

# Do Nutrient Limitation Patterns Shift from Nitrogen Toward Phosphorus with Increasing Nitrogen Deposition Across the Northeastern United States?

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## ABSTRACT

Atmospheric nitrogen (N) deposition is altering biogeochemical cycling in forests and interconnected lakes of the northeastern US, and may shift nutrient

limitation from N toward other essential elements, such as phosphorus (P). Whether this shift is occurring relative to N deposition gradients across the northeastern US has not been investigated. We used datasets for the northeastern US and the Adirondack sub-region to evaluate whether P limitation is increasing where N deposition is high at two geographic scales, based on N:P mass ratios. Using a model-selection approach, we determined that foliar N for dominant tree species and lake dissolved inorganic N (DIN) increased coincident with increasing N deposition, independent of relationships between foliar N or lake DIN and precipitation or temperature. Foliar P also increased with N deposition across the northeastern US for seven of eight deciduous species, but changed less across the Adirondacks. Foliar N:P

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therefore declined at the highest levels of N deposition for most deciduous species across the region (remaining nearly constant for most conifers and increasing only for black cherry and hemlock), but increased across all species in the Adirondacks. Ratios between DIN and total P (DIN:TP) in lakes were unrelated to N deposition regionally but increased across the Adirondacks. Thus, nutrient limitation patterns shifted from N toward P for dominant trees, and further toward P for predominantly P-limited lakes, at the sub-regional but not regional scale. For the northeastern US overall, accumulated N deposition may be insufficient to drive nutrient limitation

from N toward P; alternatively, elements other than P (for example, calcium, magnesium) may become limiting as N accumulates. The consistent Adirondack foliar and lake response could provide early indication of shifts toward P limitation within the northeastern US, and together with regional patterns, suggests that foliar chemistry could be a predictor of lake chemistry in the context of N deposition across the region.

**Key words:** nutrient limitation; nitrogen deposition; phosphorus; northeastern US; forest; lake; Adirondacks.

## INTRODUCTION

Atmospheric deposition of nitrogen (N) due to fossil fuel combustion and agricultural activities is influencing forest and aquatic ecosystems across the northeastern US (for example, Aber and others 2003; Galloway and others 2003). Excess N deposition has a range of negative effects on these ecosystems, such as increased vulnerability to drought, winter damage, insect herbivory, or competitive exclusion; release of gaseous N oxides; and acidification of surface waters or soils, which can release potentially toxic substances such as aluminum (Aber and others 1989; Fenn and others 1998; Driscoll and others 2003). Over the long term, N deposition can lead to N saturation (Agren and Bosatta 1988; Aber and others 1989, 1998), in which increased N may first alleviate N limitation typical of many forests and some lakes in the northeastern US (Vadeboncoeur 2010; Baron and others 2011). After this initial fertilization effect, continued N accumulation may result in nitrate leaching from terrestrial ecosystems, nutrient imbalances, and possibly shifts in nutrient limitation patterns with implications for the productivity and species composition of both forest and lake ecosystems (Lovett and others 2000; Baron and others 2011; Lovett and Goodale 2011).

In forests of the northeastern US, predicted increases in foliar N concentrations and plant growth in response to N deposition (Aber and others 1989, 1998) have been observed for some species and geographic scales, but are not always evident. Foliar N has increased with increasing N deposition for dominant tree species across sub-regional deposition gradients (for example, the Adirondack Mountains; McNeil and others 2007); regionally across broadleaf deciduous and ever-

green coniferous species groups (Pardo and others 2006); and for sensitive species at high elevations (McNulty and others 1991; Boggs and others 2007; Pardo and others 2007). Responses have not been consistent for dominant species across the northeastern US, however, potentially because of spatial heterogeneity, interannual variability in foliar N, and factors such as climate and disturbance (Aber and others 2003). Similarly, across the northeastern and north-central US, N deposition stimulated growth of nearly half of 24 tree species examined, consistent with fertilization from added N; however, three species showed reduced growth with N deposition and eight showed decreased survivorship, consistent with direct or indirect negative impacts of N addition (Thomas and others 2010). In a meta-analysis of N amendment experiments in deciduous forests of the northeastern US, 75% of evaluated tree species increased production in response to N addition, whereas 70% responded to multiple elements, suggesting that N alone did not determine productivity (Vadeboncoeur 2010). Atmospheric N deposition both varies across the landscape (Weathers and others 2000, 2006; Nanus and others 2008) and influences plant growth and survivorship at a regional scale (Thomas and others 2010); variability in species response to added N, however, suggests a need to also consider the role of other essential elements.

The lack of positive growth response to N deposition by some dominant tree species may suggest a transition toward a later stage of N saturation, where N no longer limits growth (for example, Aber and others 1989). Nutrient imbalances stimulated by N deposition may induce shifts in nutrient limitation from N toward other elements, such as phosphorus (P), which also has been shown to limit or co-limit production in terrestrial

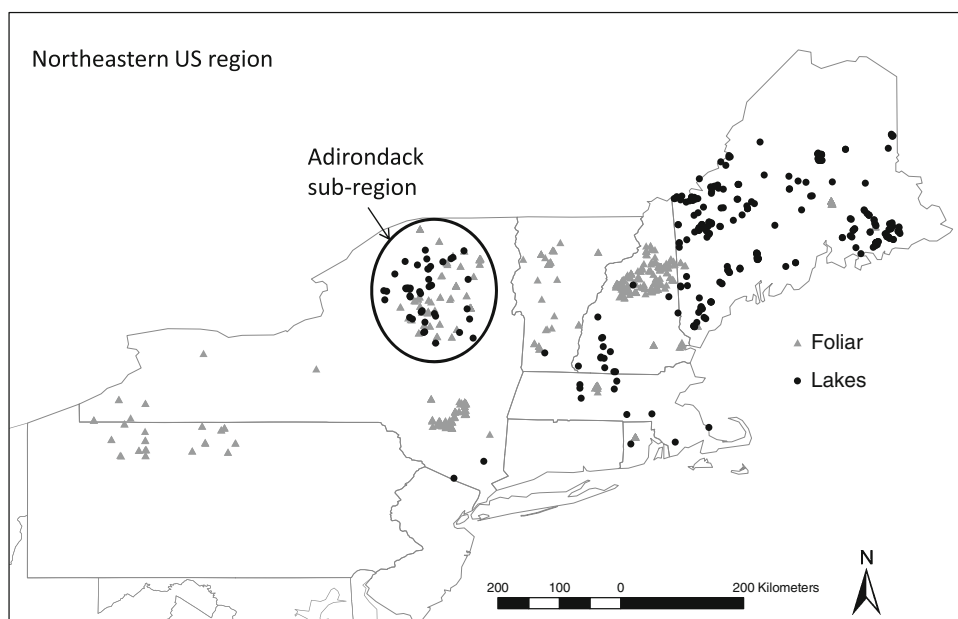
ecosystems (Elser and others 2007). Geochemical sinks for P limit its accessibility in soils, and rapid assimilation of P following mineralization from organic matter (Yanai 1992) suggests a need for efficient P uptake by northeastern species. Soil acidification associated with N addition may inhibit P mineralization and therefore availability, however (Compton and Cole 1998). Moreover, added N may decrease fine-root biomass (Nadelhoffer 2000) and mycorrhizal activity (Wallenda and Kottke 1998; Nilsson and Wallander 2003; Treseder 2004, although responses vary), potentially leading to reduced P uptake or P limitation (Vitousek and others 2010). A shift toward P limitation following N deposition or experimental N addition has been observed in some forest studies (Mohren and others 1986; Tessier and Raynal 2003; Gress and others 2007; Braun and others 2010) but not others (Finzi 2009; Weand and others 2010b).

For lake ecosystems, studies only recently have begun to consider the effects of N deposition on nutrient limitation, likely because lakes have been considered predominantly limited by P (Schindler 1977; Schindler and others 2008). Recent work has found evidence of N limitation in a subset of lakes in northern Europe and across the US, however, particularly where N deposition is low (Elser and others 2009a; Baron and others 2011). In addition, increasing P limitation of P-limited lakes has the potential to influence factors such as phytoplankton diversity or food web functioning (Elser and others 2009a). In Europe and the western US, Elser and others (2009b, 2010) have shown N deposition effects on stoichiometry of lake biota, with shifts

from N toward P limitation of phytoplankton and zooplankton. Whether a transition is occurring from N toward P limitation for forests, or toward greater P limitation for lakes, across the broad regional scale of the northeastern US has not yet been evaluated.

