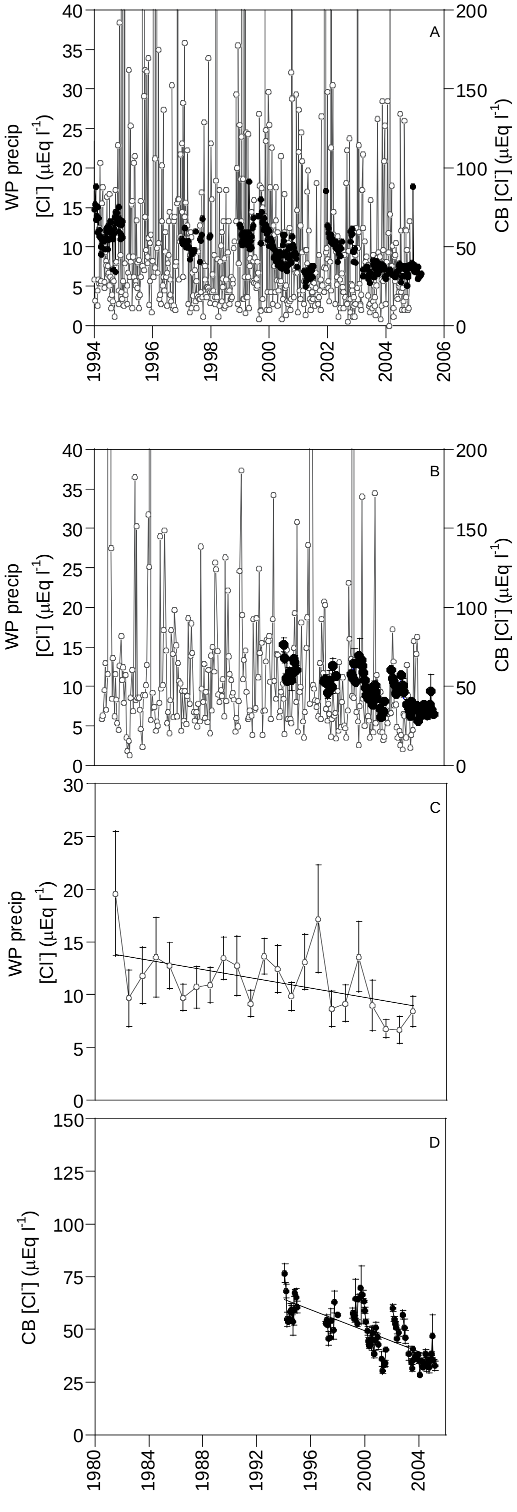
Figure 11


A
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CB [Cl$^-$] (µEq l^{-1})
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2002
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2006
B
WP precip [Cl$^-$] (µEq l^{-1})
CB [Cl$^-$] (µEq l^{-1})
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C
WP precip [Cl$^-$] (µEq l^{-1})
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D
CB [Cl$^-$] (µEq l^{-1})
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2004

Figure 12

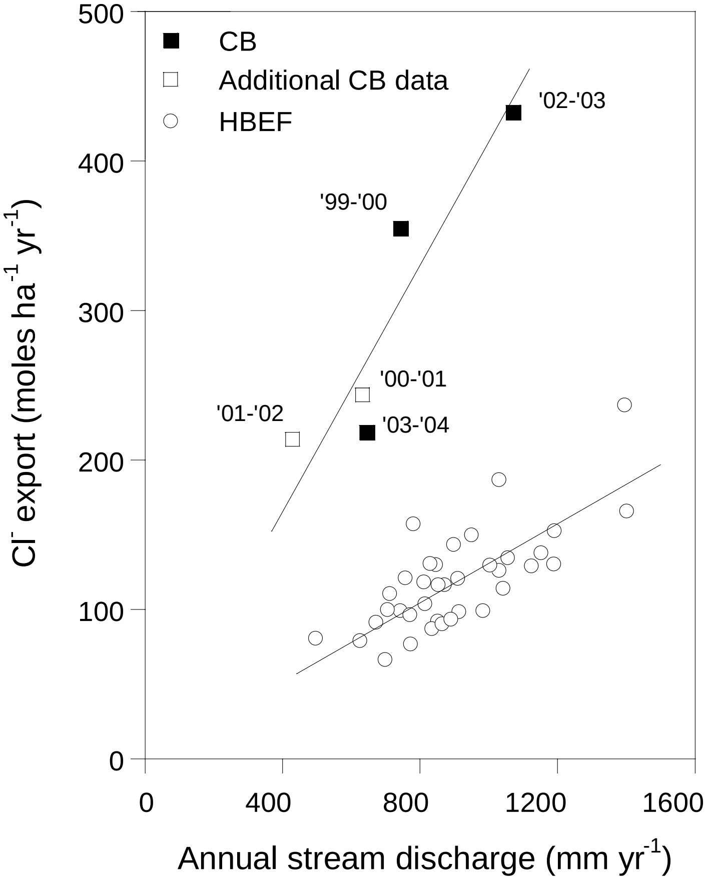
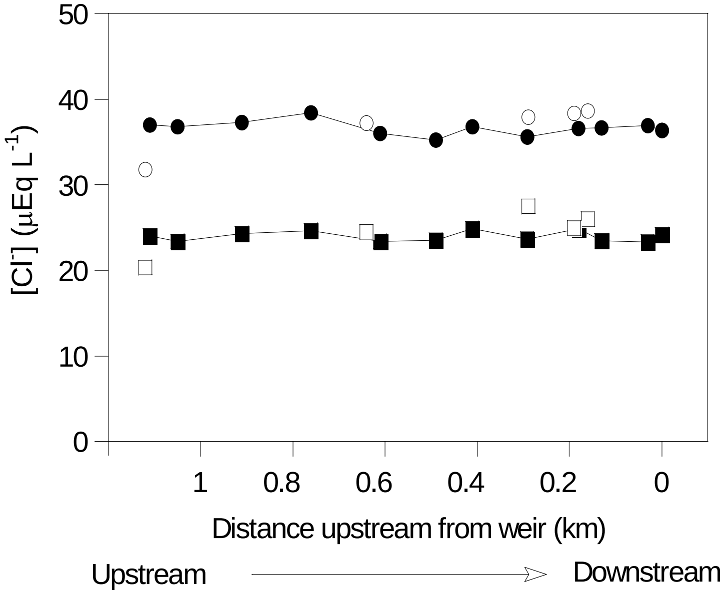


Figure 13



CHAPTER 3

Hydrogen ion, sulfate, nitrate and ammonium in precipitation near West Point, NY: decadal decreases in acidic deposition and regional emissions of SO_2 and NO_x

J. B. Shapiro[1, 2,] *, H. J. Simpson[1, 2] K. L. Griffin[1, 2] and W. S. F. Schuster[3]

[1]Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964

[2] Department of Earth and Environmental Sciences, Columbia University, New York, NY 10027

[3] Black Rock Forest, 129 Continental Road, Cornwall, NY 12518

*Author for correspondence: Phone: (845) 365-8395; Email: jbs59@ldeo.columbia.edu

Abstract

Wet deposition of acidic precipitation in the northeastern USA can have important impacts on terrestrial and aquatic ecosystems. National Atmospheric Deposition Program (NADP) precipitation chemistry data near West Point, NY (1980-2003) were examined here. Seasonally, precipitation near West Point (mean annual pH = 4.29) was more acidic in summer (4.09) and less acidic in winter (4.5), consistent with [SO_4^{2-}] and [NO_3^-] summer maxima and winter minima. Additionally, seasonal patterns in the [SO_4^{2-}]/[NO_3^-] of summer maximum and winter minimum values were consistent with alternating low and high NO_x photochemical regimes. The late spring/early summer peak in [NH_4^+] occurred earlier than that of [H^+], [SO_4^{2-}] and [NO_3^-], probably related to the difference in emissions sources for NH_3 vs. SO_2 and NO_x. Averaged over two decades, annual NO_3^--N comprised ~ 67% of total fixed N wet deposition, although the proportion from NH_4^+ has risen in recent years. From 1981-2003, [SO_4^{2-}], [NO_3^-] and [H^+] wet deposition decreased significantly while [NH_4^+] increased. Decadal trends in precipitation [SO_4^{2-}], [NO_3^-] and [H^+] at West Point were similar to trends reported for other long-term research sites in the northeastern USA. H^+ wet deposition near West Point decreased by 38% from 1981 to 2003 consistent with decreases in SO_4^{2-} (37%) and NO_3^- (23%) wet deposition, resulting in current [H^+] levels likely at the lowest average concentration since the late 1930's. Per unit area, SO_4^{2-} wet deposition was ~ 20% of local and regional SO_2 emissions indicating that appreciable amounts of SO_4^{2-} were likely deposited regionally as dry deposition and as wet and dry deposition at locations beyond the northeastern USA. In general, wet deposition decadal trends reported here were consistent with those for local, state and regional SO_2, NO_x and NH_3 emissions, indicating that average precipitation chemistry near West Point has been responsive to temporal changes in large spatial scale upwind emissions.

Keywords: wet deposition, precipitation chemistry, NADP, Black Rock Forest

Introduction

Deposition of anthropogenic acids H_2SO_4 and HNO_3 in the northeastern USA have had significant impacts on sensitive terrestrial and aquatic ecosystems (Likens, *et al.*, 1972; Siccama, *et al.*, 1982; Likens, *et al.*, 1996) such as acidification of soil and lake waters, discoloration of leaves or needles, tree dieback and leaching of vital nutrient cations from soils (Driscoll, *et al.*, 2001; Tomlinson, 2003). Specific to reduced tree growth, it has been shown that acid deposition increases the flux of base cations, such as Ca^{2+}, into soil solution, subsequently leading to increased Ca^{2+} outflow in streams, which decreases availability for biomass uptake (Lawrence, *et al.*, 1995; Shortle, *et al.*, 1997; Tomlinson, 2003). In an effort to reduce these and other detrimental effects, the 1990 Clean Air Act Amendments (CAAA) were designed to significantly lower emissions of SO_2 and NO_x from electricity generating stations. These reactive gases are subsequently oxidized and hydrolyzed in the atmosphere, resulting in acidic precipitation and therefore lowering large point source emissions should lessen impacts on downwind ecosystems (Holland, *et al.*, 1999; Lynch, *et al.*, 2000b).

Long-term records of bulk deposition and wet only $[SO_4^{2-}]$ in precipitation have reported appreciable temporal declines in the northeastern USA, consistent with substantial reductions in point source SO_2 emissions (Lynch, *et al.*, 2000b; Butler, *et al.*, 2001; Likens, *et al.*, 2001; Park, *et al.*, 2003). Bulter *et al.*, (2001) found nearly a one to one correspondence between decreases in SO_2 emissions in the northeastern USA and decreases in precipitation $[SO_4^{2-}]$ in the region. However, percentage decreases in NO_x emissions have been considerably less than for SO_2 and appreciable reductions in regional precipitation $[NO_3^-]$ have not been consistently observed (Lynch, *et al.*, 2000b;

Lynch, *et al.*, 2000a; Butler, *et al.*, 2003). Unlike SO_2, NO_x emissions are attributed mostly to non-point sources such as vehicle emissions (USEPA, 2002) which are not regulated by the 1990 CAAA. During the period from 1991-1997, among 15 states reported as the largest NO_x emitters, only CA, NY and PA had significant reductions in NO_x emissions. Temporal trends in NO_x emissions for the 12 remaining states were either constant (TX, OH, FL, IN, MI, LA, KY, GA, and NC) or increasing (IL, TN, and AL) (Butler, *et al.*, 2001)

The objectives of this study were to characterize seasonal and decadal (1981-2003) trends in precipitation [H^+], [SO_4^{2-}], [NO_3^-] and [NH_4^+] and wet deposition of these ions near West Point, NY. Trends in precipitation chemistry were also compared to local, state and regional SO_2, NO_x and NH_3 emissions. A precipitation monitoring station near West Point, NY was chosen for this investigation because: 1) it is in close proximity (~ 70 km) to the center of a huge urban complex (NYC) and therefore potentially affected by "local" emissions, and 2) it is also very near (~ 5 km) a relatively pristine forested area (Black Rock Forest) in the Hudson Highlands where a wide-range of ecological, physiological and hydrological experiments are being conducted (e.g. Engel, *et al.*, 2002; Nagel, Griffin, 2004; Whitehead, *et al.*, 2004).

Methods

The National Atmospheric Deposition Program (NADP) maintains a network of > 200 sampling stations in North America that collect weekly wet-only composite precipitation for measurement of chemical composition (Lamb, Bowersox, 2000). NADP site NY99, (41º35' N, 74º05' W, 201 m elevation) is located on the West Point Military Reservation, in the Lower Hudson Valley, Orange County, New York (Fig. 1). The location for NY99 is at Camp Buckner, which is on the grounds of the West Point Military Reservation but ~ 8 km west of West Point proper. West Point proper extends to the edge of the Hudson River. The actual location of NY99 is therefore closer to the border of the BRF (< 3 km) and the towns of Highlands Falls (7 km), Fort Montgomery (6 km), Central Valley (6 km) and Highland Mills (5 km). Therefore, the meteorological conditions at these monitoring stations reflect much more the conditions typical of the Black Rock Forest and surrounding Hudson Highlands than they do the corridor along the Hudson River where West Point is located.

Data from NY99, appended with compositions from nearby NY51 for about three years prior to the onset of sample collection at NY99 (9/13/83), provide continuous weekly composite chemistry from July 1, 1980 through February 3, 2004 (NADP, 2004). Data from NY51 for the initial year of operation (6/26/79-7/1/80) were excluded here, based primarily on the presence of a number of weeks of data with unusually high Na^+/Cl^- ratios. We concluded that the first year of operation at NY51 may have had appreciable contamination of samples, at least for Na^+ (Shapiro, *et al.*, 2005) An infilled version of the NADP NY51/NY99 data was used here to calculate amount-weighted mean concentrations as well as wet deposition values for H^+, SO_4^{2-}, NO_3^- and NH_4^+. Values were infilled for 167 of the 1231 weeks included here. For a description of the combined NY51/NY99 data and infilling procedures refer to Shapiro *et al.*, (2005).

A separate, screened version of the NY51/NY99 chemistry data was derived to establish relationships internal to the data set (i.e. correlations between ions). The screening process removed concentrations for weeks with: 1) very low amounts of precipitation (< 2mm) (Gilliland, *et al.*, 2002); 2) charge balance differences > 3σ of the mean charge balance difference for the entire data set; and 3) samples designated by NADP as being invalid (Shapiro, *et al.*, 2005). A total of 242 of the 1231 weeks were removed for these reasons with invalid NADP data accounting for 147 of the 242 screened weeks. Comparisons between these two data sets indicate no statistically significant differences in mean annual $[H^+]$ (μEq L^{-1}) (1981-2003) (Fig. 2) between infilled and screened data, indicating that the infill procedures did not bias the annual mean values of the NADP data. A linear regression between annual means of the two sets yielded a statistically significant R^2 value of 0.87. Similar conclusions can be drawn for $[SO_4^{2-}]$, $[NO_3^-]$, and $[NH_4^+]$ (μEq L^{-1}) infilled and screened mean annual values (1981-2003) (data not shown).

In this study, $[SO_4^{2-}]$ values include sea-salt and non sea-salt $[SO_4^{2-}]$ components in precipitation, such as anthropogenic as well as volcanic, terrestrial and marine biogenic sulfur emissions. Using the sea-water ratio of SO_4^{2-}/Na^+ (0.121) (equivalents units) as indicative of the sea-salt SO_4^{2-} contribution (Berner, Berner, 1996), the non sea-salt component, of primary interest here, accounts for a mean of ~ 97% of total weekly $[SO_4^{2-}]$ measured near West Point. The mean SO_4^{2-}/Na^+ ratio in precipitation measured near West Point was 19.7, a factor of ~163 times greater than the sea water ratio. Additionally, in this study, total fixed nitrogen refers specifically to input from NO_3^- and NH_4^+, for which empirical data were available for NY99 and does not include contributions from organic nitrogen.

Regional source emissions relevant to the West Point area are defined here as those derived for New York State in Butler *et al*., (2001), and Butler *et al*., (2003), using the NOAA Air Resources Laboratory's Hysplit-4 model (Draxler, Rolph, 2003; Rolph, 2003). The results of these model transport calculations indicate that SO_2 and NO_x emissions from NY, NJ, PA, OH and WV are the primary sources for New York State deposition based on 9-12 hour air mass back-trajectories (Fig. 3). Using this time interval for the back-trajectories, Butler *et al.,* (2001) found a nearly one to one relationship between changes in SO_2 emissions and precipitation [SO_4^{2-}] from the early vs. the late 1990's. Local emissions are defined here as counties in NY, NJ and PA within 100 km of West Point that are consistent with the most frequent directions of air mass back-trajectories. Support for this first order assumption is reported in Ho *et al*., (1998) where prevailing wind directions for Black Rock Forest (~ 5 km north of West Point) were regionally representative and averaged over a year were primarily from the NW, SW and S.

County, state and regional emissions data for SO_2, NO_x and NH_3 were obtained from the USEPA, Emission Factor and Inventory Group (McMullen, Personal Communication, 2004) for 1990 and for 1996-2000. These emissions data reflect up-to-date emissions estimates and are designated here as "corrected data". In addition, emissions estimates from the online USEPA National Emissions Trends (NET) database (USEPA, 2004) for years 1990-1999 are also discussed here. Although generally similar, the absolute values do not represent the most recent emissions estimates and are therefore designated here as "uncorrected data" and included for derivation of semi-quantitative trends since 1990. All SO_2, NO_x and NH_3 emissions were reported in short tons yr^{-1} by the USEPA but converted to kg yr^{-1} for this study.

Results

Measured values of $[H^+]$, $[SO_4^{2-}]$, $[NO_3^-]$ and $[NH_4^+]$ at NY51 and NY99 for the 55 week overlap period (9/13/1983-10/2/1984) were quite similar and differences were non-systematic [Fig. 4]. R^2 statistics for linear regressions forced through zero comparing data at the two sites for $[H^+]$, $[SO_4^{2-}]$, $[NO_3^-]$ and $[NH_4^+]$ were 0.81, 0.87, 0.93 and 0.86 respectively. Precipitation amounts (mm wk^{-1}) at the two sites over this period (Fig. 4E) yielded a linear regression slope of 1.0 and a R^2 value of 0.99 (Shapiro, *et al.*, 2005).

Calendar month mean precipitation amounts (mm) for NY51/NY99 (1981-2003) were 106 ± 4 mm $month^{-1}$ (maximum in November (125 ± 10 mm), minimum in February (80 ± 9 mm)), for an annual average of 1288 ± 49 mm $year^{-1}$. Calendar month mean and median concentrations for $[H^+]$, $[SO_4^{2-}]$ and $[NO_3^-]$ (Fig. 5) were relatively low during winter, progressively increasing to a maxima in late summer, followed by a sharp decline in September. The seasonal trend in $[NH_4^+]$ is generally similar (Fig. 5D), however, peak concentrations occurred in May and June whereas maxima in $[H^+]$, $[SO_4^{2-}]$ and $[NO_3^-]$ occurred during mid to late summer. Calendar month mean values for $[H^+]$, $[SO_4^{2-}]$, $[NO_3^-]$ and $[NH_4^+]$ all had comparatively low concentrations in November, possibly reflecting the precipitation amount maximum in November. December concentrations were slightly higher than November and January for all four species. Seasonal patterns similar to these trends in calendar month patterns are evident in wet deposition fluxes (mEq m^{-2}) for each of these ions (Table 1). The ratio of SO_4^{2-}/Cl^- (equivalents units) in precipitation near West Point ranged from a minimum of ~ 3 in winter to ~ 15 in mid-summer (Fig. 5E), while the ratio of SO_4^{2-}/NO_3^- (equivalence units) also had a consistent seasonal pattern with the highest values during the summer and the lowest values during winter (Fig. 5F). Scatter plots of [SO_4^{2-}] vs. [NO_3^-] during summer and winter indicate appreciably higher slopes and R^2 values during summer (slope = 1.7; y-intercept = 13.95; R^2 = 0.71) vs. those in winter (slope = 0.47; y-intercept = 21.66; R^2 = 0.35) (Fig. 6). The annual mean pH for data measured near West Point (1981-2003) was 4.29 ([H^+] = 51 μEq L^{-1}) with a maximum pH of 4.5 ([H^+] = 32 μEq L^{-1}) during November and a minimum pH of 4.09 ([H^+] = 81 μEq L^{-1}) during August.

Annual mean values in [H^+], [SO_4^{2-}], [NO_3^-] and [NH_4^+] (1981-2003) (Fig. 7) indicate significant decreasing temporal trends in [H^+] (R^2 = 0.55; slope = -1.05; $p < 0.0001$), [SO_4^{2-}] (R^2 = 0.49; slope = -0.92; p = 0.0002) and [NO_3^-] (R^2 = 0.28; slope = -0.34; p = 0.01), and a non-statistically significant increasing trend in [NH_4^+] (R^2 = 0.12; slope = 0.13; p = 0.1). Wet deposition trends for SO_4^{2-}, NO_3^-, H^+ and NH_4^+ (Fig. 7) are similar in sign and statistical significance to trends for amount-weighted mean concentrations.

Annual wet deposition of SO_4^{2-} and NO_3^- have a weak, yet statistically significant relationship with annual precipitation amount (mm) (1981-2003) (R^2 = 0.24; p= 0.019 and R^2 =0.29; p = 0.008 for SO_4^{2-} and NO_3^- respectively) (data not shown). Residuals for annual SO_4^{2-} and NO_3^- wet deposition derived from the regressions between SO_4^{2-} wet deposition vs. precipitation amount and NO_3^- wet deposition vs. precipitation amount indicate statistically significant decreasing trends over the decadal record (1981-2003) (Fig. 8) (R^2 = 0.62; slope = -1.12; $P < 0.0001$ and R^2 = 0.24; slope = -0.35; P = 0.015 for SO_4^{2-} and NO_3^- residuals, respectively). Statistically significant trends in residuals for SO_4^{2-} and NO_3^- indicate that there is variability in the wet deposition record that cannot be attributed to variability in annual precipitation amount. Therefore, temporal trends in

SO_4^{2-} and NO_3^- wet deposition probably also result from additional factors, such as changes in annual SO_2 and NO_x emissions.

H^+ is the dominant cation in annual wet deposition at NY51/NY99 (61 mEq m^{-2}) followed by NH_4^+ (15 mEq m^{-2}) (Table 1). Sulfate is the dominant anion at NY51/NY99 (Table 1; Fig. 9), followed by NO_3^-, with NO_3^- -N accounting for an average of ~ 67% of the total fixed nitrogen in wet deposition near West Point (Table 1). The percentage annual contribution of $[SO_4^{2-}]$ to total anion charge decreased over the record (1981-2003) while the percentage annual contribution of $[NO_3^-]$ to total anion charge increased (Fig. 9). These decadal trends are reflected in seasonally aggregated $[SO_4^{2-}]/[NO_3^-]$ ratios, which show a small but statistically significant decreasing trend in $[SO_4^{2-}]/[NO_3^-]$ (1981-2003) ($R^2 = 0.06$; slope = -0.003; $p = 0.015$) (Fig. 10). A consistent peak in $[SO_4^{2-}]/[NO_3^-]$ ratios during summer is an indication of the larger percentage range in monthly mean $[SO_4^{2-}]$ values throughout the calendar year, increasing from a value comparable to that of $[NO_3^-]$ in winter to twice that for $[NO_3^-]$ in summer (Figs. 5 and 10).

The long-term temporal trend (1981-2003) in $[Cl^-]$ was slightly negative and statistically significant ($R^2 = 0.23$; slope = -0.22; $p = 0.02$) although the decreasing trend in Cl^- wet deposition was not statistically significant ($R^2 = 0.08$; slope = -0.29; $p = 0.18$). Seasonal $[SO_4^{2-}]/[Cl^-]$ vs. year (1981-2003) and calendar month $[SO_4^{2-}]/[Cl^-]$ plots indicate maxima in $[SO_4^{2-}]/[Cl^-]$ ratios during summer, reflecting high summer $[SO_4^{2-}]$ coinciding with low summer $[Cl^-]$ (Figs. 5E and 11) (Shapiro, *et al.*, 2005). Clearly, anion chemistry of precipitation near West Point was systematically variable with season, reflecting the dominance of acidic gas oxidation during summer and marine aerosol sources exhibiting more importance during winter.

Qualitatively, SO_2 emissions at the regional, state and county levels for corrected and uncorrected data (Fig. 12A, B, C) indicate generally decreasing emissions over time (1990-2000). Temporal changes in NO_x emissions (Fig. 12D, E, F) are not as dramatic as for SO_2 but do indicate decreasing regional and county emissions and somewhat lesser decreases in New York State emissions for corrected and uncorrected data. Temporal trends in corrected and uncorrected NH_3 emissions (Fig. 12G, H & I) were increasing at all three spatial scales.

For first order comparisons based on continuous 10-year uncorrected emissions data, percentage changes in emissions for SO_2, NO_x and NH_3 (1990-1999) were calculated using values for 1990 and 1999 derived from linear regression equations fit to all of the uncorrected emissions data. Results from this approach indicate that SO_2 emissions, at the county, state and regional level have decreased by ~ 31-36%, NO_x emissions have decreased by ~ 9-17% and NH_3 emissions have increased by ~ 12-28% (Table 2). These emissions trends are generally consistent with corresponding percentage changes in [SO_4^{2-}] and SO_4^{2-} wet deposition (-22% and -33%, respectively), [NO_3^-] and NO_3^- wet deposition (-13% and -26%, respectively), and [NH_4^+] and NH_4^+ wet deposition (+15 and +11%, respectively) measured near West Point when derived from the same approach over the same time period (1990-1999).

Discussion

It is instructive to compare precipitation chemistry measured near West Point with temporal trends in emissions on several spatial scales, given the goal of CAAA to reduce harmful effects of acid rain on terrestrial ecosystems by lowering point source emissions. Additionally, trends derived for this site near West Point can provide proxy precipitation chemistry data for nearby locations in the lower Hudson valley, such as Black Rock Forest.

Calendar month trends in [H^+], [SO_4^{2-}] and [NO_3^-] and wet deposition fluxes [Fig. 5; Table 1] near West Point indicate minimum concentrations in fall/winter and maximum concentrations in summer, which can be attributed primarily to the temporal pattern in photochemical oxidation of SO_2 and NO_x gases in the troposphere (Calvert, *et al.*, 1985; Stein, Lamb, 2003). Reactions of these acidic gases occur more rapidly in summer due to a larger pool of oxidizing species from photochemical reactions of volatile organic compounds in the atmosphere (Calvert, *et al.*, 1985; Hindy, 1994; Stein, Lamb, 2003). Additionally, maximum concentrations of [H^+], [SO_4^{2-}] and [NO_3^-] in precipitation occur in July/August, concurrent with seasonal peaks in air temperature. General calendar month trends in precipitation [H^+], [SO_4^{2-}] and [NO_3-] near West Point are similar to those measured at the Institute of Ecosystem Studies (IES), in Millbrook, NY, a research site ~ 60 km northeast of West Point (Kelly, *et al.*, 2002), indicating regional coherence in trends for these ions.

Seasonal and calendar month trends in [SO_4^{2-}]/[NO_3^-] indicate minimum values during winter months, and maximum values during summer months (Figs. 5F & 10); this temporal pattern is consistent with alternating high and low NO_x photochemical regimes (Stein, Lamb, 2003). During winter, which can be characterized as a high NO_x regime, NO_x emissions are greater than the supply of available oxidizing species. The primary sink for radicals is therefore the oxidation of NO_x gases to HNO_3, which inhibits peroxide production (Stein, Lamb, 2003). These atmospheric conditions favor NO_3^- production over SO_4^{2-} production, which is reflected in the relatively low [SO_4^{2-}]/[NO_3^-] ratios measured during winter. Conversely, during summer, which is a low NO_x regime, the potential pool of oxidizing species is greater than NO_x emissions and thus there are abundant radicals available for peroxide production, which are required for aqueous phase SO_4^{2-} production (Stein, Lamb, 2003). Stein and Lamb (2003) estimate hydrogen peroxide production rates for summer (2.1 x 10^5 molecules cm^{-1} s^{-1}) and winter (7.0 x 10^2 molecules cm^{-1} s^{-1}), which indicate 300-fold greater availability during summer, consistent with significantly greater summer SO_4^{2-} production. Low NO_x regime conditions are reflected in the relatively high $[SO_4^{2-}]/[NO_3^-]$ ratio during summer months (Figs 5F & 10). Furthermore, the greater slope for scatter plots of $[SO_4^{2-}]$ vs. $[NO_3^-]$ during summer than winter (Fig. 6) illustrate this difference in atmospheric oxidizing potential and the relative production of SO_4^{2-} and NO_3^- with SO_4^{2-} production greatly exceeding NO_3^- production during summer whereas SO_4^{2-} production was much lower relative to NO_3^- during winter.

This seasonal pattern of alternating high and low NO_x regimes occurring during winter and summer has been reported for 16 precipitation monitoring sites in the eastern USA (Stein, Lamb, 2003). Comparison of the average weekly $[SO_4^{2-}]$ vs. $[NO_3^-]$ for these 16 regional sites with that reported here for a site near West Point, NY (1981-2004) indicate that for summer and winter, the relative concentrations of SO_4^{2-} and NO_3^- reported here were generally consistent with regional patterns in the concentration of these ions (Fig. 13), averaging near the middle of the range for both of these acidic anions. The periods of averaging for the regional stations were not identical to that for the site near West Point.

Calendar month (1999) New York State SO_2 point source emissions were compared to seasonal patterns in [SO_4^{2-}] in precipitation. Emissions, per calendar month, in 1999 for New York State from 29 large electricity generating stations (USEPA, 2005), which accounted for 77% of the 1999 uncorrected point source SO_2 emissions for the state, show both January and July maxima in SO_2 emissions (Fig. 14). The presence of two peaks in monthly emissions contrasts with the single large maximum in calendar month precipitation [SO_4^{2-}] (Fig. 5B). This qualitative comparison between SO_2 emissions and [SO_4^{2-}] in precipitation is consistent with the conclusion that the calendar month trend in [SO_4^{2-}] primarily reflects atmospheric photochemistry rather than a linear response to variations in seasonal SO_2 emissions.

The monthly pattern in [NH_4^+] (Fig. 5D) probably reflects seasonal NH_3 emissions from agriculture in general and especially livestock production, which account for more than ~ 80% of NH_3 emissions in the USA (Battye, *et al.*, 1994; USEPA, 2000). Annual mean trends precipitation [NH_4^+] measured near West Point indicate a moderate increase from 1980-2003. Although not statistically significant, this trend is opposite to that reported for IES, which the authors conclude was probably a response to a decrease in dairy cattle numbers within Dutchess County, NY (1984-1999) (Kelly, *et al.*, 2002). In contrast, NH_3 emissions from uncorrected EPA data (1990-1999) for Orange County and New York State indicate increasing NH_3 emissions from agriculture and forestry, consistent with the overall increasing trend in total NH_3 emissions reported here. The contrasting temporal trends for the West Point site and the IES could reflect the relatively short tropospheric lifetime of NH_3, which has been estimated to be hours to days (Krupa, 2003). Approximately 50% of NH_3 deposition can occur within 50 km of the point of emission and thus [NH_4^+] in precipitation and wet deposition probably reflects more local emissions than [NO_3^-], [SO_4^{2-}] and [H^+] (Ferm, 1998).

Anion equivalents in precipitation measured near West Point are dominated by [SO_4^{2-}] (Fig. 9) even though the temporal trend over two decades indicates that the percentage of total anions provided by [SO_4^{2-}] has decreased while the percentage for total anions from [NO_3^-] has increased (Fig. 9). This difference in anion chemistry temporal trends appears to result from differences in relative rates of decrease of SO_2 and NO_x emissions. Temporal trends at West Point for SO_4^{2-} and NO_3^- percentage of total anions are consistent with trends at the Hubbard Brook Experimental Forest, NH (HBEF) (1964-2000) when compared over the same time period (Lovett, *et al.*, 2005). Precipitation chemistry data from the HBEF represents the longest continuous record in North American and therefore offers a valuable comparison with other locations, such as the station near West Point.

The data since 1981 for precipitation [SO_4^{2-}] measured near West Point indicate a significant decreasing trend over time of 35% (-0.92 μEq L^{-1} yr^{-1}; Fig. 7B). The annual rate of decrease in [SO_4^{2-}] was similar to the trend at the HBEF (-0.88 μEq L^{-1} yr^{-1}; 1978-1998) (Likens, *et al.*, 2001) although the periods reported differ slightly for the two sites. When calculated over the same time periods, the rate of decrease in precipitation [SO_4^{2-}] near West Point was slightly less than at other locations in the region. For example from 1981-1998 the mean annual decrease in [SO_4^{2-}] measured near West Point was –0.93 μEq L^{-1} yr^{-1}, compared to –1.02 μEq L^{-1} yr^{-1} at Bridgeton, ME (NADP site ME02), and –1.18 μEq L^{-1} yr^{-1} at Underhill, VT (NADP site VT01) (Likens, *et al.*, 2001). Additionally, the decrease in [SO_4^{2-}] from 1983-2001 at the Huntington Wildlife Forest in the Adirondack

Mountains, NY was similar to that measured near West Point over the same period (-0.79 μEq L^{-1} yr^{-1} and -0.68 μEq L^{-1} yr^{-1}, respectively).

The two-decade trend near West Point of decreasing precipitation $[NO_3^-]$ (-24%) (Fig. 7C) and NO_3^- wet deposition (-23%) are in general agreement with results from other locations in New York State, including the Huntington Wildlife Forest in the Adirondack Mountains (Park, *et al.*, 2003) and the Institute of Ecosystem Studies (Kelly, *et al.*, 2002). This coherence is worthy of note since ~ 10% declines in NO_x emissions in the northeastern region from 1991-2000 have been reported (Butler, *et al.*, 2003), which is considerably less than the ~ 24% decrease in SO_2 emission reported for NY from the early to the late 1990's (Butler, *et al.*, 2001). The lower percentage of NO_x decrease has been suggested to result from the competing effects of decreasing NO_x emissions from electricity generating stations vs. the constant or increasing NO_x emission from vehicles, the latter of which makes up > 50% of total NO_x emissions (Butler, *et al.*, 2003).

One feature in the data representing West Point annual mean values worthy of note is the conspicuously low $[H^+]$, $[SO_4^{2-}]$, $[NO_3^-]$ and $[NH_4^+]$ during 1982, 1983 and 1984 (Fig. 7). Analysis of a similar feature at the HBEF indicates that low annual mean $[SO_4^{2-}]$ in precipitation during 1983 and 1984 was a consequence of differences in seasonal amounts of precipitation, with 1983 and 1984 having low summer precipitation amounts and thus low annual $[SO_4^{2-}]$ (Likens, *et al.*, 1990). However, neither annual, seasonal nor calendar month variability in precipitation amounts measured near West Point during 1982-1984 can consistently account for markedly low ion concentrations during those years and therefore it remains unclear as to the origin of this feature in the temporal trends measured near West Point.

In comparing annual SO_4^{2-} -S, NO_3^- -N and NH_4^+ -N wet deposition (kg ha^{-1}) (Table 1) measured near West Point to other sites in the northeastern USA, deposition amounts are within the ranges reported for Millbrook, NY (Kelly, *et al.*, 2002) and somewhat greater than those reported for the Huntington Wildlife Forest (Park, *et al.*, 2003); possibly reflecting the closer proximity of West Point to major emissions sources. NO_3^- -N and NH_4^+ -N wet only deposition (kg ha^{-1}) for the West Point site are also similar to those at the HBEF (Table 1) (Campbell, *et al.*, 2004). The reported annual average SO_4^{2-} -S wet deposition measured near West Point (8.9 kg ha^{-1}) is somewhat lower than the 10.8 kg ha^{-1} of SO_4^{2-} -S measured at the HBEF, as would be expected since the HBEF reports SO_4^{2-} -S as bulk deposition (Table 1) (Likens, *et al.*, 2002). A first order comparison (Fig. 15) of decadal trends in SO_4^{2-} wet deposition measured near West Point (1981-2003), SO_4^{2-} bulk deposition at the HBEF (1965-1998) (Likens, *et al.*, 2002) and total SO_2 emissions for the USA (1940-1998) (USEPA, 2000) indicate that decadal trends measured near West Point and at the HBEF are generally in good agreement and that both precipitation chemistry trends are consistent with temporal trends in national SO_2 emissions. Estimates of national emissions of SO_2 for the late 1990's were similar to the lowest values for any years since the late 1930's. Given the continued decrease in SO_4^{2-} wet deposition (37%) measured near West point from 1981 through 2003, it appears likely that average $[H^+]$ levels in precipitation are now probably lower than they have been in more than 60 years.

The limited amount of corrected EPA emissions data makes detailed comparisons difficult between precipitation concentrations or wet deposition and corresponding emissions amounts. However, rates of decrease in SO_2 and NO_x corrected and uncorrected emissions are in general agreement with statistically significant decreasing trends in SO_4^{2-} and NO_3^- precipitation-weighted mean concentrations, wet deposition fluxes and residuals of wet deposition fluxes, when compared over the same time periods.

There is apparent coherence between the substantial decrease in uncorrected regional SO_2 emissions data for 1995 (Fig. 12A), reflecting the first year of implementation of Phase I of the CAAA (Lynch, *et al.*, 2000b), and a marked drop in SO_4^{2-} wet deposition at NY99 in 1995 (Fig. 7G). This might indicate that changes in SO_4^{2-} wet deposition measured near West Point are more sensitive to regional rather than state or more local emissions. However, in the subsequent year, 1996, there was a large increase in SO_4^{2-} wet deposition despite no appreciable increase in SO_2 emissions at any of the spatial scales represented. Lynch *et al.* (2000b) conclude that wet deposition fluxes are strongly influenced by variability in precipitation amount, a relationship that is supported by SO_4^{2-} wet deposition data reported here as well as SO_4^{2-} bulk deposition data at the HBEF (Likens, *et al.*, 2001). This could account for the relatively high SO_4^{2-} wet deposition in 1996, which had the second highest annual precipitation on record (1981-2003) with 65% more precipitation than in 1995 and 67% more than in 1997. Additionally, precipitation amount during the summer of 1996 was 36% greater than the long-term average (1981-2003). In general, 1996 was a very wet year both in the northeastern and midwestern USA (Butler, *et al.*, 2001). Higher precipitation amount could increase the fraction of atmospheric SO_4^{2-} removed as wet deposition and therefore appear as an anomalously high year in the wet deposition time series. This set of circumstances was also reported for HBEF, where SO_4^{2-} bulk deposition was relatively high in 1996, while a decrease occurred in regional SO_2 emissions (CT, DE, MA, ME, NH, NJ, NY, OH, PA, VA, VT, WV) (Likens, *et al.*, 2001).

