

Atmospheric inputs and nitrogen saturation status in and adjacent to Class I wilderness areas of the northeastern US

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Abstract Atmospheric inputs of N and S in bulk deposition (open collectors) and throughfall (beneath canopy collectors) were measured in and adjacent to two Class I wilderness areas of the northeastern US. In general, atmospheric S inputs followed our expectations with throughfall S fluxes increasing with elevation in the White Mountains, New Hampshire and throughfall S fluxes being greater in coniferous than deciduous stands in both sites. In contrast, throughfall N fluxes decreased significantly with elevation. Throughfall NO_3^- fluxes were greater in coniferous than deciduous stands of Lye Brook, Vermont, but were greater in deciduous than coniferous stands of the White Mountains. We found overlap in the range of values for atmospheric N inputs between our measurements and monitoring data [National Atmospheric Deposition Program (NADP) and Clean Air Status and Trends Network (CASTNET)] for wet and total (wet + dry) deposition at Lye Brook. However, our measurements of total S deposition in the White Mountains and bulk (wet) deposition at both Lye Brook and the White Mountains were significantly lower than NADP plus CASTNET, and NADP data, respectively. Natural abundance ^{18}O in throughfall and bulk deposition were not significantly different, suggesting that there was no significant biological production of NO_3^- via nitrification in the canopy. NO_3^- concentrations in streams were low and had natural abundance ^{18}O values consistent with

microbial production, demonstrating that atmospheric N is being biologically transformed while moving through these watersheds and that these forested watersheds are unlikely to be N saturated.

Keywords Bulk deposition · Critical load · Throughfall · Ion-exchange resin · Lye Brook Wilderness, Natural abundance stable isotopes, Mixing models, Presidential Range-Dry River Wilderness

Introduction

N and S emissions are the major sources of N and S deposition onto forests of the northeastern US (e.g., Galloway et al. 1995; Driscoll et al. 2001; Weathers et al. 2006). S deposition has been declining in the northeastern US since the enactment of the Clean Air Act Amendments in the 1990s [National Atmospheric Deposition Program (NADP) 2014]. While rates of N deposition to this region have also been declining over recent years (NADP 2011), they remain significantly elevated by almost an order of magnitude over pre-industrial levels. Initially, deposited N can lead to increased forest productivity since this element is an essential nutrient for plants and microorganisms. However, excess N can lead to a syndrome of responses known as “N saturation.” Symptoms of N saturation include increased NO_3^- leaching to nearby streams, which can lead to nutrient imbalances in trees, reductions in biodiversity (Bobbink et al. 2010; Clark et al. 2013), acidification of stream water, and other detrimental impacts on forest ecosystems (Agren and Bosatta 1988; Aber et al. 1989, 1998; Stoddard 1994; Peterjohn et al. 1996).

It is important to quantify inputs of S and N to forest ecosystems for many reasons, including assessing the effects of deposition (e.g., Pardo et al. 2011) and using mass balance

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approaches to understand catchment function (e.g., Mitchell et al. 2011). Further, assessment of the role of N deposition in influencing the N saturation status of forest ecosystems is reliant upon accurate input measurements. The occurrence of N saturation in many forest ecosystems has prompted considerable interest among ecologists and land managers to determine both the rate of atmospheric inputs across broad spatial scales, since they are the ultimate drivers of saturation, and the N saturation status of these systems. While there are published S and N deposition estimates for the northeastern US that show patterns of deposition over broad spatial scales (kilometers), they cannot account for finer-scale (tens to hundreds of meters) spatial differences in deposition (Ollinger et al. 1993; Weathers et al. 2006). Recently, Weathers et al. (2006) developed an empirical model to predict total deposition based on such landscape features as elevation and vegetation type. This model, built on measurements made in Acadia and Great Smoky Mountains National Parks, shows that total deposition can vary tenfold over tens of meters and is greater than what is predicted by monitoring stations and existing deposition models (Weathers et al. 2006). These results suggest that determining rates of atmospheric deposition on scales finer than previously modeled is necessary for predicting total atmospheric deposition to ecosystems in heterogeneous terrain.

Despite the need for spatially explicit, reasonably accurate estimates of N inputs, there are few such data available for the northeastern US, especially in Class I wilderness areas. Class I areas include federal lands such as wilderness areas, which federal land managers are mandated to protect under special air quality protections under Section 162(a) of the federal Clean Air Act. Forested watersheds in these areas are particularly susceptible to relatively high rates of atmospheric deposition because of their complex terrain, high elevations and the presence of conifer forests, landscape features that have been shown to have high rates of atmospheric deposition (e.g., Weathers et al. 2000). It is therefore important to know the amount of atmospheric pollutants being deposited and the ability of forest ecosystems within Class I wilderness areas to retain excess N.

Past studies show that most N losses from northeastern US forest ecosystems occur as NO_3^- in stream water (Aber et al. 2003; Campbell et al. 2004). Through measuring natural abundance stable isotopes of O and N in NO_3^- , several studies have shown that most of the NO_3^- exported in stream water in this region is produced microbially within the ecosystem as opposed to moving without transformation from the atmosphere, through the canopy and soils, to streams (Kendall et al. 1996; Burns and Kendall 2002; Pardo et al. 2004). A greater proportion of NO_3^- in stream water coming directly from nitrification, rather than directly from deposition, has been interpreted to mean that adjacent forested watersheds are not N saturated.