Nutrient limitation is most reliably evaluated via fertilization experiments (Pardo and others 2011), but experimental approaches are difficult to apply at a large spatial scale. The degree of limitation by N versus P is therefore often assessed by less direct indices such as ratios between N and P, such that higher or lower N:P suggests limitation by P or N, respectively (for example, Tessier and Raynal 2003; Güsewell 2004). Ratios between N and P have been used to indicate degree of nutrient limitation for marine, freshwater aquatic, and terrestrial ecosystems (for example, Redfield 1958; Koerselman and Meuleman 1996; Tessier and Raynal 2003; Güsewell 2004; Elser and others 2009a; Bergstrom 2010; Baron and others 2011). Although questions remain about whether N:P thresholds can be used to directly infer N or P limitation of growth, due to complications from factors such as inter-specific differences or nutrient co-limitation (Davidson and Howarth 2007; Townsend and others 2007; Craine and others 2008; Craine 2009), analysis of variation in N:P ratios remains a valuable tool for assessing potential patterns in nutrient limitation across broad landscapes.

Our objective was to evaluate whether increased limitation by P is linked to N deposition for forest and interconnected lake ecosystems over an N deposition gradient across the northeastern US,



**Figure 1.** Map of the northeastern US region and Adirondack sub-region, indicating foliar chemistry and lake site locations.

considering two geographic scales: the region as a whole (approximately 400,000 km<sup>2</sup>) and the Adirondack sub-region (25,000 km<sup>2</sup>; Figure 1). We examined the following specific hypotheses:

1. For forests across the northeastern US, foliar N concentrations (foliar N) for dominant tree species will increase along a spatial gradient of increasing N deposition, as has been shown previously for specific sub-regions, species, or groups of species. This pattern will be evident over and above any relationships between foliar N and climate variables (annual precipitation and mean annual temperature (MAT)) that may have confounded some previous analyses of the effects of N deposition on foliar N (for example, Aber and others 2003).
2. In contrast, foliar P concentrations (foliar P) will decline or remain unchanged at both regional and sub-regional scales.
3. Therefore, foliar N:P ratios will increase with increasing N deposition, suggesting a pattern of greater P limitation of growth.
4. In lakes, dissolved inorganic N (DIN) and therefore ratios of DIN:TP (total P) will also increase along a spatial gradient of increasing N deposition, indicating increasing P limitation across coupled aquatic and forest ecosystems.

In examining nutrient limitation patterns in forest and lake ecosystems individually, we also sought to identify parallel patterns of response to N deposition between regional forest and lake ecosystems that might suggest linkages between them. Lakes integrate nutrient cycling processes occurring in the upland watershed, their chemistry ultimately reflecting the transformations and transport of nutrients from adjacent uplands, wetlands, and streams, in addition to in-lake processing (Moldan and Cerny 1994). Corresponding foliar and lake patterns in response to increasing N deposition across the northeastern US and the Adirondacks could suggest meaningful cross-system linkages.

## METHODS

### Foliar and Lake Chemistry Data

For the northeastern US, we used foliar and lake chemistry data from 1990 to 2006 mainly compiled by the Northeastern Ecosystem Research Cooperative (NERC) (NERC 2010a, b; Weand and others 2010b) (Figure 1; online Appendix 1), subsets of which have previously been described by Aber and others (2003) and Pardo and others (2006). To generate a representative measure for each variable

per site and to minimize effects of temporal variability, we averaged individual measures across sampling times and locations (for example, across sampling months within a year, across sampling years, across multiple sampling locations within a lake, or across trees within a site). Due to variability among data sources, site extent varied from the scale of an individual tree, to a sampling plot (approximately 400–1,000 m<sup>2</sup>), to a watershed (thousands of square meters to thousands of hectares). Regionally, sites ranged in elevation from 13 to 1,576 m above sea level (5–95th percentiles: 87–1,032 m; median: 600 m).

For the sub-regional scale of the Adirondacks, we analyzed a foliar chemistry dataset based on samples collected in 2003 from 75 30 × 30-m sampling locations placed to span a previously defined southwest-to-northeast gradient from high to low wet inorganic N deposition (McNeil and others 2007). Elevations of these sites ranged from 366 to 1,405 m above sea level, with only two sites above 1,000 m (5–95th percentiles: 430–839 m; median: 564 m). Adirondack lake chemistry data were derived from 43 lakes sampled from 1991 to 2003 through the US Environmental Protection Agency (EPA) Temporally Integrated Monitoring of Ecosystems (TIME) Program in conjunction with the Adirondack Long-term Monitoring Program (<http://www.adirondacklakesurvey.org/>). (Because lakes were not co-located with Adirondack foliar chemistry sites, we could not include an exactly correspondent, independent lake data set.) We included the sub-regional as well as the regional scale of analysis because of the greater consistency in sampling time (foliar chemistry data from a single growing season), sampling area (sites of consistent area), and spatial factors such as geology, soil characteristics (sites representing a consistent physiographic region), climate, and disturbance history for the Adirondacks relative to the northeastern US as a whole. Analysis of data from a single study at the sub-regional scale thus might be expected to reduce the confounding effects of such factors, and reveal patterns potentially obscured in analysis of compiled data representing the regional scale (Aber and others 2003).

To assess nutrient limitation patterns, we selected the best regionally available indicators for forest and lake ecosystems. Measures of foliar chemistry included percent N and percent P in green leaf tissue, with foliar N:P ratios calculated on a mass basis as the most frequently used foliar indicator of nutrient limitation (for example, Gusewell 2004). Measures of lake chemistry included DIN (N from nitrate (NO<sub>3</sub><sup>-</sup>-N) plus ammonium (NH<sub>4</sub><sup>+</sup>-N)) and TP (organic plus inorganic P),



with lake DIN:TP ratios also calculated on a mass basis (for example, Bergstrom 2010; Baron and others 2011). Although ratios of total N to total P (TN:TP) often are recommended (for example, Dodds 2003), some recent studies have used DIN:TP ratios to detect nutrient limitation patterns in relation to spatial N deposition gradients (Bergstrom 2010; Baron and others 2011). In a comparison of TN:TP versus DIN:TP ratios, Bergstrom (2010) determined that DIN:TP ratios showed greater variability in relation to N deposition and were better indicators of N versus P limitation by phytoplankton. Similarly, Morris and Lewis (1988) found DIN:TP to be the most effective indicator of phytoplankton nutrient limitation of nine indices tested, including combinations of inorganic, organic, dissolved, particulate, and total N and P. In addition, DIN:TP appears more sensitive than TN:TP to variations in N deposition because it is less influenced by catchment characteristics such as forest and wetland cover that strongly influence organic N in surface waters (Ito and others 2005). Although seston N:P ratios would be more analogous to those of foliage (that is, providing a measure of nutrients taken up by the biota), issues regarding what seston represents (for example, algal biomass, bacteria biomass, detritus), what size fraction is appropriate for remote forest watersheds (Adams and others 2009), and the limited availability of regional seston data sets prevented use of this measure. Given that we assessed qualitative patterns within ecosystems, it was reasonable in this case to use differently derived indices for lakes than for forests. Sampling and analytical methods used to measure N and P are detailed for each study in citations listed in online Appendix 1 and via the NERC web site (NERC 2010a, b).

The regional foliar P data set consisted of 1,538 total data points. Before analysis, we removed six sites (23 estimates of foliar P from eight tree species) from Buttermilk Falls in the Catskills region of NY, because foliar P concentrations were 2–5 times higher than those of other sites in the area for unknown reasons (Weand and others 2010b). For the Adirondacks, we removed 8 of 251 data points due to unusually low foliar P (<0.01%) and correspondingly high foliar aluminum, as foliar chemistry at these sites appeared heavily influenced by aluminum dynamics.