SO_2 emissions from 2000 corrected data were calculated per unit area for regional, state and county sources (Table 3). These data indicate that annual emissions per unit area for local (23 counties) as well as regional (5 states) data were quite similar (119 x 10^3 and 132 x 10^3 moles SO_2 km^{-2}, respectively), while wet deposition per unit area near West Point (25 x 10^3 moles SO_4^{2-} km^{-2} yr^{-1}) was ~ 20% of the rate of S emissions at both the local and regional scale. This comparison indicates that appreciable amounts of SO_2 emissions can also reach land surfaces as dry deposition, and that large amounts are also transported beyond the northeastern USA into the northwestern Atlantic Ocean and beyond.

Conclusions

1) Based on national SO_2 emissions data, annual average $[H^+]$ measured near West Point is probably lower at present than it has been at any time since the late 1930's. Acidity in precipitation ($[H^+]$) near West Point has decreased substantially (~ 36%) from 1981 to 2003, reflecting parallel decreases in both $[SO_4^{2-}]$ (~ 35%) and $[NO_3^-]$ (~ 24%) in precipitation.

2) NO_3^- has contributed on average more than two thirds of fixed nitrogen to wet deposition measured near West Point from 1981-2003, but temporal trends show declining $[NO_3^-]$ and increasing $[NH_4^+]$ such that NH_4^+ in 2003 accounted for ~ 37% of fixed N deposition.

3) Seasonal and calendar month patterns of high $[SO_4^{2-}]/[NO_3^-]$ during the summer and low $[SO_4^{2-}]/[NO_3^-]$ during the winter are consistent with alternating low

(summer) and high NO_x (winter) regimes, reflecting the very large annual variation in photochemical oxidation rates.

4) Large seasonal shifts in $[SO_4^{2-}]/[Cl^-]$ in wet deposition, from summer ratios of ~ 10-15, to winter ratios of only ~ 1-3 reflect the dominant influence of rapid oxidation of acidic S gases during the summer vs. major storms with marine air sources during the winter.

5) Although $[SO_4^{2-}]$ in precipitation contributes the largest percentage of total anion concentration in all seasons, this percentage is decreasing, while the fraction derived from $[NO_3^-]$ is increasing despite an overall decrease in $[NO_3^-]$ and in local, state and regional NO_x emissions.

6) Temporal trends in mean annual precipitation chemistry measured near West Point, which can be used as proxies for precipitation chemistry for nearby ecosystems in the lower Hudson valley region, are generally consistent with those from other sites in the northeastern USA.

7) Temporal trends in local, state and regional SO_2, NO_x and NH_3 emissions are consistent with percentage changes in $[SO_4^{2-}]$, $[NO_3^-]$ and $[NH_4^+]$ and wet deposition of these ions, indicating a consistent relationship between emissions upwind of the site at a range of spatial scales and the mean annual composition of precipitation chemistry near West Point.

8) Wet deposition of SO_4^{2-} measured near West Point is ~ 20% of SO_2 emissions per unit area on local (23 counties) and regional (5 states) spatial scales. This suggests that a significant portion of SO_2 emissions are likely deposited: 1)

regionally as dry deposition; and 2) as wet and dry deposition in areas beyond the northeastern USA.

Acknowledgements

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Table Captions

Table 1: Mean ± sem wet deposition fluxes (1981-2003) aggregated seasonally and annually for H^+, SO_4^{2-}, NO_3^- and NH_4^+ (mEq m^{-2} and kg ha^{-1}) measured near West Point, NY. For comparison, wet deposition fluxes are aggregated annually for data reported from: [a]The Institute of Ecosystem Studies (IES) in Millbrook, NY (1988-1999) (Kelly, *et al.*, 2002); [b]The Huntington Wildlife Forest, (HWF) NY (1995-2000) (Park, *et al.*, 2003); [c]The Hubbard Brook Experimental Forest (HBEF) (1979-1998) (Campbell, *et al.*, 2004); [d]data for SO_4^{2-} -S at the HBEF was for bulk deposition (1964-1998) (Likens, *et al.*, 2002).

Table 2: Percentage change in 1999 for SO_2, NO_x and NH_3 uncorrected emissions data (1990-1999) derived from linear regressions of emissions vs. year. Regional emissions are defined here as the total from NY, NJ, PA, OH and WV; county emissions are the sum from 23 counties 100km upwind of West Point, NY. For comparison, the percentage change in precipitation-weighted mean concentrations and wet deposition for SO_4^{2-}, NO_3^- and NH_4^+ measured at the NADP station near West Point were calculated in the same way as for emissions and are derived over the corresponding time period.

Table 3: Area (km^2), 2000 calendar year "corrected" EPA SO_2 emissions (moles $year^{-1}$) and SO_2 emissions per unit area (10^3 moles SO_2 km^{-2}) for: A) five states designated here as the regional SO_2 source emissions area for West Point, NY (NY, NJ, PA, WV, OH) and; B) counties in NY, NJ and PA that are ~100 km upwind of West Point. For comparison, SO_4^{2-} wet deposition for the 2000 calendar year was 25 x 10^3 moles SO_4^{2-} km^{-2}.

Figure Captions

Figure 1: Regional map of selected NADP sites discussed here. The circle includes the general location of the highest population densities and most of the large emissions sources in the NYC metropolitan region.

NADP site	Latitude	Longitude	Elevation (m)	Start Date	End Date	Distance from NY99 (km)
NY99	41.35	-74.05	201	9/13/1983		0
NY51	41.35	-74.04	186	6/26/1979	10/2/1984	1
PA72	41.33	-74.82	212	12/27/1983		64
NY12	42.38	-73.50	406	1/2/1980	8/6/1985	123
NJ99	40.32	-74.85	72	8/4/1981		133

Figure 2: Mean ± sem annual (1981-2003) $[H^+]$ amount-weighted (μEq L^{-1}) concentrations for infilled combined NY51/NY99 data (closed circles/solid line; total of 1064 weeks) and screened combined NY51/NY99 data (open circles/dashed line; total of 989 weeks). A linear regression between the two variables yielded an R^2 value of 0.87.

Figure 3: Map of states and counties included in regional and local emissions estimates, respectively. Counties included in local emissions are shaded in gray. The black circle indicates the location of West Point, NY.

Figure 4: Concentrations for NY99 (solid circles/solid line) and NY51 (open circles/dashed line) for 55 week period of data overlap (9/13/83-10/2/84) for: A) $[H^+]$ $R^2 = 0.81$; B) $[SO_4^{2-}]$ $R^2 = 0.87$; C) $[NO_3^-]$ $R^2 = 0.93$; D) $[NH_4^+]$ $R^2 = 0.86$ and E) precipitation amount (mm wk^{-1}) for NY99 (solid circles/solid line) and NY51 (open circles/dashed line) for the same period ($R^2 = 0.99$) (Shapiro, *et al.*, 2005).

Figure 5: Calendar month mean ± sem (solid circles/solid line) and median (open circles/dashed line) amount-weighted concentrations for infilled data set: A) $[H^+]$; B) $[SO_4^{2-}]$; C) $[NO_3^-]$; D) $[NH_4^+]$; E) $[SO_4^{2-}]/[Cl^-]$ and F) $[SO_4^{2-}]/[NO_3^-]$.

Figure 6: Linear regressions of weekly screened $[SO_4^{2-}]$ vs. $[NO_3^-]$ for: A) summer (slope = 1.7; y-intercept = 13.95; $R^2 = 0.71$); and B) winter (slope = 0.47; y-intercept = 21.66; $R^2 = 0.35$).

Figure 7: Annual mean ± sem for amount-weighted mean concentrations for infilled data in μEq L^{-1} (1981-2003): A) $[H^+]$; B) $[SO_4^{2-}]$; C) $[NO_3^-]$; and D) $[NH_4^+]$; annual sum of wet deposition for infilled data in mEq m^{-2} (1981-2003): E) H^+; F) SO_4^{2-}; G) NO_3^-; and H) NH_4^+.

Figure 8: Residuals vs. year (1981-2003) from the linear regression of: A) SO_4^{2-} wet deposition (mEq m^{-2}) vs. mean annual precipitation amount (mm) (solid squares) (1981-2003) ($R^2 = 0.62$; slope = -1.12; $P < 0.0001$) and B) NO_3^- wet deposition (mEq m^{-2}) vs. mean annual precipitation amount (mm) (open squares) (1981-2003) ($R^2 = 0.24$; slope = -0.35; $P < 0.015$).

Figure 9: Percentage of annual total anion charge attributed to SO_4^{2-} (solid circles), NO_3^- (open circles) and Cl^- (open triangles) (1981-2003).

Figure 10: Temporal (1981-2003) trend for infilled $[SO_4^{2-}]/[NO_3^-]$ ratios aggregated seasonally ($R^2 = 0.06$; slope = -0.003; p = 0.015). Vertical dashed lines indicate winter (DJF).

Figure 11: Temporal (1981-2003) trend for infilled $[SO_4^{2-}]/[Cl^-]$ ratios aggregated seasonally. Vertical dashed lines indicate winter (DJF).

Figure 12: Total regional (5 state) annual emissions for NY, NJ, PA, OH and WV (10^7 kg yr^{-1}) from 1990-2000 for EPA corrected (solid circles) and uncorrected (open circles) data for: A) SO_2; D) NO_x; G) NH_3. Total annual emission for New York State (10^7 kg yr^{-1}) from 1990-2000 for EPA corrected (solid circles) and uncorrected (open circles) data for: B) SO_2; E) NO_x; H) NH_3. Total annual emissions for 23 counties 100 km upwind of West Point (10^7 kg yr^{-1}) from 1990-2000 for EPA corrected (solid circles) and uncorrected (open circles) data for: C) SO_2; F) NO_x; I) NH_3.

Figure 13: Mean [SO_4^{2-}] vs. [NO_3^-] weekly screened data (1981-2003) (open circles) (μEq l^{-1}) measured near West Point graphed with corresponding mean concentrations from 16 additional NADP monitoring sites in the eastern United States (closed circles) reported in Stein and Lamb (2003) for: A) summer and B) winter. The periods represented for these latter sites were not identical to that for the West Point data.

Figure 14: Calendar month SO_2 emissions (10^7 kg $month^{-1}$) during 1999 for 29 large generating stations in New York State, accounting for 77% of point source SO_2 emissions and 51% of total SO_2 emissions.

Figure 15: Comparison of trends in SO_4^{2-} wet deposition measured near West Point (1981-2003) (solid circles/solid line), SO_4^{2-} bulk deposition at the HBEF (1965-1998) (open squares/dashed line), and SO_2 emissions for the USA (1940-1998) (10^7 kg yr^{-1}), (open triangles, solid line).

Table 1

Location		H^+ (mEq m^{-2})	H^+ (kg ha^{-1})	SO_4^{2-} (mEq m^{-2})	SO_4^{2-}-S (kg S ha^{-1})	NO_3^- (mEq m^{-2})	NO_3^- -N (kg N ha^{-1})	NH_4^+ (mEq m^{-2})	NH_4^+ -N (kg N ha^{-1})
West Point	winter	9.9 ± 0.6	0.1 ± 0.01	7.6 ± 0.5	1.2 ± 0.08	5.2 ± 0.2	0.7 ± 0.03	1.5 ± 0.1	0.2 ± 0.01
West Point	spring	16.0 ± 0.9	0.2 ± 0.01	15.3 ± 0.8	2.5 ± 0.1	8.7 ± 0.3	1.2 ± 0.05	5.0 ± 0.6	0.7 ± 0.08
West Point	summer	22.9 ± 1.4	0.2 ± 0.01	21.7 ± 1.2	3.5 ± 0.2	11.3 ± 0.7	1.6 ± 0.1	5.7 ± 0.4	0.8 ± 0.05
West Point	fall	11.8 ± .7	0.1 ± 0.01	10.9 ± 0.6	1.8 ± 0.1	5.7 ± 0.3	0.8 ± 0.04	2.6 ± 0.2	0.4 ± 0.02
West Point	annual	60.7 ± 1.9	0.6 ± 0.02	55.6 ± 0.6	8.9 ± 0.3	30.9 ± 0.9	4.3 ± 0.1	14.8 ± 0.7	2.1 ± 0.1
IES[a]	annual	-	-	-	~5.0-10.0	-	~3.0-5.0	-	~1.0-3.0
HWF[b]	annual	-	-	-	5.0	-	3.3	-	1.6
HBEF[c]	annual	-	-	-	10.8[d]	-	4.3[c]	-	1.8[c]

Table 2

	Regional SO_2 emissions	NY state SO_2 emissions	County SO_2 emission	West Point: $[SO_4^{2-}]$	West Point: SO_4^{2-} wet deposition
1990-1999 % change	- 36%	- 36%	- 31%	- 22%	- 33%
p-value	< 0.01	< 0.01	< 0.01	0.07	0.05

	Regional NOx emissions	NY state NOx emissions	County NOx emission	West Point: $[NO_3^-]$	West Point: NO_3^- wet deposition
1990-1999 % change	- 14%	- 9%	- 17%	- 13%	- 26%
p-value	0.02	0.06	< 0.01	0.09	0.14

	Regional NH_3 emissions	NY state NH_3 emissions	County NH_3 emission	West Point: $[NH_4^+]$	West Point: NH_4^+ wet deposition
1990-1999 % change	+ 12%	+ 22%	+ 28%	+ 15%	+ 11%
p-value	< 0.01	< 0.01	< 0.01	0.29	0.73

Table 3

A. State	Area (km^2)	SO$_2$ Emissions (moles year^{-1})	SO$_2$ Emissions (10^3 moles SO$_2$ km^{-2} yr^{-1})
NY	1.22E+05	7.70E+09	63
NJ	1.92E+04	1.85E+09	96
PA	1.16E+05	1.68E+10	145
WV	6.24E+04	9.60E+09	154
OH	1.06E+05	2.04E+10	193
total for 5 states	4.26E+05	5.64E+10	
mean for 5 state area^{-1}			132

B. State/County	Area (km^2)	SO$_2$ emission (moles year^{-1})	SO$_2$ emission (10^3 moles SO$_2$ km^{-2} yr^{-1})
NY			
Bronx	1.09E+02	9.27E+07	852
Delaware	1.71E+03	1.17E+07	7
Kings	1.84E+02	1.93E+08	1050
New York	5.96E+01	4.01E+08	6740
Orange	2.11E+03	4.53E+08	215
Queens	2.82E+02	2.70E+08	957
Richmond	1.50E+02	1.48E+07	99
Rockland	4.51E+02	1.90E+08	422
Sullivan	2.51E+03	8.54E+06	3
Ulster	2.92E+03	5.16E+07	18
NJ			
Bergen	6.06E+02	1.09E+08	179
Essex	3.26E+02	1.12E+08	343
Hudson	1.22E+02	3.82E+08	3140
Middlesex	8.03E+02	7.28E+07	91
Morris	1.21E+03	5.14E+07	42
Passaic	4.79E+02	5.94E+07	124
Somerset	7.90E+02	3.41E+07	43
Sussex	1.35E+03	1.21E+07	9
Union	2.67E+02	8.10E+07	304
Warren	9.27E+02	1.34E+07	14
PA			
Monroe	1.58E+03	1.91E+07	12
Pike	1.42E+03	5.01E+06	4
Wayne	1.89E+03	1.04E+07	6
total for 23 counties	2.22E+04	2.65E+09	
mean for 23 county area $^{-1}$			119

Figure 1

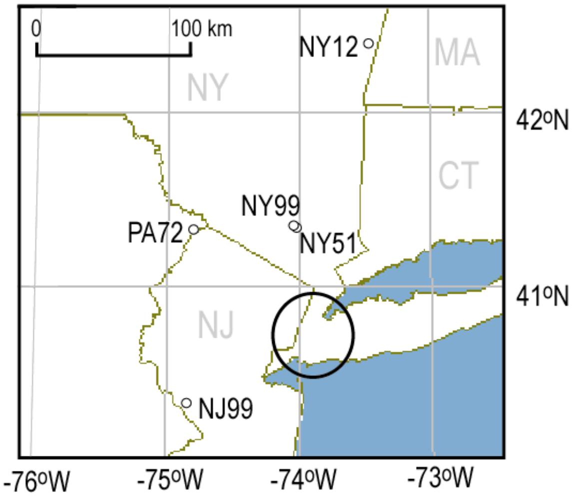


Figure 2

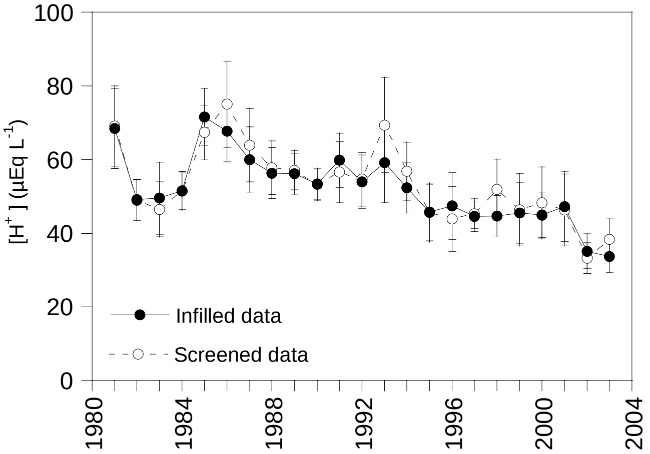


Figure 3

Figure 4

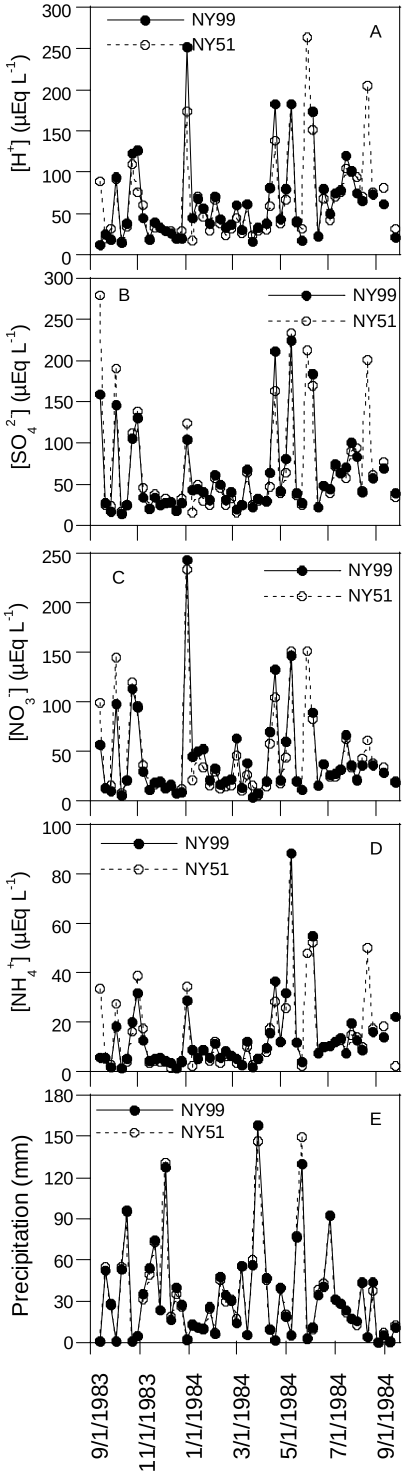


Figure 5

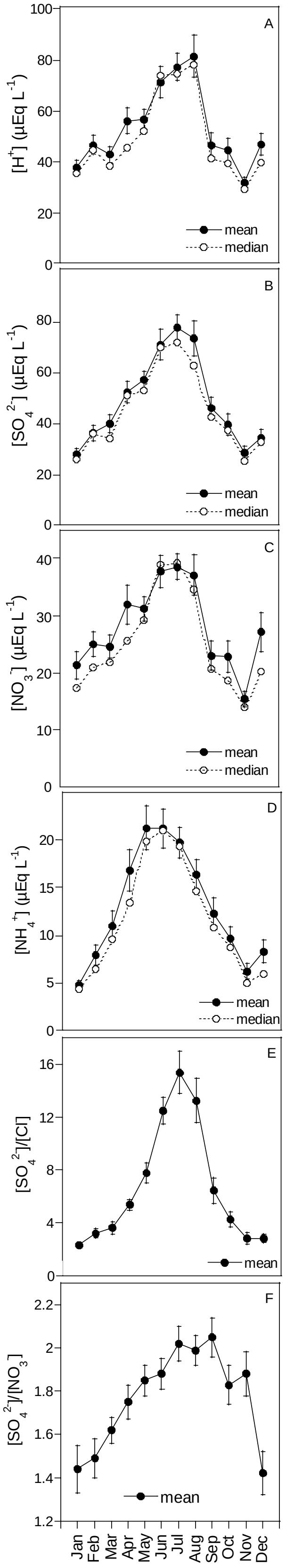


Figure 6

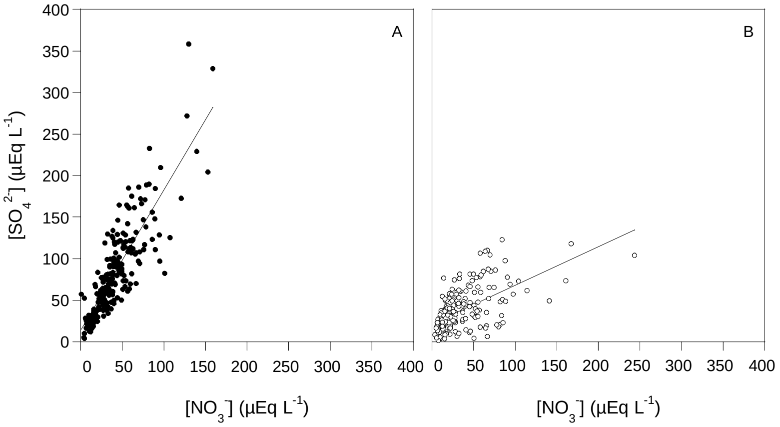

A
B
400
350
300
250
200
150
100
50
0
$[SO_4^{2-}]$ (µEq L^{-1})
0
50
100
150
200
250
300
350
400
$[NO_3^-]$ (µEq L^{-1})
0
50
100
150
200
250
300
350
400
$[NO_3^-]$ (µEq L^{-1})

Figure 7

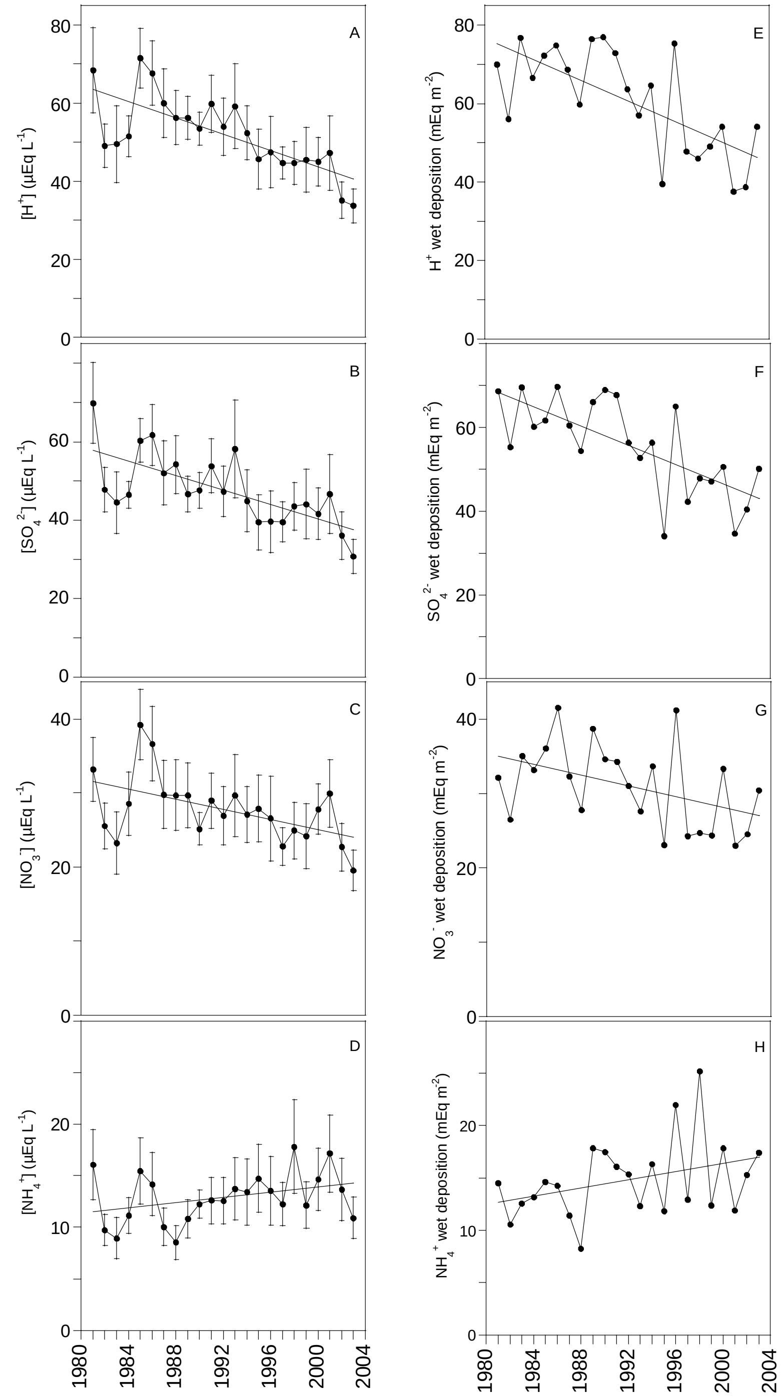

A
[H+] (μEq L-1)
0
20
40
60
80
B
[SO4 2-] (μEq L-1)
0
20
40
60
C
[NO3 -] (μEq L-1)
0
20
40
D
[NH4 +] (μEq L-1)
0
10
20
1980
1984
1988
1992
1996
2000
2004
E
H+ wet deposition (mEq m-2)
0
20
40
60
80
F
SO4 2- wet deposition (mEq m-2)
0
20
40
60
G
NO3 - wet deposition (mEq m-2)
0
20
40
H
NH4 + wet deposition (mEq m-2)
0
10
20
1980
1984
1988
1992
1996
2000
2004

Figure 8

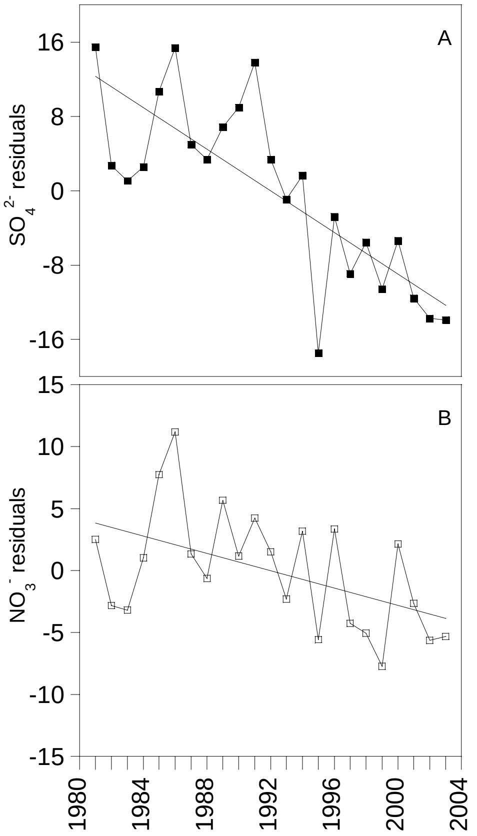


Figure 9

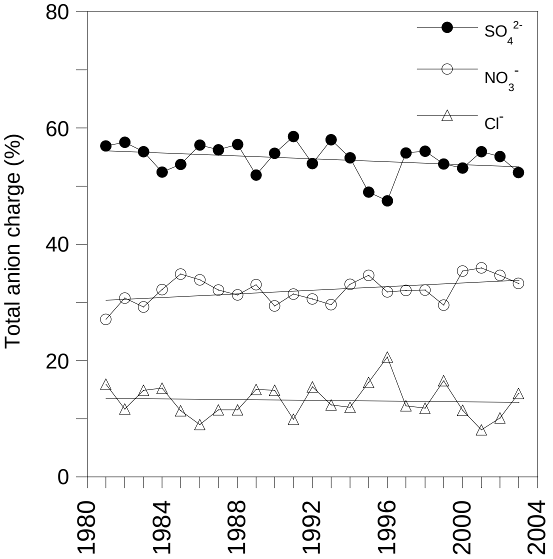


Figure 10

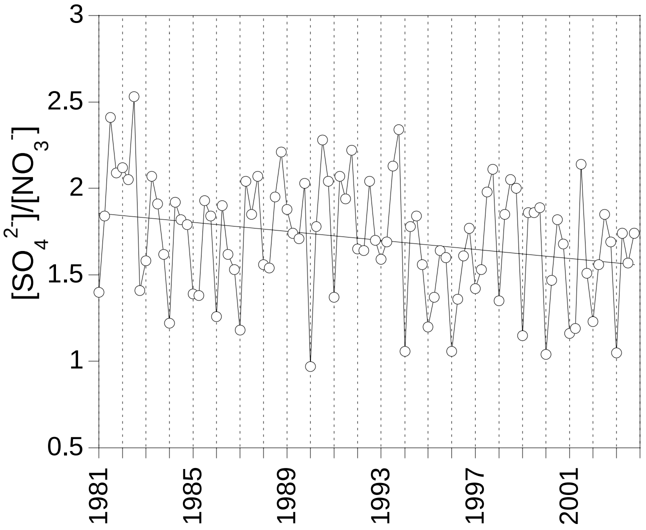


Figure 11

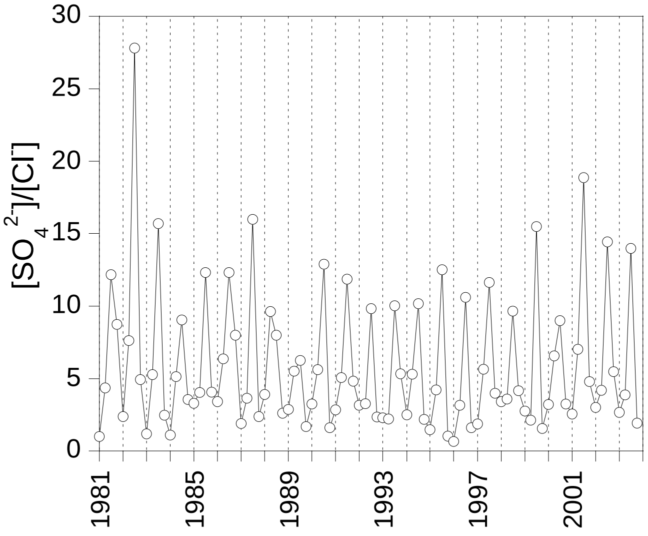


Figure 12

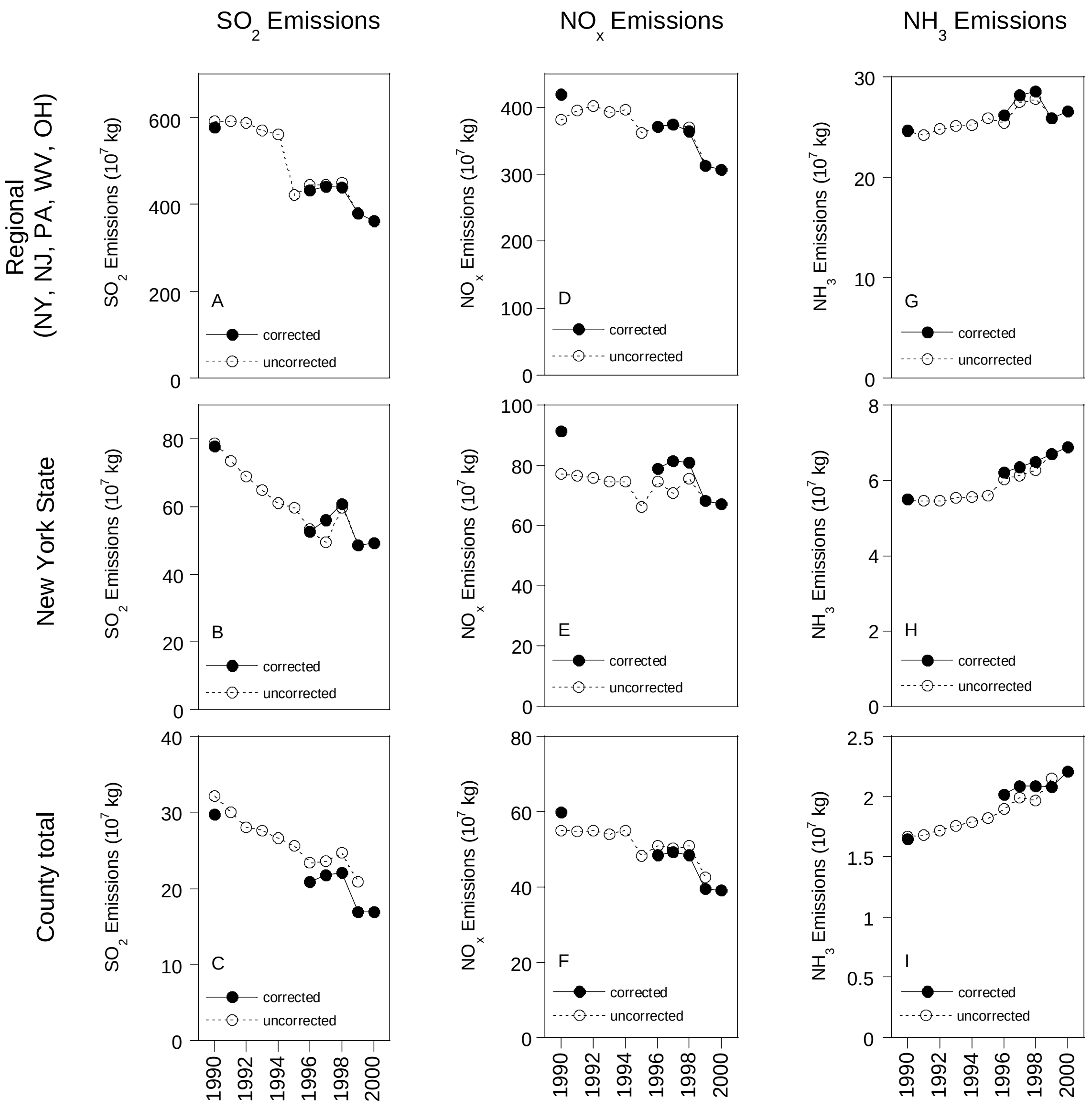

SO2 Emissions
NOx Emissions
NH3 Emissions
Regional (NY, NJ, PA, WV, OH)
New York State
County total
SO2 Emissions (10^7 kg)
NOx Emissions (10^7 kg)
NH3 Emissions (10^7 kg)
A
B
C
D
E
F
G
H
I
corrected
uncorrected
0
200
400
600
20
40
60
80
10
30
100
300
2
4
6
8
0.5
1
1.5
2.5
1990
1992
1994
1996
1998
2000

Figure 13

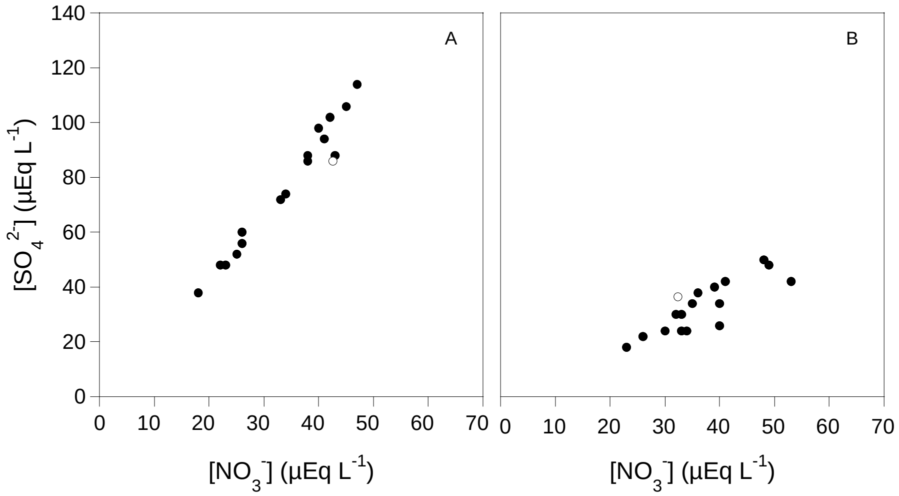


Figure 14

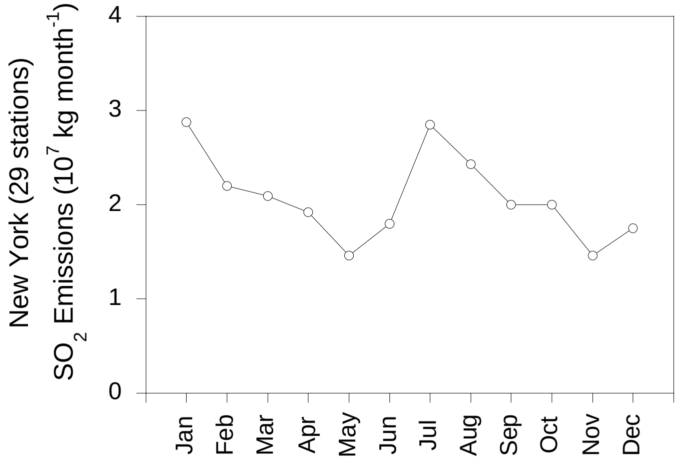
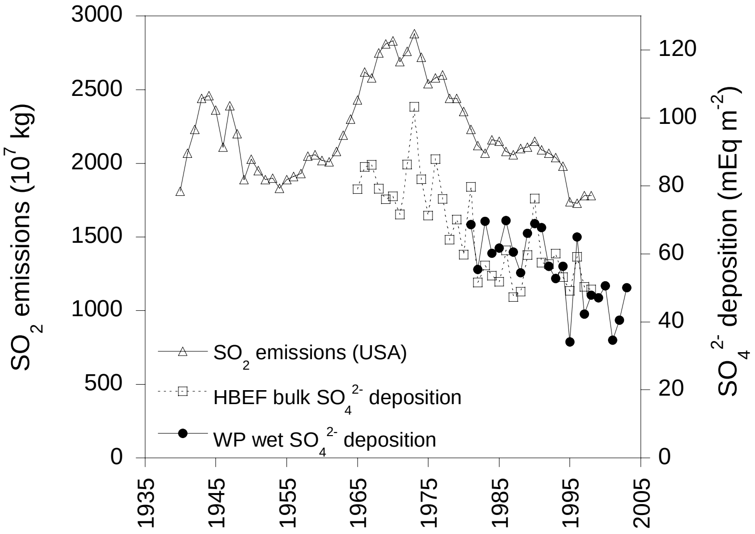


Figure 15



SO_2 emissions (10^7 kg)
0
500
1000
1500
2000
2500
3000
SO_4^{2-} deposition (mEq m^{-2})
0
20
40
60
80
100
120
1935
1945
1955
1965
1975
1985
1995
2005
SO_2 emissions (USA)
HBEF bulk SO_4^{2-} deposition
WP wet SO_4^{2-} deposition

CHAPTER 4

Sulfate and SO_2 wet and dry deposition from forest network stations near West Point, NY

J. B. Shapiro[1, 2] *, H. J. Simpson[1,2], K. L. Griffin[1,2], and W. S. F. Schuster[3]

[1]Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964

[2] Department of Earth and Environmental Sciences, Columbia University, New York, NY 10027

[3] Black Rock Forest, 129 Continental Road, Cornwall, NY 12518

*Author for correspondence: Phone: 845 365 8395; Email: jbs59@ldeo.columbia.edu

Abstract

Wet deposition of dissolved SO_4^{2-} and dry deposition of particulate SO_4^{2-} and SO_2 gas were measured at a site surrounded by deciduous forest on the West Point Military Reservation in the lower Hudson River Valley, NY concurrently during 1985-1997 as part of several long-term monitoring programs. Interannual variability in wet and dry S deposition during these years show appreciable coherence. Total S deposition (wet SO_4^{2-}-S + dry SO_2-S + dry SO_4^{2-}-S) was dominated by SO_4^{2-}-S wet deposition particularly during spring and summer months, reflecting the importance of atmospheric oxidant chemistry on SO_4^{2-} deposition. However, dry deposition was an important source of S year round and was at least as, or even more important than wet deposition during winter months and during periods of low precipitation, respectively. Total S dry deposition (SO_2-S + SO_4^{2-}-S) was dominated by SO_2-S compared to SO_4^{2-}-S, possibly as a result of more local sources for SO_2 as well as a shorter atmospheric residence times (or greater deposition velocities) for SO_2. While SO_2-S dominated S dry deposition year round, SO_4^{2-}-S dry deposition was at a maximum of ~ 20% of total S dry deposition during summer months. In contrast to the pattern of maximum SO_4^{2-}-S wet deposition occurring during summer months, total S dry deposition (SO_2-S + SO_4^{2-}-S) was relatively consistent throughout the year as a result of high atmospheric [SO_2] occurring during winter (usually attributed to elevated energy demand for winter heating) and high SO_2 deposition velocity occurring during summer (attributed to growing season increases in factors such as leaf area index). Total S dry deposition (SO_2-S + SO_4^{2-}-S) averaged 4.3 ± 0.4 kg S ha^{-1} yr^{-1}, approximately 50% of the 8.9 ± 0.6 kg S ha^{-1} yr^{-1} SO_4^{2-}-S wet deposition and 33% of total S (wet + dry) deposition over a period of 9 years. These relationships could potentially be used to estimate dry deposition during years for which only wet deposition data were available. Regionally, dry S deposition estimates reported here represent an intermediate flux compared to those measured at a location in central PA, which reports generally higher seasonal deposition velocities and ~ 2-fold greater SO_2 emissions per unit area than for NY state and a more remote site in northern NY, which had comparatively low annual atmospheric S concentrations.