Previous studies have used measurements of natural abundance ^{18}O and ^{15}N in NO_3^- in samples collected from national monitoring network sites, such as the National Atmospheric Deposition Program (NADP), to represent the “precipitation” source for their isotopic mixing models (Elliott et al. 2007, 2009). However, national network monitoring sites are sparsely distributed in the northeastern US. Given that rates of atmospheric deposition can vary up to tenfold within much smaller geographic areas than those monitored by the national networks (Weathers et al. 2006), it is important to know whether the stable isotopic signatures of atmospheric deposition are equally variable in order to interpret stream isotopic values in the context of N saturation. Also, the data on isotopic signatures from analyses of NADP samples include only wet deposition, which often accounts for only one third to one half of total deposition (<http://www.epa.gov/castnet/deposition.html>). Dry and/or cloud deposition inputs, along with any additional canopy processing, could alter the isotopic signature of below-canopy NO_3^- inputs (throughfall). While microbial transformation of N within the canopy is not likely to be as large in magnitude as soil microbial processing, it is possible that ignoring the potential effect of canopy processes (e.g., plant N exchange or microbial processes) will result in an underestimation of the degree to which forest ecosystems have become N saturated. For example, if isotopic signatures of NO_3^- in stream water are similar to that of NO_3^- produced microbially, it is possible that either microbial processing in the canopy or the isotopic signature of dry or cloud deposition is obscuring the fact that biological processes within the forest floor have become overwhelmed or “saturated.” Campbell et al. (2006) showed that canopy processing of N is not significant within the winter months (leaf off) for forested watersheds of the Adirondack Mountains, New York, but the impact of canopy processing of N on natural abundance ^{15}N and ^{18}O in NO_3^- reaching the forest floor within the growing season is not yet known.

Here we used the dual isotope ^{15}N and ^{18}O approach to examine the relationship between below-canopy N deposition and indices of N saturation directly in and adjacent to Class I areas of the northeastern US. We quantified bulk deposition and throughfall fluxes across elevation and vegetation type (deciduous vs. coniferous) and also measured the isotopic signatures of precipitation entering the canopy and forest floor to gain a more complete understanding of the saturation status for multiple forest sites within the northeastern US. Based on Weathers et al. (2006), we predicted that total deposition (wet + dry, as indicated by S in throughfall) in these regions would be higher than deposition estimates from the nearest monitoring station [e.g., NADP/Clean Air Status and Trends Network (CASTNET)] and that stream samples from the highest elevations would exhibit symptoms of N saturation, meaning that NO_3^- in

streams would have isotopic compositions reflecting direct deposition sources, rather than production via microbial nitrification.

Materials and methods

Site description

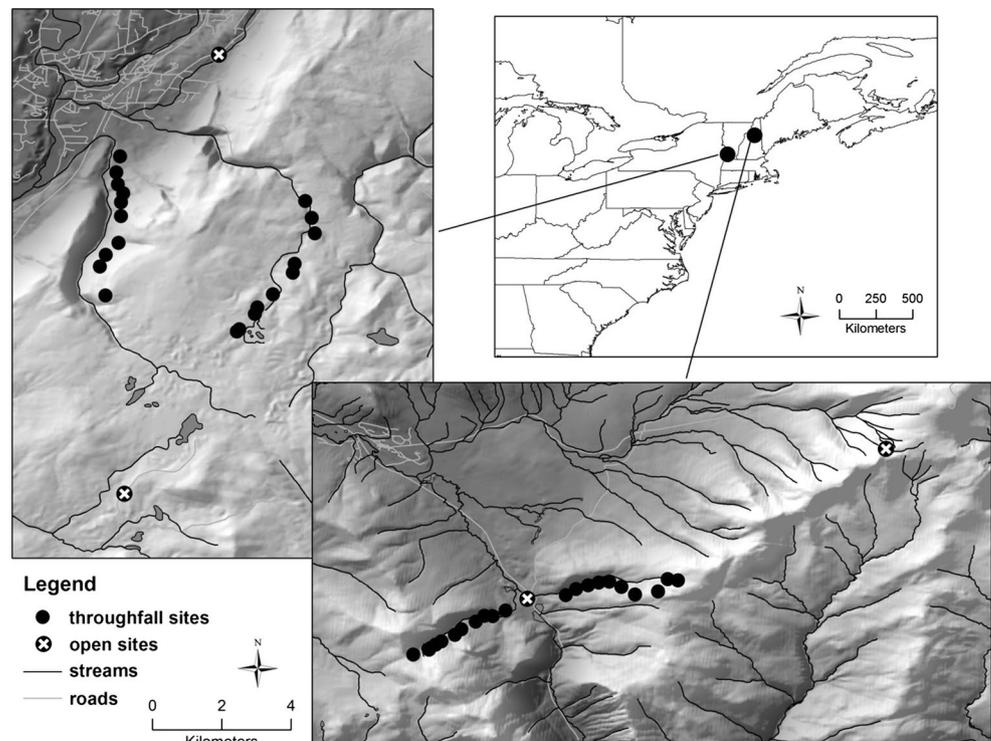
Field collections were made in four watersheds in Vermont and New Hampshire (Fig. 1). Two of the watersheds were located in Lye Brook Wilderness, Manchester, Vermont in the southern part of Green Mountain National Forest, an area designated as wilderness area in 1975. Elevations within Lye Brook Wilderness range between 275–885 m. Dominant vegetation cover includes *Fagus grandifolia*, *Betula* spp., *Acer* spp., *Tsuga canadensis*, and *Picea rubens*. Soils are derived from glacial deposits, composed of both spodosols and inceptisols, are generally acidic and loamy, and are poorly buffered due to their low base cations (Campbell et al. 2002). The coordinates of the base of the two watersheds we examined in Lye Brook are 43.152°N, 73.037°W and 43.141°N, 72.989°W and elevation ranges were 294–757 and 685–786 m, respectively. The other two watersheds (Crawford Brook and Gibbs Brook) were located just outside the Class I Wilderness Presidential Range-Dry River Wilderness, Crawford Notch, New Hampshire in White Mountain National Forest. This area was designated as wilderness in 1975. Dominant vegetation