## N Deposition and Climate Variables

For the northeastern US as a whole, we estimated total inorganic N deposition (wet plus dry deposition; referred to hereafter as total N deposition)

from site latitude, longitude, and elevation using the spatial regression model ClimCalc (Ollinger and others 1993, 1995), which covers Maine, New Hampshire, Vermont, Massachusetts, Connecticut, Rhode Island, New Jersey, New York, and Pennsylvania. As ClimCalc is based on atmospheric N concentration estimates from the 1980s and early 1990s, we used it to approximate relative N deposition patterns for sites within its range rather than to estimate precise values. Because ClimCalc estimates are static, they are more accurate when deposition is not changing rapidly; in the eastern US, total N oxide (NO<sub>x</sub>) emissions declined only 7–12% from 1991 to 2000 (Butler and others 2003), suggesting that ClimCalc predictions were applicable for the data included here. To estimate regional climate variables, we used 30-year averages (1971–2000) of annual precipitation and MAT, interpolated to plot locations from PRISM climate data (Boyer and others unpublished; PRISM Climate Group, <http://prism.oregonstate.edu>).

For the Adirondacks, we estimated inorganic wet N deposition (referred to hereafter as wet N deposition) from latitude, longitude, and elevation using a spatial regression model developed specifically for this sub-region (Ito and others 2002; McNeil and others 2007). We used this model because it accounts for local variation in wet N deposition in the Adirondacks better than does ClimCalc (Ito and others 2002). Using this model required the assumption that patterns of dry deposition, cloud-water and fog deposition, and organic N deposition (which are not included in the model) reflect patterns of wet N deposition at the intermediate elevations represented by these sites (McNeil and others 2007; Bedison and McNeil 2009), 95% of which were at or below 839 m elevation.

## Maximum Likelihood Analysis of Foliar Chemistry Relationships

We analyzed foliar N, foliar P, and foliar N:P for the 12 most frequent tree species at 718 sites across the northeastern US, and for the seven most frequent tree species at 75 sites in the Adirondacks (Figure 1; Table 1). Each analysis encompassed the entire data set for the region or sub-region, including all study species within all available sites, such that the total number of data points was 1,308–1,684 for the northeastern US and 243 for the Adirondacks (Table 1).

In the analysis for the northeastern US, we used a model-selection approach to determine whether inclusion of total N deposition improved models that related foliar N, foliar P, or foliar N:P to species

**Table 1.** Species and Numbers of Sites Included in the Analysis

Code	Latin name	Common name	Ecol attrib.	No. sites per species (foliar chemistry)			
				Northeastern US			Adks
				N	P	N:P	N, P, & N:P
ABBA	<i>Abies balsamea</i> (L.) Mill.	Balsam fir	EC, EM	103	97	87	24
ACRU	<i>Acer rubrum</i> L.	Red maple	BD, AM	144	116	93	21
ACSA	<i>Acer saccharum</i> Marsh.	Sugar maple	BD, AM	276	261	230	35
BEAL	<i>Betula alleghaniensis</i> Britt.	Yellow birch	BD, EM	254	243	205	45
BEPA	<i>Betula papyrifera</i> Marsh.	Paper birch	BD, EM	162	162	137	
FAGR	<i>Fagus grandifolia</i> Ehrh.	American beech	BD, EM	211	192	163	51
FRAM	<i>Fraxinus americana</i> L.	White ash	BD, AM	91	91	78	
PIRU	<i>Picea rubens</i> Sarg.	Red spruce	EC, EM	186	166	141	41
PIST	<i>Pinus strobus</i> L.	White pine	EC, EM	47	27	27	
PRSE	<i>Prunus serotina</i> Ehrh.	Black cherry	BD, AM	54	42	41	
QURU	<i>Quercus rubra</i> L.	Northern red oak	BD, EM	64	45	45	
TSCA	<i>Tsuga canadensis</i> (L.) Carr.	Eastern hemlock	EC, EM	92	73	61	26
				1,684	1,515	1,308	243

Species information includes abbreviation codes, Latin names, common names, and ecological attributes for 12 dominant tree species of the northeastern US. EC = evergreen conifer, BD = broadleaf deciduous, AM = arbuscular mycorrhizal, EM = ectomycorrhizal.

identity or climate (here indicated by two variables, precipitation and MAT). Collinearity between N deposition and climate variables can challenge our ability to isolate relationships between foliar chemistry and N deposition from relationships between foliar chemistry and climate (Aber and others 2003). Bivariate relationships between N deposition, precipitation, and MAT showed high variability and very little collinearity, however, enabling all three variables to be included meaningfully in the same model. We employed the following multiple linear regression model and subsets of this model to examine relationships between N deposition and foliar chemistry independent of climate effects:

$$y_{is} = \beta_s + \beta_1 \text{precip}_i + \beta_2 \text{MAT}_i + \beta_3 \text{Ndep}_i + \varepsilon_{is}$$

where  $y_{is}$  was the foliar N, P or N:P ratio of species  $s$  at site  $i$ ;  $\beta_s, \beta_1, \beta_2, \beta_3$  are species-specific regression coefficients;  $\text{precip}_i, \text{MAT}_i,$  and  $\text{Ndep}_i$  are the average annual precipitation, mean annual temperature, and annual total N deposition rates at site  $i$ ; and  $\varepsilon_{is}$  is an error term.

We solved for the maximum likelihood estimates of model parameters for a set of alternate forms of this equation that would predict foliar N, P, or N:P in relation to: (a) a grand mean for the data set; (b) individual means and variances by species; (c) species-specific, linear relationships with either climate variables (precipitation and/or MAT) or N deposition alone; and (d) species-specific, linear relationships with both climate variables and N

deposition. We compared this sequence to indicate the strength of support for sequentially including species identity, the two climate variables, and N deposition in a model to explain variability in foliar N, P, or N:P. To assess the extent to which the relationships between foliar N, P, or N:P and N deposition might be nonlinear rather than linear, we also included versions of the model modified to include a power or polynomial function to describe the effects of N deposition. Nonlinearity could occur as a function of saturation or decline at high N deposition, reflecting a negative effect of N deposition on plant functioning (Aber and others 1989, 1998). We considered nonlinear models for the relationships between foliar chemistry and climate variables as well. Bivariate relationships between foliar chemistry, precipitation, and MAT showed no evidence of nonlinear relationships, however, and a model including nonlinear relationships between foliar N and the two climate variables received much less support than the linear model. We therefore used a linear model throughout to fit climate relationships with foliar chemistry.

We solved for model parameters using simulated annealing (Goffe and others 1994), a global optimization procedure, using the R software likelihood package (R Version 2.10, <http://www.r-project.org/>). Variances were homogeneous, and residuals were normally distributed or sufficiently normal as not to affect conclusions. Use of species-specific variances improved support for all models tested, so they were applied throughout the anal-

ysis. We used the  $R^2$  of the regressions as a measure of overall goodness of fit, and we compared alternative models using the Akaike Information Criterion (AIC), such that a lower value of AIC (that is, demonstrating a more parsimonious model) indicates more support for the given model; a difference in AIC of 2 is considered meaningful and a difference of 10 provides very strong support (Burnham and Anderson 2002). Because our most complex models included fewer than 40 samples per model parameter, we used the corrected AIC ( $AIC_c$ ) for all model comparisons (Burnham and Anderson 2002). In addition, we used two-unit support intervals (approximately comparable to a 95% confidence interval) to assess the strength of support for each model parameter estimate.

Analyses of Adirondack foliar chemistry data were generally as described above, but omitted climate variables. In the Adirondacks, scatterplots between the independent variables showed strong collinearity between precipitation and wet N deposition gradients that prevented separation of their effects on foliar chemistry. In contrast, for the entire region the predominant precipitation gradient is from northwest to southeast, and N deposition instead increases from northeast to southwest (Ollinger and others 1993), minimizing collinearity between these variables. Because we could detect effects of N deposition independent of the effects of precipitation or MAT on foliar chemistry regionally, and the Adirondack data were also consistent with a relationship between foliar chemistry and N deposition, we included only species and N deposition effects in the sub-regional analysis. Although this could result in steeper slopes between foliar N and N deposition for the Adirondacks, at the regional scale, precipitation effects were small and did not change our conclusions.