Keywords: AIRMoN, DDIM, deposition velocity, Huntington Forest, NY, State College, PA, Black Rock Forest

Introduction

Acidic deposition is of considerable interest in the northeastern USA, where damaging effects of acid rain have been reported in a number of sensitive terrestrial and aquatic ecosystems (Likens, *et al.*, 1972; Siccama, *et al.*, 1982; Likens, *et al.*, 1996). Measurements of wet-only deposition for ions associated with acidic deposition, such as SO_4^{2-}, have been extensively reported and are currently conducted by the National Atmospheric Deposition Program (NADP) at > 200 stations across the USA (Lamb, Bowersox, 2000). Dry deposition fluxes of aerosols and gases, which can contribute comparable amounts to that for wet deposition (Lovett, 1994) are much more complicated to estimate and the derived fluxes have greater uncertainty (Hicks, *et al.*, 1991; Meyers, *et al.*, 1991).

Key factors that influence the rate of dry deposition include: 1) atmospheric concentrations of gases and aerosols of interest; 2) temporal variability in local meteorology (e.g. turbulence in the lower atmosphere) and; 3) variation in site-specific vegetative characteristics (Ollinger, *et al.*, 1993; Lovett, 1994). Aerosol dry deposition occurs by gravitational settling and wind induced impaction for particles > 5μm, and by diffusion across the boundary layer of surfaces for smaller particles. For gases, dry deposition occurs via boundary layer diffusion and subsequent vegetative absorption (Lovett, 1994).

SO_4^{2-}-S wet deposition at NADP monitoring site, NY99, situated on a site surrounded by deciduous forest in the West Point Military Reservation in the lower Hudson Valley of NY averaged 8.9 kg ha^{-1} yr^{-1} during 1981-2003, with deposition decreasing significantly (-37%) over this time period (Shapiro, *et al.*, 2005a), a temporal trend consistent with those reported for a number of locations in the northeastern USA (Butler, *et al.*, 2001; Likens, *et al.*, 2001). Collocated dry deposition data from the Atmospheric Integrated Research Monitoring Network (AIRMoN) of NOAA during 1985-1997 can be used to compare dry deposition with wet deposition and total sulfur (SO_4^{2-}-S wet + SO_4^{2-}-S dry + SO_2-S dry) deposition for a number of years. Access to collocated wet and dry deposition data over the same years for the NY99 station is particularly valuable since dry deposition estimates reflect a number of site-specific meteorological and vegetative data as well as concentrations of gases and aerosols.

Some goals of this investigation include: 1) compile and compare data for dry deposition of SO_2-S and SO_4^{2-}-S near West Point (WP), NY (1985-1997); 2) compare calendar month and interannual trends in SO_2-S and SO_4^{2-}-S dry deposition with those for collocated measurements of SO_4^{2-}-S wet deposition, atmospheric [SO_2] and [SO_4^{2-}] and precipitation [SO_4^{2-}]; 3) estimate the fraction of total S deposition attributed to dry S deposition based on these monitoring data, and; 4) compare dry deposition reported here to SO_2-S and SO_4^{2-}-S dry deposition data reported at proximal locations. In this study, total S deposition was defined as wet plus dry deposition and excludes S deposited via cloud or fog interception. These data can be used to estimate dry deposition and total deposition for WP and nearby ecosystems in the lower Hudson Valley with similar vegetative characteristics, such as the adjacent Black Rock Forest (BRF) where related ongoing ecological research has been conducted (Engel, *et al.*, 2002; Barringer, Clemants, 2003; Nagel, Griffin, 2004; Whitehead, *et al.*, 2004; Shapiro, *et al.*, 2005a) and for which the deposition of particles and aerosols may be an important source of S.

Methods

Dry deposition of particulate SO_4^{2-} and gaseous SO_2 have been estimated by AIRMoN using the dry deposition inferential measurement (DDIM) approach. AIRMoN has operated ~ 20 stations nationally, the majority of which were in the eastern USA, with 3 active stations as of September 2005 (Oak Ridge, TN, Bondville, IL, Wye, MD) (Hicks, *et al.*, 2001; Artz, 2005). The DDIM derives an estimate for dry deposition from the product of measured concentrations in air and model derived deposition velocities (Hicks, *et al.*, 1991; Meyers, *et al.*, 1991; Lovett, 1994; Meyers, *et al.*, 1998). This approach can be useful for obtaining estimates of dry deposition for sites where direct atmospheric fluxes to the surface by eddy correlation or gradient techniques are not available (Lovett, 1994).

A filterpack system is used to measure SO_4^{2-}, SO_2, NO_3^- and HNO_3 in ambient air to obtain concentrations for calculating dry deposition of each of these species. Detailed descriptions of the filterpack system are available elsewhere (e.g. Hicks, *et al.*, 1991; Meyers, *et al.*, 1991). In brief, ambient air is drawn through 20 cm of Teflon tubing at a rate of 3.0 L min^{-1} to a series of filters for separation and collection of specific particles and gases. The tubing effectively serves as a “pre-filter” for particles > 5 μm in diameter to settle under the influence of gravity. These particles are not subsequently analyzed since contributions from large particles are not a goal of the AIRMoN dry deposition network. Assessment of the large particle (5 μm) flux conducted at the Hubbard Book Experimental Forest concluded that they did not add significant amounts of SO_4^{2-} to S deposition since concentrations in collocated bulk and wet only collectors were not statistically different (Martin, *et al.*, 2000; Likens, *et al.*, 2002). Within the filterpack system, after passing through the initial Teflon tubing, air first encounters a Teflon filter (4.7 cm diameter) that collects SO_4^{2-} and NO_3^- particles (> 2 μm), then a nylon filter (4.7 cm diameter) that removes HNO_3 vapor and finally a K_2CO_3 treated cellulose filter (4.7 cm diameter) that removes SO_2 (Hicks, *et al.*, 1991). Filters were routinely collected and replaced on Tuesdays at 9 am and therefore measured concentrations are reported as weekly averages. Each of the filters were subsequently extracted and analyzed for SO_4^{2-} and NO_3^- by ion chromatography (Hicks, *et al.*, 1991).

Deposition velocities for each atmospheric species of interest were calculated as the inverse of the sum of several resistances: 1) aerodynamic resistance, which is the relative resistance imposed on a gas or aerosol by turbulence in the atmosphere; this parameter was calculated as a function of mean wind speed and the standard deviation of wind direction; 2) boundary layer resistance, which is the resistance of the layer of air near a surface (i.e. leaf or soil) that is affected by the presence of that surface; 3) surface resistance of vegetation, soils and water to gas and aerosol uptake (Meyers, Yuen, 1987; Hicks, *et al.*, 1991; Meyers, *et al.*, 1991; Lovett, 1994; Meyers, *et al.*, 1998). These resistances are a function of local meteorological and vegetative characteristics such that calculation of deposition velocities requires a variety of site-specific data including solar radiation, wind speed at 10 m, the standard deviation of wind direction, temperature, humidity, surface wetness, precipitation, leaf area index (LAI), the type and height of vegetation as well as stomatal resistance and response to light and temperature variation (Hicks, *et al.*, 1991; Meyers, *et al.*, 1991; Meyers, *et al.*, 1998). The suite of site-specific data, were compiled as 15-minute and 1 hour averages (Hicks, *et al.*, 1991). Weekly deposition velocities were averages of hourly measurements (Matt, Meyers, 1993; Meyers, *et al.*, 1998).

The DDIM was originally developed as a "big leaf" (single layer) vegetation model but has since been elaborated and currently divides the canopy into 20 layers to obtain more resolution of the differential effects of light and wind at various heights within a forest canopy (Meyers, *et al.*, 1991; Meyers, *et al.*, 1998). Comparison of modeled vs. direct measurements of dry deposition using techniques such as eddy flux correlation and concentration gradients have served to further improve model calculations (Meyers, *et al.*, 1991). Uncertainties in dry deposition of SO_4^{2-} and SO_2 are attributed primarily to uncertainties in calculated deposition velocities, the errors for which are estimated to be on the order of 30% (Hicks, *et al.*, 1991).

Weekly SO_4^{2-} and SO_2 dry deposition data for a site near WP, NY (41°35' N, 74.05° W) (1984-1997) were obtained from the NOAA, AIRMoN web site (http://www.arl.noaa.gov/research/projects/airmon_data.html). The location of the NOAA and NADP deposition monitoring stations was at Camp Buckner; a site surrounded by deciduous forest on the grounds of the WP Military Reservation but ~ 8 km west of WP proper. WP proper extends to the edge of the Hudson River. The location of these monitoring stations are closer to the border of the BRF (< 3 km) and the towns of Highlands Falls (7 km), Fort Montgomery (6 km), Central Valley (6 km) and Highland Mills (5 km). Therefore, meteorological conditions at these monitoring stations reflect much more the conditions typical of the BRF and surrounding Hudson Highlands than they do the corridor along the Hudson River where West Point proper is located.

Gaps in SO_4^{2-} and SO_2 dry deposition data were infilled with values derived from linear interpolation for gaps of one or two weeks; gaps longer than two weeks were not infilled. Linear interpolation was used to provide values for 25 weeks during 1985-1997. Because annual dry deposition represents a summation, only years with reported and infilled weekly data for ≥ 92% of the year (i.e. ≥ 48 weeks) were included to derive annual dry deposition estimates (i.e. 1988 (100%), 1989 (100%), 1990 (100%), 1991 (100%), 1992 (100%), 1993 (98%), 1994 (96%), 1995 (94%) and 1997 (92%)). For comparison of temporal patterns in dry deposition to those measured at proximal sites, SO_4^{2-} and SO_2 data were obtained from the NOAA, AIRMoN web site for the two monitoring stations closest to West Point: 1) the Huntington Forest (HF) (43°59' N, 74°25' W) (1990-1997), located in the Adirondack Mountains of northern NY, the vegetation of which is mixed northern hardwoods with conifers along lower slopes (Park, *et al.*, 2003); and, 2) State College (SC) in central PA, (40.79° N 77.95° W) located on an experimental farm under the supervision of Pennsylvania State University, where corn, wheat and soybeans are grown (1985-1997) (Fig. 1) (Meyers, *et al.*, 1991; Hicks, *et al.*, 2001). These two sites were 249 and 332 km from the NOAA monitoring station on the WP Military Reservation, respectively. Seasonal variations in total atmospheric S concentrations (SO_2-S + SO_4^{2-}-S) were similar in general trends for these three sites, with two maxima in total S concentration; a winter peak in atmospheric [SO_2] usually attributed to elevated energy demand for winter heating and a second peak attributed to summer [SO_4^{2-}] associated with atmospheric oxidant chemistry (Hicks, *et al.*, 2001).

Atmospheric [SO_4^{2-}] and [SO_2] measured by AIRMoN at the WP monitoring station during 1985-1997 (Hicks, *et al.*, 2001) are discussed here for comparison with calendar month and interannual trends in SO_4^{2-} and SO_2 dry deposition, SO_4^{2-} wet deposition and precipitation SO_4^{2-} amount-weighted mean concentration. Decadal and calendar month trends in SO_4^{2-} wet deposition and precipitation amount-weighted concentrations for the NADP NY99 precipitation monitoring station near WP have been reported in Shapiro *et al.*, (2005).

In addition, atmospheric [SO_2] and [SO_4^{2-}] and dry deposition data (1987-1993) from the Clean Air Status and Trend Network (CASTNet) monitoring system near WP, NY were also included here. CASTNet dry deposition fluxes were estimated using an analogous approach to AIRMoN, where measured atmospheric concentrations from a filterpack system were combined with deposition velocities estimated using a multi-layer model calibrated with site-specific meteorological and vegetative data (USEPA, 1998; USEPA, 2003). There are currently > 70 active CASTNet monitoring stations with data available from an EPA web site (http://cfpub.epa.gov/gdm/index.cfm?fuseaction=iss.isshome). To compare spatial patterns in calendar month variability, atmospheric [SO_2] data for the two CASTNet sites closest to WP, NY were included. These two stations are Claryville, NY and Washington Crossing, NJ, 78 and 135 km from the CASTNet WP monitoring site, respectively (Fig. 1).

One goal of CASTNet is to monitor temporal patterns in deposition as they relate to emissions, particularly for SO_2 (Baumgardner*, et al.*, 2002). Locations for CASTNet monitoring sites were chosen primarily to measure regionally-representative pollution concentrations (Hicks*, et al.*, 2001; Sickles, Shadwick, 2002). Preliminary comparison of data between the AIRMoN and CASTNet filterpack systems indicate that systematic differences are relatively small for sulfur species, although differences may arise during periods of high humidity (Hicks, *et al.*, 2002). For data measured at the WP monitoring stations, a linear regression forced through zero of weekly atmospheric [SO_2] measured by CASTNet and AIRMoN during years when both filterpack systems were operational (1/6/1987-9/28/1993) yielded a slope of 0.97 and an R^2 value of 0.75. Although the two filterpack systems generally report similar [SO_2], weekly data indicate that for weeks with relatively high [SO_2] the CASTNet filterpack concentrations were higher relative to those reported by the AIRMoN filterpack system. A linear regression forced through zero comparing [SO_4^{2-}] measured by the two monitoring systems yielded a slope of 1.00 and an R^2 value of 0.75 (Fig. 2).

Results

Comparison of temporal trends in SO_4^{2-}-S wet deposition for 1981-2003 (Shapiro, *et al.*, 2005a) and total S dry deposition (SO_4^{2-}-S + SO_2-S) for 1988-1995 and 1997 (Fig. 3) indicate appreciable coherence in interannual features. In particular, relatively low deposition during 1988, higher deposition in 1989-1991 and lower deposition in 1992 through 1997 were evident in both the NADP-wet and AIRMoN-dry deposition data. The average annual total S dry deposition for AIRMoN data near WP, NY during 1985-1987 (Meyers, *et al.*, 1991) are included (Fig 3) to extend the length of the time series displayed here, and were generally consistent with the wet deposition time series. Additionally, CASTNet total S dry deposition data for 1989-1992 were included for comparison with those from AIRMoN. CASTNet data were comparable in magnitude to AIRMoN data but interannual variability differed with CASTNet data showing a linear decrease during 1989-1991 while AIRMoN data was relatively constant for that period.

Throughout the years of overlap, dry deposition was significantly less than wet deposition (Fig. 3). A linear regression forced through zero of AIRMoN total S dry deposition (SO_4^{2-}-S + SO_2-S) vs. annual NADP SO_4^{2-}-S wet deposition (Fig. 4) for 1988-1995 and 1997 indicates that S dry deposition was ~ one half of SO_4^{2-}-S wet deposition (slope = 0.49; $R^2 = 0.7$; $P < 0.001$). On average, S dry deposition (SO_2-S + SO_4^{2-}-S) was 4.3 ± 0.4 kg S ha^{-1} yr^{-1} and S total deposition (SO_4^{2-}-S wet + SO_2-S dry + SO_4^{2-}-S dry) was 13.2 ± 1.0 kg S ha^{-1} yr^{-1} indicating that S dry deposition (SO_2-S + SO_4^{2-}-S) accounted for ~ 33% of total S deposition at WP, NY during 1988-1995 and 1997.

The percentage of weekly total (wet + dry) S deposition attributed to total S dry deposition (SO_2-S + SO_4^{2-}-S) decreased as corresponding weekly precipitation amount increased (Fig. 5). An exponential function ($y = 56.3e^{-0.0182x}$) used to characterize the relationship yielded an R^2 value of 0.46.

Comparison of calendar month means for SO_4^{2-}-S wet deposition and S dry deposition (SO_2-S + SO_4^{2-}-S) (1984-1997) reveal much greater seasonal variability in wet deposition than for dry deposition, which was relatively constant throughout the year (Fig. 6A). Values for wet and dry S deposition were similar during winter but wet deposition was significantly greater during spring, summer and fall, with maximum wet deposition during July (Fig. 6A) with average values ~ 3.4 times that of dry S deposition. Calendar month means in the percentage of S dry deposition (SO_2-S + SO_4^{2-}-S) to total S deposition (SO_4^{2-}-S wet + SO_2-S dry + SO_4^{2-}-S dry) indicate that although the annual average was ~ 33%, this percentage ranged from a high of 49% during winter to a low of 24% during summer (Fig. 6B).

In addition, calendar month means indicate that total S dry deposition was dominated by SO_2-S dry deposition throughout the year (Fig. 7A). On an annual basis, SO_2-S and SO_4^{2-}-S account for an average of ~ 86% and ~ 14% of total S dry deposition, respectively. During the calendar year, SO_2-S dry deposition displays two moderate peaks with maxima in winter and late spring/summer. The calendar month trend in SO_4^{2-}-S dry deposition had a single maximum during summer months, when SO_4^{2-}-S dry deposition represented ~20% of total S dry deposition.

To facilitate comparison between temporal patterns in calendar month dry deposition fluxes presented here, collocated data for calendar month atmospheric [SO_2-S] and [SO_4^{2-}-S] (Hicks, *et al.*, 2001), as well as precipitation [SO_4^{2-}-S] (Shapiro, *et al.*, 2005a), are presented together (Fig. 7B). Calendar month mean trends in aerosol and precipitation [SO_4^{2}] are both consistent with a single summer peak in SO_4^{2-}-S dry deposition. However, calendar month means in gas phase [SO_2-S] indicate a single maximum during winter, whereas SO_2-S dry deposition had two maxima (winter and summer).

A scatter plot of weekly SO_4^{2-}-S dry deposition vs. SO_2-S dry deposition, grouped into summer and winter fluxes (Fig. 8B), illustrates that higher SO_4^{2-}-S dry deposition occurred during summer and that ranges in SO_2-S dry deposition fluxes were comparable during both seasons at the WP site. For comparison, these fluxes at HF (Fig. 8A) indicate that the range in SO_4^{2-}-S dry deposition was comparable to that for WP during both summer and winter, while the range in SO_2-S dry deposition during summer and winter was much less than at WP. In contrast, data from SC, PA (fig. 8C) indicate that although the relationship between weekly SO_4^{2-}-S and SO_2-S dry deposition during summer was comparable to WP, the winter relationship between SO_4^{2-}-S and SO_2-S was substantially different, with much higher weekly SO_2-S dry deposition fluxes than at WP or HF.

To explore individual components contributing to seasonal variability in S dry deposition fluxes among these three AIRMoN sites (HF, WP and SC), calendar month mean ± sem SO_2 deposition velocities, atmospheric [SO_2] and SO_2-S dry deposition (Fig. 9) were compared. Relatively consistent values for calendar month dry deposition of S at the station near WP resulted from two opposing factors: 1) significantly greater atmospheric [SO_2] during winter vs. summer months; and, 2) significant greater SO_2 deposition velocities during summer vs. winter months (Fig. 9). Similarly, there was a low degree of calendar month variability in SO_2-S dry deposition at HF, although atmospheric [SO_2] for HF were significantly lower throughout the year, resulting in lower absolute values for SO_2-S dry deposition at HF compared to WP. In contrast, there was a high degree of calendar month variability in SO_2-S dry deposition for SC, likely due to significantly higher deposition velocities for SO_2 at SC during all months except July and August combined with high atmospheric [SO_2] during fall and winter months. A similar examination of patterns in calendar month means for SO_4^{2-} deposition velocities, atmospheric [SO_4^{2-}] and SO_4^{2-}-S dry deposition among these three sites (Fig. 10) indicates relatively minor spatial variability, with differences in SO_4^{2-}-S dry deposition (Fig. 10C) mostly dependent upon variability in local atmospheric [SO_4^{2-}] (Fig. 10B). Interestingly, SO_4^{2-} deposition velocities peak during April, May and June, which are months that precede peaks in atmospheric [SO_4^{2-}] (July and August) and SO_2 deposition velocities (May through September).

AIRMoN atmospheric [SO_2] and [SO_4^{2-}] had annual averages of 3.0 and 2.7 μg m^{-3} for HF (1990-1997), 11.6 and 4.6 μg m^{-3} for WP (1985-1997) and 14.1 and 6.0 μg m^{-3} for SC, PA (1985-1997), respectively (Hicks, *et al.*, 2001). The average annual S dry deposition for HF (1.3 kg S ha yr^{-1}) (1995-2000) was 21% of total (wet + dry) S deposition (Park, *et al.*, 2003), and the average annual S dry deposition for SC, PA (11.3 and 8.6 kg S ha yr^{-1} during 1990-1993 and 1997-2000, respectively) was consistently 53% of total (wet + dry) S deposition (Baumgardner, *et al.*, 2002). Percentages for HF and SC were respectively less than and greater than the 33% reported here for the monitoring station near WP.

For a first-order comparison of the degree of spatial variability in atmospheric [SO_2], the two AIRMoN and the two CASTNet sites in closest proximity to WP were compared with AIRMoN and CASTNet data for the monitoring stations near WP (Fig. 11). Calendar month variability (mean ± sem) indicates that in general atmospheric [SO_2] at SC (AIRMoN), Washington Crossing, NJ (CASTNet), and WP (AIRMoN and CASTNet) display a similar pronounced seasonal pattern with maximum concentrations occurring during winter and minimum concentrations occurring during summer. In contrast, atmospheric [SO_2] measured in Claryville, NY (CASTNet) and HF (AIRMoN), had markedly lower values in general and also less pronounced seasonal variations. It should be noted that the years of available data for these six locations were not identical, thus this comparison should be considered as a preliminary indication of geographical trends.

Discussion

It is striking that interannual variation in S deposition for NADP wet and AIRMoN dry deposition at WP (Fig. 3) show generally comparable trends (1988-1995 and 1997), considering that measurements of wet and dry deposition are totally independent, with wet deposition being a more direct measurement and dry deposition estimates involving calculation of a number of model dependent parameters. The general coherence indicates that although S wet deposition primarily occurs during spring and summer, while S dry deposition is more evenly distributed by month (Fig. 6), both had similar patterns of interannual variability in S deposition. The percentage of weekly total S dry deposition (SO_2-S + SO_4^{2-}-S) with respect to total (wet + dry) S deposition decreased appreciably as weekly precipitation amount increased (Fig. 5). This pattern illustrates the dependence of the relative contributions of dry and wet S deposition on week-to-week variability in local precipitation amount.

Estimates of wet and dry S deposition near WP, NY indicate that total S deposition was dominated by SO_4^{2-}-S wet deposition and that wet deposition was greatest during spring and summer (Figs. 3 and 6A). During these warmer months, photo-oxidation of atmospheric SO_2 occurs more rapidly due to higher ambient temperatures and a greater pool of oxidizing species from atmospheric reactions with volatile organic compounds (Calvert, *et al.*, 1985; Meyers, *et al.*, 1991; Hindy, 1994) thus generating higher aerosol [SO_4^{2-}-S], and a summer peak in precipitation [SO_4^{2-}] (Fig. 7B).

However, S dry deposition was dominated by SO_2-S relative to SO_4^{2-}-S during all calendar months (1998-1995 and 1997) (Fig. 7A), a pattern consistent with WP AIRMoN data for 1985-1987 (Meyers, *et al.*, 1991), WP CASTNet data during 1989-1992

(USEPA, 2005), as well as estimates for S dry deposition reported for CASTNet sites in the northeast USA (Baumgardner, *et al.*, 2002). Meyers *et al.*, (1991) suggest that dominance of SO_2-S dry deposition results from the difference in origin for atmospheric SO_2 vs. SO_4^{2-} with SO_2 reflecting more local sources and SO_4^{2-} originating from an appreciably larger area (Hicks, *et al.*, 2001). This is consistent with estimates of shorter annual average atmospheric residence times for SO_2 of ~ 1 - 2 days versus a ~ 4 - 5 day annual average atmospheric residence time for SO_4^{2-} (Rasch, *et al.*, 2000). Furthermore, deposition velocities calculated for particulate SO_4^{2-} (< 0.5 cm s^{-1}) average less than for SO_2 (0.2 to >1.0 cm s^{-1}) (Lovett, 1994; Likens, *et al.*, 2002). This difference results in fine SO_4^{2-} particles (≤ 2 μm median diameter) depositing less readily than SO_2 onto leaves and other forest receptors (Lovett, 1994; Likens, *et al.*, 2002).

One effect of variability in deposition velocities and how they change by season can be seen in the difference in calendar month trends for SO_2-S dry deposition and atmospheric [SO_2] (Figs. 7A & B), which both exhibit high values in winter whereas SO_2 dry deposition also has a second maximum during summer. Spring/summer SO_2 deposition velocities in the DDIM have been shown to increase by a factor of ~ 2.5 in summer compared to winter in response to factors such as changes in LAI, solar radiation, temperature and surface wetness (Matt, Meyers, 1993), all factors which tend to increase during the spring/summer growing season. Changes in these meteorological and vegetative characteristics contribute to an increase in SO_2-S dry deposition during summer near WP, NY, despite lower atmospheric [SO_2]. Similar seasonal trends have been reported for other AIRMoN dry deposition monitoring sites in New York, Pennsylvania, Virginia and Illinois (Meyers, *et al.*, 1991).

The annual average for total S dry deposition was ~ 50% of wet deposition and ~ 33% of total (wet + dry) S deposition near WP, NY during 1988-1995 and 1997. These percentages were equal to the 50% and 33% percentages, respectively, for CASTNet WP data during 1989-1992 (USEPA, 2005) and similar to percentages reported in Meyers *et al.,* (1991) for WP during 1985-1987 of 54% and 35% respectively. The general consistency at WP in annual percentage of S dry deposition relative to wet deposition (50-54%) could be useful for estimating S dry deposition at WP, and nearby locations for years where only SO_4^{2-}-S wet deposition data were available. Assuming 50% for the relationship between these two fluxes, a mean ± sem flux of 3.6 ± 0.2 kg S ha^{-1} yr^{-1} for S dry deposition was estimated based on wet deposition measured near WP during the period from 1998 to 2003.

The 33-35% S dry deposition estimate relative to total S deposition at WP was within the range of 30-60% reported for other AIRMoN sites (Meyers*, et al.*, 1991) and consistent with an average of 38% S dry deposition for sulfur species measured at 30 CASTNet sites in the eastern USA (Baumgardner*, et al.*, 2002). In comparison, the mean annual percentage of S dry deposition relative to total S deposition for HF, NY (21%) (Park*, et al.*, 2003) was lower and the mean annual percentage for SC, PA (53%) (Baumgardner*, et al.*, 2002) was higher than reported here for the WP site. The variability in the percentage of dry S deposition relative to total S deposition at these three locations is consistent with trends reported in Meyers *et al.*, (1991) where percentages of S dry deposition relative to total S deposition were relatively low for locations with lower atmospheric concentrations of sulfur species. Atmospheric S concentrations measured by AIRMoN decreased from relatively high concentrations at

SC, PA, to somewhat lower concentrations at WP, NY to relatively low concentrations measured at HF, NY (Hicks, *et al.*, 2001).

Seasonal and spatial patterns in the relationship between SO_4^{2-}-S dry deposition and SO_2-S dry deposition for HF, WP and SC indicate a decreasing flux of winter SO_2-S dry deposition as distance from SC increased (Fig. 8). In examining the individual components relevant to SO_2-S dry deposition (Fig. 9), it appears that major differences in SO_2-S dry deposition for SC result from a combination of an unusual calendar month pattern in deposition velocities along with greater atmospheric $[SO_2]$ at SC during winter and fall. The differences in calendar month variability of SO_2 deposition velocity at SC compared to HF and WP could result from differences in their respective local terrains: SC is an agricultural site while both HF and WP are forested sites. Additionally, the greater atmospheric $[SO_2]$ measured at SC during winter and fall may reflect greater annual emissions per unit area reported for PA compared to NY (Table 1). Annual emissions estimates for 1990-1993 and 1997-2000 indicate that SO_2 emissions per unit area averaged ~ 2 times greater in PA than in NY (Table 1). Relative to the atmospheric $[SO_2]$ at the SC and HF sites, the atmospheric $[SO_2]$ at WP had a transitional value that was somewhat less than the annual maximum concentrations at SC but appreciably greater than those measured at HF, consistent with the relatively proximities of these three locations to states with major SO_2 emissions (Baumgardner, *et al.*, 2002).

In contrast, spatial variability in SO_4^{2-}-S dry deposition appears to be a function of atmospheric $[SO_4^{2-}]$ with similar SO_4^{2-} deposition velocities for the three sites examined here in some detail. The difference in the relative coherence for SO_2 deposition velocities vs. SO_4^{2-} deposition velocities for the three sites examined here could be a result of site and species-specific factors differentially affecting calculated deposition velocities for aerosols (SO_4^{2-}) and gases (SO_2). However, in general, the difference in the magnitude of SO_4^{2-}-S and SO_2-S dry deposition among these sites is consistent with greater atmospheric residence times and lower deposition velocities for SO_4^{2-} compared to SO_2. Additionally, the lower degree of variability in atmospheric [SO_4^{2-}] more likely reflects the regional origin of SO_4^{2-} to these sites whereas the greater variability in atmospheric [SO_2] among these three sites, was likely a response to more local origins for SO_2 emissions.

In assessing S dry deposition fluxes estimated from the DDIM, it is important to note uncertainties reported for AIRMoN protocols used to measure concentrations as well as to calculate deposition velocities. Comparison between weekly composite samples used in AIRMoN versus an hourly air sampling protocol indicated that weekly samples underestimated annual SO_2 dry deposition by ~ 20% due to a large negative difference (40%) during the growing season (Matt, Meyers, 1993). The impact of utilizing weekly average SO_2 dry deposition measurements in lieu of segregated day and night measurements has also been investigated. Matt and Meyers (1993) found that weekly composite samples underestimated SO_2 dry deposition by ~ 41% compared with systems that measure day and night concentration separately. In contrast, Meyers and Yuen (1987) report that there was no significant difference associated with using separate day and night systems.

Regarding modeled vs. measured SO_2 deposition velocities using eddy correlation measurements, some appreciable differences have been reported between the two methods but systematic biases between modeled and measured values for soybean, pasture and corn fields were relatively low (~10%) (Meyers, *et al.*, 1998; Baumgardner, *et al.*, 2002). For deciduous and mixed deciduous/conifer forests the systematic bias between methods was reported to be significantly greater, with 10-50% lower deposition velocities for the DDIM compared to eddy covariance measurements (Finkelstein, *et al.*, 2000; Baumgardner, *et al.*, 2002). Considering these findings along with underestimated total S dry deposition during several years presented here with gaps in weekly deposition data, dry deposition estimates from the DDIM method for the site near WP (~ 4.3 kg S ha^{-1} yr^{-1}) should probably be considered as minimum values for the flux of S from the atmosphere to forested ecosystems within the Hudson Highlands, NY. Conversely, a mass balance approach applied to the Cascade Brook watershed located within Black Rock Forest ~ 5 km from the West Point AIRMoN and CASTNet monitoring stations indicate an upper limit for S dry deposition (SO_4^{2-}-S export - SO_4^{2-}-S wet deposition) of 14 - 17 kg S ha^{-1} yr^{-1} during water years 1999-2000, 2002-2003 and 2003-2004 (Shapiro, *et al.*, 2005b). These flux estimates are ~ 3.2 - 4.0 times that derived from the DDIM and assume that no other sources besides wet and dry deposition contribute to total S export within this watershed, which may not necessarily be accurate.

In conclusion, annual values of wet and dry S deposition near WP, NY tended to covary during 1988-1995 and 1997, a period when networks measuring wet deposition (NADP) and dry deposition (AIRMoN) were both operational at this location. During these years, total S dry deposition was ~ 50% of wet S deposition and ~33% of total S deposition. These data could be useful for estimating S dry deposition at locations naear WP, NY during years for which wet deposition of SO_4^{2-} has been measured. Dry S deposition estimates reported for WP represent intermediate values compared to fluxes measured at a location in central PA, which report generally higher annual deposition velocities and greater winter/fall atmospheric [SO_2] and a site in northern NY, which reports appreciably lower annual atmospheric S concentrations.

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Table Caption

Table 1: Annual average SO_2 emissions per unit area (tons km^{-2} yr^{-1}) for PA and NY during 1990-1993 and 1997-2000 (Baumgardner, *et al.*, 2002).

Table 1	SO_2 emissions/area (tons km^{-2} yr^{-1}) 1990-1993 average	SO_2 emissions/area (tons km^{-2} yr^{-1}) 1997-2000 average
PA	12.93	11.19
NY	6.45	5.08
ratio of PA:NY	2.00	2.20

Figure Captions

Figure 1: Map with locations of AIRMoN (filled circles), CASTNet (open circles) and both AIRMoN and CASTNet (filled star) dry deposition monitoring stations referred to here. HF = Huntington Forest, NY; SC = State College, PA; WP= West Point, NY; CAT175 = Claryville, NY; WSP144 = Washington Crossing, NJ.

Figure 2: Linear regressions forced through zero for weekly concentration data measured at West Point, NY by CASTNeT and AIRMoN monitoring systems (1/6/1987 - 9/28/1993) for: A) [SO_2], slope = 0.97 and $R^2 = 0.75$; and B) [SO_4^{2-}], slope = 1.00 and $R^2 = 0.75$.

Figure 3: Wet and dry deposition measured near West Point, NY. SO_4^{2-}-S wet deposition (filled circles) from the NADP precipitation chemistry network (1981-2003) (Shapiro, *et al.*, 2005a); total S dry deposition (SO_2-S + SO_4^{2-}-S) (open circles) from AIRMoN (1988-1995 and 1997); total S dry deposition from AIRMoN reported in Meyers *et al.*, (1991) (open squares) (1985-1987); total S dry deposition at West Point measured by CASTNet (filled triangles) (1989-1992) (USEPA, 2005).

Figure 4: Total S dry deposition (SO_4^{2-}-S + SO_2-S) (kg ha^{-1} yr^{-1}) vs. SO_4^{2-}-S wet deposition (kg ha^{-1} yr^{-1}) for 1988-1995 and 1997 (slope = 0.49; $R^2 = 0.7$; $P < 0.001$).