includes *Betula* spp., *Acer* spp., *Picea rubens*, and *Abies balsamea*. Soils of the White Mountains are also derived from glacial till and are composed mostly of spodosols. The coordinates of the base of the watersheds we examined in the White Mountains are 44.221°N, 71.402°W and 44.217°N, 71.418°W and elevation ranges were 718–1,187 and 633–1,061 m, respectively. The four watersheds were chosen to maximize the elevation gradient and mix of vegetation cover types as well as accessibility via trails to the streams.

Throughfall and bulk-precipitation collection

Ten throughfall plots were located along each of the four elevation gradients (i.e., four watersheds) in a stratified random placement; one plot was randomly placed in each of ten evenly distributed elevation bands using geographic information system digital elevation model and vegetation cover data. Plots were established out of sight of trails and in relatively uniform vegetation cover of deciduous or coniferous trees away from any dramatic changes in slope or vegetation cover to reduce edge effects (Weathers et al. 1995). Within each of the four watersheds, five plots were located in deciduous and five in coniferous stands. Each plot contained one anion-exchange resin collector and three mixed bed ion-exchange resin collectors arranged randomly around the center point. Bulk deposition plots were placed in clearings near the lower and upper elevation bounds of the watersheds and contained one anion

Fig. 1 Map of site locations. Black circles represent locations of throughfall collectors and stream samples. Circles with a cross represent bulk resin column collectors in the open (no canopy cover). Lye Brook is located in Vermont and the White Mountains in New Hampshire



and two mixed bed resin collectors. We had a total of 40 locations within the forest and four locations total for bulk deposition. We measured throughfall S beneath the canopy because it has been shown to be a reasonable surrogate for total atmospheric deposition [wet, dry and cloud (Lindberg and Lovett 1992; Weathers et al. 1992, 1995, 2006; Lovett 1994)].

Each throughfall collector consisted of a 20-cm-diameter plastic funnel attached to a 20-ml disposable chromatography column and set on top of a polyvinyl chloride pipe so that collectors were each 1.5 m aboveground (after Simkin et al. 2004; Templer and McCann 2010). The 20-ml disposable chromatography columns were packed with either Dowex Monosphere MR-3 UPW mixed ion-exchange resin or Dowex Monosphere 550-A anion-exchange resin (Dow Chemical Company, Midland, MI) and had a 30- μm pore-size filter at the bottom of each resin column. Poly wool was placed at the neck of the funnel to prevent debris from entering the resin column. The funnel collected rainwater and canopy throughfall and channeled it through the resin column where charged N and S compounds (specifically NO_2^- , NO_3^- , NH_4^+ , SO_4^{2-}) were adsorbed to the resin. To prevent saturation of the resin beads, we replaced the resin columns every 5–8 weeks between 25 May 2007 and 13 October 2007. Thus, for each of the four watersheds, we prepared 46 resin columns ($n = 4$ for each of the ten throughfall plots and $n = 3$ for each of the two bulk deposition sites) for each of the three sampling periods at Lye Brook and two sampling periods in the White Mountains. We have a continuous record of bulk or throughfall fluxes throughout the growing season at all sites since new resin columns were installed immediately within the same locations after removing old ones. Continuous measurements of throughfall and bulk deposition permitted us to reduce uncertainty related to short-term variation in atmospheric inputs (Zimmerman and Zimmerman 2014).

We compared our measurements of bulk deposition and throughfall in Lye Brook to wet deposition measured at NADP monitoring station VT01 and dry deposition modeled from measurements made at CASTNET station HWF187, which are 35 and 135 km from the Lye Brook sites, respectively, for the same period that we sampled throughfall and bulk deposition. We compared our measurements of bulk deposition and throughfall in the White Mountain site to wet deposition measured at NADP station NH02 and dry deposition modeled from measurements made at CASTNET WST109 station, which are both 40 km from our sites in the White Mountains. While NADP ME08 is 5 km closer to our sites in the White Mountains than NH02, we chose NH02 since it is more similar in topography and elevation to our sites in the White Mountains. We gap filled missing NADP data using the concentration means of the remainder of the growing season and

the recorded precipitation for those missing weeks for each site (3 out of 21 weeks for VT01 and 1 out of 15 weeks for NH02).

Stream collection

Samples of the main stream of each watershed (all first- or second-order streams) were taken near each throughfall plot where accessible during each throughfall resin collection. Unfiltered samples were taken for pH and filtered samples were taken for analysis of NH_4^+ , NO_3^- and NO_2^- . Samples were filtered in the field using a 0.45- μm -membrane syringe filter.