In addition to the full linear and nonlinear models described above, for the Adirondacks we also considered two simplified linear models of the relationship between foliar chemistry and N deposition: (a) an ANCOVA model with species-specific intercepts but a single slope; (b) an ANCOVA-like model with species-specific slopes but a single intercept. For the regional analysis we made similar comparisons, but do not present those results here because the full linear model always received the greatest support.

### Maximum Likelihood Analysis of Lake Chemistry

We analyzed lake DIN, TP, and DIN:TP for 331 lake data points across the northeastern US and a subset

of 43 lakes in the Adirondack sub-region (Figure 1). To examine relationships between DIN, TP, and DIN:TP and N deposition at the regional scale, we used model selection to determine whether inclusion of N deposition improved models relating lake chemistry to annual precipitation and/or MAT. As in the foliar chemistry analysis, for the Adirondacks we omitted the two climate variables, and evaluation of models was as described above. We used linear models to fit the relationships between lake chemistry and independent variables, with all lake chemistry data log-transformed to improve normality of residuals. Although we considered nonlinear models as well, these models received less support and are not presented here.

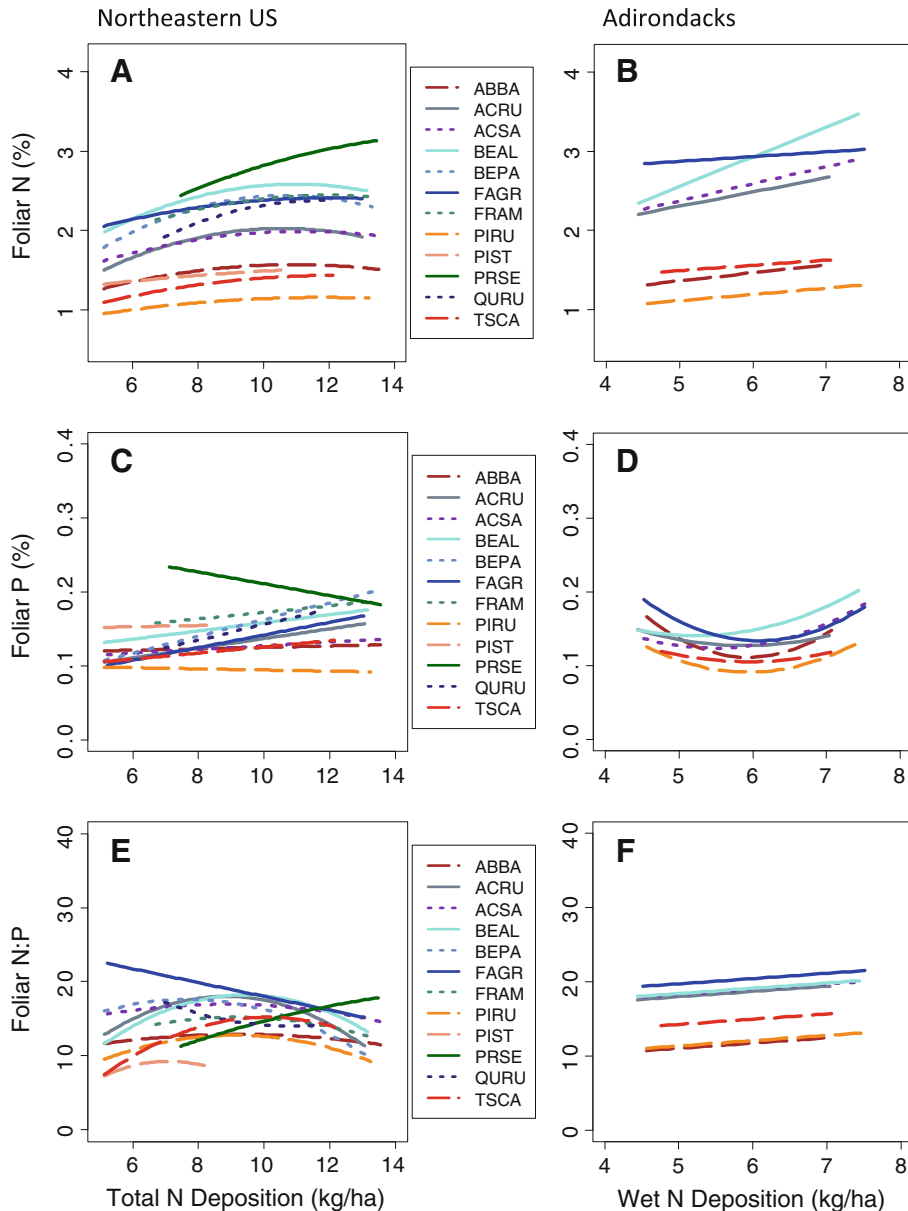
## RESULTS

### Foliar N

Across the northeastern US, foliar N increased with increasing N deposition as expected for each of the 12 most frequently represented tree species (Figures 2A, 3; Table 2; online Appendices 2 and 3). In addition, all models that included N deposition received more support (lower  $AIC_c$ ) than did a model including species, annual precipitation, and MAT alone (Table 2). This indicated that effects of N deposition on foliar N were meaningful independent of relationships between precipitation or MAT and foliar N. At the regional scale, variability in foliar N was better explained by a polynomial than by a linear model. Foliar N initially increased with increasing N deposition, followed by a saturation response beginning at N deposition of 9–10 kg N ha<sup>-1</sup> y<sup>-1</sup> for most species, with an apparent decline in foliar N at estimated total N deposition above 12 kg N ha<sup>-1</sup> y<sup>-1</sup> (Figures 2A, 3; Table 2; online Appendices 2 and 3). The magnitude and shape of the regional foliar N response to N deposition was species-specific (Figure 2A; online Appendix 2).

For the Adirondacks, maximum likelihood analysis showed that foliar N increased with N deposition across the seven most frequent tree species, and in contrast to the regional analysis, indicated more support for a linear model than for a power or polynomial relationship (Figures 2B, 4; Table 3). Thus, there was no evidence to support saturation or decline of foliar N at high N deposition in the Adirondacks, although the Adirondack gradient did not reach the level of N deposition where foliar N appeared to decline regionally.

Across the northeastern US, broadleaf deciduous species showed the steepest initial increase in foliar N with increasing N deposition and evergreen



**Figure 2.** Species-specific relationships between N deposition and **A, B** foliar N, **C, D** foliar P, and **E, F** foliar N:P (by mass) for the northeastern US and the Adirondacks.

Relationships between foliar chemistry variables and total inorganic N deposition (for the northeastern US) or inorganic wet N deposition (for the Adirondacks) are plotted using the linear or nonlinear model with the greatest support (lowest AIC<sub>c</sub>; Tables 2, 3). For the northeastern US, relationships are plotted at an average annual precipitation and MAT per species. Coniferous species are in red and orange colors and indicated by long-dashed lines, and species abbreviations are defined in Table 1.