Figure 5: Weekly total S dry deposition (SO_2-S + SO_4^{2-}-S) as a percentage of weekly total S deposition (wet SO_4^{2-}-S + dry SO_2-S + dry SO_4^{2-}-S) vs. weekly precipitation

amount (mm) 1984-1997. The exponential function, $y = 56.3e^{-0.0182x}$, yielded an R^2 value of 0.46.

Figure 6: A) Calendar month mean ± sem for SO_4^{2-}-S wet deposition (1984 – 1997) (filled circles) (Shapiro, *et al.*, 2005a) and total S dry deposition (1984 – 1997) (SO_2-S + SO_4^{2-}-S) (open circles); B) Calendar month total S dry deposition (SO_2-S + SO_4^{2-}-S) as a percentage of total S deposition (wet + dry).

Figure 7: A) Calendar month mean ± sem for total S dry deposition (SO_2-S + SO_4^{2-}-S) (open circles), SO_2-S dry deposition (filled squares) and SO_4^{2-}-S dry deposition (open triangles) (kg ha^{-1}); B) Calendar month averages ± sem for [left-hand y-axis] atmospheric [SO_2] (filled squares) and [SO_4^{2-}] (open triangles) (μg m^{-3}) (Hicks, *et al.*, 2001) and [secondary y-axis] precipitation-weighted [SO_4^{2-}] (filled circles) (mg L^{-1}) (Shapiro, *et al.*, 2005a).

Figure 8: Weekly SO_4^{2-}-S dry deposition (kg ha^{-1}) vs. weekly SO_2-S dry deposition (kg ha^{-1}) for summer (open circles) and winter (filled circles): A) Huntington Forest, NY (HF); B) West Point, NY (WP) and; C) State College, PA (SC).

Figure 9: Calendar month mean ± sem for AIRMoN data at Huntington Forest (filled triangles), West Point (open circles) and State College (filled circles): A) SO_2 deposition velocity (cm sec^{-1}), B) atmospheric [SO_2] (μg m^{-3}), and C) SO_2-S dry deposition (kg ha^{-1}).

Figure 10: Calendar month mean ± sem for AIRMoN data at Huntington Forest (filled triangles), West Point (open circles) and State College (filled circles): A) SO_4^{2-} deposition velocity (cm sec^{-1}), B) atmospheric [SO_4^{2-}] (μg m^{-3}), and C) SO_4^{2-}-S dry deposition (kg ha^{-1}).

Figure 11: Calendar month mean ± sem atmospheric [SO_2] (µg m^{-3}) at Huntington Forest (AIRMoN) (filled triangles), West Point (AIRMoN) (open circles), West Point (CASTNet) (open triangles), State College (AIRMoN) (filled circles), Washington Crossing, NJ (CASTNet) (grided squares) and Clayrville, NY (CASTNet) (open squares).

Figure 1

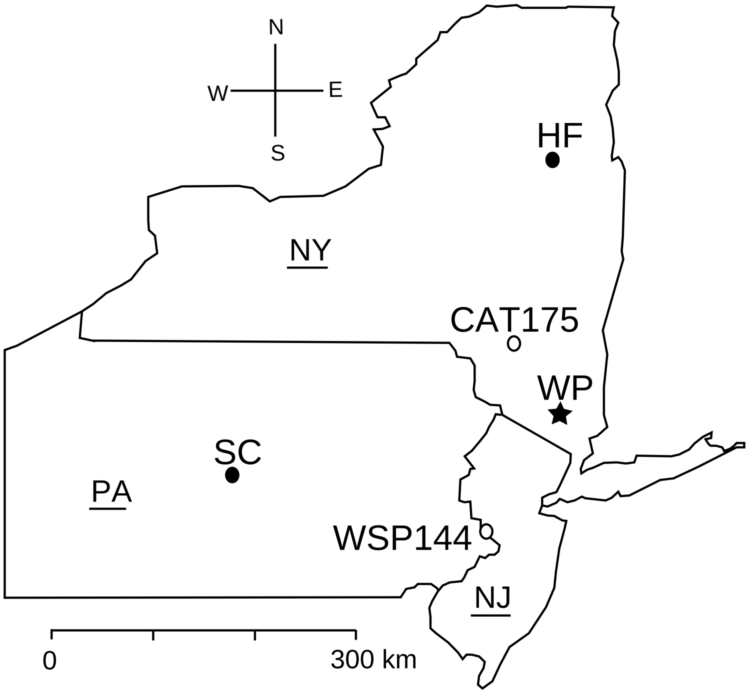
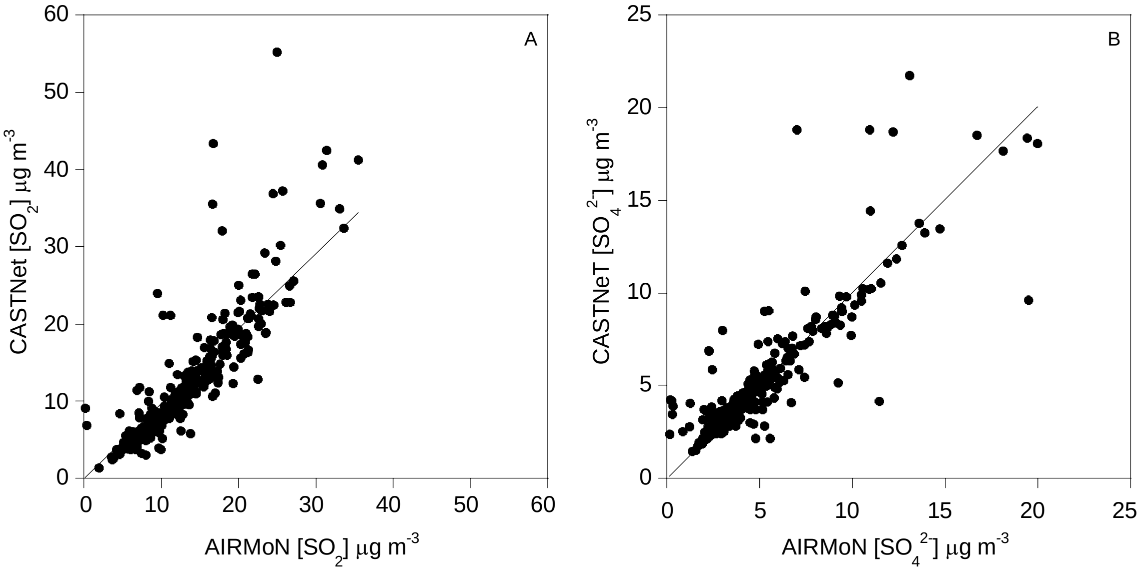


Figure 2



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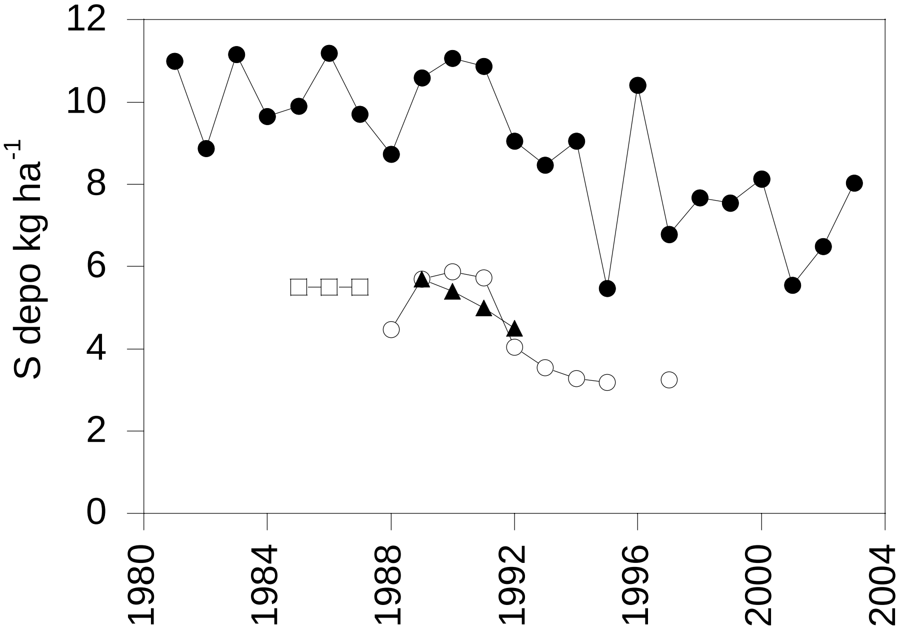

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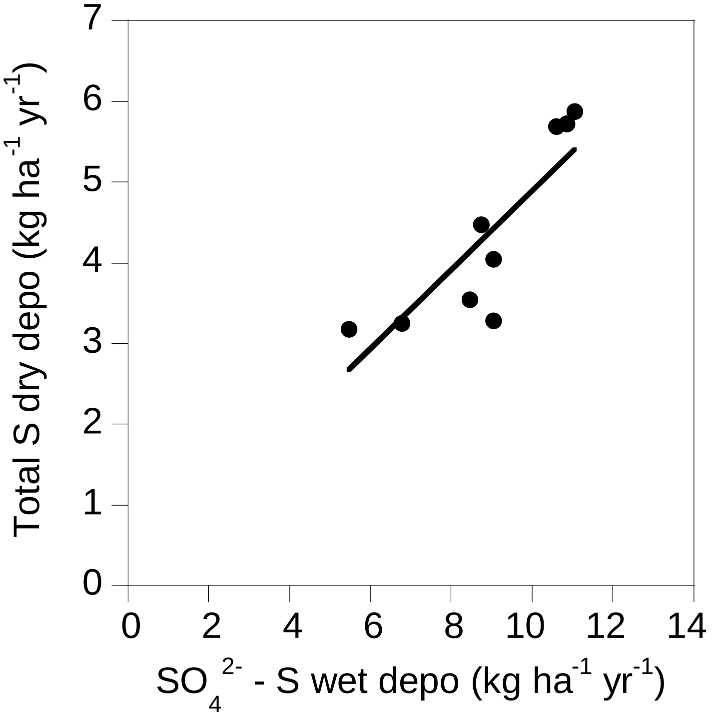

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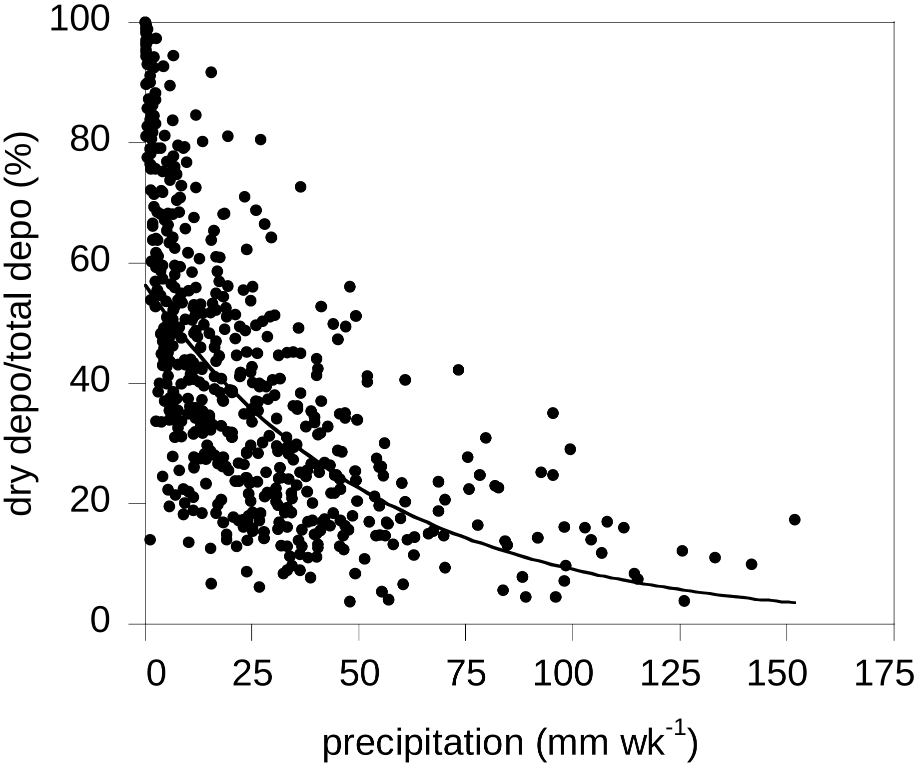


dry depo/total depo (%)
100
80
60
40
20
0
0
25
50
75
100
125
150
175
precipitation (mm wk-1)

Figure 6

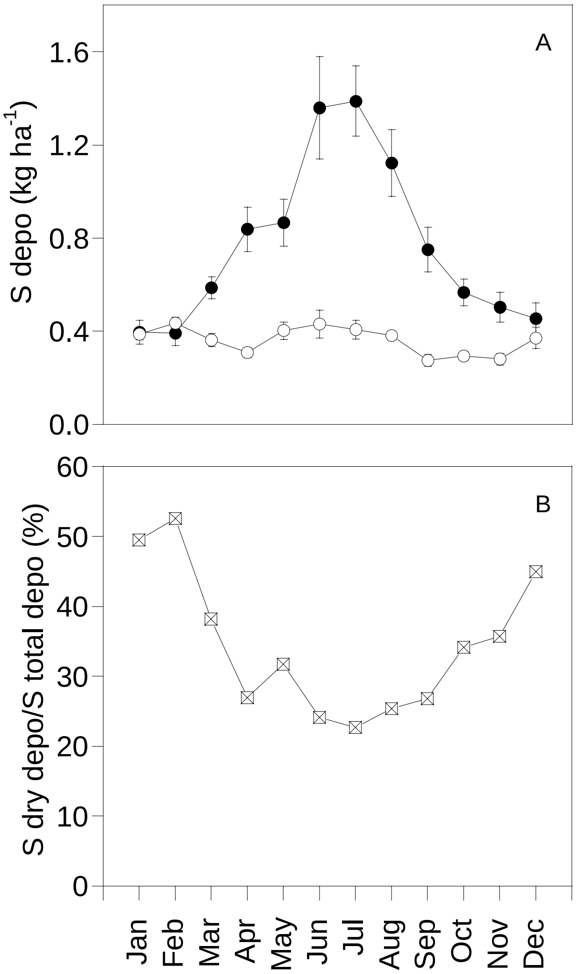

A
S depo (kg ha^{-1})
0.0
0.4
0.8
1.2
1.6
B
S dry depo/S total depo (%)
0
10
20
30
40
50
60
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

Figure 7

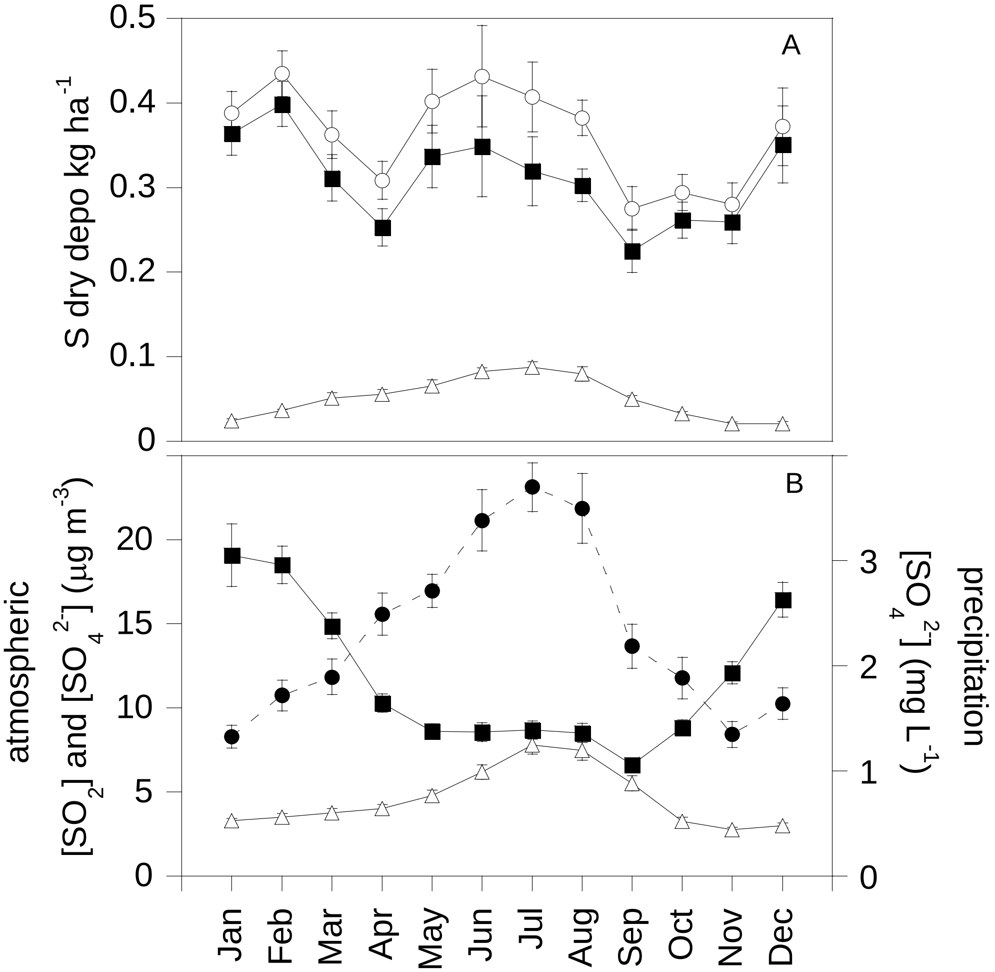

A
B
S dry depo kg ha^{-1}
0.5
0.4
0.3
0.2
0.1
0
atmospheric
[SO$_2$] and [SO$_4$$^{2-}$] (μg m^{-3})
20
15
10
5
0
precipitation
[SO$_4$$^{2-}$] (mg L^{-1})
3
2
1
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

Figure 8

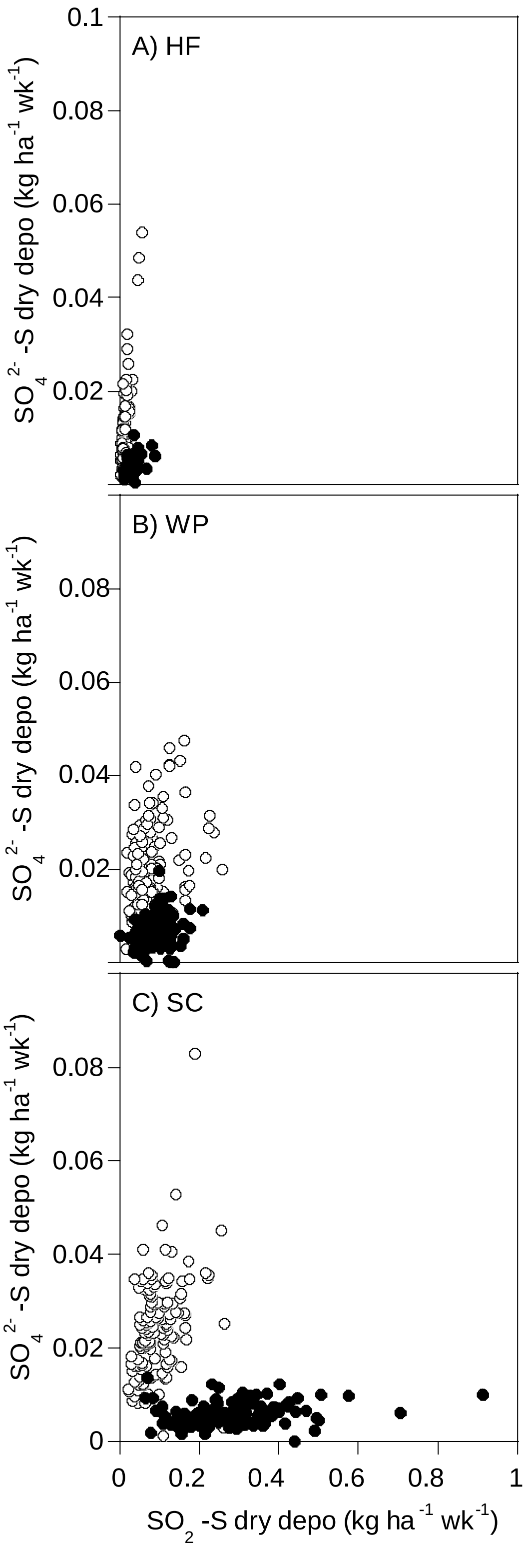

0.1
0.08
0.06
0.04
0.02
0
A) HF
B) WP
C) SC
SO_4^{2-} -S dry depo (kg ha^{-1} wk^{-1})
0
0.2
0.4
0.6
0.8
1
SO_2 -S dry depo (kg ha^{-1} wk^{-1})

Figure 9

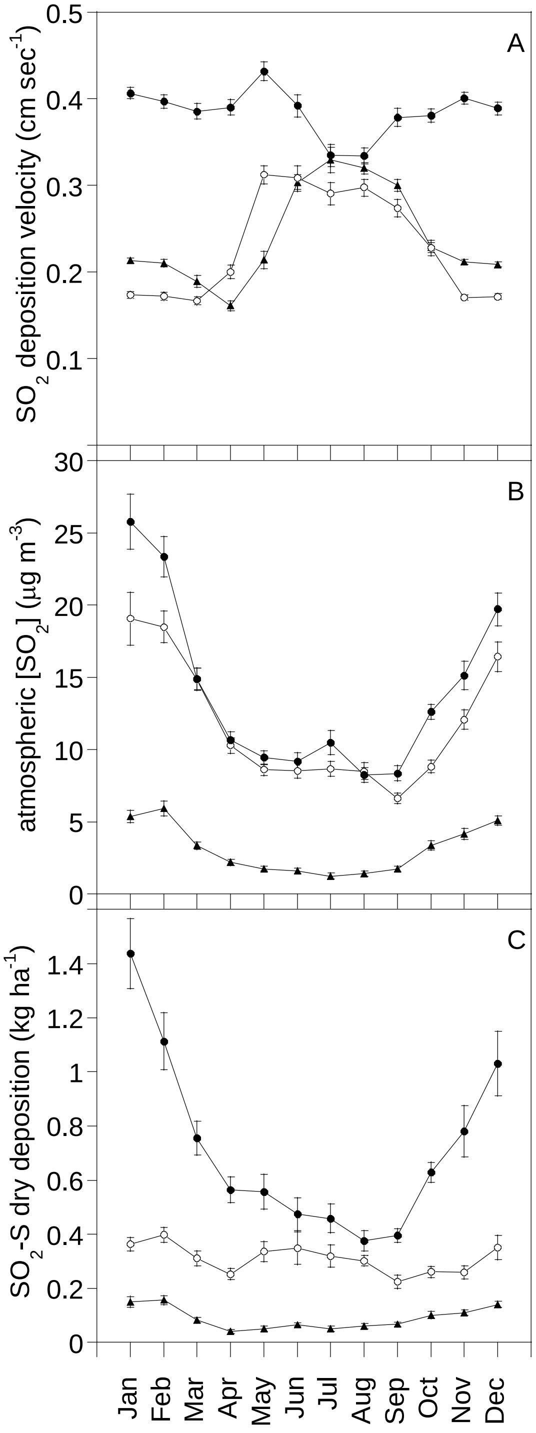

A
B
C
SO_2 deposition velocity (cm sec^{-1})
atmospheric [SO_2] (μg m^{-3})
SO_2-S dry deposition (kg ha^{-1})
0.5
0.4
0.3
0.2
0.1
30
25
20
15
10
5
0
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

Figure 10

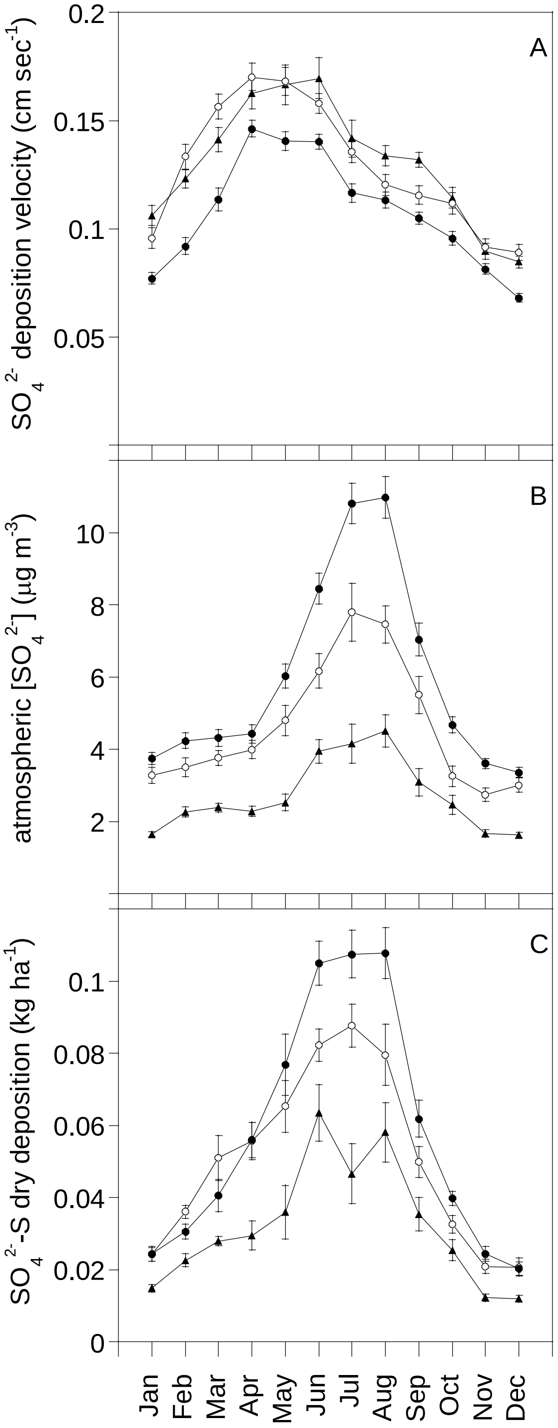
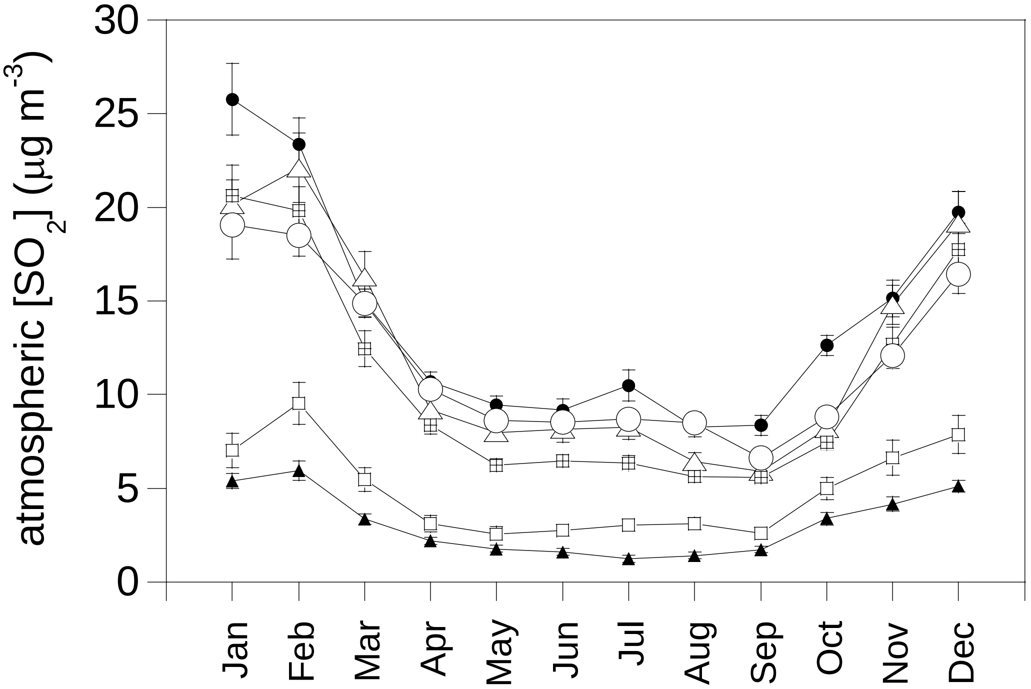

0.2
0.15
0.1
0.05
SO$_4^{2-}$ deposition velocity (cm sec^{-1})
A
10
8
6
4
2
atmospheric [SO$_4^{2-}$] (µg m^{-3})
B
0.1
0.08
0.06
0.04
0.02
0
SO$_4^{2-}$-S dry deposition (kg ha^{-1})
C
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

Figure 11


atmospheric $[SO_2]$ (µg m^{-3})
0
5
10
15
20
25
30
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

CHAPTER 5

Sulfate budgets in a small pristine watershed in Black Rock Forest, NY

J. B. Shapiro[1, 2] *, H. J. Simpson[1,2], K. L. Griffin[1,2], M. Stute[1,3] and W. S. F. Schuster[4]

[1]Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964

[2] Department of Earth and Environmental Sciences, Columbia University, New York, NY 10027

[3] Department of Environmental Science, Barnard College, New York, NY 10027.

[4] Black Rock Forest, 129 Continental Road, Cornwall, NY 12518

*Author for correspondence: Phone: 845 365 8395; Email: jbs59@ldeo.columbia.edu

Abstract

A mass balance approach was applied to derive an upper limit for dry deposition of sulfur to Cascade Brook, a relatively small oak dominated watershed (135-ha) within the 1500-ha Black Rock Forest in the Hudson Highlands of NY. Mean values for wet-only and dry deposition fluxes during water years 1999-2000, 2002-2003 and 2003-2004 were previously estimated to be 8.0 kg S ha^{-1} yr^{-1} and 4.0 kg S ha^{-1} yr^{-1}, respectively; the latter being derived from a dry deposition inferential technique. Stream water [SO_4^{2-}] upstream and downstream of a forest/shrub wetland within the watershed displayed different temporal patterns, with upstream concentrations relatively insensitive to discharge amount. Conversely, [SO_4^{2-}] downstream of the wetland often varied substantially with discharge, particularly during low flow periods. Variability in [SO_4^{2-}] at the downstream location was consistent with SO_4^{2-} reduction occurring within the wetlands during summer low discharge conditions and SO_4^{2-} oxidation of previously reduced SO_4^{2-} occurring in the wetlands during drought conditions with no stream discharge. Temporal variability in monthly flux-weighted mean [SO_4^{2-}] in stream water upstream (171 uEq l^{-1}; RSD ~ 10%) and downstream (163 uEq l^{-1}; RSD ~ 20%) of the wetlands was appreciably less than corresponding variability in monthly volume-weighted precipitation mean [SO_4^{2-}] (41 ueq l^{-1}; RSD = 58%). This difference in temporal variability was likely due to the dampening effects of SO_4^{2-} sorption reactions, organic S mineralization and storage of soil moisture SO_4^{2-} within the watershed. Separate SO_4^{2-} export fluxes were estimated for the site upstream and downstream of the wetlands during water years 1999-2000, 2002-2003 and 2003-2004 yielding mean fluxes of 25 and 22 kg S ha^{-1} yr^{-1}, respectively, indicating that annually an average of ~ 3.0 kg S ha^{-1} yr^{-1} or 12% of SO_4^{2-}-S was stored within the wetlands. During water years examined here, SO_4^{2-}-S export exceeded input from wet deposition by an average ratio of 3.1-to-1 at the site upstream and 2.8-to-1 at the site downstream of the wetland, respectively, indicating significant contributions to S export in addition to that derived from wet deposition. If dry deposition were the only important additional source of S, the magnitude of dry deposition would be ~ 14 - 17 kg S ha^{-1} yr^{-1}, or ~ 3.5 - 4.3 times the independent estimate derived from the inferential technique. However, we conclude that although wet and dry S deposition likely provide the largest contributions to stream S export, there are additional plausible watershed processes which may contribute measurable amounts of SO_4^{2-}-S including: 1) chemical weathering of S-bearing minerals; 2) desorption of SO_4^{2-} from the mineral soil layer; and 3) mineralization of organic S.

Key words: sulfate reduction, SO_4^{2-} desorption, organic S mineralization, NADP, sulfur dry deposition, Black Rock Forest

Introduction

SO_4^{2-} deposition via acid precipitation is a topic of considerable interest due to the associated negative impacts on sensitive terrestrial and aquatic ecosystems (Likens et al. 1972; Driscoll et al. 2001; Norton and Vesely 2003). Such effects include acidification of soil and stream waters, leaching of nutrient cations, such as Ca^{2+} from soils, mobilization of toxic Al^{+3}, tree dieback and alteration of biotic communities (Shortle et al. 1997; Driscoll et al. 2001; Norton and Vesely 2003; Tomlinson 2003). Estimating input of SO_4^{2-} via wet deposition is relatively straightforward, based on composite precipitation samples collected and analyzed on a weekly basis by the National Atmospheric Deposition Program (NADP) at > 200 sites in the United States (Lamb and Bowersox 2000). Using mass balance approaches, forested ecosystems in the northeastern USA have reported greater SO_4^{2-} export compared to input via either wet or bulk deposition (Stoddard and Murdoch 1991; Likens et al. 2002; Park et al. 2003) (Table 1) indicating that there are significant additional sources of S to these ecosystems. One additional category of S input to ecosystems is from dry deposition of sulfur bearing aerosols and gases, the net flux from which is much more difficult to quantify and may be at least as large as that from wet deposition (Lovett 1994).

The Black Rock Forest (BRF), a relatively pristine 1500-ha preserve in the Hudson Highlands of NY ~ 70 km north of New York City, is the site of a variety of ongoing geochemical and ecological investigations, including acid rain monitoring and watershed ion budgets (Stieglitz et al. 2003; Nagel and Griffin 2004; Whitehead et al. 2004; Shapiro et al. 2005a; Shapiro et al. 2005d). During 1981-2004 SO_4^{2-}, measured at an NADP monitoring station adjacent to BRF (~5 km SSW), was the dominant anion in precipitation with concentration and wet deposition decreasing by 35% and 37% respectively during this period; this total decrease was consistent with reductions in local and regional SO_2 emissions (Shapiro et al. 2005a). Compared to the 8.9 kg S ha^{-1} yr^{-1} mean annual SO_4^{2-} wet deposition (1981-2004) measured at West Point, an independent estimate from a collocated dry deposition monitoring station indicated that S dry deposition to BRF could contribute 4.5 kg S ha^{-1} yr^{-1} (1988-1997), which is an additional 50% of that provided by wet deposition (Shapiro et al. 2005a; Shapiro et al. 2005c). Considerable uncertainties are associated with dry deposition estimates derived from inferential techniques as was used here; thus additional methods of deriving dry deposition have also been investigated (Hicks et al. 1991; Meyers et al. 1991; Likens et al. 2002). In this study, a watershed mass balance approach was used to provide a second independent estimate of S dry deposition to BRF.

Several specific goals of this study include: 1) measure seasonal and interannual variations in stream water [SO_4^{2-}] within the Cascade Brook (CB) watershed of BRF; 2) examine possible spatial and temporal variability in [SO_4^{2-}] measured upstream and downstream of the wetlands within CB; 3) compare stream water [SO_4^{2-}] and SO_4^{2-} export to precipitation [SO_4^{2-}] and SO_4^{2-} wet deposition; 4) estimate S dry deposition to CB using a watershed S mass balance approach; 5) compare mass balance dry S deposition estimates with a dry deposition estimate previously derived from the Dry Deposition Inferential Measurement (DDIM); and 6) examine potential additional sources of SO_4^{2-} consistent with SO_4^{2-} export in excess of wet deposition.

Methods

Description of Black Rock Forest

BRF (41°23 N, 73°59 W – location of the CB weir) is a 1500-ha ecological preserve near the west bank of the Hudson River, adjacent to Cornwall, NY. Bedrock within the forest is primarily metamorphic Pre-Cambrian gneiss (Schuberth 1968; Isachsen and Gates 1991). Areas of exposed bedrock are common throughout the forest. The regional climate can be described as humid continental with a range in monthly mean temperatures from a maximum of 23°C in July to minimum of -3°C in January (Engel et al. 2002) and a relatively constant rate of mean calendar month precipitation (106 ± 4 mm month^{-1}) (Shapiro et al. 2005a).

The CB watershed (135ha) (Fig. 1) is situated in the SE corner of BRF. Soils within the watershed are medium texture loams and are relatively thin with a mean depth (excluding areas of exposed bedrock) of 28 cm at elevations > 400m and a mean depth of 32 cm downstream near the weir gauging station (i.e downstream of Glycerine Hollow) (Nagel et al. 2002; Pederson 2005a). Within CB there are two sites from which stream water samples have been collected on a weekly basis: 1) North Bridge (NB), which is upstream of Glycerine Hollow, an eight hectare red maple-hardwood swamp forested wetlands (Reschke 1990), and 2) Old West Point Road (OWPR), which is downstream of the wetlands and includes a sitting pool, a v-notch weir (120°) and stage recording station.

Stream discharge

Hourly stage height has been measured at the OWPR site since 1999 and calibration test confirm that discharge meets the stage-discharge relationship characteristic of a sharp-crested 120° v-notch weir (Hertzler 1938). Discharge amounts were normalized to watershed area and converted to mm yr^{-1}. For 19 days during 1999-

2004, stream levels at the weir exceeded the height of the 0.61 m vertical distance of the v-notch. For these 19 days a compound weir approach was used to estimate total discharge (i.e. sum of discharge within and above the top of the v-notch constrained with perpendicular rock walls) (Grant and Dawson 1997).

Discharge amounts and stream chemistry for water years 1999-2000, 2002-2003 and 2003-2004 were used in our budget analysis. There were large gaps in 2000-2001 and 2001-2002 stage height data (95 and 64 days, respectively). Water years were defined here as October 1st to September 31st with minor variations due to precipitation measurements occurring on Tuesdays. A gap of 17 days in the 1999-2000 water year, corresponding to ~ 3% of annual discharge, was infilled using previously derived outputs from a hydrologic model, TOPMODEL, for CB (Shaman et al. 2002). Minor gaps in hourly discharge data during the three water years used here were infilled by linear interpolation. For more description of the equations used to convert stage height to discharge as well as infill methods for discharge refer to Shapiro *et al.* (2005d).