Sample analysis

Anion resin columns were extracted with 1 M KI solution using the method described in Simkin et al. (2004). The extracts were analyzed for SO_4^{2-} on a Dionex DX-500 ion chromatograph, in the Cary Institute Analytical Laboratory, with a detection limit of 0.02 mg L⁻¹. For mixed bed ion-exchange resin extraction, we added 50 ml of 2 M KCl to the 10 g of resin beads three times sequentially (a total of 150 ml) and filtered with Whatman no. 1 filter paper. NH_4^+ , NO_3^- , NO_2^- concentrations were determined on a Lachat QuikChem 8000 flow injection analyzer in the Templer Laboratory at Boston University. We used the salicylate method (E10-107-0602-A) for NH_4^+ concentrations in solution and the NO_3^- 8000 method (E10-107-04-1-C) for determining NO_3^- and NO_2^- (hereafter NO_3^-) concentrations in solution. We used an external calibration standard, Environmental Resource Associates catalog no. 505.

Samples with concentrations higher than the detection limits were diluted. Stream water samples were diluted with deionized water, while throughfall and bulk collector samples were diluted with resin extract solution. Diluted samples were reanalyzed on the Lachat QuikChem 8000 flow injection analyzer.

We summed NH_4^+ , NO_3^- , and SO_4^{2-} of each resin collector for the 2007 summer sampling season (May–October for Lye Brook and June–September for the White Mountain sites) to estimate total atmospheric N and S inputs, respectively. Atmospheric inputs were converted to fluxes using the dimensions of the funnel (20-cm diameter) attached to each resin collector. We report values for stream N concentrations, and not fluxes, since hydrologic fluxes were not measured in this study.

We used the denitrifier method (Casciotti et al. 2002; Templer and Weathers 2011) to determine the natural abundance isotope composition of NO_3^- in atmospheric inputs, throughfall, and stream water for those samples that had sufficient NO_3^- concentrations (>0.1 mg N L⁻¹). The stable isotope composition (δ) of N and O in N_2O gas

Table 1 Total deposition measured from National Atmospheric Deposition Program (NADP; wet deposition, NADP VT01 and NH02) and Clean Air Status and Trends Network (CASTNET; dry deposition, CASTNET HWF187 and WST109) monitoring sites and throughfall collectors (coniferous and deciduous stands) at Lye Brook and White Mountain (White Mtns) sites

	Site	<i>n</i>	NH ₄ ⁺ -N	NO ₃ ⁻ -N	Total inorganic N	SO ₄ ²⁻ -S
Total deposition (wet + dry)						
NADP + CASTNET	VT01, HWF187	1	3.54	3.14	6.72	8.54
Coniferous throughfall	Lye Brook	10	3.37 ± 0.47	3.80 a ± 0.71	7.15 ± 1.13	7.85 a ± 1.19
Deciduous throughfall	Lye Brook	10	3.89 ± 0.35	2.37 b ± 0.18	6.24 ± 0.48	6.50 b ± 0.29
NADP + CASTNET	NH0 ₂ , WST109		3.80	2.88	6.68	8.94
Coniferous throughfall	White Mtns	10	1.44 ± 0.22	0.99 a ± 0.18	2.44 ± 0.36	6.02 a ± 0.37
Deciduous throughfall	White Mtns	10	1.52 ± 0.12	1.46 b ± 0.06	2.96 ± 0.16	4.75 b ± 0.30
Wet deposition						
NADP	VT01	1	3.25	2.99	6.24	8.18
Bulk collectors (this study)	Lye Brook	2	3.38 ± 1.13	1.89 ± 0.13	5.27 ± 1.26	4.85 ± 0.93
NADP	NH0 ₂	1	3.69	2.70	6.42	8.65
Bulk collectors (this study)	White Mtns	2	4.07 ± 0.20	2.17 ± 0.24	6.24 ± 0.04	5.55 ± 0.95
Stream water						
	Site	<i>n</i>	NH ₄ ⁺ -N	NO ₃ ⁻ -N	pH	
	Lye Brook	15	0.013 ± 0.002	0.13 ± 0.02	4.66	
	White Mtns	15	0.004 ± 0.00018	0.12 ± 0.01	4.91	

Data also included those for wet deposition measured from NADP sites and bulk collectors in this study. Units for atmospheric inputs are kg ha⁻¹ year⁻¹ for N and S (means ± SE); units for stream water chemistry are mg N L⁻¹. Different letters indicate statistically significant differences in throughfall flux for N or S for coniferous vs. deciduous stands within Lye Brook or the White Mtns

produced by the bacteria was measured on a SerCon Cryoprep trace gas concentration system interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (SerCon, Cheshire, UK) at the University of California Davis Stable Isotope Facility. We used US Geological Survey standards nos. 32, 34 and 35.