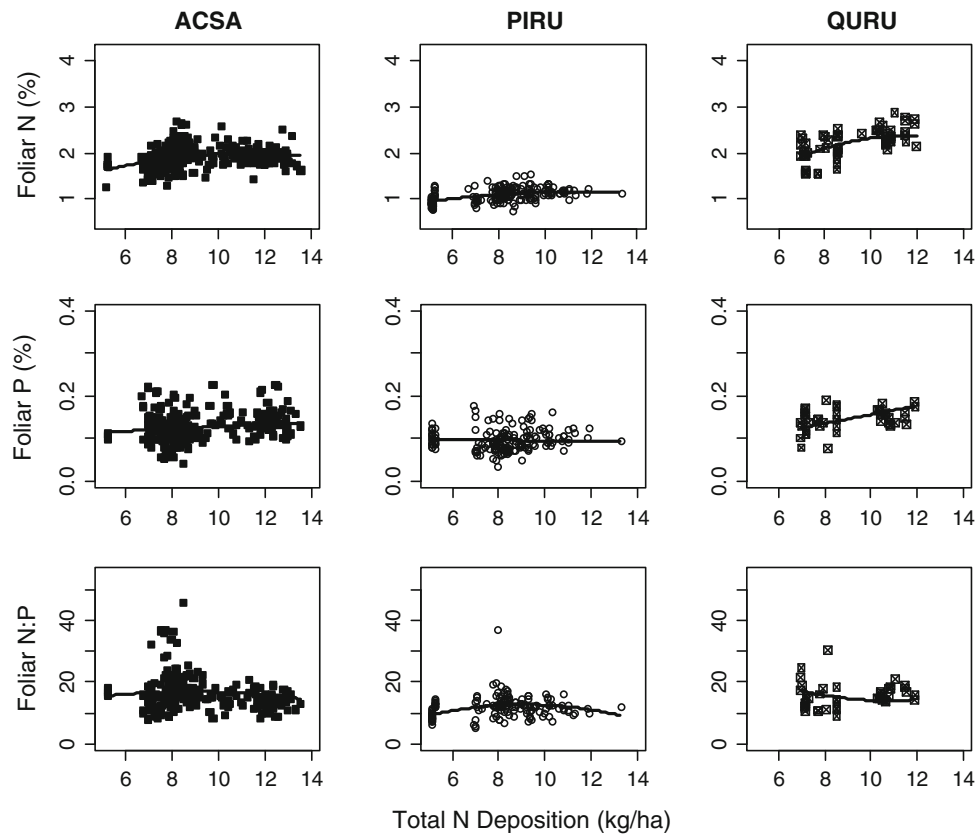
coniferous species the shallowest (Figure 2A; online Appendix 2). For the strongest responders (red oak, paper birch, and yellow birch), foliar N increased  $1.0\text{--}1.2\text{ mg N g}^{-1}$  per  $\text{kg N ha}^{-1}\text{ y}^{-1}$  of deposition, whereas for the weakest responders (red spruce, white pine, and hemlock), foliar N increased  $0.3\text{--}0.5\text{ mg N g}^{-1}$  per  $\text{kg N ha}^{-1}\text{ y}^{-1}$  of deposition. The mean percent increase in foliar N with increasing N deposition across the region was similar between species groups, however, ranging from 15 to 36% for deciduous species and from 13 to 31% for conifers (Figure 2A), relative to a mean increase in total N deposition of 69–123% across deciduous species versus 107–137% for conifers. For the Adirondacks, American beech, red spruce, and hemlock showed limited response to N depo-

sition, whereas yellow birch responded most (Figure 2B; online Appendix 4); however, note that black cherry, red oak, and paper birch occurred in too few plots to be analyzed for the Adirondacks, and increases in foliar N relative to wet N deposition estimates for the sub-region are not directly comparable to the regional estimates above. Across the Adirondacks, the mean increase in foliar N with increasing N deposition ranged from 6 to 49% for broadleaf deciduous species and from 11 to 21% for evergreen conifers (Figure 2B).

### Foliar P

Contrary to expectations, foliar P increased linearly with increasing N deposition across the northeast-





**Figure 3.** Representative relationships between total inorganic N deposition and foliar N, foliar P, and foliar N:P (by mass) across the northeastern US for sugar maple (ACSA; broadleaf deciduous species with limited response to N deposition), red spruce (PIRU; representative evergreen coniferous species), and red oak (QURU; broadleaf deciduous species with strong response to N deposition). Relationships between foliar chemistry variables and total N deposition are plotted using the linear or nonlinear model with the greatest support (lowest AIC<sub>c</sub>; Table 2), at an average annual precipitation and MAT per species. Individual graphs for all species are provided in online Appendix 2.

**Table 2.** Comparisons of AIC<sub>c</sub> for Sequential Northeastern US Foliar Chemistry Models

Model	AIC <sub>c</sub>		
	Foliar N (%)	Foliar P (%)	Foliar N:P
Grand mean across species	10509.7	1655.2	8061.3
Species-specific means & variances	7800.0	1142.3	7633.1
+ N deposition	7493.0	1054.4	7594.7
+ MAT	7637.7	1061.2	7555.8
+ Precipitation	7550.2	1102.7	7606.9
+ Climate (MAT & precipitation)	7491.1	1047.4	7530.5
+ N deposition (linear)	7314.7	<b>986.6</b>	7521.3
+ N deposition (power)	7271.0	1023.8	7533.8
+ N deposition (polynomial)	<b>7261.5</b>	1000.2	<b>7503.9</b>
Number of parameters (best model)	72	60	72
<i>n</i>	1684	1515	1308
<i>R</i> <sup>2</sup> (best model)	0.86	0.37	0.34

In each series of models explaining variability in foliar N, P, or N:P, a “+” in front of a variable indicates that it was included in the model in addition to variable(s) at the previous level of analysis. Models with the lowest AIC<sub>c</sub> have the most support and are indicated in bold.

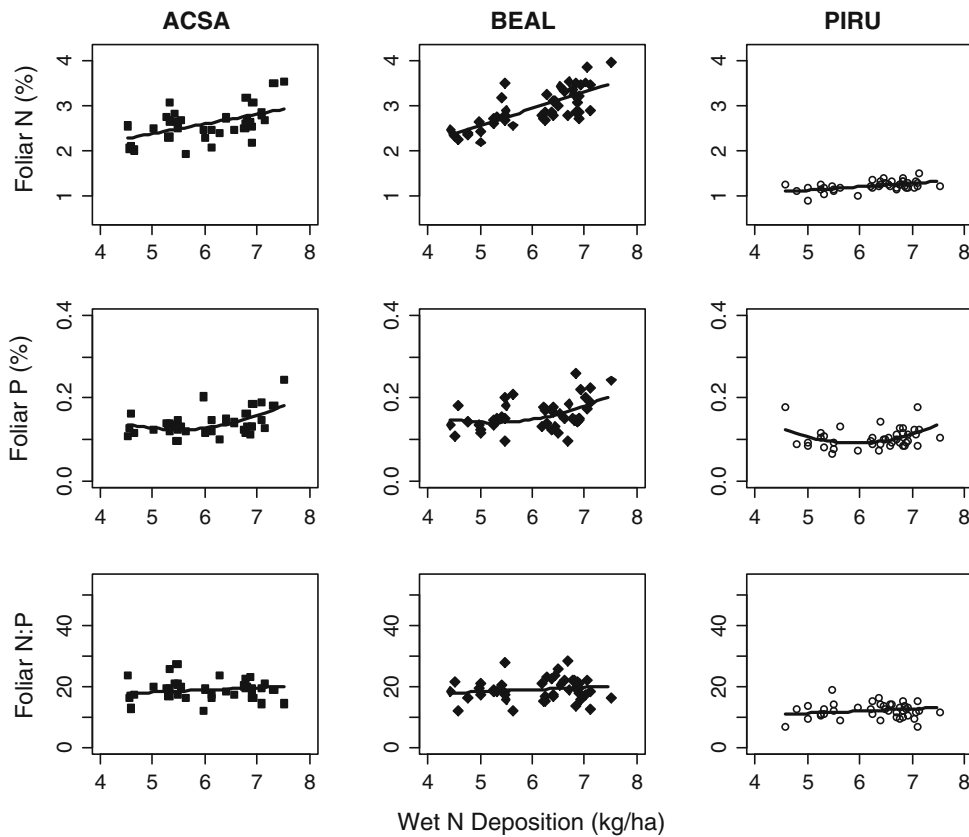


Figure 4. Representative relationships between inorganic wet N deposition and foliar N, foliar P, and foliar N:P (by mass) across the Adirondacks for sugar maple (ACSA), yellow birch (BEAL), and red spruce (PIRU). Species were selected to correspond to those in Figure 3 where possible, with yellow birch replacing red oak as a species with a strong foliar N relationship with N deposition. Individual graphs for all species are provided in online Appendix 4.