Additionally, during 1999, discharge (m^3 s^{-1}) at NB and OWPR (Fig. 2) were estimated from weekly water velocity measurements (digital water velocity meter, FP101, Global Water Instrumentation, Inc., CA) coupled with cross sectional area measurements and used here to derive a relationship between the relative amount of discharge at these two locations. The equation from a linear regression of discharge at NB vs. OWPR was $y = 0.5746x - 0.0016$ and yielded an $R^2 = 0.96$. This relative relationship between discharge at NB and OWPR was used to estimate discharge amounts normalized for upstream watershed area (mm wk^{-1}) for NB during all weeks with available discharge data measured by stage height at OWPR as previously detailed.

Having separate discharge amounts for NB and OWPR makes it possible to estimate unique SO_4^{2-} export fluxes for each site. The equation between discharge at these two sites was subsequently inverted to better represent the physical relationship between discharge at OWPR vs. North Bridge ($y = 1.6796x + 0.0041$). This second equation reflects the relative difference in upstream area for both sites in that discharge at OWPR is significantly greater than at NB. The positive y-intercept indicates that there are events with discharge occurring at OWPR when none occurs at NB. This is consistent with the differences in topography along the stream axis with the area upstream of NB being steeper and possibly reflecting a greater fraction of event runoff and the area downstream of NB being relatively flat and likely reflecting more baseflow conditions as measured at OWPR.

Stream chemistry

Weekly stream samples were collected in high density polyethylene (HDPE) bottles during 1997 to 2005 at the NB and OWPR sites, filtered using a 0.4μm Whatman® nuclepore® polycarbonate membrane and refrigerated (~3-4°C) prior to analysis with the exception of 9 weeks worth of samples collected during 1997 and 36 weeks worth of samples collected during 2002, which were stored at room temperature for one or more months. Water samples were analyzed using ion chromatography, (Dionex, DX-100; Dionex Corporation, Sunnyvale, CA) where the relative standard deviation (RSD) (stdev/mean*100) for a $[SO_4^{2-}]$ of 156.2 $\mu Eq\ l^{-1}$ was ~ 2%. All stream samples were analyzed during the period from November 2004 - June 2005. We conducted a SO_4^{2-} storage experiment to asses possible storage effects on $[SO_4^{2-}]$ samples collected prior to November 2004. On January 4, 2005 five stream water samples (250 ml) were collected in HDPE bottles from the OWPR site, filtered and measured by ion chromatography. The mean ± sem of the five samples yielded a [SO_4^{2-}] of 167.1 ± 1.34 μEq l^{-1}. The stream samples were subsequently refrigerated and each of the five samples were re-measured on a weekly basis for 27 subsequent weeks. During that time, there did not appear to be any systematic changes from the original mean [SO_4^{2-}] for the five stored samples (mean [SO_4^{2-}] ± sem of 140 samples = 161.7 ± 0.3 μEq l^{-1}; RSD = 1.9%) (Fig. 3). Additionally, independent estimates for evaporative water vapor loss from a full 250ml HDPE bottle were minor, with a maximum of ~ 2.09 ml during 8 years of storage (1997-2005) at 22-24ºC (Kennan 1991). It is likely that this estimate is considerably greater than actual losses for refrigerated samples. These observations are consistent with results from the Hubbard Brook Experimental Forest (HBEF) where measured values of [SO_4^{2-}] in stream water samples from 1978 were compared to concentrations from re-analysis of the same samples in 1994 (slope = 0.93; R^2 = 0.93). The authors conclude that there were no systematic differences between the two sets of measurements (Alewell et al. 1999). Additionally, results from a storage experiment of soil water from a hemlock stand in Ulster County, NY indicated stable concentrations for a range of SO_4^{2-} concentrations (~ 80 to 140 μEq l^{-1}) over a 16-week period (Yorks and McHale 2000). Thus we assume that measured [SO_4^{2-}] in CB stream water samples collected prior to November 2004 represent unbiased stream water [SO_4^{2-}] from the data collected.

Although relatively complete, there were minor gaps in the NB [SO_4^{2-}] data during water years 1999-2000, 2002-2003 and 2003-2004, the water years used here to construct SO_4^{2-} export budgets. Two methods were used to infill missing [SO_4^{2-}] data:

1) If a single week in the NB data was missing it was infilled with a value derived from linear interpolation of the prior and subsequent weeks. This method infilled one week during 1999-2000, two weeks during 2002-2003 and six weeks during 2003-2004.

2) For gaps longer than one week, a calendar month average of [SO_4^{2-}] from NB (1997-2004) was used as an infill value. This method was used to infill 20 weeks during 2002-2003 and three weeks during 2003-2004.

An additional consideration for [SO_4^{2-}] at NB concerns the use of monthly mean SO_4^{2-} concentrations for analysis of calendar month and interannual trends as opposed to using flux-weighted SO_4^{2-} concentrations. Flux-weighted concentrations (c_w) were calculated as follows:

$$c_w = \frac{\sum_1^n c_i q_i}{\sum_1^n q_i}$$

where n is the number of weeks per month, c_i is the weekly ion concentration (μEq l^{-1}) and q_i is the weekly stream discharge amount at NB. It would be preferable to exclusively use flux-weighted SO_4^{2-} concentrations but the difference in the length of the discharge and SO_4^{2-} time series would exclude [SO_4^{2-}] data prior to 1999 from being utilized in this analysis. However, there was no statistical difference between SO_4^{2-} monthly mean concentrations and SO_4^{2-} flux-weighted concentrations when calculated over the same time period (1999-2004) ($p = 0.64$). Furthermore, a linear regression forced through zero between the two data sets exhibits a close statistical relationship (slope = 1.0; $R^2 = 0.93$)

(Fig. 4). Similar conclusions can be drawn for the relationship between monthly mean [SO_4^{2-}] and flux-weighted SO_4^{2-} concentrations at OWPR.

Additionally, gaps in the OWPR [SO_4^{2-}] data during water years 1999-2000, 2002-2003 and 2003-2004 were infilled using the following methods:

1) Gaps of one week in the OWPR data were infilled with a value derived from a linear interpolation of the prior and subsequent weeks. This method infilled one week during 1999-2000 and six weeks during 2003-2004.

2) For gaps longer than one week, infill values were generated from calendar month means for months indicating a relatively insensitive relationship between OWPR [SO_4^{2-}] (μEq l^{-1}) and OWPR discharge amount (mm wk^{-1}) (i.e. January, February, March, April and December (data not shown)). This method infilled 17 weeks during 2002-2003 and four weeks during 2003-2004.

3) For gaps longer than one week during June and July, which on first order were months indicating appreciable sensitivity in the relationship between OWPR [SO_4^{2-}] (μEq l^{-1}) and OWPR discharge amount (mm wk^{-1}) (data not shown), SO_4^{2-} concentrations were estimated on a case by case basis from linear trendlines of [SO_4^{2-}] during weeks surrounding each data gap. This method was used to infill three weeks during 2002-2003 and two weeks during 2003-2004. Because of the variability in [SO_4^{2-}] during these two months, infilled data estimated for these five weeks may misrepresent actual (unmeasured) [SO_4^{2-}]. Despite this shortcoming, it is unlikely that these five weeks significant contribute to annual SO_4^{2-} export at OWPR since weekly discharge during these five weeks averaged 0.8 ± 0.3 mm wk^{-1}, an amount which was appreciably less than the 15.7 ± 1.1 mm wk^{-1} average

discharge amount for all weeks at OWPR with non-zero discharge measured during 1999-2005.

Finally, SO_4^{2-} export fluxes for NB and OWPR were calculated as the product of site-specific discharge from 10am Tuesday until 9am the following Tuesday times the weekly $[SO_4^{2-}]$ (NB or OWPR) corresponding to the stream sample taken at 9am on the second Tuesday of the measurement period. Export budgets reported here include infilled $[SO_4^{2-}]$ and discharge data unless otherwise specified.

Precipitation composition and amounts

Weekly precipitation amounts for the CB watershed were estimated as an unweighted average of precipitation measured at the NADP station on the West Point Military Reservation, NY and at the Old Forest Headquarters within BRF, which are ~ 5 km SSW and 3 km NNW from the CB watershed respectively (Fig. 1). A detailed description of precipitation data sets can be found in Shapiro *et al.* (2005d). Data for amount-weighted precipitation $[SO_4^{2-}]$ and SO_4^{2-} wet deposition were obtained from the NADP collection station at West Point (NY51/NY99) (NADP 2004). An infilled version of NADP data was produced to provide estimates of $[SO_4^{2-}]$ during weeks that reported non-zero amounts of precipitation but that had no corresponding chemistry data. A detailed description of infilling procedures can be found in Shapiro *et al.* (2005b). This infilled version was used to derive precipitation $[SO_4^{2-}]$ and SO_4^{2-} wet deposition for watershed SO_4^{2-} budgets estimated here. There was no statistically significant difference between the annual precipitation $[SO_4^{2-}]$ (1981-2004) for the infilled version of the data compared to a screened version of the data that eliminated weeks in the NADP data that reported invalid ion chemistry, very low precipitation amounts (< 2mm) or an excess (>

3σ) charge imbalance (Shapiro et al. 2005a). This comparison between data sets confirms that infilling procedures did not bias the mean annual values of the NADP [SO_4^{2-}] data included here.

Results

[SO_4^{2-}] within Cascade Brook

Weekly [SO_4^{2-}] data (1997-2005) (Fig. 5) indicate relatively stable SO_4^{2-} concentrations at NB with a low degree of week-to-week variability (mean ± sem = 176.1 ± 1.1 μEq l^{-1}), whereas concentrations at the OWPR site were much more variable, with periods of both high and low SO_4^{2-} concentrations (mean ± sem = 172.7 ± 4.5 μEq l^{-1}). The difference in variability for these two data sets can be represented by comparing relative standard deviations (RSD), (RSD = 10.3 % and 42.2%, respectively) which differ by ~ a factor of four. For comparison, weekly mean ± sem for precipitation [SO_4^{2-}] (1997-2004) was 57.7 ± 2.7 μEq l^{-1} with a high degree of weekly variability as indicated by a RSD of 91.6%.

[SO_4^{2-}] (μEq l^{-1}) vs. discharge (mm wk^{-1}) for NB and OWPR indicate substantially different trends, with NB [SO_4^{2-}] relatively insensitive to discharge, whereas OWPR [SO_4^{2-}] has very large range of values associated with low discharge periods (Fig. 6). An example of the variable temporal pattern of [SO_4^{2-}] at NB and OWPR with discharge amount is evident during the 2000 calendar year (Fig. 7). During winter and early spring, [SO_4^{2-}] at NB and OWPR were both relatively stable and had comparable values. In contrast, during late-spring through mid-fall [SO_4^{2-}] values at NB and OWPR diverged substantially, with OWPR [SO_4^{2-}] systematically much lower and appear highly responsive to discharge amounts. Scatter plots of [SO_4^{2-}] (μEq l^{-1}) vs. discharge (mm wk^{-}

^{1}) during the 2000 calendar year for NB and OWPR further confirm this differential response (Fig. 8), where [SO_4^{2-}] at OWPR was quite variable with discharge amount during low discharge periods while [SO_4^{2-}] at NB was relatively constant.

Conversely, an example of considerably elevated [SO_4^{2-}] at OWPR compared to NB (> 2 fold) occurred during January 2002 (Fig. 9). Prior to January 2002, there were 20 consecutive weeks during 2001 (7/24/2001 – 12/11/2001) where measured stream discharge was zero indicating extended drought conditions within the CB watershed. Although there was a period of missing data in the measured discharge record for 1/2/2002 through 2/12/2002, stream samples for these weeks were collected, indicating that stream discharge had resumed. From January 2, 2002 through January 22, 2002, SO_4^{2-} concentrations at OWPR were much higher than those at NB, after which concentrations at the two sites converged again.

Additionally, spatial and temporal variability in [SO_4^{2-}] can be seen in comparing weekly [SO_4^{2-}]/[Cl^-] ratios measured in precipitation and in stream water samples from NB and OWPR (Fig. 10). The regular annual pattern in precipitation [SO_4^{2-}]/[Cl^-] indicates higher ratios during summer and lower ratios during winter, corresponding to SO_2 oxidation dominating during summer when corresponding Cl^- deposition displays an annual minimum (Shapiro et al. 2005a). The low degree of variability in NB [SO_4^{2-}]/[Cl^-] is consistent with low temporal variability in [SO_4^{2-}] and correspondingly, the higher degree of variability in OWPR [SO_4^{2-}/[Cl^-] reflects the generally higher degree of variability in stream water [SO_4^{2-}]. Furthermore, both NB and OWPR [SO_4^{2-}]/[Cl^-] indicate a high degree of dampening of the [SO_4^{2-}]/[Cl^-] ratio of incident precipitation.

Calendar month mean ± sem [SO_4^{2-}] measured in NB stream water were consistently and substantially greater than corresponding amount-weighted precipitation [SO_4^{2-}], with the mean monthly value for NB stream water (176.1 ± 1.1 μEq l^{-1}) ~ 4.3 times that of amount-weighted precipitation (40.5 ± 2.4 μEq l^{-1}) (1997-2004) (Fig. 11). It should be noted that calendar month means for NB [SO_4^{2-}] (1997-2005) are estimates using non-infilled data and therefore data gaps occur during weeks when no stream water sample was collected due to zero discharge or inaccessible conditions. On average 21 measurements contribute to each calendar month [SO_4^{2-}] mean. With respect to variability, the 10% RSD of NB stream water was considerably less than the ~ 58% RSD for monthly amount-weighted precipitation indicating the low degree of variability in NB stream water [SO_4^{2-}] as reflected in the lack of a marked calendar month pattern. In comparison, precipitation [SO_4^{2-}] displayed a distinct calendar month pattern with relatively low values during fall and winter and maximum concentrations during summer. These large differences in temporal variability were also evident in the long-term [SO_4^{2-}] stream and precipitation time series aggregated monthly (1997-2005) (Fig. 12A) where appreciable dampening of the precipitation temporal variation was evident in monthly NB stream water [SO_4^{2}].

Monthly mean [SO_4^{2-}] measured at NB during 1997 through 2005 indicate a decreasing trend over time (slope = -0.37 μEq l^{-1} $month^{-1}$; $R^2 = 0.52$), consistent with the multi-decadal (1981-2004) decrease in annual [SO_4^{2-}] (slope = -0.92 μEq l^{-1} yr^{-1}; $R^2 = 0.49$) (Figs. 12B, C) (Shapiro et al. 2005a). It would be preferable to compare annual [SO_4^{2-}] for both stream water and amount-weighted concentrations; however the discontinuous stream chemistry record inhibits such analysis; thus monthly values were used to illustrate multi-year trends. Predicted values derived from linear regression equations indicate that during years of overlapping data (1997-2003) precipitation and stream water [SO_4^{2-}] decreased by 2.1% and 2.3% per year, respectively.

Cascade Brook SO_4^{2-} budgets

Mean annual evapotranspiration (ET), (precipitation – discharge) within CB during water years 1999-2000, 2002-2003 and 2003-2004 varied from 41% of precipitation at NB to 47% of precipitation at OWPR. This spatial variability in ET likely reflects differences in upstream topography at NB vs. OWPR, respectively, with generally steep topography upstream of NB and a greater prevalence of flatter watershed topography between NB and OWPR. SO_4^{2-} export fluxes for the 1999-2000, 2002-2003 and 2003-2004 water years indicate a relatively large range in values for NB (17.5 to 33.3 kg S ha^{-1} yr^{-1}) and OWPR (15.7 to 29.8 kg S ha^{-1} yr^{-1}) with mean fluxes of 24.9 ± 4.6 kg S ha^{-1} yr^{-1} and 22.0 ± 4.1 kg S ha^{-1} yr^{-1}, respectively (Table 2). The ratio of SO_4^{2-} stream export/SO_4^{2-} wet deposition averaged 3.1 (range = 2.0 to 4.3) at NB and 2.8 (range = 1.8 to 3.9) at OWPR indicating at least one other significant source of SO_4^{2-}-S in addition to wet deposition. On average during water years 1999-2000, 2002-2003 and 2003-2004, SO_4^{2-}-S export measured at OWPR was 2.9 ± 0.5 kg S ha^{-1} yr^{-1} or 11.6% less than the corresponding SO_4^{2-}-S export at NB, suggesting that significant amounts of S were stored within the wetlands situated between the two stream sampling stations. As a comparison using non-infilled data, the amount of SO_4^{2-}-S export measured at OWPR was an average of 3.0 ± 0.6 kg S ha^{-1} yr^{-1} (data not shown) or 14.9% less than the corresponding SO_4^{2-}-S export at NB, confirming that net S storage reported here was not an artifact of infilling processes. Consistent with these differences in SO_4^{2-} export at OWPR and NB, the monthly flux-weighted mean [SO_4^{2-}] at OWPR (163.4 ± 4.6; RSD = 20.4%) was less than that measured at NB (170.7 ± 2.8 RSD = 10.3%).

SO_4^{2-} export budgets at NB and OWPR during the relatively dry water years 2000-2001 and 2001-2002 (which had 142 and 72 days with zero discharge respectively) have not been addressed thus far because of gaps in the water discharge data during these years. However, approximations can be used to infill missing discharge data to facilitate first order comparisons with three years of relatively high quality SO_4^{2-} export budgets. Individual linear regression equations for each calendar month of discharge vs. precipitation were used to estimate discharge amount from precipitation during weeks with gaps in discharge data. Additionally, gaps in NB [SO_4^{2-}] were infilled by calendar month averages for 13 weeks during water year 2000 - 2001 and four weeks during 2001-2002. Gaps in OWPR [SO_4^{2-}] were infilled by calendar month averages for three weeks during 2001 - 2001 and 17 weeks during 2002 - 2003 and extrapolations from linear trend lines were used for one week during 2001 - 2002 and three weeks during 2002 - 2003. Sulfate export budgets for these two years yield SO_4^{2-} export/SO_4^{2-} wet deposition ratios of 2.1 and 2.2 at NB and 1.8 and 2.5 at OWPR during water years 2000 - 2001 and 2001 - 2002, respectively. Although of lesser quality, these additional years fall within the range of those reported here for the other three water years, indicating a relatively consistent relationship between stream SO_4^{2-} export and SO_4^{2-} wet deposition at CB.

Discussion

Cascade Brook [SO_4^{2-}] upstream and downstream of Glycerine Hollow

Weekly [SO_4^{2-}] at NB was relatively consistent throughout the measurement period (RSD ~ 10%) whereas much greater variability was evident in [SO_4^{2-}] at OWPR

(RSD ~ 42%) (Fig. 5). Differences in temporal variability have also been reported in Ontario, Canada at sites that consider the effect of stream discharge on stream water [SO_4^{2-}] (Eimers et al. 2004) where SO_4^{2-} export was higher during years reporting drought conditions. Additionally, some studies compare stream water [SO_4^{2-}] of watersheds with and without wetlands (Schiff et al. 2005). One catchment containing wetlands reported relatively low [SO_4^{2-}] during summer seasons whereas relatively high [SO_4^{2-}] in stream water was reported during periods following extended drought conditions (Schiff et al. 2005). Drought conditions were on the order of weeks to several months (Dillon et al. 1997; Schiff et al. 2005). In analyzing the concentration and $\delta^{34}S$ signature of stream SO_4^{2-}, Schiff *et al.* (2005) concluded that systematic variations in stream water [SO_4^{2-}] were consistent with microbial SO_4^{2-} reduction in the upper peat layer of wetlands during summer low flow conditions. During such conditions, incomplete microbial reduction of SO_4^{2-} within the wetlands appear to have resulted in comparatively low stream water [SO_4^{2-}] with a correspondingly high $\delta^{34}S$-SO_4^{2-} signature. Conversely, oxidation of previously reduced SO_4^{2-} in the upper peat layer appears to have occurred during low water table drought conditions, resulting in relatively high stream [SO_4^{2-}] and relatively low $\delta^{34}S$ when surface water discharge resumed (Schiff et al. 2005). It is plausible that a similar sequence of processes accounts for the divergence of [SO_4^{2-}] at NB compared to [SO_4^{2-}] at OWPR, since the latter lies downstream of the Glycerine Hollow wetlands. One example occurred during the spring and summer of 2000 in CB, where [SO_4^{2-}] at OWPR was appreciably lower than at NB (Fig. 7). Additionally, [SO_4^{2-}] measured at OWPR was much more variable during low discharge conditions than at NB (Figs. 6, 8). This pattern of variable [SO_4^{2-}] at low stream discharges is consistent with summer sulfate reduction within Glycerine Hollow acting as a short-term sink for SO_4^{2-}, yielding low [SO_4^{2-}] at OWPR compared to that at NB (Figs. 5, 7).

Conversely, during an extended drought within CB it is plausible that lower water levels within the wetlands permitted oxidation of previously reduced sulfur. This set of circumstances would result in appreciably higher [SO_4^{2-}] during subsequent discharge events at OWPR compared to NB, as occurred during January 2002 (Fig. 9). There were three other events in the 1997-2005 data set with high [SO_4^{2-}] at OWPR compared to NB, but the lack of corresponding discharge and/or low resolution [SO_4^{2-}] data during these additional events inhibits more detailed analysis.

On an annual basis, it appears that a maximum of ~ 3 kg S ha^{-1} yr^{-1} or ~ 12% of S exported from NB was stored within Glycerine Hollow as reduced inorganic S during water years analyzed here. This suggests that potential positive effects for terrestrial ecosystems associated with significant reductions in SO_4^{2-} wet deposition may not be immediately transferred to watersheds containing wetlands storing appreciable amounts of S, such as reported here for CB.

Dampening of SO_4^{2-} variability in stream water introduced via precipitation

The lack of seasonal variability in stream water [SO_4^{2-}] and [SO_4^{2-}]/[Cl^-] at NB compared to the considerable calendar month variability in precipitation [SO_4^{2-}] and [SO_4^{2-}]/[Cl^-] (Figs. 10, 11) suggests that there are mechanisms within the watershed that dampen the variability introduced by precipitation influxes of SO_4^{2-}. This lack of consistent seasonal variability in stream water [SO_4^{2-}] has also been reported for watersheds within the HBEF in NH, and the Huntington Wildlife Forest (HWF) in the

Adirondacks (Alewell et al. 1999; Likens et al. 2002; Park et al. 2003). Seasonal variability in precipitation [SO_4^{2-}] reflects the much greater photochemical oxidation of SO_2 in the troposphere during spring and summer due to a larger pool of oxidizing species during these warm seasons (Calvert et al. 1985; Stein and Lamb 2003). The subsequent dampening of this seasonal signal in stream [SO_4^{2-}] is consistent with the integrated impacts that organic S mineralization and SO_4^{2-} sorption reactions can have within the organic and mineral soil layers as water travels through the watershed (Mitchell et al. 1992; Alewell et al. 1999). The net result of such mechanisms is to apparently eliminate the temporal variability in [SO_4^{2-}] introduced by precipitation.

Dry S deposition and other potential sources of S to Cascade Brook

With regard to the mean flux-weighted [SO_4^{2-}] of NB stream water (~ 171 μEq l^{-1}), which is ~ 4.2 times that of precipitation (~ 41μEq l^{-1}), the concentration effect due to evaporation losses in the CB watershed upstream of NB (~ 41%) accounts for less than half of this difference. This excess component of [SO_4^{2-}] in stream water is consistent with the mean ratio of SO_4^{2-} stream export/SO_4^{2-} wet deposition reported for NB of 3.1-to-1, indicating appreciable sources of SO_4^{2-} to stream water in addition to SO_4^{2-} wet deposition. A SO_4^{2-} mass balance for a watershed in the HWF (1995-2000) also supported the conclusion that SO_4^{2-}-S export in stream water was greater than input via wet deposition with an export/wet deposition ratio of 3:1 (Park et al. 2003) (Table 1). Similarly, during 33 of 34 years of measurements (1964-1998) at the HBEF SO_4^{2-} export in stream water was appreciably greater than SO_4^{2-} input from bulk deposition with a long term average bulk deposition/stream export ratio of SO_4^{2-} of ~ 1.5:1 (Likens et al. 2002).

Atmospheric and watershed sources of SO_4^{2-} consistent with excess SO_4^{2-} export in stream water relative to SO_4^{2-} input via wet deposition include: 1) dry deposition of S bearing aerosols and gases; 2) weathering of S bearing minerals in bedrock, glacial till or soils within the watershed; 3) desorption of previously adsorbed SO_4^{2-} within the soils; and 4) SO_4^{2-} input from the mineralization of soil organic matter.

Using SO_4^{2-} export fluxes from OWPR and NB a watershed mass balance was estimated to provide an upper limit range for S dry deposition to CB. This approach attributes 14 - 17 kg S ha^{-1} yr^{-1} of total S stream export (22 - 25 kg S ha^{-1} yr^{-1}) from OWPR and NB respectively, to input from dry deposition. This approach assumes no other sources within the watershed contribute S to CB. These mass balance estimates are ~ 3.5 – 4.3 times greater than the 4.0 kg ha^{-1} yr^{-1} (1988-1997) S dry deposition estimate derived using a relationship between wet and dry S deposition from a dry deposition inferential measurement (DDIM) technique based on S aerosol and gas measurements from a site adjacent to BRF (Shapiro et al. 2005c). During 1985-1997 independent wet and dry S deposition monitoring stations were active at the West Point Military Reservation, 5km SSW of the CB watershed. Total S dry deposition was estimated using a DDIM, which combines measured concentrations of gaseous SO_2-S and particulate SO_4^{2-}-S with modeled deposition velocities parameterized with site-specific meteorological and vegetative data (Hicks et al. 1991; Meyers et al. 1991; Meyers et al. 1998). Model estimates from 9 years of collocated wet and dry S measurements indicate that S dry deposition was ~ 33% of total deposition or ~ 50% of wet S deposition (Shapiro et al. 2005c). Similar results have been reported for the HBEF, which indicate that S dry deposition calculated by a watershed mass balance approach was ~ 4 times that estimated from a DDIM approach (Likens et al. 2002). Comparing mass balance and DDIM estimates for S dry deposition within Cascade Brook suggests that the range of this flux derived from two independent methods is quite large and perhaps could be considered as upper and lower limits (Matt and Meyers 1993) for dry deposition, respectively.

A second potential source contributing to SO_4^{2-} stream export within CB is S release from chemical weathering. There have not been systematic studies of S weathering of bedrock, glacial till or soil minerals within BRF and thus this flux cannot be evaluated directly. However, a first-order attempt to assess the approximate magnitude of this flux was made by sampling at a number of sites along the stream axis from the headwater of CB downstream to the gauging station (Fig. 13). As water contact time with soil and bedrock increases progressively with lower elevation within the watershed, if chemical weathering contributes large amounts of S to stream water then $[SO_4^{2-}]$ along the stream transect would probably increase. Results from two sampling transects do not reveal a systematic increase in $[SO_4^{2-}]$ along the stream axis (Fig. 13) despite an 11-15% increase in dissolved silica (data not shown). Estimates of S contribution from weathering at the HBEF, which is known to be underlain by relatively S-rich bedrock (1.92 to 8.34 mg g^{-1}), yield a range from 0.64 to 1.6 kg S ha^{-1} yr^{-1} (Likens et al. 2002; Bailey et al. 2004). Applying this range of S weathering to CB SO_4^{2-} export constrains an upper limit of S contribution from weathering of ~ 2.6% to 7.3% of the annual average SO_4^{2-} export reported here, suggesting that S from chemical weathering is unlikely to be a major source of dissolved $[SO_4^{2-}]$.

Desorption of SO_4^{2-} from soil mineral surfaces has also been suggested as a source of SO_4^{2-} in stream water (Likens et al. 2002). Desorption of soil SO_4^{2-} may currently be occurring in response to decreasing SO_4^{2-} wet deposition (Likens et al. 2002), which has been measured to be -37% during 1981-2003 at a site adjacent to BRF (Shapiro et al. 2005a). Adsorption/desorption of SO_4^{2-} to mineral surfaces is considered to be pH dependent (Fuller et al. 1987; Welsch et al. 2004); thus, if soil pH increases in response to declining acidic deposition, desorption of soil SO_4^{2-} could temporarily contribute additional [SO_4^{2-}] to stream waters. This flux would potentially be a component of the the “excess” SO_4^{2-} export relative to SO_4^{2-} wet deposition input flux but this desorption flux may not be large enough dominate the long-term secular trend in stream water [SO_4^{2-}]. Results from soil chemistry model simulations for HBEF conclude that SO_4^{2-} desorption was a relatively small flux (~1 kg S ha^{-1} yr^{-1}) and unable to account for the significant imbalance in the HBEF SO_4^{2-} input:export budget (Driscoll et al. 1998; Gbondo-Tugbawa et al. 2001; Likens et al. 2002). A soil S inventory at a watershed within the HBEF indicated that the pool of adsorbed SO_4^{2-} was ~ 6% of total soil S (1478 kg S ha^{-1}) whereas the organic soil S pool accounted for ~ 93% of total soil S (Mitchell et al. 1989; Driscoll et al. 1998). For CB, a SO_4^{2-} desorption flux on the order of 1 kg S ha^{-1} yr^{-1} would account for ~ 4 to 4.5 % of the average annual SO_4^{2-} export.

Another plausible source for excess SO_4^{2-} export in CB may be from mineralization (oxidation) of soil organic S (Likens et al. 2002). Systematic variability in the $\delta^{34}S$ and $\delta^{18}O$ of precipitation and soil water SO_4^{2-} suggests that SO_4^{2-} likely cycles through vegetation prior to export in stream water (Mayer et al. 1995; Novak et al. 1996; Alewell et al. 1999; Likens et al. 2002; Bailey et al. 2004). For example, Mayer et al.

(1995) concluded that the comparatively depleted $\delta^{18}O$ signature of soil water SO_4^{2-} versus the relatively enriched $\delta^{18}O$ of coincident precipitation SO_4^{2-} indicated that soil water SO_4^{2-} was primarily a result of the mineralization of organic soil sulfur utilizing soil water oxygen, which has an appreciably lighter isotopic signature than atmospheric oxygen. At CB, SO_4^{2-} from organic mineralization could plausibly contribute to excess SO_4^{2-} export since: 1) presently tree growth rates within BRF have apparently declined since the early 1990's and biomass accumulation has declined since 2000 (Pederson 2005b; Schuster 2005). Thus, SO_4^{2-} derived from soil organic S mineralization could be greater than storage of S via assimilation and as such may appear in stream water as a net SO_4^{2-} source; and 2) the S:C ratio of presently formed organic material could be lower than that formed during periods with greater S deposition. Consequently, SO_4^{2-} derived from current mineralization of organic material formed during earlier years with greater SO_4^{2-} deposition would appear as a temporary source of excess SO_4^{2-} in stream water. This mechanism would require a temporal decline in SO_4^{2-} wet deposition, which is consistent with the observed -37% decrease over the period from 1981 to 2004 in local SO_4^{2-} wet deposition (Shapiro et al. 2005a). Estimates from HBEF indicate that during 1993-1998 as much as 2.21 kg S ha^{-1} yr^{-1} of SO_4^{2-}-S export at HBEF may be attributed to SOM mineralization (Likens et al. 2002). This flux was ~ 26% of bulk S deposition at HBEF (1993-1998) (Likens et al. 2002). Using the percentage of S from mineralization of SOM relative to S bulk deposition at HBEF, we calculate a first order estimate of 2.08 kg S ha^{-1} yr^{-1} for SO_4^{2-}-S from SOM mineralization at CB. This approach assumes a linear relationship between the ratios of HBEF SO_4^{2-}-S from SOM mineralization: SO_4^{2-}-S bulk deposition and CB SO_4^{2-}-S from SOM mineralization: SO_4^{2-}-S wet deposition.

The magnitude of this flux (2.08 kg S ha^{-1} yr^{-1}) would account for ~ 8 to 10% of the mean annual SO_4^{2-}-S export at CB.

Independent estimates of S weathering, SO_4^{2-} adsorption/desorption and soil organic S mineralization within BRF have not been measured, which inhibits quantitative allocation of excess SO_4^{2-} export to each of these plausible sources. Order of magnitude estimates for CB based on comparisons to HBEF data are presented here to preliminarily address the large discrepancy in the CB SO_4^{2-} input:export budget. We therefore conclude for CB that the average water year SO_4^{2-}-S export (22.0 – 24.9 kg S ha^{-1} yr^{-1}) likely reflects significant contributions from SO_4^{2-} wet deposition (8.0 kg S ha^{-1} yr^{-1}) and S dry deposition (4.0 – 17.0 kg S ha^{-1} yr^{-1}) with additional contributions from S weathering (0.64 - 1.6 kg S ha^{-1} yr^{-1}), SO_4^{2-} desorption (1 kg S ha^{-1} yr^{-1}) and soil organic S mineralization (2.08 kg S ha^{-1} yr^{-1}).

Long-term trends in Cascade Brook [SO_4^{2-}]

The multi-year temporal trend in [SO_4^{2-}] at the NB sampling site (1997-2005) was negative with a slope of -0.37 μEq l^{-1} $month^{-1}$. This rate of decrease was equivalent to -4.4 μEq l^{-1} yr^{-1} which was ~ 4.8 times the -0.92 μEq l^{-1} yr^{-1} slope of annual precipitation [SO_4^{2-}] (Shapiro et al. 2005a). This comparison is consistent with the ~ 4.3 times difference in average concentration of stream water compared to precipitation reported here (Fig. 11). Additionally, the predicted rates of annual decrease in [SO_4^{2-}] derived from linear regression equations for precipitation (2.1% yr^{-1}) and stream water (2.3% yr^{-1}) at NB during 1997-2003 indicate similar trends. This coherence indicates that in general, the CB watershed as measured by NB stream water has responded directly to decreasing regional and local SO_2 emissions and decreasing precipitation [SO_4^{2-}] during the period from 1981 to 2004 (Shapiro et al. 2005a). Decreasing stream water [SO_4^{2-}] has also been observed at the HBEF, which reports a 31% decrease in stream water [SO_4^{2-}] during 34 years of measurement (1964-1998) (Likens et al. 2002). At CB, analysis of long-term trends in OWPR [SO_4^{2-}] indicates that the predicted annual rate of decrease during 1997-2003, derived from a linear regression of calendar month means, was 3.2% (data not shown). This greater rate of decrease at OWPR than that estimated for NB likely reflects the appreciable amounts of S storage with Glycerine Hollow and therefore absolute [SO_4^{2-}] and SO_4^{2-} export measured at OWPR were less than at NB.

Additional uncertainties

Uncertainties associated with watershed SO_4^{2-} budgets for three years include: 1) the use of calendar month means to infill gaps in the [SO_4^{2-}] data; 2) the assumption that CB bedrock is impermeable and that water losses via deep seepage are negligible; 3) that there have been no assessment of possible additions of S via cloud or fog interception; and 4) no direct estimates for input and /or export of organic S in export budgets. Infilling gaps in the NB [SO_4^{2-}] data with calendar month averages are not likely to appreciably perturb SO_4^{2-} export budgets for NB since the relative standard error (RSE) for monthly average stream [SO_4^{2-}] averaged ~ 2%. Likewise, the RSE for calendar month means used to infill gaps in the OWPR [SO_4^{2-}] data during months that were relatively insensitive to discharge (i.e January, February, March, April and December) was reasonably low at 3.1%. A second issue, water loss via deep seepage, is relevant to our assumption that precipitation reaching the CB watershed leaves predominantly via evapotranspiration or surface runoff. Evapotranspiration during the water years analyzed here was estimated to average ~ 41 - 47% (Shapiro et al. 2005d), a proportion consistent with 40-50% evapotranspiration losses estimated for three forested watersheds in Vermont and New Hampshire, including the HBEF (Hornbeck et al. 1997). Therefore, although some water loss from deep seepage in the CB watershed probably occurs to a limited extent, it appears likely that this accounts for a very small water flux compared to surface runoff. With respect to additional S deposition via cloud or fog interception with the canopy, there have not been measurements of this flux to Cascade Brook or Black Rock Forest, although it is possible that during such meteorological conditions, S deposition may occur via this pathway. The fourth issue concerns organic S fluxes in CB, which have not been considered in the analysis presented here. Estimates of organic S input to temperate forests via precipitation are considered to be negligible (Homann et al. 1990) although organic S output ranged from 1.6 – 15 % of total S in stream water at the HBEF during 1986 (Mitchell et al. 1989). If organic S contributed an additional 15% to mean S export in CB, total S export for the three water years analyzed here would increase to a maximum of ~ 29.3 kg S ha^{-1} yr^{-1}

Conclusions

1) Weekly SO_4^{2-} concentrations in stream water at the OWPR sampling site were much more variable than those at the NB sampling site. These fluctuations appeared to be sensitive to water discharge rates and primarily occurred during low discharge periods. Relatively low [SO_4^{2-}] at OWPR were consistent with SO_4^{2-} reduction in upstream wetlands during low flow summer periods, whereas relatively high [SO_4^{2-}] were consistent with oxidation of previously reduced sulfur for periods following drought conditions.

2) Comparison of SO_4^{2-}-S export fluxes at NB and OWPR suggest a storage of ~ 3 kg S ha^{-1} yr^{-1} or 12% of the NB SO_4^{2-}-S export flux was stored within the Glycerine Hollow wetlands.

3) Comparison of variability in stream water and precipitation [SO_4^{2-}] indicates significant dampening of the seasonal pattern introduced by precipitation [SO_4^{2-}] in weekly and flux-weighted stream water [SO_4^{2-}]. Processes consistent with this dampening in stream water include SO_4^{2-} sorption reactions and soil organic S cycling.

4) Stream water [SO_4^{2-}] and SO_4^{2-} export budgets upstream and downstream of the wetlands indicate significant excess SO_4^{2-} in stream water compared with SO_4^{2-} wet deposition. If dry deposition were to account for the entire difference between S export and S input via wet deposition, S dry deposition would be ~ 14 - 17 kg S ha^{-1} yr^{-1}; this flux is 3.5 – 4.3 times greater than an independent estimate of S dry deposition derived from an inferential technique based on S aerosol and gas measurements. It is plausible that these independent estimates represent upper and lower limits for S dry deposition to the CB watershed.

5) Processes in addition to SO_4^{2-} wet and total S dry deposition that are likely to contribute to SO_4^{2-}-S export include: chemical weathering, SO_4^{2-} desportion reactions and SO_4^{2-} from soil organic S mineralization.