We estimated the relative contributions of atmospheric inputs and nitrification to streams in each of the four watersheds using the natural abundance isotope composition of NO₃⁻ in a two end-member mixing model (Pardo et al. 2004; Templer and McCann 2010). The following equation was used to partition the sources of NO₃⁻ in streams between atmospheric inputs and nitrification:

$$\% \text{ NO}_3^- \text{ from atmospheric inputs} = \left(\frac{\delta^{18}\text{O}_{\text{loss}} - \delta^{18}\text{O}_{\text{nitrification}}}{\delta^{18}\text{O}_{\text{input}} - \delta^{18}\text{O}_{\text{nitrification}}} \right) \times 100$$

where δ¹⁸O_{loss} is the value of δ¹⁸O in streams, δ¹⁸O_{input} is the value of δ¹⁸O in atmospheric inputs and δ¹⁸O_{nitrification} is the published value of δ¹⁸O for nitrification (Kendall and McDonnel 1998; Pardo et al. 2004).

Statistical analysis

We examined potential correlations between elevation and fluxes of N and S using Spearman’s rank correlation analysis, a non-parametric procedure, since fluxes were not

normally distributed. To examine potential differences in N and S fluxes across forest type (i.e., coniferous, deciduous), we conducted a Kruskal–Wallis rank sums test with forest type as the main effect. Similarly, we examined natural abundances of ¹⁵N and ¹⁸O across elevation in atmospheric fluxes and stream water using Spearman’s rank correlation analysis and across forest types using a Kruskal–Wallis rank sums test. We used SAS JMP software (version 10.0.0, 2012) for all statistical analyses.

Results

Throughfall and atmospheric deposition

Fluxes of throughfall NH₄⁺, NO₃⁻, total inorganic N (NH₄⁺-N + NO₃⁻-N), and S were all significantly greater in Lye Brook than at the White Mountain sites (*P* < 0.001, <0.001, <0.001, and 0.0002, respectively; Table 1; Fig. 2). Throughfall fluxes of NH₄⁺ decreased (*R* = -0.031; *P* = 0.016) significantly with elevation in Lye Brook, while there were no significant patterns of throughfall NO₃⁻, total dissolved inorganic N, or S with elevation in Lye Brook (Fig. 2). At the White Mountain sites, throughfall fluxes of NH₄⁺ (*R* = -0.33; *P* = 0.012), NO₃⁻ (*R* = -0.59; *P* < 0.0001) and total dissolved inorganic N (*R* = -0.46; *P* = 0.0002) decreased significantly with elevation, while throughfall fluxes of S (*R* = 0.78; *P* < 0.0001) increased significantly with elevation.

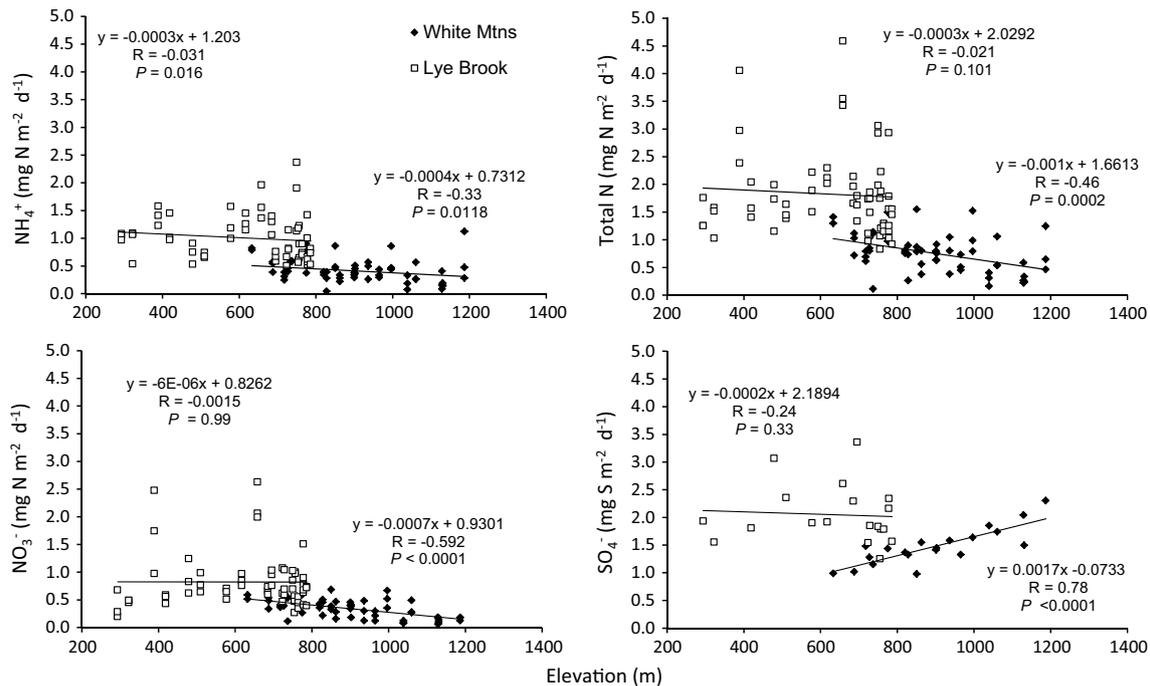


Fig. 2 NH₄⁺, NO₃⁻, total inorganic N, and S fluxes in throughfall along elevation gradients in Lye Brook, Vermont and White Mountains, New Hampshire. $n = 3$ per plot for mixed bed resin collectors (NH₄⁺, NO₃⁻ and total inorganic N) and $n = 1$ per plot for anion resin collectors (S)

Within Lye Brook, throughfall fluxes of NO₃⁻ and S were significantly greater below coniferous than deciduous stands ($P < 0.05$; Table 1). In the White Mountains, throughfall fluxes of NO₃⁻ were greater below deciduous than coniferous stands, while throughfall fluxes of S were greater below coniferous than deciduous stands ($P < 0.05$; Table 1). There were no significant differences in throughfall NH₄⁺ or total dissolved inorganic N among forest types at Lye Brook or the White Mountains.

