

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

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 (14 for each of the ten throughfall plots and 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^+

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 NO_3^- 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

Within Lye Brook, throughfall fluxes of NO_3^- and S were significantly greater below coniferous than deciduous stands ($P < 0.05$; Table 1). In the White Mountains, throughfall fluxes of NO_3^- 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 NH_4^+ or total dissolved inorganic N among forest types at Lye Brook or the White Mountains.

Comparison of throughfall and

were significantly greater than in throughfall and bulk precipitation ($P < 0.0001$). Natural abundance ^{18}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 ^{18}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 ^{15}N values were greater in deciduous stands

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 ^{15}N and ^{18}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 ^{18}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 ^{18}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 $8 \text{ kg N ha}^{-1} \text{ year}^{-1}$, 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

of inorganic nitrogen for 24 forest watersheds in the northeastern

- Weathers KC, Lovett GM, Likens GE (1992) The influence of forest edge on cloud deposition. In: Schwartz SE, Slinn WGN (eds) *Precipitation scavenging and atmosphere-surface exchange*, vol. 3, The summer volume: applications and appraisals. Hemisphere, Washington, DC, pp 1415–1423
- Weathers KC, Lovett GM, Likens GE (1995) Cloud deposition to a spruce forest edge. *Atmos Environ* 29:665–672
- Weathers KC, Lovett GM, Likens GM, Lathrop R (2000) The effect of landscape features on deposition to Hunter Mountain, Catskill Mountains, New York. *Ecol Appl* 10:528–540
- Weathers KC, Simkin SM, Lovett G, Lindberg SE (2006) Empirical modeling of atmospheric deposition in mountainous landscapes. *Ecol Appl* 16:1590–1607
- Yanai RD, Vadeboncouer MA, Hamburg SP, Arthur MA, Fuss CB, Groffman PM, Siccama TF, Driscoll CT (2013) From missing source to missing sink: long-term changes in the nitrogen budget of a northern hardwood forest. *Environ Sci Technol* 47:11440–11448
- Zimmerman A, Zimmerman B (2014) Requirements for throughfall monitoring: the roles of temporal scale and canopy complexity. *Agric For Meteorol* 189–190:125–139