6) A decreasing temporal trend in monthly stream water [SO_4^{2-}] (1997-2005) was consistent with a decreasing trend (1981-2004) in precipitation [SO_4^{2-}] indicating that stream waters were responsive to declines in precipitation [SO_4^{2-}], which

have been shown to be responsive to reductions in SO_2 emissions on several spatial scales.

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Table 1: SO_4^{2-}-S input and export budgets from the Huntington Wildlife Forest (HWF) in the Adirondack Mountains (1995-2000) (Park et al. 2003); the Hubbard Brook Experimental Forest (HBEF), NH (1964-1998) (Likens et al. 2002); and the Biscuit Brook (BB) watershed within the Catskill Mountains (Stoddard and Murdoch 1991). [a] wet deposition; [b] bulk deposition.

Table 1

	SO_4^{2-}-S wet or bulk deposition	SO_4^{2-}-S export	SO_4^{2-}-S export/ SO_4^{2-}-S wet deposition
	(kg S ha^{-1} yr^{-1})	(kg S ha^{-1} yr^{-1})	
HWF	5[a]	15.2	3.04
HBEF	10.8[b]	15.9	1.47
BB	11.8[a]	18.2	1.54

Table 2: SO_4^{2-} budget components for water years 1999-2000, 2002-2003 and 2003-2004. Hydrologic data (denoted by [a]) is reprinted here from Shapiro *et al.* (2005d). Evapotranspiration was calculated by difference.

Table 2

North Bridge

Water Year	Precipitation [a]	Discharge	Evapotranspiration	Evapotranspiration [a]	SO_4^{2-} wet deposition	SO_4^{2-}-S wet deposition	SO_4^{2-} export	SO_4^{2-}-S export	SO_4^{2-} export/ SO_4^{2-} wet deposition	Net SO_4^{2-}-S difference (NB-OWPR)	Net SO_4^{2-}-S difference (NB-OWPR)
	(mm)	(mm)	(mm)	(% of precipitation)	(mEq m^{-2} yr^{-1})	(kg ha^{-1} yr^{-1})	(mEq m^{-2} yr^{-1})	(kg ha^{-1} yr^{-1})		(kg ha^{-1} yr^{-1})	(% of NB export)
1999-2000	1371	821	550	40.1	48.2	7.7	148.2	23.8	3.1	3.2	13.6
2002-2003	1704	1196	508	29.8	48.0	7.7	207.7	33.3	4.3	3.5	10.5
2003-2004	1537	704	833	54.2	53.5	8.6	109.4	17.5	2.0	1.8	10.5
average	1537	907	630	41.4	49.9	8.0	155.1	24.9	3.1	2.9	11.6
± sem	96	148	102	7.1	1.8	0.3	28.6	4.6	0.7	0.5	1.0
2000-2001	1016	509	507	49.9	42.1	6.8	88.8	14.2	2.1	2.0	14.1
2001-2002	884	411	473	53.5	35.9	5.8	77.6	12.4	2.2	-1.7	-13.7

Old West Point Road

Water Year	Precipitation [a]	Discharge [a]	Evapotranspiration [a]	Evapotranspiration [a]	SO_4^{2-} wet deposition	SO_4^{2-}-S wet deposition	SO_4^{2-} export	SO_4^{2-}-S export	SO_4^{2-} export/ SO_4^{2-} wet deposition
	(mm)	(mm)	(mm)	(% of precipitation)	(mEq m^{-2} yr^{-1})	(kg ha^{-1} yr^{-1})	(mEq m^{-2} yr^{-1})	(kg ha^{-1} yr^{-1})	
1999-2000	1371	744	627	45.7	48.2	7.7	128.0	20.5	2.7
2002-2003	1704	1071	633	37.1	48.0	7.7	185.8	29.8	3.9
2003-2004	1537	644	893	58.1	53.5	8.6	97.9	15.7	1.8
average	1537	820	717	47.0	49.9	8.0	137.2	22.0	2.8
± sem	96	129	88	6.1	1.8	0.3	25.8	4.1	0.6
2000-2001	1016	466	550	54.1	42.1	6.8	76.1	12.2	1.8
2001-2002	884	415	469	53.1	35.9	5.8	88.0	14.1	2.5

Figure captions

Figure 1: A) New York State map with locations of Black Rock Forest, the Hudson River and Mohawk River, which is the largest tributary to the Hudson River. B) Black Rock Forest boundary map, indicating the Old Forest Headquarters (OFHQ), the Open Lowland (OL) and the Ridge Top (RT) precipitation collectors, as well as the site of the National Atmospheric Deposition Program (NADP NY99) composite precipitation amount and chemistry collector. The boundary for the Cascade Brook watershed (CB) is also indicated, C) Contour map (intervals of 10 m of elevation) of the Cascade Brook watershed within BRF. Two stream sampling sites, North Bridge (NB) and Old West Point Road (OWPR), are identified (open squares) as is the Glycerine Hollow (GH) wetlands.

Figure 2: Weekly discharge (m^3 s^{-1}) during 1999 at both North Bridge and Old West Point Road sampling from water velocity and cross sectional area measurements. The linear regression ($y= 0.5746x-0.0016$; $R^2 = 0.96$) does not include the circled data point (0.27, 0.06).

Figure 3: Mean ± sem of five stream water samples from Old West Point Road collected on January 4, 2005, measured for [SO_4^{2-}] and re-analyzed on a weekly basis for 28 consecutive weeks to investigate possible effects on [SO_4^{2-}] from long-term storage.

Figure 4: Monthly mean [SO_4^{2-}] ± sem vs. monthly flux-weighted [SO_4^{2-}] for North Bridge samples (1999-2004) ($p = 0.64$; $R^2 = 0.93$; slope = 1.0).

Figure 5: Weekly [SO_4^{2-}] (1997-2005) at the North Bridge (closed circles) and the Old West Point Road sites (open circles).

Figure 6: Weekly [SO_4^{2-}] vs. stream discharge during 1999-2004: A) North Bridge (closed circles); and B) Old West Point Road (open circles). Note: one point not included in Fig. 6B (0.04 mm wk^{-1}, 442.7 μEq l^{-1}).

Figure 7: A) [SO_4^{2-}] at North Bridge (closed circles) and Old West Point Road (open circles) and; B) weekly discharge during calendar year 2000. Shaded area represents weeks during late-spring through mid-fall.

Figure 8: Weekly [SO_4^{2-}] vs. stream discharge during calendar year 2000: A) North Bridge (closed circles); and B) Old West Point Road (open circles).

Figure 9: A) [SO_4^{2-}] μEq l^{-1} at North Bridge (closed circles) and Old West Point Road (open circles) and; B) weekly discharge (mm wk^{-1}) during May 2001-July 2002. The light gray box indicates an extended period of no water discharge (20 weeks of drought) in the Cascade Brook watershed; the dark gray box indicates the period following the drought with stream chemistry but no recorded stage measurements.

Figure 10: A) weekly [SO_4^{2-}]/[Cl^-] for precipitation (dark line), NB stream samples (closed circles) and OWPR (open circles); B) same data as in (A) with enlarged y-axis showing weekly [SO_4^{2-}]/[Cl^-] for NB stream samples (closed circles) and OWPR (open circles) with the mean annual precipitation-weighted [SO_4^{2-}]/[Cl^-] (1997-2004) (dark-dashed line).

Figure 11: Mean ± sem (closed circles) calendar month North Bridge stream [SO_4^{2-}] (μEq l^{-1}) (1994 - 2004) and mean ± sem (open circles) calendar month precipitation [SO_4^{2-}] (μEq l^{-1}) (1994 - 2004). Note that due to incomplete stream water

sampling resulting from zero discharge or inaccessible conditions, an average of 21 measurements were used for each calendar month mean.

Figure 12: A) Monthly amount-weighted mean precipitation [SO_4^{2-}] (μEq l^{-1}) during 1980-2004 (open circles) and monthly mean ± sem (closed circles) North Bridge [SO_4^{2-}] (μEq l^{-1}) during 1997-2005. B) Annual mean ± sem (open circles) precipitation [SO_4^{2-}] (μEq l^{-1}) during 1981-2004 (Shapiro et al. 2005a) ($R^2 = 0.49$; slope = -0.92 μEq l^{-1} yr^{-1}); C) Monthly mean ± sem (closed circles) North Bridge [SO_4^{2-}] (μEq l^{-1}) during 1997-2005. ($R^2 = 0.52$; slope = -0.37 μEq l^{-1} $month^{-1}$). Note: for all three graphs the scale for stream water [SO_4^{2-}] is four times that for precipitation [SO_4^{2-}] corresponding to the mean difference in [SO_4^{2-}] of these sources.

Figure 13: Stream water samples taken along a transect of Cascade Brook from the headwaters downstream to the weir gauging station (0 km). Solid circles from 2/11/05, open circles were tributary samples on the same date; solid squares from 3/29/05, open squares were tributary samples on the same date. Discharges at the weir during these two dates were 3.7 mm day^{-1} (2/11/05) and 33.5 mm day^{-1} (3/29/05).

Figure 1

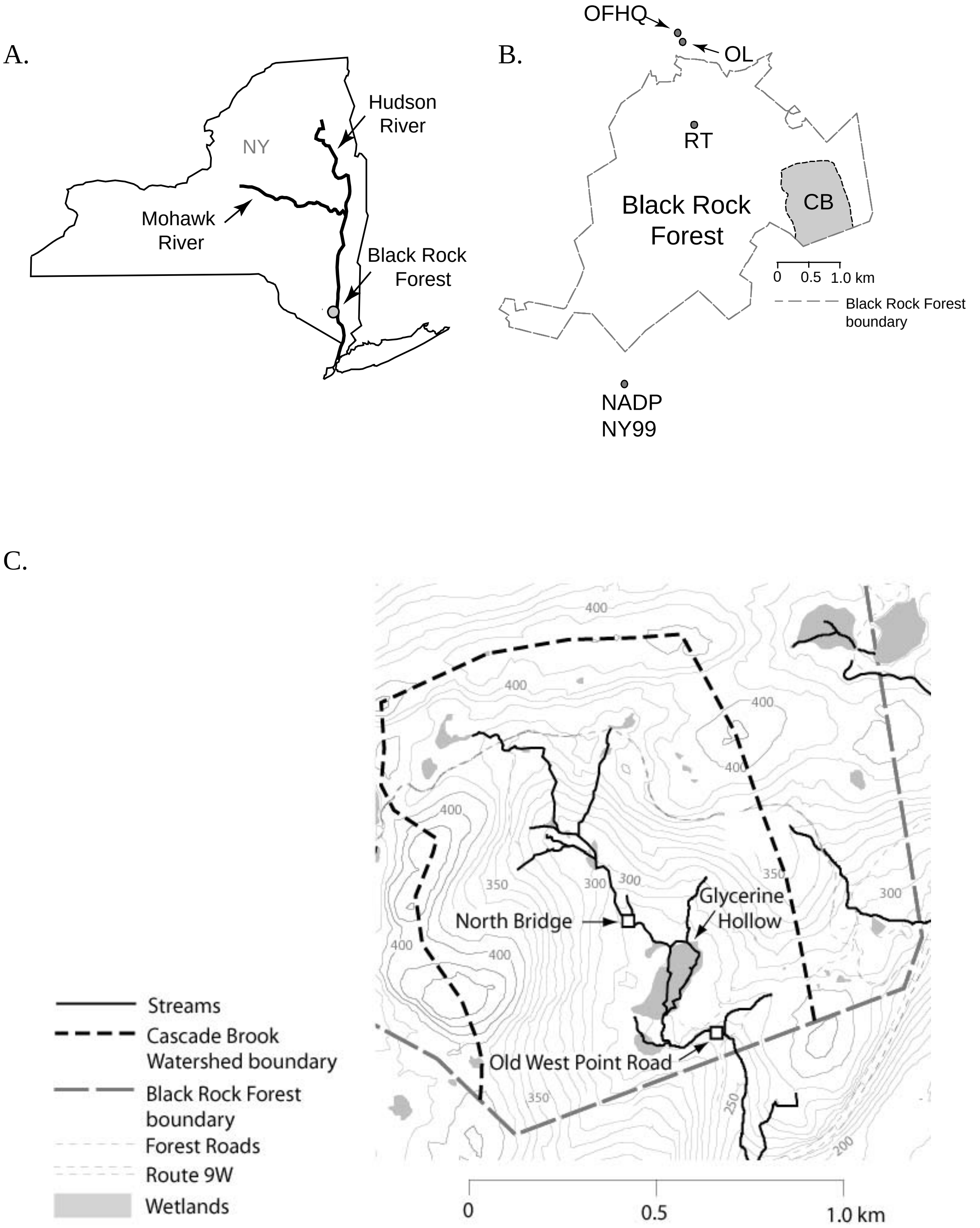
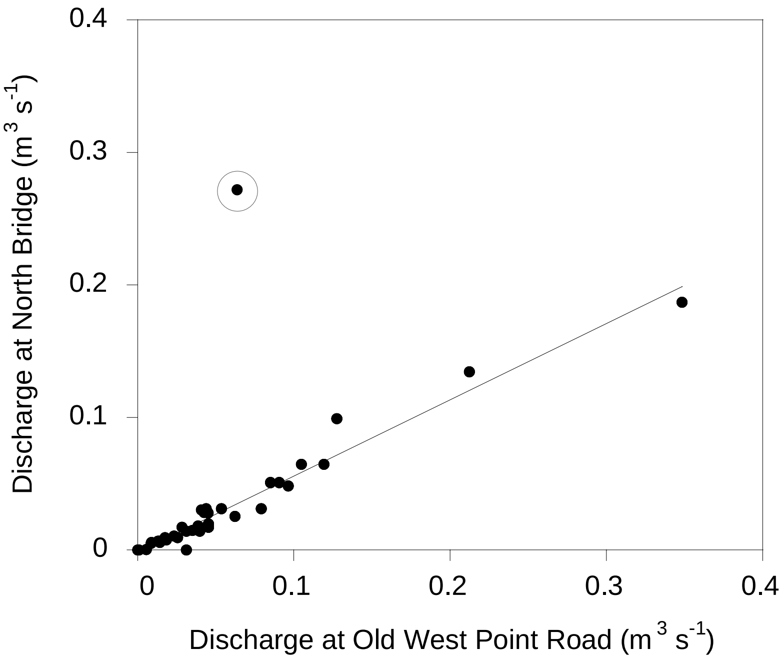

A.
NY
Hudson River
Mohawk River
Black Rock Forest
B.
OFHQ
OL
RT
Black Rock Forest
CB
0
0.5
1.0 km
Black Rock Forest boundary
NADP NY99
C.
400
350
300
250
200
North Bridge
Glycerine Hollow
Old West Point Road
Streams
Cascade Brook Watershed boundary
Black Rock Forest boundary
Forest Roads
Route 9W
Wetlands
0
0.5
1.0 km

Figure 2



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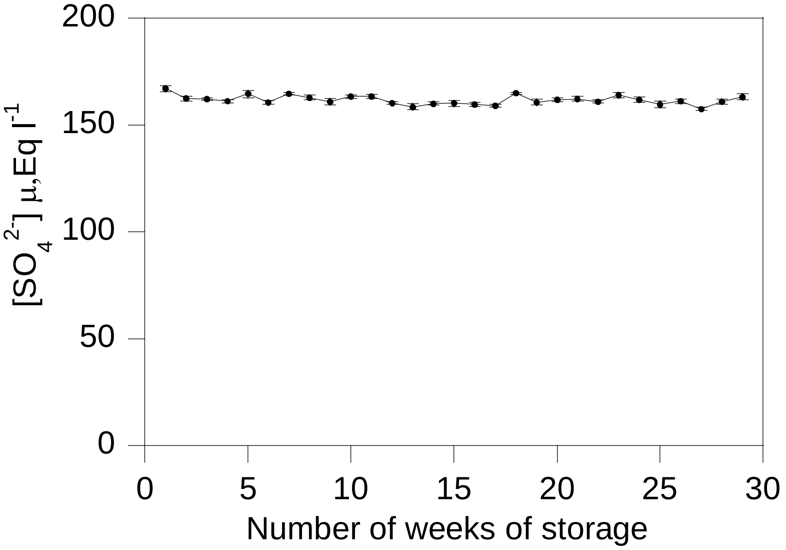

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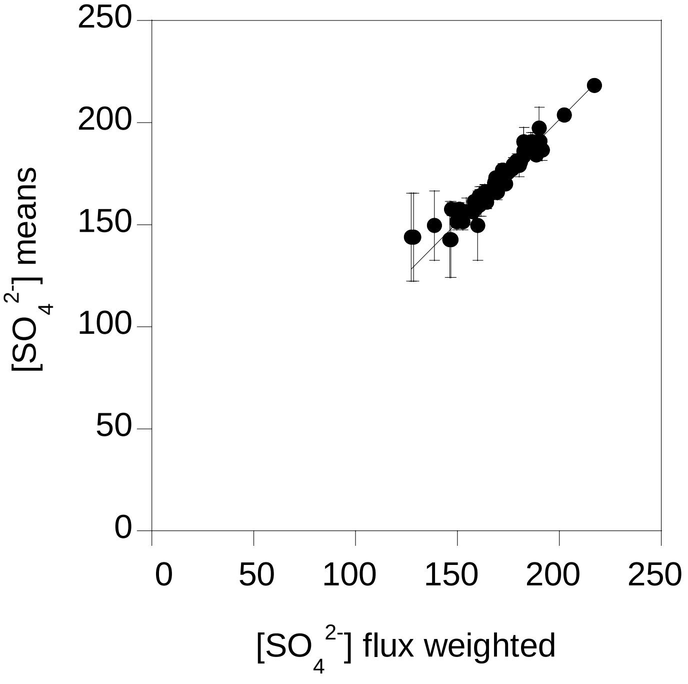

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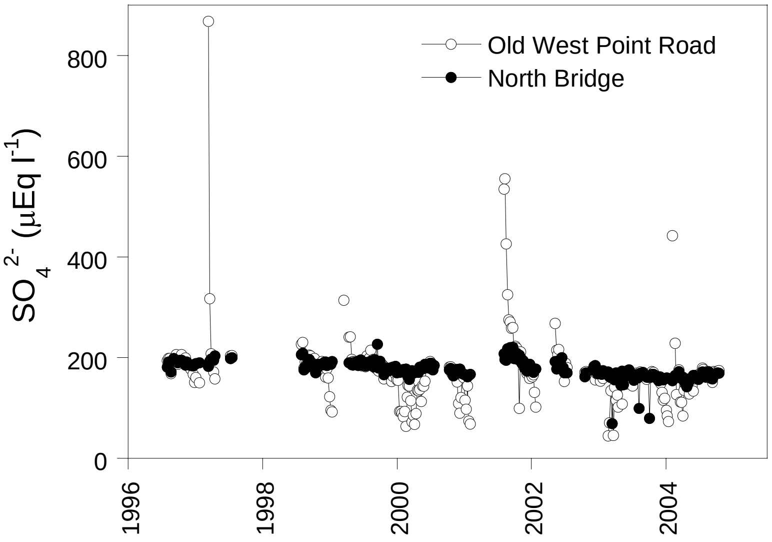


Figure 6

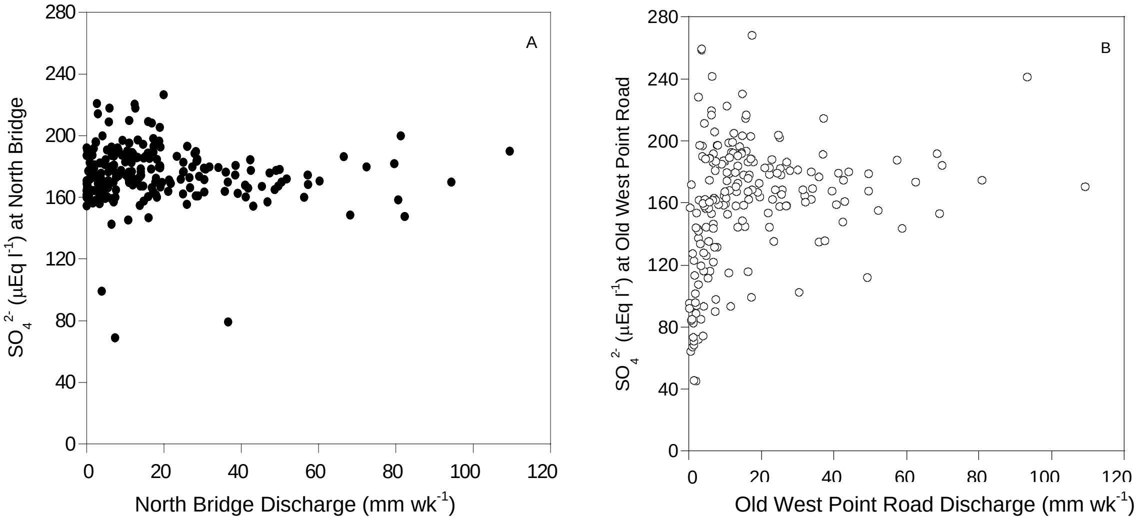

A
SO$_4^{2-}$ (µEq l^{-1}) at North Bridge
0
40
80
120
160
200
240
280
0
20
40
60
80
100
120
North Bridge Discharge (mm wk^{-1})
B
SO$_4^{2-}$ (µEq l^{-1}) at Old West Point Road
0
40
80
120
160
200
240
280
0
20
40
60
80
100
120
Old West Point Road Discharge (mm wk^{-1})

Figure 7

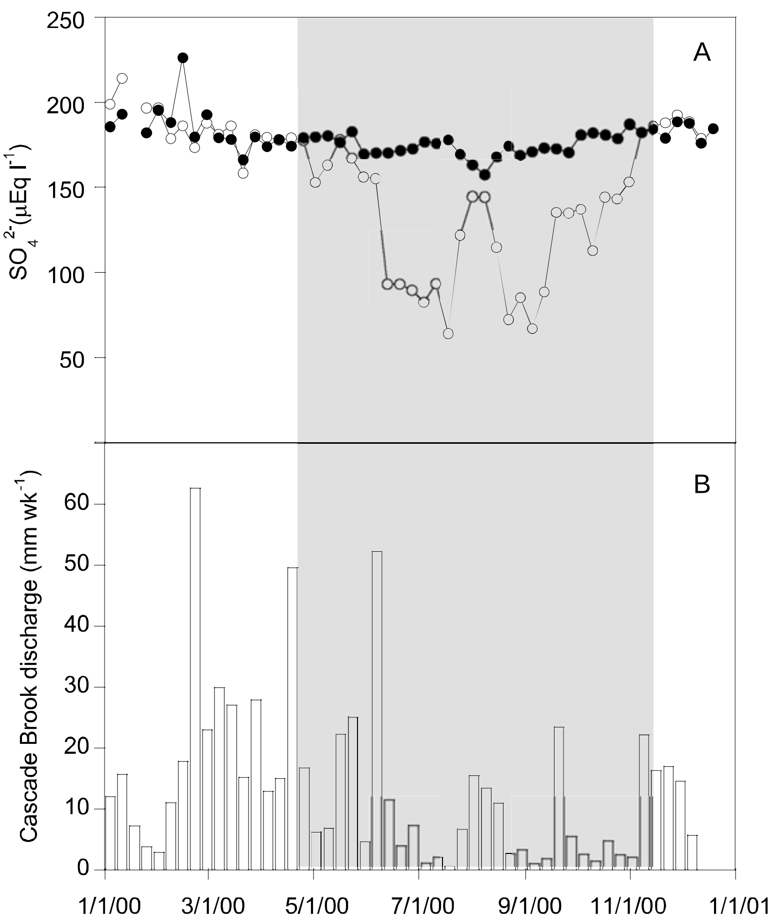

250
200
150
100
50
SO$_4^{2-}$(μEq l^{-1})
A
60
50
40
30
20
10
0
Cascade Brook discharge (mm wk^{-1})
B
1/1/00
3/1/00
5/1/00
7/1/00
9/1/00
11/1/00
1/1/01

Figure 8

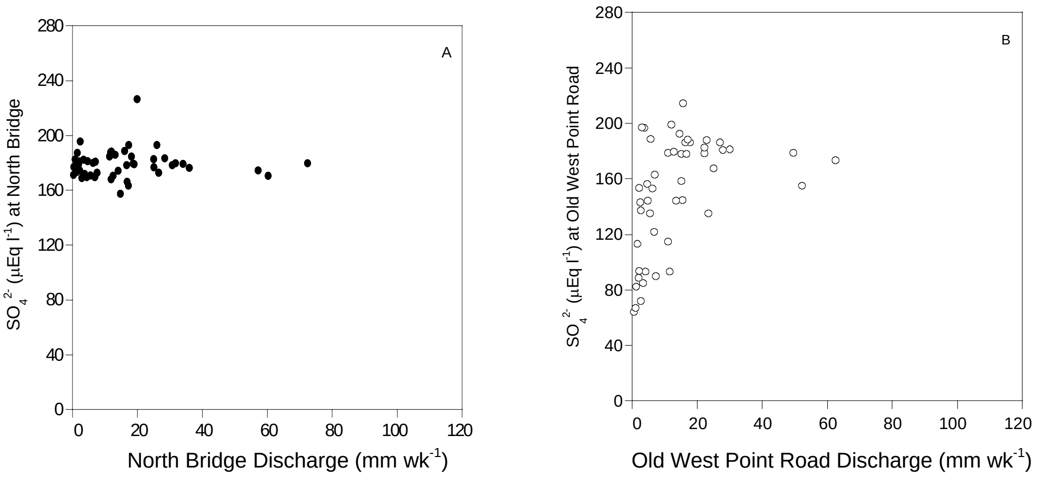

A
280
240
200
160
120
80
40
0
0
20
40
60
80
100
120
North Bridge Discharge (mm wk^{-1})
SO$_4^{2-}$ (µEq l^{-1}) at North Bridge
B
280
240
200
160
120
80
40
0
0
20
40
60
80
100
120
Old West Point Road Discharge (mm wk^{-1})
SO$_4^{2-}$ (µEq l^{-1}) at Old West Point Road

Figure 9

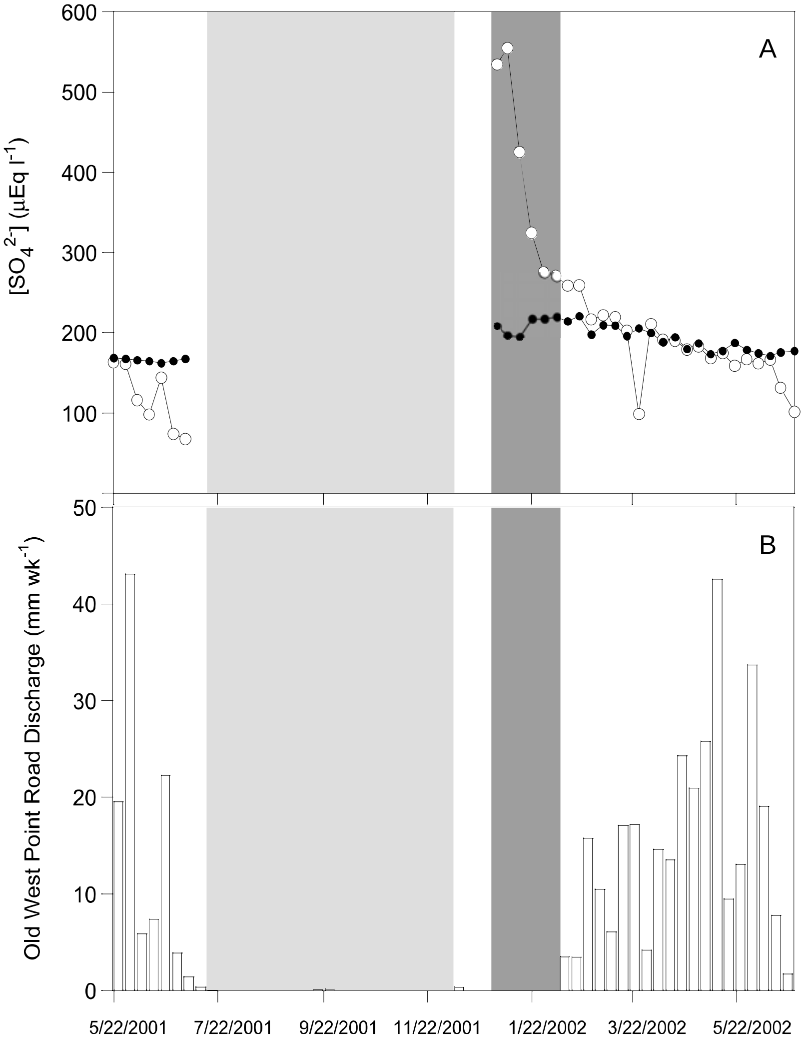

600
500
400
300
200
100
[SO$_4^{2-}$] (µEq l^{-1})
A
50
40
30
20
10
0
Old West Point Road Discharge (mm wk^{-1})
B
5/22/2001
7/22/2001
9/22/2001
11/22/2001
1/22/2002
3/22/2002
5/22/2002

Figure 10

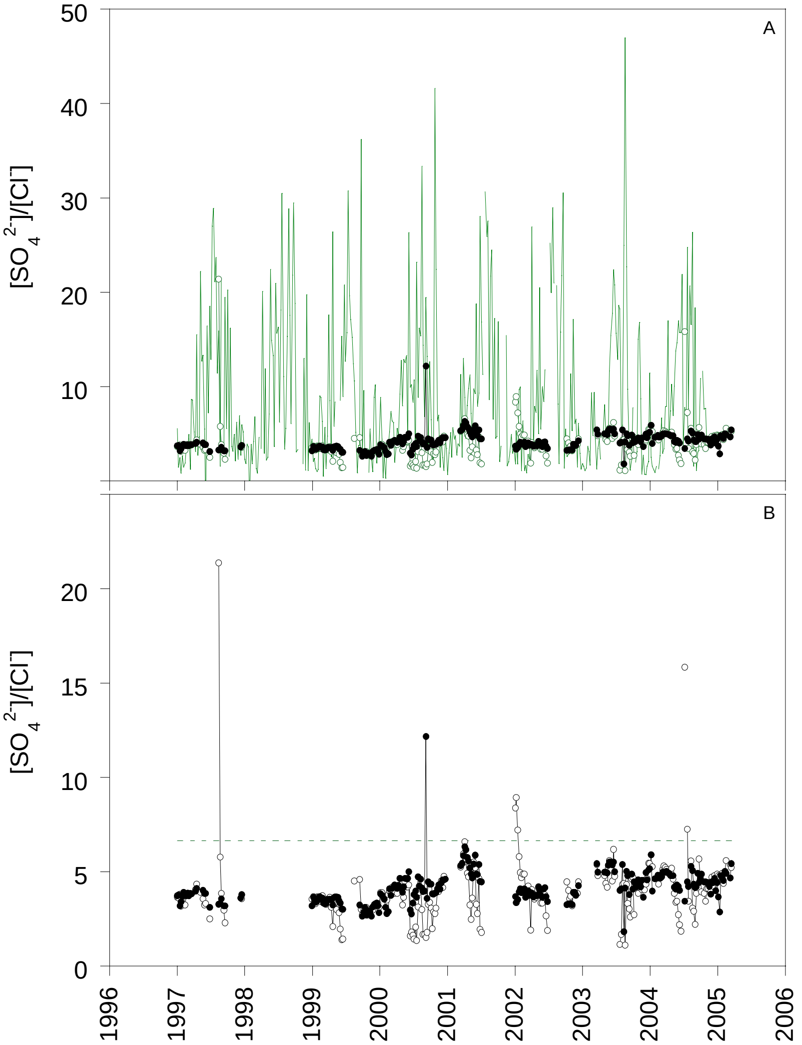


Figure 11

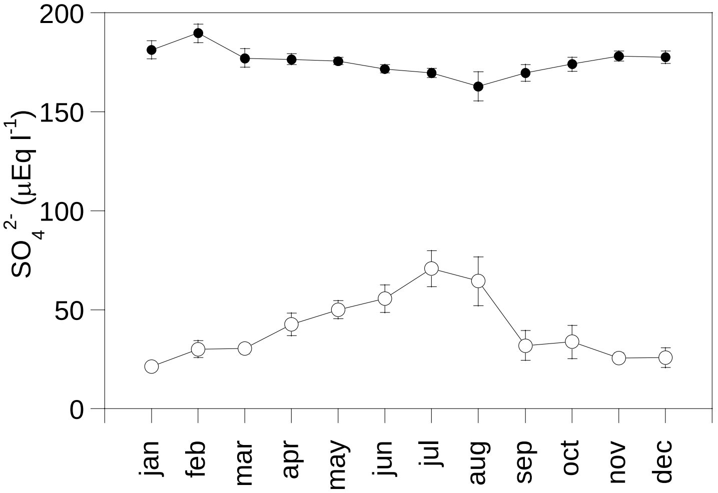


Figure 12

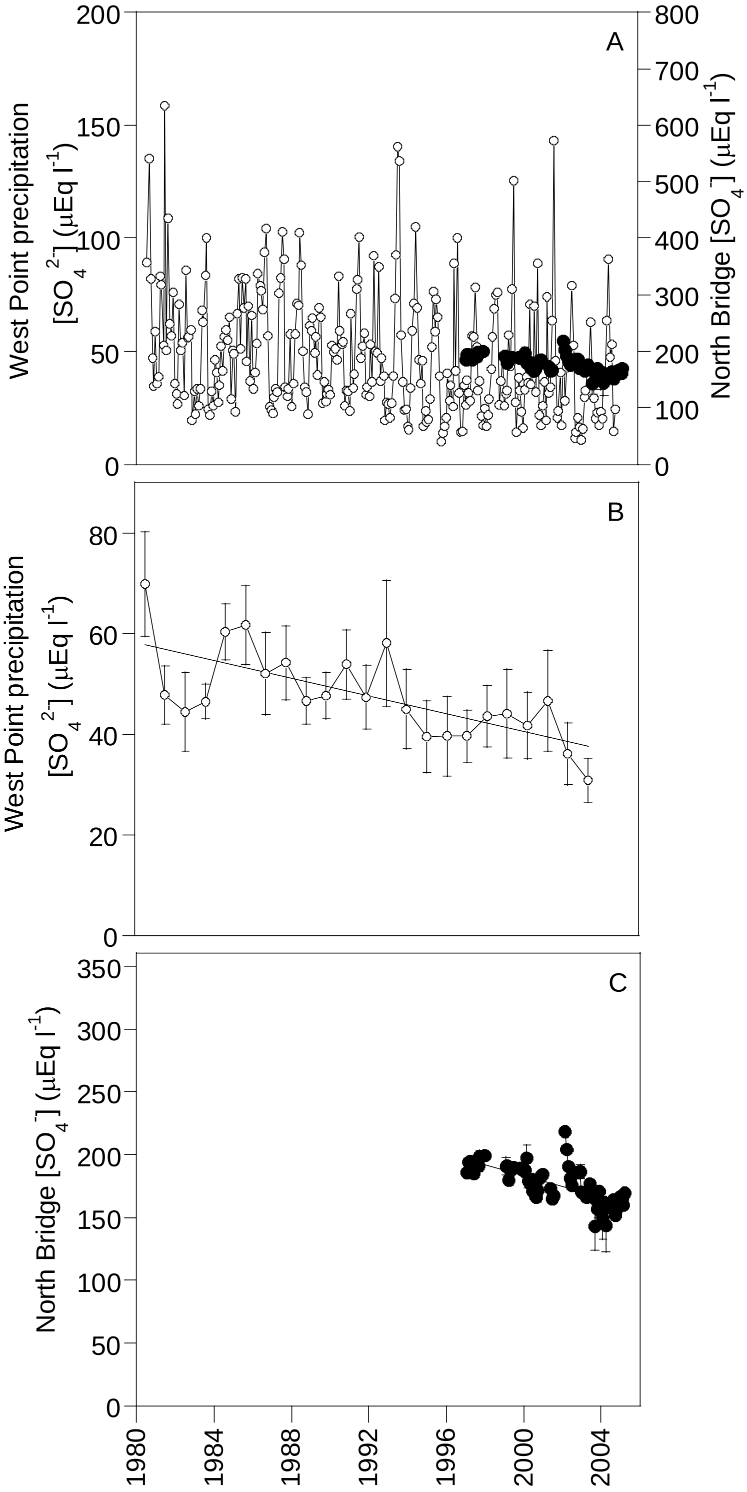
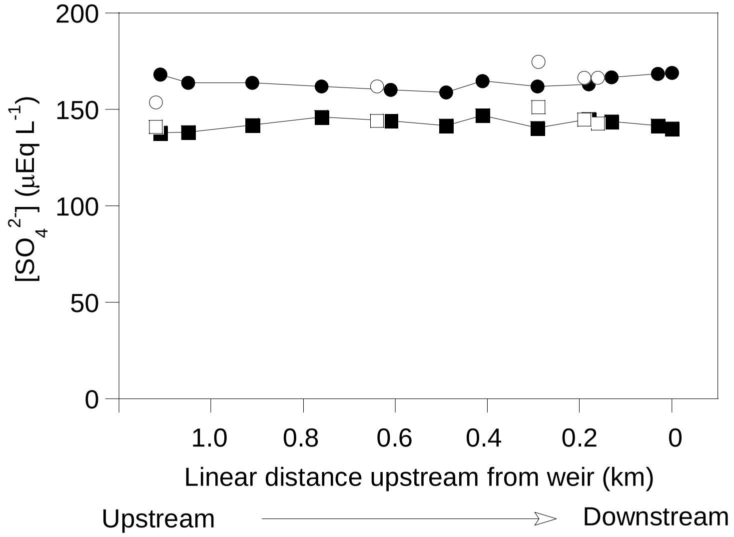

A
B
C
West Point precipitation [SO$_4^{2-}$] (μEq l^{-1})
North Bridge [SO$_4^{-}$] (μEq l^{-1})
0
50
100
150
200
0
100
200
300
400
500
600
700
800
0
20
40
60
80
0
50
100
150
200
250
300
350
1980
1984
1988
1992
1996
2000
2004

Figure 13


200
150
100
50
0
$[SO_4^{2-}]$ (μEq L^{-1})
1.0
0.8
0.6
0.4
0.2
0
Linear distance upstream from weir (km)
Upstream
Downstream

CONCLUSIONS AND POTENTIAL AREAS OF FUTURE RESEARCH

The research presented here attempts to quantify or constrain approximate magnitudes of deposition via precipitation of specific dissolved ions, cumulative dry deposition of relevant aerosols and gases and the export of corresponding ions in stream water from the Cascade Brook watershed within Black Rock Forest. As part of this effot, watershed mass balance budgets for Cl^- and SO_4^{2-} and atmospheric input budgets for NO_3^- and NH_4^+ wet deposition were developed. Cascade Brook is an excellent candidate for watershed studies because: 1) it is located in Black Rock Forest, which is a relatively pristine forested ecosystem within the Hudson Highlands of NY; 2) Black Rock Forest is relatively close (~70 km) to a huge urban center (NYC) and thus is vulnerable to potential impacts from industrial emissions; and 3) Black Rock Forest in general and Cascade Brook in particular host an expanding range of ongoing scientific investigations.