Comparison of throughfall and atmospheric deposition to NADP and CASTNET

Wet deposition dominated total (wet + dry) N and S inputs at both Lye Brook and the White Mountains for the time period of our study, as indicated by the data collected from nearby NADP and CASTNET monitoring stations and the relatively small difference in the amount of S we found in throughfall relative to bulk deposition, which is often used as a measure of dry deposition (Table 1). Our measurements of bulk and throughfall deposition are consistent with some, but not all, monitoring program data. At Lye Brook, for example, there was overlap in the range of values between our measurements of throughfall N and S for the same time period compared to total deposition estimates from nearby NADP and CASTNET network sites (Table 1). Further, there was overlap between our bulk deposition N measurements for the same time period compared

to wet deposition estimates from nearby NADP network sites at both Lye Brook and the White Mountains. In contrast, our measurements of bulk S deposition were lower than those of wet deposition estimates from nearby NADP network sites at both Lye Brook and the White Mountains.

Stream chemistry

Stream water NH₄⁺ concentrations increased ($R = 0.38$; $P = 0.029$) and pH decreased ($R = -0.58$; $P = 0.0003$; data not shown) with elevation in Lye Brook. There was a trend for reduced concentrations of NO₃⁻ with elevation in Lye Brook, but the pattern was not statistically significant ($R = -0.32$; $P = 0.062$). Stream water pH decreased with elevation at the White Mountain sites ($R = -0.78$; $P < 0.0001$), but concentrations of NH₄⁺ ($P = 0.26$) and NO₃⁻ ($P = 0.43$) did not vary significantly with elevation. Stream water NH₄⁺ and NO₃⁻ concentrations were 0.013 ± 0.002 and 0.13 ± 0.02 mg N L⁻¹, respectively, in Lye Brook and 0.004 ± 0.00018 and 0.12 ± 0.012 mg N L⁻¹, respectively, at the White Mountain sites (Table 1).

Isotopic composition

Natural abundance $\delta^{18}\text{O}$ values of NO₃⁻ in throughfall and bulk precipitation were significantly greater than in stream water ($P < 0.0001$), while $\delta^{15}\text{N}$ values of stream water

were significantly greater than in throughfall and bulk precipitation ($P < 0.0001$). Natural abundance $\delta^{18}\text{O}$ values of throughfall did not vary between the two forest types and the bulk collectors in the open ($P = 0.85$; Fig. 3), but were significantly greater in Lye Brook compared to the White Mountain sites ($P = 0.0012$). The $\delta^{18}\text{O}$ values of throughfall and bulk deposition were similar within Lye Brook (71.5 ± 0.48 ‰ in throughfall and 71.95 ± 1.52 ‰ in bulk collectors) and the White Mountains (69.6 ± 0.48 ‰ in throughfall and 69.8 ± 1.1 ‰ in bulk collectors). Throughfall $\delta^{15}\text{N}$ values were greater in deciduous stands and open areas ($P = 0.031$) and were greater in Lye Brook than at the White Mountain sites ($P < 0.0001$). There were no significant differences in $\delta^{15}\text{N}$ ($P = 0.54$) or $\delta^{18}\text{O}$ ($P = 0.21$) values among streams comparing Lye Brook to the White Mountains. There were no significant differences in $\delta^{15}\text{N}$ ($P = 0.15$) or $\delta^{18}\text{O}$ ($P = 0.85$) with elevation at Lye Brook or the White Mountains ($P = 0.50$ for $\delta^{15}\text{N}$ and 0.86 for $\delta^{18}\text{O}$).

Discussion

Atmospheric deposition

In this study, we estimated rates of total (wet + dry) and wet deposition to two Wilderness regions in the northeastern US and explored how these rates vary between coniferous and deciduous forest types, across elevation gradients, and how they compared to regional monitoring and modeling data (NADP and CASTNET). Based on previous research, we used S flux in throughfall as a reasonable estimate of total deposition. Measured N flux in throughfall, however, is unlikely to reflect solely atmospheric deposition to forest canopies because of uptake and leaching of N within canopies (Johnson and Lindberg 1992). We compared throughfall measurements to estimates of total deposition from the closest NADP and CASTNET sites to our sampling sites in Vermont and New Hampshire, and we compared our measurements of bulk deposition outside of the forest to wet deposition from the closest NADP sites.