**Table 3.** Comparisons of  $AIC_c$  for Sequential Adirondack Foliar Chemistry Models

Model	$AIC_c$		
	Foliar N (%)	Foliar P (%)	Foliar N:P
Grand mean across species	1684.5	204.8	1457.4
Species-specific means & variances	1138.9	140.6	1301.9
+ N deposition (linear)			
ANCOVA: spp.-specific intercepts	1092.3	142.1	<b>1294.8</b>
ANCOVA-like: spp.-specific slopes	1102.1	137.1	1300.4
Full linear model	<b>1072.2</b>	136.6	1302.4
+ N deposition (power)	1092.0	147.8	1311.5
+ N deposition (polynomial)	1082.6	<b>119.4</b>	1299.5
Number of parameters (best model)	21	28	15
$n$	243	243	243
$R^2$ (best model)	0.91	0.42	0.52

In each series of models explaining variability in foliar N, P, or N:P, a "+" in front of a variable indicates that it was included in the model in addition to variable(s) at the previous level of analysis. Models with the lowest  $AIC_c$  have the most support and are indicated in bold. spp. = species.

ern US for seven of the eight deciduous species considered, the only exception being black cherry (Figure 2C; online Appendix 2). With the exception of hemlock, slopes of the relationship between foliar P and N deposition were nearly flat for coniferous species, as expected (Figure 2C; online

Appendix 2). The best model to explain patterns in foliar P across the northeastern US was a full linear model that included N deposition, species, annual precipitation, and MAT (Table 2). Thus, positive regional relationships between foliar P and N deposition were meaningful despite relationships

between foliar P and the two climate variables, and the responses showed no evidence of saturation or decline.

For the Adirondack sub-region, model selection supported a species-specific, polynomial relationship between foliar P and N deposition, in which foliar P was lowest at intermediate levels of N deposition (Figures 2D, 4; Table 3). American beech, balsam fir, and red spruce drove this pattern. Yellow birch and sugar maple showed a more consistently positive relationship between foliar P and N deposition, and red maple and hemlock showed little response (Figure 2D; online Appendix 4).

### Foliar N:P

Also contrary to expectations, foliar N:P did not increase consistently with increasing N deposition across the northeastern US. Relationships between foliar N:P and N deposition varied by species in magnitude and direction (Figure 2E; online Appendix 2) and exhibited a non-linear (polynomial) shape, with the highest foliar N:P generally at intermediate levels of N deposition, approximately  $9 \text{ kg N ha}^{-1} \text{ y}^{-1}$  (Figure 2E; Table 2). Foliar N:P predominantly declined with increasing N deposition for sugar maple, paper birch, American beech, and red oak but increased for hemlock and black cherry (Figure 2E; online Appendix 2). Similar to foliar N and P, variation in foliar N:P at the regional scale was better explained by a model that included N deposition, species, and the two climate variables than by one including species and climate alone.

In contrast to regional patterns, across the Adirondacks foliar N:P increased with increasing N deposition as hypothesized for all seven species

examined (Figure 2F; online Appendix 4). Increases in foliar N drove this response, despite the shallow polynomial relationships between foliar P and N deposition. An ANCOVA model with species-specific intercepts but a consistent slope received the most support (Table 3), such that across species, foliar N:P increased by 0.710 (0.643–0.770 support interval) per  $\text{kg N ha}^{-1} \text{ y}^{-1}$  (online Appendix 5).

### Lake Patterns

Across the northeastern US and for the Adirondacks, lake DIN increased with increasing N deposition ( $\Delta\text{AIC}_c = 945.4$  and  $\Delta\text{AIC}_c = 118.0$ , respectively, relative to grand mean models; Tables 4 and 5; online Appendix 6). Regionally, a model including both N deposition and MAT had greater support than one including MAT alone (the next strongest model,  $\Delta\text{AIC}_c = 2.6$ ; Table 4). This indicated that the positive relationship between N deposition and lake DIN was meaningful over and above relationships between lake DIN and either precipitation (positive) or MAT (negative). Model selection showed no evidence for a relationship between lake TP and N deposition for the Adirondacks (Table 5) or at the regional scale (Table 4). A positive relationship between lake DIN:TP and N deposition was strongly supported for the Adirondacks ( $\Delta\text{AIC}_c = 11.2$ ) but not for the northeastern US as a whole (Tables 4, 5; online Appendix 6).

## DISCUSSION

### Foliar N Responses to N Deposition

Observed increases in foliar N with increasing N deposition for 12 dominant tree species in the northeastern US, at regional and sub-regional

**Table 4.** Comparisons of  $\text{AIC}_c$  for Sequential Northeastern US Lake Chemistry Models

Model	$\text{AIC}_c$		
	DIN (mg N/l)	TP (mg P/l)	DIN:TP
Grand mean across samples	1801.5	1964.4	982.1
N deposition	856.2	748.2	983.0
MAT	856.6	745.9	972.5
+ N deposition	<b>854.0</b>	747.7	971.9
Precipitation	860.6	743.0	975.6
+ N deposition	858.2	<b>742.9</b>	977.3
Climate (MAT & precipitation)	858.3	743.8	<b>967.4</b>
+ N deposition	855.9	743.7	969.2
Number of parameters (best model)	4	4	4
$n$	331	331	330
$R^2$ (best model)	0.04	0.056	0.057

In each series of models explaining variability in DIN, TP, or DIN:TP, a “+” in front of a variable indicates that it was included in the model in addition to variable(s) at the previous level of analysis. Models with the lowest  $\text{AIC}_c$  have the most support and are indicated in bold.

**Table 5.** Comparisons of AIC<sub>c</sub> for Sequential Adirondack Lake Chemistry Models

Model	AIC <sub>c</sub>		
	DIN (mg N/l)	TP (mg P/l)	DIN:TP
Grand mean across samples	225.9	<b>84.3</b>	151.1
N deposition	<b>107.8</b>	99.7	<b>139.9</b>
Number of parameters (best model)	3	3	3
<i>n</i>	43	43	43
<i>R</i> <sup>2</sup> (best model)	0.33	0.13	0.29

*Models with the lowest AIC<sub>c</sub> have the most support and are indicated in bold.*

scales, support hypothesis 1 that foliar N should increase with increasing N deposition. These results corroborate and extend prior analyses that found positive correlations between foliar N and N deposition at the regional scale for deciduous and coniferous species groups (Pardo and others 2006) and for sensitive species at high elevations (McNulty and others 1991; Boggs and others 2007; Pardo and others 2007). McNeil and others (2007) also found positive linear relationships between foliar N and N deposition for dominant tree species in the Adirondack sub-region. Our results contrast with the analysis of Aber and others (2003), who suggested that confounding effects of interacting climate gradients and other landscape variability limited detection of foliar N response to N deposition by sugar maple or black spruce across the northeastern US in their study. The current analysis uses a larger and more comprehensive dataset to demonstrate that observed increases in foliar N in relation to spatial gradients in N deposition are meaningful over and above the effects of climatic factors that often co-vary with N deposition and contribute to variability in foliar N (Yin 1993; Magill and others 2000; Aber and others 2003; Reich and Oleksyn 2004).

Across the northeastern US, the increase and saturation of foliar N with increasing N deposition suggests that several species have reached a maximum response to N addition in terms of their stoichiometric flexibility. This nonlinear response accords with Aber and others' (1989) conceptual model for N saturation, but not with the Aber and others (1998) revised model, which predicts a continuous increase in foliar N with increasing N deposition. Lovett and Goodale (2011) suggest that limited stoichiometric plasticity may prevent a continuous increase in foliar N for many species. They found a maximum foliar N increase of 20% in an N addition study in an oak forest, and other long-term N amendment studies have found similar limitations (for example, Gundersen and others

1998; Magill and others 2004), although foliar N has increased up to 100% with N addition in some studies of evergreen conifers (Magill and others 2004; McNulty and others 2005).

In this study, the apparent decline in foliar N at the highest levels of N deposition may suggest the beginnings of impairment of plant functioning and therefore N uptake. Such impairment is not yet evident in the regional growth response (Thomas and others 2010), however, and a comparable decline in foliar N is evident in only a subset of fertilization studies (Elvir and others 2005; Lovett and Goodale 2011). Of the species for which foliar N decreased most (yellow birch, paper birch, red maple, sugar maple, balsam fir; Figure 2A, online Appendix 2), only yellow birch had a decline in foliar N supported also by a lack of growth response (Thomas and others 2010; Vadeboncoeur 2010) and decreased survivorship in response to increasing N deposition (Thomas and others 2010). Yellow birch has experienced a region-wide decline in recent decades that is thought to be initiated by freezing damage to roots (Zhu and others 2000). Reductions in birch root biomass with N addition (Pettersson and others 1993) or via toxicity from aluminum or manganese (Hoyle 1971) released at low pH where N deposition is high could exacerbate freeze-induced root damage and serve as an unrecognized contributor to species decline.