During the process of data collection and analysis much has been learned concerning the sources of a number of ions to and within this forested ecosystem, which has furthered our collective understanding of the cycling of these ions from atmospheric input to export via surface water discharge. In addition, the research presented here has brought to light several new questions that could be posed within Cascade Brook in an effort to build on what has been developed thus far.

Concerning Cl^- budgets, chapter 1 describes calendar month variability in Cl^- and Na^+ ions in precipitation measured at a precipitation monitoring station on the West Point Military Reservation, NY (~ 5 km from Cascade Brook). Concentration and wet deposition of these ions were appreciably greater during winter than summer months, a temporal pattern likely associated with the greater frequency of marine storms during cold seasons in the West Point area. Interestingly, calendar month variability in precipitation [Cl^-]/[Na^+] indicated that this ratio exceeded the [Cl^-]/[Na^+] seawater ratio throughout the year and reached a maximum of twice the seawater ratio during summer months. This suggests that sources in addition to unfractionated sea salt contribute significant amounts of Cl^- to total annual Cl^- wet deposition. Using the ratio of [Cl^-]/[Na^+] in seawater to estimate an annual amount of "excess" Cl^- as well as including a correction to account for terrestrial-derived Na^+, we conclude that as much as 24% (~ 1.17 kg ha^{-1} yr^{-1}) of annual Cl^- wet deposition to West Point, NY can be attributed to sources other than unfractionated sea salt. Regional sources known to contribute to atmospheric Cl^- include: 1) HCl emissions from coal combustion, 2) HCl emissions from industrial and domestic waste incineration, and 3) HCl produced by sea-salt dechlorination, which results from the interaction of sea-salt aerosols with acidic atmospheric gases (i.e. $H_2SO_4^{2-}$ and HNO_3). When two systematic errors associated with Na^+ contamination in the reported NADP data were take into account, the relative contributions to total excess Cl^- for each additional source of Cl^- ranged from: 29-50% for HCl emissions attributed to coal combustion, 5-9% for HCl emissions from waste incineration and 40-65% for HCl production as a result of sea-salt dechlorination.

With concentrations and fluxes of Cl^- delivered via precipitation documented on calendar month and interannual time scales, chapter 2 incorporated this input information with Cascade Brook surface water [Cl^-] and Cl^- export data to develop a Cl^- budget for the Cascade Brook watershed. There was much greater weekly and monthly variability in precipitation [Cl^-] than in surface water [Cl^-] owing to the integrating spatial and temporal effects of watershed soils and associated stream water [Cl^-]. Furthermore, in comparing the relative concentrations and wet deposition fluxes of precipitation and stream water Cl^-, appreciably greater concentrations and discharge fluxes of stream water Cl^- indicated that there was at least one other significant source of Cl^- contributing to Cascade Brook in addition to Cl^- input via rain and snow. Using a watershed mass balance approach, the magnitude of the "additional" source(s) in Cl^- export was 22 mEq Cl^- m^{-2} yr^{-1}, which was approximately twice the 11.7 mEq Cl^- m^{-2} yr^{-1} derived from wet deposition during the water years examined here. This amount (22 mEq Cl^- m^{-2} yr^{-1}) should represent an upper limit for Cl^- derived from dry deposition of Cl^- bearing aerosols and gases to Cascade Brook. However, we conclude that the "additional" flux of Cl^- may also include a significant contribution of Cl^- from mineralization of soil organic matter (SOM) formed during prior years with greater atmospheric deposition of Cl^- as probably occurred during the 1960's and 1970's. As a result, minimum values of 5.8 and 4.0 mEq Cl^- m^{-2} yr^{-1} were estimated for the contribution of dry deposition and SOM mineralization to Cl^- export, respectively. Finally, the mean monthly flux-weighted $[Cl^-]$ of Cascade Brook (44 ± 1.6 μEq l^{-1}) was compared to the $[Cl^-]$ of several other Hudson River tributaries in the region (560 - 6300 μEq l^{-1}). The concentrations in Cascade Brook within Black Rock Forest were significantly less than these other streams as well as for $[Cl^-]$ measurements taken along Highland Brook downstream of Black Rock Forest. These comparisons indicated that surface waters in the Cascade Brook catchment were relative unaffected by anthropogenic contamination, such as winter road salting and waste water effluent, both of which have been documented to have significantly affected a number of tributaries along the Hudson River.

In developing watershed budgets for SO_4^{2-}, the first step was to document decadal and calendar month patterns in precipitation [SO_4^{2-}] and wet deposition relevant to Cascade Brook. The resource for this data, the National Acid Deposition Program (NADP) precipitation monitoring station near West Point, NY also permitted the analysis of these same trends for H^+, NO_3^- and NH_4^+ delivered via precipitation. One motivation for assessing SO_4^{2-}, NO_3^- and H^+ was that wet deposition of these ions, which are associated with acidic deposition, could have significant negative impacts on sensitive terrestrial and aquatic ecosystems, particularly in the northeastern USA. NH_4^+ was also included for analysis to gain insights into fixed nitrogen deposition in addition to NO_3^- deposition. Calendar month trends in precipitation [H^+], [SO_4^{2-}] and [NO_3^-] and wet deposition consistently indicated minimum values during fall and winter with annual maximum occurring during summer months. This temporal pattern can be attributed primarily to the seasonal changes in rates of photochemical oxidation of SO_2 and NO_x gases in the troposphere. The seasonal pattern in [SO_4^{2-}]/[NO_3^-], with relatively low values during winter and relative high values during summer, was consistent with alternating high and low NO_x photochemical regimes; a pattern that has been measured at 16 other precipitation monitoring sites in the northeastern USA region. The annual maximum in [NH_4^+] and wet deposition occurred somewhat earlier than that for acidic ions, probably reflecting differences in emissions sources for NH_3 vs. SO_2 and NO_x gases. In general, contributions of NH_4^+-N to total N wet deposition were less than one third during the 1981-2003 measurement period, although the fraction of total fixed N contribution tended to increase in recent years. Long term trends in annual [H^+], [SO_4^{2-}], [NO_3^-] and wet deposition indicate appreciable decreases during 1981-2003 such that

$[H^+]$ is now probably at the lowest concentration measured at this location since the late 1930's. These significant decreases in precipitation $[H^+]$, $[SO_4^{2-}]$, $[NO_3^-]$ and wet deposition are comparable to the percentage decreases in SO_2 and NO_x emissions over similar time periods indicating that concentrations and wet deposition of ions associated with acid rain have been generally responsive to reductions in local and regional emissions of associated gases. Additionally, we estimate that per unit area, SO_4^{2-} wet deposition has been approximately 20% of regional and local SO_2 emissions per unit area, indicating that a significant amount of SO_4^{2-} could have been deposited regionally as dry deposition or as wet and dry deposition at locations beyond the northeastern USA.

We were also able to obtain independent estimates of annual S dry deposition from an Atmospheric Integrated Research Monitoring Network (AIRMoN) dry deposition station that was operated at the West Point Military Reservation during 1985-1997. This provided an opportunity to compare collocated wet and dry S deposition data during overlapping time periods since dry deposition measurements include a number of site-specific meteorological and vegetative characteristics. In brief, S dry deposition fluxes for SO_2-S and SO_4^{2-}-S, derived by the AIRMoN network, were the product of locally measured atmospheric concentrations of SO_4^{2-} and SO_2 and modeled deposition velocities derived from a multi-layer forest canopy model specific for each S species. In analyzing interannual trends in wet and dry S deposition during 1985-1997, there was appreciable coherence between wet and dry fluxes, which is noteworthy because measured parameters for each flux were quite dissimilar and independent. Over the 9 years examined in detail, average annual wet S deposition (8.9 kg S ha^{-1} yr^{-1}) was ~ twice the annual average for total S dry deposition (SO_2-S + SO_4^{2-}-S) (4.3 kg S ha^{-1} yr^{-1}). It may be possible to use this ~ 2:1 relationship between S wet deposition and total S dry deposition during years when only S wet deposition data are available. Additionally, S wet deposition displayed greater calendar month variability than total S dry deposition, which was relative constant throughout the calendar year. Total S dry deposition was dominated by SO_2-S, probably as a result of more local sources for SO_2 as well as a shorter atmospheric residence times and thus greater deposition velocities for SO_2 than SO_4^{2-}. Regionally, dry S deposition estimates reported for the site near West Point, NY represent an intermediate flux compared to those measured at a location in central PA, which reports generally higher seasonal deposition velocities and ~ 2-fold greater SO_2 emissions per unit area than measured in NY state and a more remote site in northern NY, which reported comparatively low annual atmospheric S concentrations.

Finally, we examined S wet and dry deposition data with surface water [SO_4^{2}] and SO_4^{2-}-S export data for Cascade Brook to develop S watershed budgets. In the process, we established that [SO_4^{2-}] measured upstream and downstream of the Glycerine Hollow wetlands within Cascade Brook had appreciable temporal differences, with [SO_4^{2-}] upstream of the wetlands relatively insensitive to discharge amount and [SO_4^{2-}] downstream of the wetlands much more sensitive to discharge amount, particularly during low discharge events. This pattern of spatial and temporal variability was consistent with sulfate reduction in the wetlands during low flow periods, followed by re-oxidation of previously reduced sulfur during drought conditions within Cascade Brook. Elevated [SO_4^{2-}] were subsequently measured when stream discharge rates increased again. During water years 1999-2000, 2002-2003 and 2003-2004 we estimate that annually ~ 3.0 kg S ha^{-1} yr^{-1} or ~ 12% of the sulfate measured upstream of the wetlands was “temporarily” stored within the wetlands. Additionally, mean annual S export amount for these two sites were ~ 25 and 22 kg S ha^{-1} yr^{-1} upstream and downstream of the wetlands, respectively. These amounts of S export were 3.1 and 2.8 times the corresponding 8.0 kg S ha^{-1} yr^{-1} S wet deposition for the same years, indicating that there was at least one significant additional source of S to Cascade Brook during this period. If all “excess” S export was attributed to S dry deposition, an annual average of ~ 14-17 kg S ha^{-1} yr^{-1} would be incident to Cascade Brook. However, these estimates should probably be considered as upper limits for S dry deposition, and are 3.5 - 4.3 times the rate of S dry deposition estimated by the DDIM. We therefore conclude that although S wet and dry deposition are probably the dominant sources of inorganic S to Cascade Brook, there are additional mechanisms that may contribute measurable amounts of S to Cascade Brook, including the chemical weathering of previously accumulated S bearing minerals, the desorption of SO_4^{2-} from mineral soils and the mineralization of soil organic matter sulfur.

On the basis of the research presented here, some promising areas of future work relevant to Cascade Brook include:

1) Continued examination of Cl^-, Na^+, H^+, SO_4^{2-}, NO_3^- and NH_4^+ ions in precipitation as measured by the NADP precipitation monitoring station at West Point, NY (NY99). Interannual and calendar month trends in these ions indicate a variety of interesting patterns. Inclusion of additional years of data could increase our understanding of the response of these ions to source strength and to regional processes known to affect the concentration of these ions in precipitation.

2) Cl^- and SO_4^{2-} ion budgets for the Cascade Brook catchment could be assessed with more confidence if data for additional water years were available. With continued measurement of stage height at the Cascade Brook weir coupled with systematic chemical analysis of stream water samples, export budgets for additional years could be compared with those documented thus far. This would allow for better long-term "average" export to wet deposition ratios as well as a better understanding of the interannual variability in the magnitude of these fluxes.

3) As presented in Chapter 5, $[SO_4^{2-}]$ at North Bridge and Old West Point Road differ appreciably, with concentrations at Old West Point Road indicating hydrologically mediated sensitivity to reduction and oxidation reactions within the upstream Glycerine Hollow wetlands. Measurement of $\delta^{34}S$ of stream water $[SO_4^{2-}]$ for North Bridge and Old West Point Road could offer insights into the magnitude of this mechanism at Cascade Brook. During summer low flow periods, when $[SO_4^{2-}]$ measured at Old West Point Road was lower than that at North Bridge, if reduction of SO_4^{2-} were occurring in the wetlands, which preferentially removes lighter isotopes, one would expect that $\delta^{34}S$ of $[SO_4^{2-}]$ measured at Old West Point Road would be heavier than that measured at North Bridge. Conversely, during higher discharge events following drought conditions, $[SO_4^{2-}]$ at Old West Point Road was significant greater than at North Bridge. If additional SO_4^{2-} were

derived from oxidation of previously reduced SO_4^{2-} within the wetlands, the $\delta^{34}S$ would reflect influx of lighter isotopes and thus the $\delta^{34}S$ in SO_4^{2-} at Old West Point Road would be expected to be lighter than at North Bridge.

4) Additional evidence for these process may also be derived from measurements of $\delta^{34}S$ in the upper peat layers of the wetlands. If reduction of SO_4^{2-} had occurred one would expect to see shallow layers of wetland cores with an elevated percentage of S and relatively low $\delta^{34}S$.

5) Also presented in chapter 5, mineralization of soil organic matter is proposed as a potentially significant source of SO_4^{2-} to stream water SO_4^{2-} export. Comparison of $\delta^{18}O$ of precipitation and stream water SO_4^{2-} could be useful for assessing the magnitude of this mechanism. If a significant amount of SO_4^{2-} were cycled through organic material prior to release in stream water, the $\delta^{18}O$ value of stream water SO_4^{2-} would be expected to be lower than that of precipitation SO_4^{2-} since the oxygen in surface water SO_4^{2-} would be introduced during the oxidation of organic sulfur and primarily derived from soil water oxygen which has a lighter $\delta^{18}O$ signature than atmospheric oxygen.

6) Data presented in Appendix A suggests that deicing road salt applied to paved roads proximal to Highland Brook may be the dominant source for significant increases in [Cl^-] as a function of distance downstream. Information concerning the amounts and composition of the road salt

applied in and around Highland Falls would aid in selecting which cations could be most helpful to measure in these stream water samples to examine whether the spatial patterns in cations were similar to those for Cl^-. If, for example, road salts were primarily NaCl, then analysis of the [Na^+] in the stream water measured at each of the 12 locations along the transect from Cascade Brook through the town of Highlands Falls could offer additional evidence to support or refute the road salt hypothesis.

7) Chapters 3, 4 and 5 have specifically included estimates of dry deposition using an atmospheric parameter model (for S) or watershed mass balance approaches (for Cl^- and S). A third method of quantifying dry deposition is by measuring the net throughfall flux (throughfall – precipitation). It would be possible to set up throughfall collectors within the Black Rock Forest canopy during the growing season and in conjunction with the ion chemistry measured at nearby NADP NY99, a net throughfall flux measurements could be derived for Cl^- and SO_4^{2-} and compared to other approaches described here.

8) Another important area of research would be to continue to develop nitrogen budgets for Cascade Brook. Precipitation inputs of NO_3^- and NH_4^+ offer a start in assessing the magnitude of these fluxes to the forest. A first order estimate of dry deposition contribution of particulate NO_3^- and nitric acid vapor could be made from the AIRMoN data set utilized here for S dry deposition. Stream water samples at

North Bridge and Old West Point Road rarely indicate a significant soluble transport of NO_3^- out of the Cascade Brook watershed. This suggests that nitrogen deposited to the forest is either immobilized as organic or inorganic material within the forest or that nitrogen is exported from the forest as NH_4^+ or as soluble and particulate organic material.

APPENDIX A

Chloride concentrations in Cascade and Highland Brooks; the evolution from a pristine forested stream to one dominated by road salt.

Introduction

Measuring surface water [Cl^-] within Cascade Brook offers the opportunity to document "background" levels of chloride within a relatively pristine watershed. Such concentrations can be compared to [Cl^-] of surface waters elsewhere, which may be influenced by anthropogenic sources such as winter road salting and effluent from wastewater treatment plants. Measurements of [Cl^-] of a number of Hudson River tributaries in the region indicate that substantial contamination attributed to these sources has occurred (Godwin, *et al.*, 2003; Hauser, 2004; Kaushal, *et al.*, 2005; Nieder, 2005). Elevated concentrations of Cl^- can have detrimental effects on nearby vegetation and vegetative communities (Hofstra, *et al.*, 1979; Panno, *et al.*, 1999; Viskari, Karenlampi, 2000; Richburg, *et al.*, 2001). In this study, Cl^- concentrations were measured in stream water samples along Highland Brook near Highland Falls, NY, as well as from three tributaries to Highland Brook, including Cascade Brook. Trends in [Cl^-] from very low concentrations within the Cascade Brook catchment of Black Rock Forest to greatly elevated concentrations along the Highland Brook stream downstream of Cascade Brook were observed.

Methods

On June 23, 2005, stream water samples were collected at six sites along the stream axis of Highland Brook, which runs parallel to Route 293, then winds alongside route 9W and along other paved roads through the village of Highland Falls and eventually discharges into the Hudson River (Fig. 1). An additional six stream water samples were taken from three Highland Brook tributaries: Cascade Brook, Stoney Lonesome Brook and stream discharge from Beaver's Pond. At each of the twelve sampling sites, electrical conductivity (EC) was measured with a hand-held field conductivity meter (WTW Cond 330i/SET, Germany), and a stream water sample was collected in a 250 ml HDPE bottle. Latitude and longitude coordinates were estimated with a handheld GPS (Garmin, 12CX) at each of the twelve sampling sites. Following fieldwork, conductivity and pH were measured in the Black Rock Forest wet lab after which samples were filtered using 0.4 μm Whatman® nuclepore® polycarbonate membranes. Samples were refrigerated (3-4°C) prior to analysis by ion chromatograph (Dionex, DX-100; Dionex Corporation, Sunnyvale, CA), which occurred within a week of sample collection.

Additionally, on May 18, 2005 a similar stream water sampling effort was conducted using identical methods as described above to collected and analyze stream water samples along Cascade Brook, Highland Brook and Stoney Lonesone Brook (Table 2). Similar results and conclusions can be drawn from the data collected on May 18 during which stream discharge was estimated to be 0.41 mm day^{-1} (Table 2). For the sake of simplicity, results for the June 23, 2005 transect are discussed herein.

Results

On june 23, 2005, [Cl^-] measured at the Cascade Brook weir gauging station was the minimum [Cl^-] measured among all 12 sampled locations (31.1 μEq l^{-1}) (site 1) (Fig. 1). [Cl^-] increased 19-fold along Cascade Brook prior to merging with Highland Brook from the minimum concentration of 31.1 μEq l^{-1} to a concentration of 592 μEq l^{-1} measured at a culvert adjacent to route 9W (site 3). The [Cl^-] of Highland Brook prior to merging with discharge from Cascade Brook was 886 μEq l^{-1} (site 4), which then decreased slightly to 805 μEq l^{-1} once the two water sources merged (site 5). The [Cl^-] of Highland Brook increased to 1,120 μEq l^{-1} further downstream at a site along route 9W (site 8), situated proximal to the Highland Falls Water Department. The Cl^- concentrations of the Stoney Lonesome Brook tributary to Highland Brook were the highest concentrations measured among all sites at 6,420 μEq l^{-1} and 6,210 μEq l^{-1} mid-stream and down-stream along Stoney Lonesome Brook, respectively (sites 6 and 7). Subsequent to discharge from Highland Brook merging with that from Stoney Lonesome Brook, [Cl^-] measured 3,090 μEq l^{-1} (site 9). A third tributary to Highland Brook was situated ~ 0.08 km downstream of where Stoney Lonesome Brook merged with Highland Brook (site 10). This tributary, which is derived from Beaver’s Pond, had a [Cl^-] of 135 μEq l^{-1}. The [Cl^-] of Highland Brook was 4,200 μEq l^{-1} (site 12) after traveling through the village of Highland Falls, NY prior to discharging into the Hudson River.

[Cl^-] μEq l^{-1} vs. distance (km) downstream from the Cascade Brook weir (Fig. 2A) for all samples taken on June 23, 2005 as well as samples taken within Cascade Brook during February 11, 2005 and March 29, 2005 indicate the high degree of variability for [Cl^-] beyond the Cascade Brook watershed along Highland Brook. [Cl^-]

from the Stoney Lonesome Brook and input from the Beaver's Pond indicate high and low concentrations, respectively along the transect relative to Highland Brook [Cl$^-$]. Similar patterns can be seen in the Electrical Conductivity (μS cm^{-1}) vs. distance (km) relationship for the same samples (Fig. 2B).

Conclusions

The very low [Cl$^-$] measured in Cascade Brook within Black Rock Forest indicates that stream water in Cascade Brook is apparently unaffected by anthropogenic sources of Cl$^-$ such as winter road salting or wastewater effluent. Concentrations of Cl$^-$ increased along Cascade Brook as proximity to Route 9W increased, reaching a maximum of 592 μEq l^{-1} at a culvert adjacent to 9W. Once discharge from Cascade Brook merged with that from Highland Brook, a small decrease in Highland Brook [Cl$^-$] indicates a modest dilution of Highland Brook [Cl$^-$] from mixing with the less concentrated [Cl$^-$] of Cascade Brook stream water. Assuming a simple two-end member mixing model utilizing [Cl$^-$] of Cascade Brook and Highland Brook, water discharge amount from Cascade Brook accounts for ~ 27% of total discharge once Cascade Brook and Highland Brook merged. [Cl$^-$] increased somewhat from 805 μEq l^{-1} to 1,120 μEq l^{-1} as Highland Brook traveled 1.2 km downstream (Fig. 1).

The [Cl$^-$] along the Stoney Lonesome Brook tributary was ~ five times that of Highland Brook [Cl$^-$] prior to merging with Stoney Lonesome Brook discharge and ~ 200 times that of the lowest [Cl$^-$] measured in Cascade Brook. The gradient in [Cl$^-$] along Stoney Lonesome Brook indicates that concentrations decreased somewhat as a function of distance downstream in Stoney Lonesome Brook. The source for the relatively high [Cl$^-$] in Stoney Lonesome Brook has not been established. The headwaters for Stoney

Lonesome Brook are located within the West Point Military Reservation. The [Cl^-] for Highland Brook had a relatively high value of 4,200 μEq l^{-1} just prior to discharging into the Hudson River. This [Cl^-] was ~ 135 times that of the lowest [Cl^-] measured in Cascade Brook.

We conclude that patterns of increases in [Cl^-] as discussed here for measurements made on June 23, 2005 along Cascade Brook and Highland Brook are consistent with substantial influence from anthropogenic Cl^- influx to surface water downstream of the pristine Black Rock Forest catchments, likely from application of deicing salts on paved roads during winter months. This proposed source appears to result in an increase in [Cl^-] measured along Highland Brook, which is proximal to route 293, 9W and other paved roads and therefore highly vulnerable to contamination from deicing salt application. In comparison to the [Cl^-] measured along Highland Brook, the [Cl^-] within the Cascade Brook watershed indicates that Cascade Brook is quite pristine and unaffected by anthropogenic sources such as winter road salting. Similar conclusions can be draw from the [Cl^-] of stream water samples collected at the same sites during May 18, 2005 (Table 2). The May 18, 2005 data corroborate that stream water within Cascade Brook is relatively pristine and that the elevated [Cl^-] along Highland Brook associated with possible contamination from deicing salts is a dominant effect during more than one sampling period.

Future work

There are two general areas for future research that would contribute appreciably to the understanding of the data presented here:

1) Detailed accounts of the amounts, composition and distribution (amount and timing) of road salts applied to routes 293, 9W and other paved roads proximal to Highland Brook during a number of years. This information would assist in examining the working hypothesis outlined here that deicing salts are primarily responsible for the steep downstream gradient in [Cl^-] measured from Cascade Brook to Highland Brook and eventually to the Hudson River.
2) Stream velocities should be measured to estimate discharge of Highland Brook at a number of sampling sites along the transect as well as the relative discharge of each of the three tributaries. For example, it would be interesting to know relative discharge for the Stoney Lonesome Brook compared to Highland Brook, considering the large disparity in [Cl^-] between these two water sources. Discharge normalized for watershed area from Cascade Brook as measured at the weir gauging station for the 24 hours of 6/23/05 was 0.39 mm day $^{-1}$.

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Table Captions

Table 1: Latitude, longitude, [Cl$^-$], electrical conductance and pH measured for samples from Cascade Brook, in Black Rock Forest through the town of Highland Falls, NY. During June 23, 2005. Sampling sites are correspondingly identified on map.

Table 2: Latitude, longitude, [Cl$^-$], electrical conductance and pH measured for samples from Cascade Brook, in Black Rock Forest through the town of Highland Falls, NY. During May 18th, 2005. Sampling sites are correspondingly identified on map with the exception of site 13 which is a site upstream on the Stoney Lonesome Brook.

Table 1

Sampling Site	Latitude (N)	Longitude (W)	Cl^- (μEq/L)	Cl^- (mg/L)	Field Conductance μS/cm	Lab Conductance μS/cm	pH
1	41 23.666	73 59.828	31.1	1.10	n/a	29.7	5.80
2	41 23.304	73 59.727	73.3	2.6	35.8	36.9	6.20
3	41 23.147	73 59.683	592	21.0	138.1	147	6.70
4	41 23.121	73 59.734	886	31.4	202	196	6.90
5	41 23.039	73 59.673	805	28.5	188	201	6.70
6	41 22.700	73 58.897	6420	228	954	970	7.20
7	41 22.586	73 58.856	6210	220	914	959	7.40
8	41 22.593	73 58.893	1120	39.8	236	234	7.20
9	41 22.567	73 58.827	3090	109	496	492	7.20
10	41 22.541	73 58.775	135	4.8	n/a	56.1	6.20
11	41 22.234	73 58.261	2478	87.8	n/a	414	7.30
12	41 22.226	73 57.788	4200	149	n/a	574	7.20

Table 2

Sampling Site	Latitude (N)	Longitude (W)	Cl^- (μEq/L)	Cl^- (mg/L)	Field Conductance μS/cm	Lab Conductance μS/cm	pH
1	41 23.666	73 59.828	32.1	1.14	30.6	30.7	5.9
2	41 23.304	73 59.727	58.4	2.07	34.3	31.9	6.0
3	41 23.147	73 59.683	758	26.9	133	137	6.5
4	41 23.121	73 59.734	1208	42.8	233	220	7.2
5	41 23.039	73 59.673	1080	38.2	222	214	7.1
6	41 22.700	73 58.897	5522	196	794	786	7.3
7	41 22.586	73 58.856	4912	174	772	737	7.4
8	41 22.593	73 58.893	1116	39.6	223	208	7.3
9	41 22.567	73 58.827	2320	82.3	398	399	7.3
10	41 22.541	73 58.775	n/a	n/a	n/a	n/a	n/a
11	41 22.234	73 58.261	1870	33.3	352	334	7.3
12	41 22.226	73 57.788	2588	91.8	441	418	7.3
13	41 23.011	73 58.805	6304	224	973	917	7.3

Figure captions

Figure 1: Approximate locations for stream water samples (1-12) taken on June 23, 2005.

Figure 2: A) [Cl$^-$] μEq l^{-1} vs. distance (km) from the headwater of Cascade Brook; and B) EC μS cm^{-1} vs. distance (km) from the headwater of Cascade Brook. For both figures: Cascade Brook data (filled squares) for transects conducted within Cascade Brook on February 11, 2005 and March 29, 2005. On June 23, 1005 samples were collected from the headwater of Cascade Brook downstream to the culvert near 9W (site 3) (open circles), additional samples were collected along Highland Brook (filled circles), Stoney Lonesome Brook (filled triangles) and from stream water originating from Beaver's Pond (open triangles). The arrow indicats the location of the Cascade Brook weir.

Figure 1

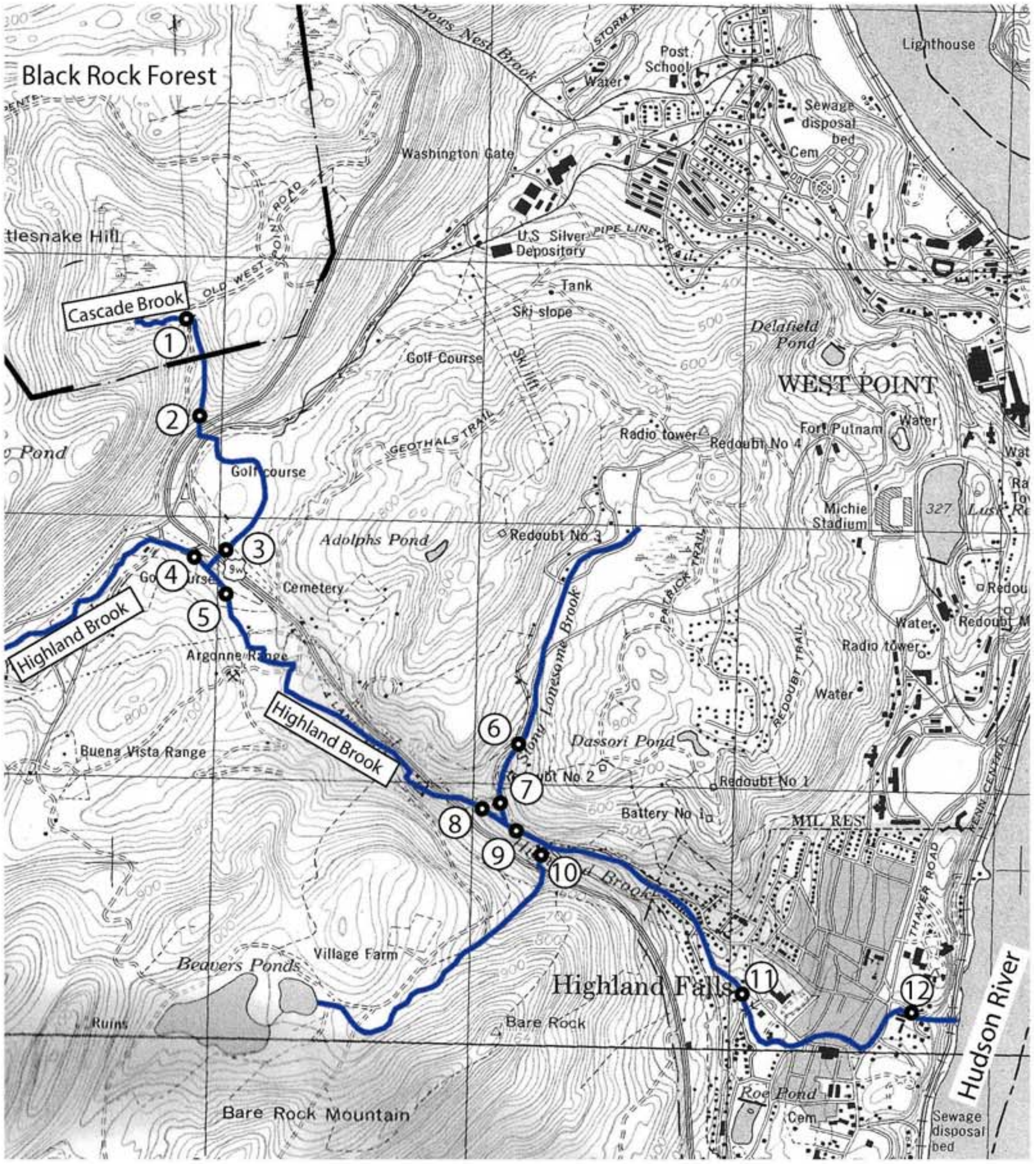
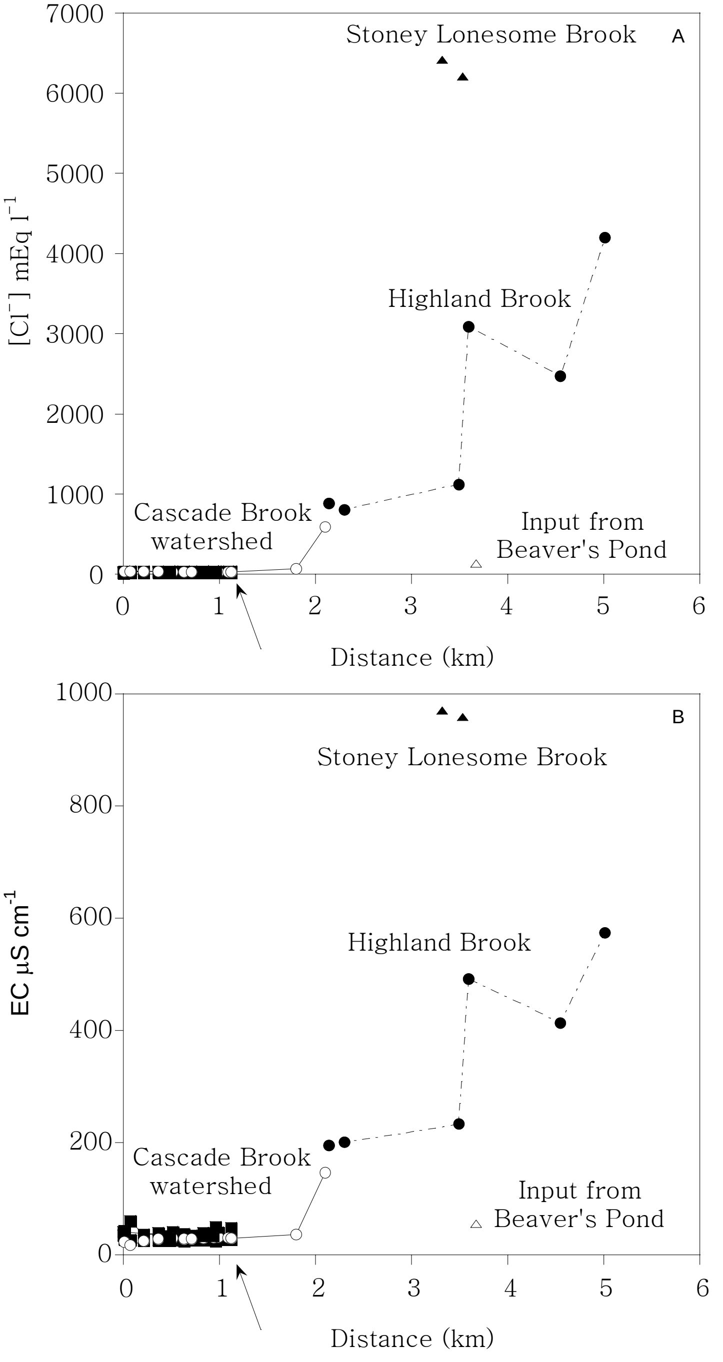

Black Rock Forest
Cascade Brook
Highland Brook
Highland Brook
Hudson River
West Point
Highland Falls
Washington Gate
U.S. Silver Depository
Golf Course
Golf course
Adolphs Pond
Redoubt No 3
Cemetery
Argonne Range
Buena Vista Range
Lonesome Brook
Dassori Pond
Redoubt No 2
Redoubt No 1
Battery No 1
Delafield Pond
Radio tower
Redoubt No 4
Fort Putnam
Michie Stadium
Beavers Ponds
Village Farm
Bare Rock
Bare Rock Mountain
Roe Pond
Lighthouse
Post School
Sewage disposal bed
Ski slope
Tank
1
2
3
4
5
6
7
8
9
10
11
12

Figure 2


A
Stoney Lonesome Brook
Highland Brook
Cascade Brook watershed
Input from Beaver's Pond
[Cl⁻] mEq l⁻¹
7000
6000
5000
4000
3000
2000
1000
0
Distance (km)
0
1
2
3
4
5
6
B
Stoney Lonesome Brook
Highland Brook
Cascade Brook watershed
Input from Beaver's Pond
EC µS cm⁻¹
1000
800
600
400
200
0
Distance (km)
0
1
2
3
4
5
6

APPENDIX B

New Phytologist

Research

Response of *Xanthium strumarium* leaf respiration in the light to elevated CO_2 concentration, nitrogen availability and temperature

J. B. Shapiro[1], K. L. Griffin[1], J. D. Lewis[2] and D. T. Tissue[3]

[1]Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA; [2]Louis Calder Center and Biological Station, Department of Biological Sciences, Fordham University, Armonk, NY 10504, USA; [3]Department of Biology, Texas Tech University, Lubbock, TX 79409, USA

Author for correspondence:
J. B. Shapiro
Tel: +44 1845 3658395
Fax: +44 1845 3658150
Email: jbs59@ldeo.columbia.edu

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Summary

- The leaf-level response of respiration in the light (R_L) is a vital component of a plant's energy and carbon balance.
- *Xanthium strumarium* (common cocklebur) plants were grown in various combinations of CO_2, nitrogen and temperature, and R_L was measured using the Kok effect method.
- R_L was significantly lower than respiration in the dark (R_D), with the lowest percentage inhibition in the elevated CO_2, high-N treatment. In general R_L increased in response to increased CO_2 concentration and N availability across all temperature treatments. However, there was a significant interactive effect of growth CO_2 concentration and measurement temperature on R_L which indicated that R_L responded more positively to temperature changes in elevated CO_2 conditions. Additionally, across all CO_2 and N treatments the percentage of respired C with respect to assimilated C increased as temperature increased.
- Collectively, these results improve our understanding of the magnitude and sensitivity to foreseen environmental changes of mitochondrial respiration during light hours.

Key words: carbon dioxide (CO_2), climate change, nitrogen, respiration, Kok effect, *Xanthium strumarium* (common cocklebur), temperature.