Our results confirm that total atmospheric deposition is higher in coniferous compared to deciduous forests (based on S fluxes), and that uptake of deposited N occurs in the canopies of both coniferous and deciduous forest stands, especially in the White Mountains (Table 1). Throughfall fluxes are typically greater in coniferous than deciduous stands (De Schrijver et al. 2007; Gundersen et al. 2009) due to their greater leaf area index resulting in greater scavenging of particles and gases (Weathers et al. 2006; Deng et al. 2013), and this was reflected in throughfall NO_3^- for Lye Brook and S data for both sites (Table 1). The greater throughfall NO_3^- fluxes within deciduous stands compared

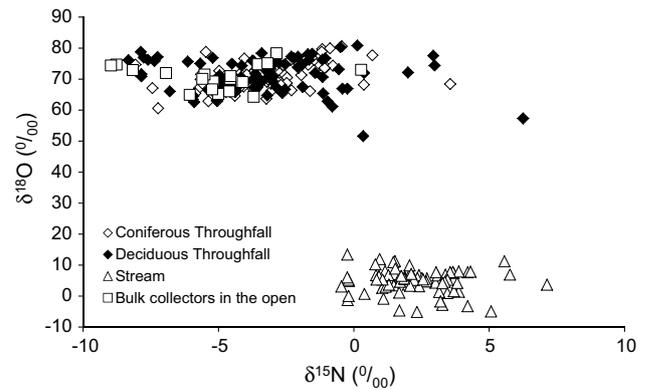


Fig. 3 Stable isotopic values of $^{15}\text{N}^{18}\text{O}_3^-$ in throughfall, bulk collectors in the open and stream samples

to coniferous stands in the White Mountains were surprising, however. Similar to coniferous forests of the Pacific Northwest, US (Fenn et al. 2013), we found canopy retention of NO_3^- in the White Mountains, but unlike the Pacific Northwest, US we observed significant amounts of NH_4^+ retention in the canopy for both coniferous and deciduous stands in the White Mountains as well.

The gradients within Lye Brook were too low in elevation (from 294 m to a maximum elevation of sampling at 786 m) to detect change or to reflect enhanced orographic or cloud inputs of S, but the White Mountain sampling locations (from 718 m to a maximum elevation of sampling at 1,187 m) showed elevation enhancement of S, as has been observed in previous studies (e.g., Lovett 1994; Weathers et al. 2000, 2006; Rustad et al. 1994). The significant decline in throughfall N flux with elevation in the White Mountains was perhaps not surprising as we might expect a greater increase in rates of net consumption of N in the canopy compared to total atmospheric N inputs at high elevation, which has been found in other studies (Lovett and Lindberg 1993).

Our measurements of bulk and throughfall deposition are consistent with some, but not all, NADP and CASTNET monitoring program data. While we expected some differences, based on our and others' work, such as higher fluxes of S and N (at least NO_3^-) at higher elevations, and larger fluxes under coniferous forest compared to deciduous forest canopies, we were surprised by some of our results. Contrary to our expectations, atmospheric S inputs in the two sites we studied were not higher than the nearest monitoring station data indicate.

We measured lower rates of bulk S deposition compared to NADP monitoring station data (59 % at Lye Brook and 64 % in the White Mountains) and measured lower rates of throughfall S inputs compared to NADP + CASTNET monitoring station data (84 % at Lye Brook and 60 % in the White Mountains). Although we cannot determine

the reasons for these differences, possibilities range from overestimating dry deposition with the CASTNET model, to sampling biases or inaccurate estimates of wet deposition from gap filling. Unfortunately, there is no additional, “true” measure of total deposition to which we can compare our data.

N fluxes compared well between our measurements and monitoring station data. This along with the fact that there was little change in throughfall N fluxes as either NH_4^+ or NO_3^- with elevation at Lye Brook suggests that using the local monitoring station data to estimate inputs at this Wilderness Area may be sufficient. In contrast, the difference between our measurements of atmospheric N throughfall fluxes compared to monitoring station data in the White Mountains, and the significantly marked increase in throughfall S fluxes with elevation in the White Mountains, suggest that fine-scale measurements of atmospheric inputs (e.g., across a watershed) in high elevation, heterogeneous terrain such as the White Mountains are important.

N saturation status and use of natural abundance stable isotopes

Decreasing stream water pH with elevation in both Lye Brook and White Mountain streams may be due to the greater rates of S deposition with elevation, especially at the White Mountain sites. Stream N concentrations were generally low across all four watersheds (Table 1). These values are within the range of values measured recently in Lye Brook (Campbell et al. 2002) and at nearby Hubbard Brook Experimental Forest, Woodstock, New Hampshire, in the White Mountain National Forest (Argerich et al. 2013) and may be low partly due to recent decreases in NO_x emissions to the atmosphere and subsequent lower atmospheric N deposition [US Environmental Protection Agency (US EPA) 2010; NADP 2011]. It should be noted that we sampled streams during baseflow events in the growing season and therefore likely missed peaks in stream N concentrations associated with early spring or large rainfall events (Campbell et al. 2002).

The values for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- in atmospheric inputs that we measured fall within the range of published isotopic values of precipitation within North America and Europe (Kendall et al. 1996; Pardo et al. 2004; Elliott et al. 2007). Results of this study validate past results that utilize NADP samples as an isotopic end member for precipitation. The fact that we found no statistically significant difference in natural abundance ^{18}O values among the throughfall samples compared to bulk collectors suggests little to no canopy production of NO_3^- via nitrification. We found greater fluxes of NO_3^- in throughfall beneath canopies than bulk deposition at Lye Brook, but the lack of significant nitrification in these canopies suggests a non-microbial

source of NO_3^- . Canopy production of NO_3^- in Lye Brook and consumption of NO_3^- in the White Mountains is similar to patterns found in California and the Pacific Northwest, US, respectively (see review by Fenn et al. 2013).