### Foliar P Responses to N Deposition

Strong regional increases in foliar P for most deciduous species considered did not support hypothesis 2, that foliar P would either decline or remain unchanged with increasing N deposition. In Swiss forests, in plots with ambient N deposition from 12 to 46 kg N ha<sup>-1</sup> y<sup>-1</sup> and in an N addition experiment, foliar P declined with increasing N from 18 to 23% for European beech (*Fagus sylvatica*) and from 14 to 19% for Norway spruce (*Picea abies*) (Braun and others 2010). The authors



attributed these effects to inhibition of mycorrhizal activity at high N. In contrast, in the US, foliar P for sugar maple and American beech was positively correlated with N deposition at high-elevation Appalachian sites (Boggs and others 2005). Foliar P for sugar maple and American beech increased similarly in the N-treated watershed at Bear Brook in Maine in the first 5–6 years of N addition, but this pattern disappeared (sugar maple) or reversed (beech) by 10–11 years of treatment (Elvir and others 2005). The authors note a lack of documentation of the effects of added N on foliar P in other long-term N amendment experiments. Available data on foliar P response to N suggest a pattern of increasing foliar P with increasing N at lower levels of N addition (via N amendment or deposition), to keep pace with N stimulation of growth, followed by a decline in foliar P as N addition increases further. Additional analysis of the response of foliar P to added N is needed to clarify the broader applicability of this pattern.

The increase in foliar P with increasing N deposition across the northeastern US, particularly for deciduous species, most likely results from stimulation of P acquisition by N fertilization (Vitousek and others 2010). In an N-limited environment, trees may acquire sufficient P to balance increased uptake of N from deposition, either from inorganic P available in the soil (typically a smaller pool) or via alternative acquisition pathways for organic P, such as mycorrhizal or phosphatase enzyme activity. N fertilization (Marklein and Houlton 2012), N deposition (Gress and others 2007), and N fixation (Houlton and others 2008) have all been shown to stimulate activity of phosphatase enzymes to release P from soil organic matter, although not in all cases (Weand and others 2010a, b). Using a linked N- and P-cycling model parameterized for several forest ecosystems, Perring and others (2008) also demonstrated that enhanced plant growth due to N addition should lead to greater P conservation in the ecosystem, which could help explain patterns of increasing foliar P with increasing N deposition across the northeastern US.

It is also possible but less likely that inorganic P could be more available for uptake at high N deposition due to acidification processes. Soil acidification is more typically considered to decrease P availability, as P is retained by clays or aluminum and iron oxides or occluded in iron and aluminum minerals (Brady and Weil 2001). At Bear Brook Watershed in Maine, Sherman and others (2006) showed that early stages of acidification mobilized P from amorphous, secondary minerals of aluminum and iron. If deciduous species are more efficient than

conifers in taking advantage of such P mobilization (Sherman and others 2006), foliar P could increase in early stages of acidification, ultimately (with tight P cycling) leading to the increased foliar P we observed for deciduous species with increasing N deposition across the region. We cannot use the regional data set to evaluate whether this mechanism applies outside Bear Brook, as we do not have time series data to evaluate release versus immobilization of P at any given site during early stages of acidification. Given that P typically becomes less available at low soil pH (Brady and Weil 2001), however, and watershed-to-watershed variability in acid-base status is high across the northeastern US, this mechanism seems unlikely to make P consistently more available across the heterogeneous regional landscape.

Finally, the observed relationship between foliar P and N deposition could be caused by factors unrelated to N deposition, such as geologic or soil conditions. If P availability were inherently greater in western portions of the region, this could help in explaining the increases in foliar P where N deposition is high. A lack of site-specific geologic data, soils data, or sufficiently precise geographic site coordinates to enable use of existing soils data sets precluded inclusion of substrate covariates in the current analysis. Overall, however, they are unlikely to influence observed patterns given the high variability in P expected both from sedimentary rock types typical in the western part of the region (conglomerates, sandstone, siltstone, shale, limestone, and dolomite) and from predominantly metamorphic rock in the eastern part of the region derived from the same sedimentary precursors (S. Bailey, personal communication).

The polynomial relationships between foliar P and N deposition across the Adirondack sub-region were unexpected but of sufficiently low magnitude as not to affect the consistent relationship between foliar N:P and N deposition across species. Notable increases in foliar P at low N deposition (observed only for American beech, balsam fir, and red spruce) were driven by a small subset of plots located either on fine-textured, glacial outwash deposits (perhaps increasing P availability via greater particle surface-to-volume ratio) or in areas with a known fire history, which ought to cause the preferential loss of N relative to P. The unique characteristics of these plots thus may have resulted in greater localized P availability and thereby foliar P. More detailed analysis of the potential effects of landscape heterogeneity (for example, with associated variation in geology, land-use history, fine scale N deposition, and so on) on P availability and

therefore foliar P is needed at both the regional and sub-regional scales, as has previously been done for N in the Adirondacks (McNeil and others 2008, 2012) and in the White Mountains (Ollinger and others 2002).

### Is P Limitation Increasing with Increasing N Deposition in Northeastern US Forests?

Overall, N:P ratios for the dominant tree species in the northeastern US did not clearly reflect N or P limitation. In a synthesis of N:P ratios for terrestrial plants, Güsewell (2004) noted increases in biomass with N fertilization at community mass-based N:P ratios less than 10, or with P fertilization at N:P ratios greater than 20, but indicated that intermediate values are not unequivocally related to N or P limitation. Furthermore, particular species have individualistic responses. In the regional data set, 83% of the data had N:P ratios between 10 and 20 (that is, not clearly tied to limitation status), 10% of N:P ratios were greater than 20, and 7% were under 10. The preponderance of N:P values within the range where limitation status is unclear suggests that tree species of the northeastern US currently obtain sufficient P to match the N available from deposition, enabling observed growth responses to N deposition (Thomas and others 2010).

At the regional scale, our hypothesis 3 that foliar N:P would increase with N deposition received support for only two species: hemlock and black cherry. Of these, hemlock appears more likely than black cherry to shift toward P limitation based on N amendment studies. Of five species considered in an N fertilization experiment in the Catskills region of New York, hemlock was the most susceptible to P limitation based on indicators of P supply and demand, which suggested a P requirement greater than available supply (Weand and others 2010b). Black cherry responded to P following N addition in a fertilization study in northwestern Pennsylvania (Auchmoody 1982), but it responded to N but not P addition in a field fertilization experiment in Connecticut, suggesting that it was not limited by P even after long-term exposure to ambient N deposition (Finzi 2009). In addition, black cherry increased in both growth and probability of survival with increasing N deposition across a regional gradient (Thomas and others 2010). The increase in foliar N:P with increasing N deposition for black cherry depended on a small number of data points at lower levels of N deposition, and therefore could be misleading (online Appendix 2).

Decreases in foliar N:P at the highest levels of N deposition for other broadleaf deciduous species

suggest that these species acquire sufficient P to more than counterbalance increases in N availability, such that increasing N deposition has not induced P limitation. These results agree with other forest studies within the northeastern US region (Finzi 2009; Weand and others 2010b), but contrast with those from outside the current study's geographic range. Other than Tessier and Raynal's (2003) study in the Catskills, which emphasized herbaceous understory rather than canopy tree species, studies detecting P limitation under high N deposition thus far have been conducted in areas such as the Haliburton region in central Ontario, Canada (Gradowski and Thomas 2006, 2008), the Fernow Experimental Forest in West Virginia, US (Gress and others 2007), and Switzerland (Braun and others 2010), where N deposition is typically higher than across the northeastern US as defined here (but see Weathers and others 2000, 2006). These contrasting results from studies inside versus outside the region suggest that N deposition across the northeastern US may not have accumulated sufficiently to drive nutrient limitation patterns from N toward P, or that up-regulation of P uptake has delayed this transition (Marklein and Houlton 2012). Observed shifts from N toward P limitation in adjacent locations may provide early indication of coming trends.