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Introduction

Motivated by projections of extensive climate change over the next century, substantial research has been conducted to characterize and understand the photosynthetic response of terrestrial vegetation to elevated CO_2 concentrations. Results from CO_2 enrichment experiments conducted on plants grown in controlled-environment growth chambers, outdoor open-top chambers and large-scale FACE rings indicate that elevated concentrations of CO_2 significantly increase photosynthetic rates (Norby *et al.*, 1999; Smith *et al.*, 2000; Herrick & Thomas, 2001). Although it has been well established that plants respire approximately half the carbon that is photosynthetically fixed (Ryan, 1991), the metabolic process of respiration has been less intensively studied with respect to its response to predicted environmental changes (Brooks & Farquhar, 1985; Thomas *et al.*, 1993; Wang *et al.*, 2001). Specifically, little is known about the extent to which elevated CO_2 concentrations, nitrogen availability and temperature change affect mitochondrial respiration that occurs in the light (Sharp *et al.*, 1984; Thomas *et al.*, 1993; Wang *et al.*, 2001; Tissue *et al.*, 2002). Obtaining a better understanding of the mechanistic response of respiration in the light to the aforementioned climate change variables has the potential to aid in producing more precise estimates of global carbon cycle budgets.

Mitochondrial respiration in the light influences, and is influenced by, various plant processes that take place only during hours of illumination. ATP derived from oxidative phosphorylation is necessary for sucrose synthesis; otherwise glucose and fructose build up in the cytosol and feed back negatively on Calvin cycle activity (Kromer, 1995). It is also thought that the respiratory electron transport chain aids in modification of the redox state of the stroma during photosynthetic activity (Foyer & Noctor, 2000). In addition, respiratory pathways produce organic precursors that are necessary for metabolic synthesis in the light; notably, C skeletons derived from the tricarboxylic acid cycle are necessary for amino acid synthesis in the light (Kromer, 1995; Villar *et al.*, 1995). These cumulative demands for energy and C skeletons can modulate the degree of mitochondrial respiration in the light (Wang *et al.*, 2001), which has the potential to change in response to variations in atmospheric CO_2 concentration, N availability and ambient temperature.

Initially, nonphotorespiratory CO_2 evolution in the light was thought to be of the same magnitude as that released during dark respiration (Graham, 1980). Additional research suggests that respiration in the light is in the range of 25–100% of respiration that occurs in darkness, indicating that respiration is partially inhibited in the light (Ishii & Murata, 1978; Brooks & Farquhar, 1985; Kirschbaum & Farquhar, 1987; McCashin *et al.*, 1988; Kromer, 1995; Wang *et al.*, 2001). It has recently been suggested that the measured reduction in respiratory efflux in the light is a result of photosynthetic re-fixation of CO_2 released from mitochondrial respiration (Loreto *et al.*, 1999; Pinelli & Loreto, 2003), and not of a direct or indirect inhibitory effect of light on CO_2 release. While this issue remains debatable, it is unlikely to explain satisfactorily the reduced efflux of CO_2 in the light. Mechanistic results indicate that the mitochondrial pyruvate dehydrogenase complex is phosphorylated in the light, which ultimately has the effect of limiting CO_2 release via the Krebs cycle (Budde & Randall, 1990; Gemel & Randall, 1992; Tovar-Méndez *et al.*, 2003). These data suggest that there is an inhibitory effect of photosynthetic products on respiratory function (Graham, 1980; Wang *et al.*, 2001; Tovar-Méndez *et al.*, 2003). Furthermore, inhibition in the mitochondrial electron chain in the light has been identified as a reduction in ATP synthase and the cytochrome pathway of electron transport, as opposed to the alternative oxidase pathway (Padmavathi & Raghavendra, 2001).

Despite the importance of respiration in the light to plant metabolism and C balance, and observed differences between dark respiration rates and respiration rates in the light, the effect of elevated CO_2 concentration on respiration in the light (R_L) has received little attention (Thomas *et al.*, 1993; Wang *et al.*, 2001; Tissue *et al.*, 2002). Results from Wang *et al.* (2001) using the herbaceous species *Xanthium strumarium* L. indicate that plants grown in elevated CO_2 conditions show a lower rate of R_L compared with respiration in darkness (R_D), and that both R_L and R_D are higher in plants grown in elevated CO_2 compared with plants grown at ambient CO_2. It is of particular significance that the percentage inhibition of R_L is lower for plants grown at elevated CO_2 (17–24%) than for those grown in ambient CO_2 (29–35%). This difference in inhibition is attributed to the greater demand for energy and C skeletons, and the greater availability of respiratory substrate in elevated vs ambient CO_2 conditions (Dewer *et al.*, 1999; Atkin *et al.*, 2000a; Wang *et al.*, 2001).

Although not studied in conjunction with the effect of elevated CO_2 concentration, data indicate a variable response of C loss through R_L and R_D to increases in temperature (Sharp *et al.*, 1984; Villar *et al.*, 1995; Atkin *et al.*, 2000b). Atkin *et al.* (2000b) report that R_L for the evergreen species *Eucalyptus pauciflora* was relatively unresponsive to increases in temperature in the range 6–30°C when measured at high irradiance. By contrast, Villar *et al.* (1995) find that R_L and R_D for deciduous species increase with increasing temperature in the range 10–30°C.

The response of respiration to climate change will be a major factor in determining whether forests are a net C source or a sink (Drake *et al.*, 1999; Valentini *et al.*, 2000). Given that respiration is clearly a fundamental factor in understanding and modeling C budgets at both leaf and ecosystem levels, consideration should be given to determining the most representative values for each individual respiratory flux, including that of mitochondrial respiration during light hours. It is therefore important that global C cycle models incorporate corrected values of respiration by using R_L in place of R_D when modeling C balance during the day, which would have the effect of increasing the total amount of C gained, and by using R_L values that are indicative of the sensitivity to variation in both temperature and CO_2 concentration. In doing so, the individual responses of R_L and photosynthesis to such environmental changes, which may be dissimilar, would be more accurately represented.

The following research investigates and quantifies the individual and interactive effects of temperature, CO_2 concentration and leaf N availability on R_L and R_D in the herbaceous species *X. strumarium*. Specifically, we hypothesized that individual increases in CO_2 concentration, N treatment and measurement temperature would affect R_L and R_D positively. Furthermore, we examined the collective effects of these variables on R_L and R_D to understand the leaf-level response of vegetation to a dynamically changing environment. Additionally, although data from previous studies have suggested that R_L and R_D are not necessarily equivalent, a further goal of this research is to confirm whether R_L is significantly lower than R_D across the aforementioned combinations of environmental conditions. The possible effect of leaf N availability on the response of R_L to CO_2 concentration and measurement temperature is studied because, in most cases, respiration can be related either to leaf N concentration or to leaf carbohydrate content, and the relative proportion of the two can vary in response to changes in environmental conditions (Amthor, 1989; Ryan, 1991).

Materials and Methods

Seed of *Xanthium strumarium* L. (common cocklebur), an annual C_3 herbaceous plant, used in this experiment were from a single population in Lubbock, TX, USA. On 1 July 2002 two seeds were planted in each of 40 6 l pots filled with sand;

10 pots were placed into each of four 1.4 m^2 controlled-environment growth chambers (E-15, Conviron Inc., Winnipeg, Manitoba, Canada) at the Lamont–Doherty Earth Observatory, Palisades, New York, USA. Seedlings emerged *c.* 7 d after planting, and were thinned to one per pot 7 d after emergence. Two of the growth chambers were programmed to supply 365 $\mu mol\ mol^{-1}$ CO_2 (ambient CO_2 treatment), and two were programmed to supply a CO_2 concentration of 730 $\mu mol\ mol^{-1}$ CO_2 (elevated CO_2 treatment). All growth chambers maintained a daytime/night-time temperature of 28/22°C and a relative humidity of *c.* 50%. Leaf-level photosynthetic photon flux density was maintained at *c.* 500 $\mu mol\ m^{-2}\ s^{-1}$ in all the chambers throughout the 9 wk experiment. Plants were maintained in their vegetative growth stage throughout the experiment with a light/dark regime of 18/6 h.

To study the effect of N availability on R_L and R_D in elevated and ambient CO_2, half the plants in each chamber were fertilized to saturation with a half-strength Hoagland's solution containing a high N concentration of 7.0 mM NH_4NO_3, and the other half were fertilized to saturation with a half-strength Hoagland's solution containing a limiting N concentration of 1.5 mM of NH_4NO_3. The concentration of the additional nutrients in both high- and low-N fertilizers were as follows: 3.0 mM K as KCl and KH_2PO_4 monobasic, 3.0 mM Ca as $CaCl_2$ dihydrate, 1.5 mM Mg as $MgCl_2$ hexahydrate, 1.0 mM P as KH_2PO_4 monobasic, 2.0 mM S as Na_2SO_4, 0.14 mM Fe as Fe-EDTA, 0.05 mM B as boric acid, 0.01 mM Mn as $MnCl_2$ 4-hydrate, 0.001 mM Zn as ZnO, 0.001 mM Cu as $CuSO_4$ and 0.05 μM Mo as MoO_3. Nutrient additions began 7 d after emergence and were repeated 3 d wk^{-1} for the remaining 7 wk of the experiment. Plants were watered until saturation with deionized water on days when they did not receive fertilizer solution.

Two methods commonly used to measure R_L are the Laisk method and the Kok method. The Laisk method measures photosynthesis at varying irradiance and at low internal CO_2 concentrations where C fixation and photorespiration are balanced; at that concentration, additional CO_2 evolution is attributed to R_L. As pointed out by Villar *et al.* (1994), the main drawback of using this method is that measurements must be made at a CO_2 concentration that is far from a given growth CO_2 concentration. Because it is not known whether there is a direct short-term effect of CO_2 concentration on R_L, we chose not to use this method in an effort to avoid unnecessary complications in interpreting the results. By contrast, the Kok method used in this study measures the response of photosynthetic rate over incrementally decreasing irradiance, and can be measured at a given growth CO_2 concentration. As applied and referred to in this experiment, the Kok method produced measurements of the long-term effect of growth CO_2 concentration on physiological function, not the short-term effect of measurement CO_2 concentration on such functions. The Kok effect, initially observed by B. Kok in 1948, specifically refers to the break in the slope of the measured photosynthetic rate in a light response (*AQ*) curve when taken with high resolution over low irradiances. At very low irradiance the slope, or quantum yield of photosynthesis, is relatively steep; at the vicinity of the light compensation point a distinct break occurs and the slope decreases. The line at irradiances below the break extends to R_D, where it is determined at 0 PAR, and the line at irradiance above the break extrapolates to R_L (Kok, 1948; Sharp *et al.*, 1984; Kromer, 1995; Padmavathi & Raghavendra, 2001; Fig. 1). At high irradiances photosynthetic rate saturates, so when calculating R_L the only points included are those in the linear section of the *AQ* curve.

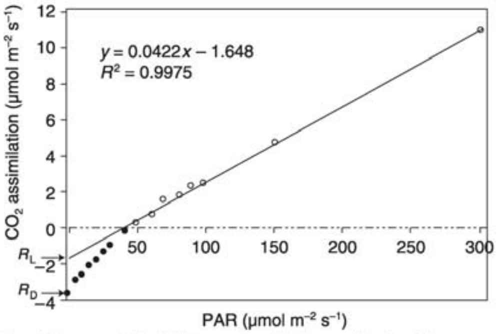

Fig. 1 Representative light-response (*AQ*) curve for *Xanthium strumarium* at relatively low PAR. Open circles represent the portion of the light response that lies above the break in the slope, these points extrapolate back to R_L. Closed circles represent the portion of the light response curve below the break in the slope and extends to the *y* axis. The value for R_D is taken at 0 PAR. Values shown are raw data and do not represent corrected values as discussed under Materials and Methods.

During the eighth week of vegetative growth *AQ* curves were measured on the youngest fully expanded leaf of three randomly selected plants per treatment per chamber, using an open-flow gas-exchange system (LI-6400, Li-Cor, Lincoln, NE, USA); however, in one of the ambient CO_2 chambers only one plant was suitable for measurement in the low-N treatment. *AQ* curves were generated using a red : blue light source (LI-6400-02B) at 20 light levels, 15 of which were < 150 $\mu mol\ m^{-2}\ s^{-1}$ in an effort to have high resolution of the photosynthetic and respiratory responses at low irradiances. For each individual plant *AQ* curves were measured at the CO_2 partial pressure of the particular growth environment (either 365 or 730 $\mu mol\ mol^{-1}$ CO_2), and were measured at three temperatures (23, 28 and 33°C) by adjusting the temperature in the cuvette and allowing conditions in the cuvette to equilibrate for *c.* 20 min before the *AQ* curve was taken. *AQ* curves were analyzed using PHOTOSYNTHESIS ASSISTANT software (version 1.1.2, 1998, Dundee Scientific, Dundee, UK) from which a value was obtained per *AQ* curve for the light-saturating rate of net photosynthesis (A_{sat}). Values for A_{sat} for each individual plant reflected the same growth and measurement conditions as those for the corresponding measurements of R_L and R_D. Leaf tissue samples for C : N analysis were taken from each plant after the *AQ* curve was completed. Samples were dried, ground and analyzed using a NCS 2500 Elemental Analyzer (Carlo Erba NCS 2500, Milan, Italy).

Vital corrections were applied to the extrapolated values of R_L as well as the measured values of R_D to compensate for suspected intrinsic limitations of employing the LI-6400 when measuring relatively low gas-exchange rates associated with leaf respiration (Pons & Welschen, 2002). In order to correct for potential overestimations of measured values of R_L and R_D when using a clamp-on leaf chamber, as opposed to a leaf chamber that accommodates an entire leaf, values for R_L and R_D were recalculated to account for the diffusion of respired CO_2 from darkened leaf material under the chamber gasket that travels into the leaf chamber. Specifically, measured values of R_D were corrected by recalculating measured values to include the inward gasket area that is in contact with the leaf during gas-exchange measurements. Pons & Welschen (2002) used a simple model that partitioned the gasket area in half, i.e. into an inward and outward gasket area, and assumed that the CO_2 evolved under the inward gasket area diffused into the leaf chamber and contributed to the measured value of R_D. Results from this model were in good agreement with measured values of R_D when taken with a cuvette that enclosed an entire leaf (Pons & Welschen, 2002). In addition, Pons & Welschen (2002) reported that overestimations of R_L using a leaf chamber that does not enclose an entire leaf are greater than those associated with measurements of R_D using the same apparatus. They attribute this to the high concentration gradient between the leaf chamber and the room in which the measurements were taken. However, the Kok method for measuring R_L used in this experiment does not rely on a difference in CO_2 concentration between the chamber and the room in which the measurement was taken any more than measuring R_D does, and it was possible to make corrections to R_L in a similar manner to those for R_D. The extrapolated value of R_L was recalculated according to the simple equation:

$$\text{recalculated value of } R_L = [(\text{extrapolated value of } R_L \times 6\ \text{cm}^2) - (\text{recalculated value of } R_D \times 3.55\ \text{cm}^2)]/6\ \text{cm}^2$$

where 6 cm^2 is the area of the window of the Li-Cor 6400 and 3.55 cm^2 is the area of the inward side of the gasket as reported by Pons & Welschen (2002). These corrections, once applied, reduced original values of R_L and R_D by an average of 1.14 (± 0.047) µmol $\text{m}^{-2}\ \text{s}^{-1}$. All values of R_D and R_L reported here refer to corrected values. Values for A_{sat} were not corrected because errors associated with diffusion through the gasket are not detectable when measuring photosynthetic rate at light saturation (Pons & Welschen, 2002).

Q_{10} values for respiration, which compare the rate of respiration at one temperature to the rate at a second temperature that is 10° C offset from the first, were calculated for R_L and R_D over the measured temperature. Interval from 23 to 33°C for each CO_2 by N treatment using the following equation:

$$Q_{10} = \frac{R_2}{R_1}^{\left(\frac{10}{T_2 - T_1}\right)} \qquad \text{Eqn 1}$$

The variables R_2 and R_1 refer to the measured respiration rate at high and low temperatures, respectively, and T_2 and T_1 refer to the specific high and low temperatures (°C) at which the respiration measurement was taken. Q_{10} values are presented primarily to facilitate comparisons with existing literature values, but in general should be used with caution (Tjoelker *et al.*, 2001; Turnbull *et al.*, 2001; Atkin & Tjoelker, 2003).

Temperature sensitivity of R_L and R_D of each treatment was calculated using a modified Arrhenius equation of the form:

$$R = R_o e^{\frac{E_o}{R_g}\left(\frac{1}{T_o} - \frac{1}{T_a}\right)} \qquad \text{Eqn 2}$$

where *R* is the respiratory rate (either R_L or R_D) measured at a specific temperature T_a (K), R_g is the molar gas constant 8.314 J $\text{mol}^{-1}\ \text{K}^{-1}$, T_o (K) is the temperature at which R_o was calculated, and E_o is a fitted parameter and represents a temperature coefficient related to the overall activation energy for the metabolic process of respiration (Lloyd & Taylor, 1994; Turnbull *et al.*, 2001). The equation was solved using a nonlinear regression function (Data Desk, Data Description, Inc., Ithaca, NY, USA, 1996).

A two-way ANOVA, with CO_2 concentration (365 vs 730 µmol mol^{-1} CO_2) and N treatment (7.0 mM vs 1.5 mM NH_4NO_3) as main effects, and respiration measurement (R_D vs R_L) and measurement temperature (23, 28 and 33°C) as repeated measures, was used to test for significance between subjects as well as within subjects. Initially the statistical model design included the CO_2 growth treatment as a nested effect within the variable designated for CO_2 growth chamber. Because the statistical significance of the chamber effect was low ($P = 0.82$) the analyses were rerun without chamber as a variable. A second ANOVA with an identical configuration was performed on $R_L : A_{sat}$ (%) and $R_D : A_{sat}$ (%) values (Data Desk). A multivariate analysis of variance (MANOVA) with R_{28} (respiration normalized to growth temperature, 28°C) and E_{o28} (temperature coefficient at 28°C) as the dependent variables, CO_2 concentration and N treatment as the main effects, and respiration measurement (R_L vs R_D) as a repeated measure variable was used to test for significance on the output of the Arrhenius model. In all analyses, effects were considered significant at $P \leq 0.10$.

Results

A main objective of this study was to determine whether R_L maintained a unique value lower than R_D over several experi-

Table 1 Summary of degrees of freedom (df), *F* ratios and statistical significance (*P* values) for the repeated-measures analysis of variance (ANOVA) on corrected values for *Xanthium strumarium for* respiration, with CO_2 concentration and nitrogen availability as the between-subject factor and respiration measurement (R_L vs R_D) and measurement temperature (23, 28 and 33°C) as the within-subject factors.

ANOVA	df	*F*-ratio	*P*-value
Between Subjects			
CO_2 Concentration (CO_2)	1	9.94	< 0.01
Nitrogen Treatment (N)	1	26.07	< 0.001
CO_2 * N	1	1.16	0.30
Within Subjects			
Respiration Measurement (R)	1	199.72	< 0.001
Measurement Temperature (T)	2	161.81	< 0.001
CO_2 * R	1	0.01	0.91
N * R	1	0.05	0.83
CO_2 * N * R	1	4.53	0.05
CO_2 * T	2	10.34	< 0.001
N * T	2	1.34	0.27
CO_2 * N * T	2	1.02	0.37
R * T	2	11.17	< 0.001
CO_2 * R * T	2	0.78	0.47
N * R * T	2	1.71	0.19
CO_2 * N * R * T	2	0.64	0.53

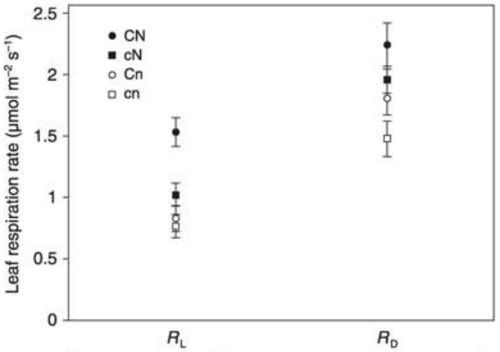

Fig. 2 Differential response of the CO_2 × nitrogen interaction specific to respiration measurement (R_L or R_D) in *Xanthium strumarium*. Points are averaged across three measured temperatures and are means ± SE of four to six replicates. CN (closed circle) = elevated CO_2, high-N treatment; cN (closed square) = ambient CO_2, high-N treatment; Cn (open circle) = elevated CO_2, low-N treatment; cn (open square) = ambient CO_2, low-N treatment.

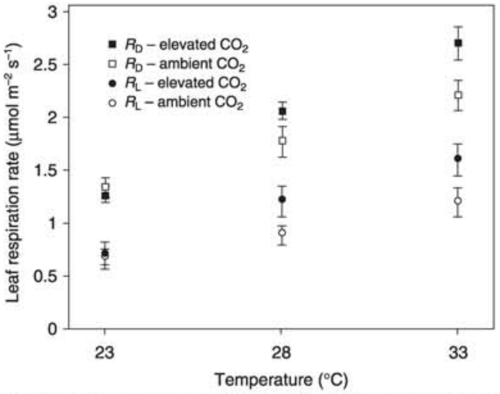

Fig. 3 Temperature-response surface of R_L and R_D in plants grown in the elevated (closed circles, R_L; closed squares, R_D) and ambient CO_2 treatments (open circles, R_L; open squares, R_D) over the three measured temperatures for *Xanthium strumarium*. Points are an average value of R_L or R_D for the high- and low-nitrogen treatments and are the mean ± SE of four to six replicates.

mentally imposed environmental variables. Statistical analyses indicate that R_L values were significantly and consistently lower than R_D values across CO_2 and N treatments and across consecutive increases in measured temperature (Table 1). Additional hypotheses addressed the individual treatment effects of CO_2 concentration and N availability across measurement temperature and forms of respiration. Both main effects were found to be significant (Table 1) such that both R_L and R_D significantly increased with an increase in CO_2 growth concentration or an increase in N availability. Furthermore, the repeated-measures effect of measurement temperature was found to be highly significant (Table 1), where an increase in measured temperature was positively associated with an increase in R_L and R_D across all CO_2 and N treatments.

Another objective of this study was to examine whether R_L and R_D differed in their relative responses to the combined effects of CO_2 and N supply. Although R_L was consistently lower than R_D across treatments, and both R_L and R_D increased with increasing CO_2 and N supply, R_L and R_D differed significantly in their relative responses to the combined effects of CO_2 and N supply (Table 1; Fig. 2). For R_L the combined effects of increasing both CO_2 and N had a strong positive effect that was substantially greater than for the other three treatments. By contrast to this interactive effect of CO_2 and N on R_L, there was no significant interaction between CO_2 and N on R_D. This differential response of R_L and R_D to the elevated CO_2, high-N treatment (CN) was similarly reflected in the percentage inhibition of R_L relative to R_D for each CO_2 × N treatment combination. The percentage inhibition of R_L relative to R_D was 28% on average for the CN treatment, but 48% for the ambient CO_2, high-N treatment (cN); 53% for the elevated CO_2, low-N treatment (Cn); and 48% for the ambient CO_2, low-N treatment (cn). The overall CO_2 × N effect on respiration measurement was constant across the three temperatures measured (Table 1).

A second set of interactions of interest in this experiment were the interactive effects of CO_2 concentration and measurement temperature on R_L and R_D. This interaction was statistically significant across R_L and R_D (Table 1), and indicated that the respiratory flux per CO_2 treatment was positively and differentially affected by measurement temperature (Fig. 3). The response of R_D and R_L to the two CO_2 treatments was not

Table 2 Treatment-specific values for *Xanthium strumarium*: calculated Q_{10} for R_L and R_D over the measured temperature interval of 23 to 33°C; normalized values for R_L at 28°C from the Arrhenius model; temperature coefficients (E_o) for R_L at 28°C from the Arrhenius model; normalized values for R_D at 28°C from the Arrhenius model; temperature coefficients (E_o) for R_D at 28°C from the Arrhenius model; and light-saturating rates of net photosynthesis. Values are means ± SE of four to six replicates

Treatment	Q_{10} for R_L	Q_{10} for R_D	R_{L28} µmol m^{-2} s^{-1}	E_{O28R_L} J mol^{-1} K^{-1}	R_{D28} µmol m^{-2} s^{-1}	E_{O28R_D} J mol^{-1} K^{-1}	A_{sat} µmol m^{-2} s^{-1}
Elevated CO_2, high nitrogen (CN)	3.33 ± 0.66	3.37 ± 0.29	1.61 ± 0.24	75199 ± 19693	2.26 ± 0.22	71794 ± 22726	54.73 ± 4.10
Ambient CO_2, high nitrogen (cN)	2.01 ± 0.44	2.00 ± 0.27	1.01 ± 0.15	53784 ± 13543	2.02 ± 0.10	37415 ± 7457	32.07 ± 3.22
Elevated CO_2, low nitrogen (Cn)	4.91 ± 0.59	3.00 ± 0.69	0.855 ± 0.14	68356 ± 15669	1.76 ± 0.11	59041 ± 3975	27.97 ± 4.07
Ambient CO_2, low nitrogen (cn)	1.89 ± 0.27	1.94 ± 0.12	0.707 ± 0.13	80143 ± 52602	1.47 ± 0.32	49857 ± 9033	20.25 ± 1.90

statistically different when measured at 23°C, but as measurement temperature increased from 23 to 28°C and from 28 to 33°C the trajectory of the response surface of the elevated and ambient CO_2 treatments diverged, with the response to the elevated CO_2 treatment becoming progressively greater.

Although N availability as a main effect had a significant positive effect on R_L and R_D across CO_2 growth concentration and measurement temperature, the interactive effect of N and measurement temperature was not statistically significant (Table 1). The relationship between respiration rates and N availability was examined further by determining whether respiration rates were correlated to leaf N concentration (%). While the statistical significance appears marginal, results indicate that R_L had a stronger positive correlation with leaf N concentration (%) in both ambient ($R^2 = 0.48$) and elevated ($R^2 = 0.45$) CO_2 treatments than those between R_D and leaf N concentration (%) ($R^2 = 0.42$ and $R^2 = 0.15$, respectively).

Q_{10} values for R_L and R_D over the measured temperature interval of 23 to 33°C were calculated (equation 1) for each of the four $CO_2 \times N$ treatments (Table 2). For plants in the cN and cn treatments, mean (± SE) Q_{10} for R_L was *c.* 2 (2.04 ± 0.44 and 1.89 ± 0.27, respectively). The Q_{10} values of R_L for plants grown in the CN and Cn treatments were substantially higher at 3.33 ± 0.66 and 4.91 ± 0.59, respectively. These latter, high Q_{10} ratios may reflect the small absolute values of R_L measured at low temperatures, and as such the relative differences in R_L become magnified over the temperature range measured. Similar trends in Q_{10} values across all treatments were observed for calculated values of R_D.

Using the modified Arrhenius equation previously described (equation 2), and the measured R_L and R_D values, normalized values of R_{28} and E_{028} for both R_L and R_D were calculated for each set of temperature measurements from each plant (Table 2). These values were used to generate temperature-sensitivity curves for each $CO_2 \times N$ treatment combination over the expanded temperature range of 20 to 35°C (Fig. 4a,b). Both CO_2 and N treatment were significant main treatment effects ($P = 0.06$ and $P < 0.01$, respectively) on R_{28} and E_{028}. Elevated CO_2 grown plants show a significantly more positive respiratory response (a steeper slope) as temperatures increase, with this effect compounded by an increase in N availability (Fig. 4) and distinct for each respiration measurement (R_D or R_L) ($P = 0.08$). This result expands on the trend observed in Fig. 3 and demonstrates the presence of treatment-specific temperature sensitivity, particularly in the elevated CO_2, high-N treatment (Fig. 4a).

Values for $R_L : A_{sat}$ (%) were consistently and significantly lower than those for $R_D : A_{sat}$ (%) across CO_2 and N treatments and short-term temperature measurements ($P < 0.001$; Fig. 5). Additionally, Fig. 5 shows that the average leaf R_L and R_D as a percentage of A_{sat} in the N × temperature treatment range in values from 2.4–4.4 and 4.6–8.1%, respectively. The statistically significant trend ($P = 0.06$) for both $R_L : A_{sat}$ (%) and $R_D : A_{sat}$ (%) values was an increase in percentage respiration with respect to A_{sat} over temperature increases across all four $CO_2 \times N$ treatments.

Discussion

Global and significant increases in mean annual temperature and CO_2 concentration and regional increases in N deposition are predicted for the near future (Vitousek *et al.*, 1997; IPCC, 2001). It is therefore imperative that studies of physiological processes of terrestrial vegetation take these environmental factors into consideration. In order to gain a complete picture of how a plant's total C balance can be affected by foreseen environmental changes, it is not sufficient to measure only the net photosynthetic response of vegetation to such climate change variables. Instead, the individual effects of both photosynthetic C gain and respiratory C loss must be taken into account if a mechanistic, predictive understanding is to be gained.

This experiment demonstrated that R_L was consistently and significantly lower then R_D across all CO_2 and N treatments and over all measured temperatures. Consistent with our hypotheses, both CO_2 concentration and N availability had significant positive effects on R_L and R_D, indicating that an increase in resource availability resulted in an increase in respiratory flux. Furthermore, there was a significant interactive effect between C and N that differentially affected R_L and R_D (Fig. 2), accounting for the broad range of values for the percentage of R_D that was inhibited in the light (28–53%). In this experiment the percentage inhibition of respiration in the

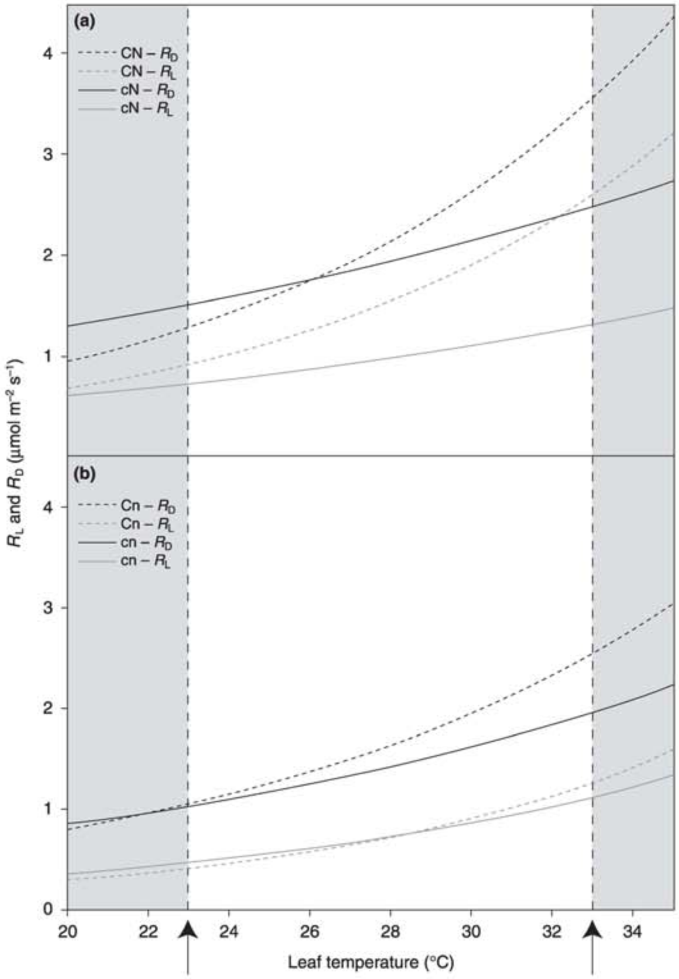

Fig. 4 Model results of R_L and R_D for *Xanthium strumarium* using a modified Arrhenius equation over the temperature range from 20 to 35°C. (a) R_D in treatment CN (dashed black line); R_L in treatment CN (dashed gray line); R_D in treatment cN (solid black line); R_L in treatment cN (solid gray line). (b) R_D in treatment Cn (dashed black line); R_L in treatment Cn (dashed gray line); R_D in treatment cn (solid black line); R_L in treatment cn (solid gray line). Arrows indicate measured temperature range; shaded regions indicate intervals of model data. Each line represents data from four to six replicates.

light in the cN and cn treatments was the same (48%), but the percentage inhibition in the Cn (53%) and CN (28%) treatments showed a nearly twofold difference. Relative inhibition of R_L for the CN and cN treatments are in accordance with those measured by Wang *et al.* (2001), who proposed that the percentage inhibition of R_L in the CN treatment is lower than that for the cN treatment, because elevated CO_2-grown plants have a greater demand for respiratory products such as energy and C skeletons. In addition, the number of mitochondria, the organelles that supply energy to the cell in the form of ATP, has been reported to be significantly higher in plants grown in elevated vs ambient CO_2 (Griffin *et al.*, 2001; Griffin *et al.*, 2004; Wang *et al.*, 2004). This suggests that plants may modulate respiratory capacity to meet a variable demand for respiratory products, which can be affected by growth CO_2 concentration.

In plants grown in the Cn treatment, R_L was highly inhibited relative to the other treatments because N limitation had a greater negative effect on R_L than the positive effect of elevated CO_2 on R_L. This general relationship between N availability and respiration rate is partially supported by the correlations between R_L and tissue N concentration (%) for all CO_2 × N treatments. However, the lack of strong statistical support precludes the use of tissue N concentration as a potential predictor of respiration rates in the light.

Although R_L and R_D responded in the same direction to the CO_2 concentration × measurement temperature interaction, the effect of CO_2 treatment on respiration varied as

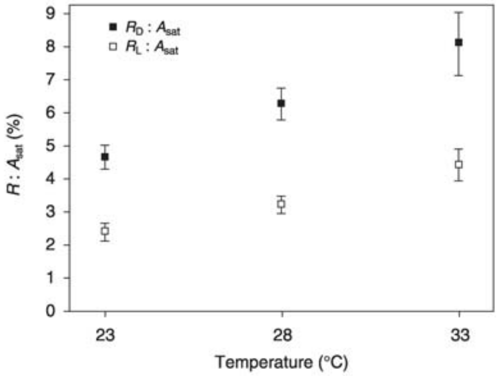

Fig. 5 Percentage leaf R_L (open squares) and R_D (closed squares) relative to light-saturating rates of net photosynthesis (A_{sat}) of *Xanthium strumarium* at three measured temperatures. Each square is the average ± SE of 22 values of $R_L : A_{sat}$ or $R_D : A_{sat}$ over all CO_2 and nitrogen treatments per temperature.

measurement temperature increased. The response surface for the elevated and ambient CO_2-grown plants (Fig. 3) indicated that, at measurement temperatures > 23°C, R_L and R_D in plants grown in elevated CO_2 responded more positively to increasing temperatures than did R_L and R_D in plants grown in ambient CO_2.

In order to explore the response of R_L and R_D to temperature more fully, two descriptive models were applied to the data and used to extrapolate the relationship beyond the temperature range measured. The models used were a Q_{10} and an Arrhenius model, chosen to allow broad comparisons with other data sets. The effect of temperature on R_L is an important factor to consider because respiration can be more responsive than photosynthesis to variations in temperature (Atkin *et al.*, 2000a). In this experiment, Q_{10} values for R_L calculated from the gas-exchange data over the measured temperature interval of 23–33°C for each of the four CO_2 × N treatments fall into two groups (Table 2). For plants grown in the ambient CO_2 concentration, the calculated Q_{10} value for R_L is *c.* 2, as is often assumed for R_D (Tjoelker *et al.*, 2001). However, for plants grown in the elevated CO_2 treatment in both high- and low-N treatments, the calculated Q_{10} value for R_L for the CN (3.33 ± 0.66) and Cn (4.91 ± 0.59) treatments were considerably higher. Q_{10} values > 3.0 have also been reported in species from both boreal and temperate forest biomes (Atkin & Tjoelker, 2003). However, an inaccuracy can arise in using a set Q_{10} over consecutive temperature intervals, as they tend to decrease with increasing temperatures, therefore overestimating C loss at high temperatures and underestimating C loss at low temperatures (Kirschbaum & Farquhar, 1984; Tjoelker *et al.*, 2001; Bruhn *et al.*, 2002).

In place of a traditional Q_{10}, a modified Arrhenius equation that uses a temperature coefficient can be used (Lloyd & Taylor, 1994). In theory, the use of the temperature coefficient should allow more robust predictions of the temperature response of respiration over a broader temperature range. Using the modified Arrhenius equation to model the temperature sensitivity of R_L we observe that R_L and R_D continue to increase appreciably as temperature increases in elevated CO_2 conditions, particularly in the high-N treatment (Fig. 4). In addition, the differences between R_D and R_L tend to get larger as temperatures increase. The marked increase in respiration with increasing temperature, especially in the elevated CO_2 treatments, has important implications for considering the simultaneous balance between photosynthetic C uptake and respiratory C loss. However, before these important short-term temperature effects can be extended to predictions of long-term temperature responses, it is crucial to consider whether or not acclimation to a new growth temperature will occur, and if so to what extent (Atkin & Tjoelker, 2003).

In analyzing the relative effect that short-term temperature change has simultaneously on both net photosynthetic C gain and respiratory C losses in the light, two important trends emerged. The first indicated that using R_L instead of R_D increased the proportion of C gained to C lost for all CO_2 × N treatments and at all measured temperatures (Fig. 5). The second, perhaps more consequential, trend suggests that in general as temperatures rise the proportion of C respired via R_L increased with respect to C gained at A_{sat}. This suggests that an increase in R_L with an increase in temperature has the potential to have a significant impact on a plant's net C balance (Graham, 1980; Sharp *et al.*, 1984).

In conclusion, the magnitude of R_L and how it changes in a variable environment is a vital factor in determining the proportion of photosynthetically fixed C that is respired, and hence in refining our estimates of ecosystems as net sinks or sources of C (Drake *et al.*, 1999; Atkin *et al.*, 2000b). This is especially important in light of the conclusion by Valentini *et al.* (2000) that ecosystem respiration was the deciding factor in categorizing 15 European forests as net C sources or sinks. In this experiment, when measuring leaf respiration rates using the Kok method, R_L was consistently and significantly lower than R_D across CO_2 and N treatments and over the experimentally measured temperature range. This difference in R_L and R_D underscores the importance of using R_L when attempting to describe accurately respiration rates that occur during light hours, and its use would increase the accuracy of estimating the total amount of C gained. In practice it may be possible to use previously measured R_D values in C models with an appropriate correction for factors such as light-induced inhibition, relative resource availability and temperature sensitivity. Such corrections could be further established with additional experimentation. If the findings in *X. strumarium* are present in other species it will be important to include these significant adjustments for respiration during hours of illumination into models that budget C balance for terrestrial ecosystems.

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