For our mixing model (equation above), we used the mean value for $\delta^{18}\text{O}$ in atmospheric inputs (71.5 ‰ for Lye Brook and 69.6 ‰ for the White Mountains) and in stream water (3.1 ‰ for Lye Brook and 4.7 ‰ for the White Mountains) and the published range of $\delta^{18}\text{O}$ values for NO_3^- produced from nitrification [−5 to +15 ‰ (Kendall et al. 1996; Pardo et al. 2004)]. We do not characterize any of the watersheds we examined as N saturated, as indicated by the relatively low stream water NO_3^- concentrations and stable isotope mixing models indicating that between 87–100 % NO_3^- in stream water comes from microbial production in soils or streams rather than directly from atmospheric deposition.

We expected that a larger proportion of NO_3^- in stream water would come directly from atmospheric inputs rather than biological production at higher elevations of the White Mountains due to higher rates of deposition (Fig. 2), cooler temperatures, thinner soil profiles, and more bedrock there compared to lower elevations. If the microbial and plant demand for N were saturated by larger rates of N inputs at higher elevations, a greater proportion of leached NO_3^- from atmospheric sources would be expected. Contrary to these expectations, although total atmospheric deposition was higher (based on throughfall S), we found lower NH_4^+ , NO_3^- and total N deposition to the forest floor at higher elevations in the White Mountains. Also, there were no significant differences in natural abundance ^{18}O or the proportion of NO_3^- in stream water coming directly from deposition vs. nitrification across elevations even though stream water NH_4^+ increased with elevation at Lye Brook and total deposition increased with elevation at the White Mountain sites.

Overall, our results demonstrate that the NO_3^- in stream water in both Lye Brook and at the White Mountain sites is produced primarily biologically via nitrification rather than coming directly from atmospheric deposition, indicating that these forested watersheds are unlikely to be N saturated. Rates of atmospheric N deposition remain elevated above pre-industrial levels, but both NO_x emissions and NO_3^- deposition have been declining in recent decades within the northeastern US (NADP 2011). Our conclusion that these forested watersheds are unlikely to be N saturated is consistent with mass budget studies showing that forested watersheds in Lye Brook accumulate N, meaning there is a greater amount of N coming in via deposition than leaving via stream water, although spikes in N export during some seasons have been observed (Campbell et al. 2000, 2002). Further, stream water is acidic and sensitive to acidification by atmospheric deposition (Adams et al. 1991). Work in the White Mountains of New Hampshire has shown declining concentrations of stream water NO_3^- and significant retention of deposited N

over the past decades, though the mechanisms behind this decline are still unclear (Goodale et al. 2003; Bernhardt et al. 2005; Bernal et al. 2012; Yanai et al. 2013).

Our observations of relatively low N leaching from Lye Brook and White Mountain sites support other studies showing some northeastern US forests in relatively undisturbed areas to have a greater capacity to retain chronic atmospheric N inputs (Driscoll et al. 2003, 2007; Dittman et al. 2007) than earlier predicted (Aber et al. 1989, 1998). In a survey across the northeastern US, Aber et al. (2003) found that NO_3^- leaching increased only above a threshold atmospheric deposition rate of $8 \text{ kg ha}^{-1} \text{ year}^{-1}$, which is above the rates measured in our study (Table 1). While the critical load [the amount of a pollutant above which causes detrimental effects on a particular organism or ecosystem process; after Pardo et al. (2011)] for stream N is not exceeded in our Lye Brook and White Mountain sites, the critical loads for other facets of these northern forested ecosystems have been exceeded, including for growth and survival of some tree species (critical load is $>3 \text{ kg N ha}^{-1} \text{ year}^{-1}$) and epiphytic lichen [critical load between 4 and $6 \text{ kg N ha}^{-1} \text{ year}^{-1}$ (Pardo et al. 2011)].

The lack of N saturation observed in the forests we studied is in contrast to other rural forests of the eastern US including the Catskill Mountains of New York (Burns et al. 2006; but see Lovett et al. 2000) and Fernow Experimental Forest in West Virginia (Peterjohn et al. 1996; Adams et al. 2006) where rates of atmospheric N deposition are considerably higher [$>10 \text{ kg N ha}^{-1} \text{ year}^{-1}$ (Weathers et al. 2000, 2006)] and NO_3^- export in streams has increased over the last two decades. Our observations are also in contrast to urban areas of the northeastern US which show signs of N saturation via high levels of N leaching. Further, some of these urban sites have natural abundance ^{18}O values indicative of NO_3^- passing through soil solution directly from the atmosphere without being biologically produced (Rao et al. 2014).

In the past, researchers considered N saturation as a phenomenon that occurs only after all biotic and abiotic sinks are overwhelmed (Agren and Bosatta 1988; Aber et al. 1989, 2003). It has become increasingly recognized that N losses to streams can occur simultaneously with uptake by biota and retention on exchange sites in soils (Lovett and Goodale 2011; Templer and McCann 2010; Rao et al. 2014). Results from our study suggest that watersheds in both Lye Brook and at the White Mountain Wilderness areas are not N saturated according to either new or old criteria. However, we cannot distinguish between NO_3^- produced in forest soils and within-stream processing based on our results from inputs and stream chemistry; it is possible that some of the N passed directly through the watershed and NO_3^- was produced in streams. Future research should determine the relative contribution of nitrification in forest soils compared to streams in this region.

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