Elements other than P, such as calcium (Ca) or magnesium (Mg), may also become limiting for some tree species as N deposition accumulates. For example, Ca deficiency has been observed for red spruce following experimentally induced N saturation (Schaberg and others 1997; 2002). Similarly, sugar maple growth was positively related to foliar Ca and Mg across the northeastern US (Long and others 2009) and to Ca fertilization (Vadeboncoeur 2010) as well as to increased N deposition (Thomas and others 2010). Although evidence for N limitation from N amendment experiments is strong for deciduous forests of the northeastern US, productivity also has tended to increase in response to addition of Ca as well as P (Vadeboncoeur 2010). If many dominant deciduous species continue to retain or acquire P within forest ecosystems as N increases (Perring and others 2008; Marklein and Houlton 2012), then N may remain a controlling factor in combination with or followed by other limiting elements.

Although our hypothesis that foliar N:P would increase with N deposition received little support at the regional scale, it was clearly supported at the sub-regional scale. Within the Adirondack sub-region, the consistent increase in foliar N:P across species suggests a greater tendency toward P limi-

tation with increasing N deposition within this geographic area. This emphasizes the importance of localized factors in determining response, possibly pointing to a particular sensitivity of this habitat, such as high soil acidity or a lack of accessible P in the soil; improved detection in a more internally consistent data set (for example, no interannual variability); or improved detection given greater landscape uniformity relative to the regional scale.

### Are Foliar Chemistry Patterns Reflected in Lakes?

The observed positive relationships between lake DIN and N deposition across the northeastern US and the Adirondack sub-region correspond to previously documented higher surface water  $\text{NO}_3^-$  with increasing N deposition, particularly above N deposition thresholds of 6–7 kg N  $\text{ha}^{-1} \text{y}^{-1}$  (for lakes and streams, Aber and others 2003; for lakes only, Baron and others 2011). The positive relationship between lake DIN:TP and N deposition at the sub-regional but not the regional scale supports hypothesis 4 only for the Adirondack sub-region, suggesting a pattern of increasing P limitation with increasing N deposition for the Adirondacks but not for the northeastern US overall. Patterns in the Adirondacks correspond to those observed by Elser and others (2009a), who found greater evidence of P limitation versus N limitation in lakes with high versus low N deposition in Norway, Sweden, and the Colorado Rocky Mountains, US. Across the northeastern US, the lack of a similar pattern could reflect variability in local factors that influence N and P supply and loss rates, such as geologic substrate, vegetation uptake, or denitrification processes (Elser and others 2009a).

The contrasting patterns in lake N:P between the Adirondacks and the larger northeastern US region match those of foliar N:P for the dominant tree species, and may suggest a particular sensitivity of the sub-region to increased N. Analysis of DIN:TP ratios for the US in relation to nutrient limitation thresholds indicated a higher percentage of P-limited lakes in the Adirondacks (84%) than in the rest of New England (66%) (Baron and others 2011). In addition, lake TP concentrations for the Adirondacks are low relative to the northeastern US overall (mean TP 2.6  $\mu\text{g/l}$  for the Adirondacks, 12.2  $\mu\text{g/l}$  regionally; NERC 2010b; Yu and others 2011), suggesting that low P supply may contribute to increasing P limitation with increasing N deposition across the sub-region in comparison to the region overall.

Corresponding patterns in nutrient limitation with increasing N deposition for forests and lakes at

both the regional and sub-regional scale suggest potential atmospheric-terrestrial-aquatic linkages that merit further investigation, and we propose two hypotheses regarding such interactions between forest and lake ecosystems. First, across the Adirondacks, parallel increases in foliar N:P and lake DIN:TP with increasing N deposition suggest the possibility that foliar chemistry may provide a signal of watershed nutrient status ultimately reflected in lake chemistry, despite many intervening nutrient pathways that might be expected to confound such a direct signal. Alternatively, strong P limitation in Adirondack lakes (Baron and others 2011), relatively high N deposition in the Adirondacks, and regional increases in foliar P with increasing N deposition together suggest that cross-ecosystem linkages may be indirect; greater P foraging by trees where N deposition is high may ultimately reduce P availability to lakes, resulting in patterns of increasing lake P limitation. Linkages between a foliar signal and lake response are difficult to assess given the mismatch in the scale at which these signals integrate ecosystem responses, as well as the intervening confounding effects of nutrient cycling processes in soils and surface waters. To address these hypotheses would require a scaleable study design using co-located foliar and surface water samples in shared watersheds across an N deposition gradient, and measuring N and P (in biomass and/or available forms) in foliage, soil water, wetlands, lake inflows, and other pools and fluxes that potentially influence foliar-lake interactions. Such further work would help determine the extent to which foliar chemistry might directly or indirectly provide a meaningful signal of lake chemistry, and thus clarify interactions between aquatic and terrestrial systems in their responses to N deposition across the region.

### CONCLUSIONS

Across the northeastern US region overall, nutrient limitation patterns do not appear to be transitioning from N toward P limitation with increasing N deposition for most dominant tree species, or further toward P for lakes. Of the tree species considered, only hemlock and black cherry showed a clear regional increase in foliar N:P, and only hemlock has been the subject of fertilization studies suggesting that it may shift from N toward P limitation with increasing N deposition in advance of other tree species. In contrast, unexpectedly strong decreases in foliar N:P at high levels of N deposition for most deciduous species indicate that they acquire sufficient P to more than counterbalance in-

creases in N availability at N deposition levels typical of the northeastern US. These results are important in suggesting either a lag in transition from N toward P limitation pending further accumulation of N from deposition across the region; or that nutrient limitation may transition from N toward elements other than P, such as Ca or Mg, particularly for deciduous species. An additional complication for trend assessment is the continued decline in N deposition due to federal regulatory changes, which may preclude future shifts toward P limitation.

At the sub-regional scale of the Adirondack Mountains, NY, concurrent patterns of increasing P limitation with increasing N deposition both for lakes and across all dominant tree species point to the importance of localized geology, land-use history, or other environmental factors in constraining nutrient limitation. The consistent lake and foliar response in the Adirondacks also suggests that this sub-region may provide an early indicator of shifts from N toward P limitation within the region overall, as N deposition continues to accumulate in the system. Parallel foliar and lake patterns of increasing P limitation in the Adirondacks, in combination with regional evidence for greater foliar P uptake with increasing N availability from deposition, suggest potential linkages between forest and lake ecosystems in the context of regional N deposition. Further investigation is needed to determine the extent to which foliar chemistry might provide a meaningful signal for watershed nutrient status, and to clarify such atmospheric-terrestrial-aquatic linkages across the region.

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#### REFERENCES

- Aber JD, Nadelhoffer KJ, Steudler P, Melillo JM. 1989. Nitrogen saturation in northern forest ecosystems. *Bioscience* 39:378–86.
- Aber J, McDowell W, Nadelhoffer K, Magill A, Berntson G, Kamakea M, McNulty S, Currie W, Rustad L, Fernandez I. 1998. Nitrogen saturation in temperate forest ecosystems—hypotheses revisited. *Bioscience* 48:921–34.
- Aber JD, Goodale CL, Ollinger SV, Smith ML, Magill AH, Martin ME, Hallett RA, Stoddard JL. 2003. Is nitrogen deposition altering the nitrogen status of northeastern forests? *Bioscience* 53:375–89.
- Adams RM, Twiss MR, Driscoll CT. 2009. Patterns of mercury accumulation among seston in lakes of the Adirondack Mountains, New York. *Environ Sci Technol* 43:4836–42.
- Agren GI, Bosatta E. 1988. Nitrogen saturation of terrestrial ecosystems. *Environ Pollut* 54:185–97.
- Auchmoody LR. 1982. Response of young black cherry stands to fertilization. *Can J For Res* 12:319–25.
- Baron JS, Driscoll CT, Stoddard JL, Richer E. 2011. Empirical critical loads of atmospheric nitrogen deposition for nutrient enrichment and acidification of sensitive US lakes. *Bioscience* 61:602–13.
- Bedison JE, McNeil BE. 2009. Is the growth of temperate forest trees enhanced along an ambient nitrogen deposition gradient? *Ecology* 90:1736–42.
- Bergstrom AK. 2010. The use of TN:TP and DIN:TP ratios as indicators for phytoplankton nutrient limitation in oligotrophic lakes affected by N deposition. *Aquat Sci* 72:277–81.
- Boggs JL, McNulty SG, Gavazzi MJ, Myers JM. 2005. Tree growth, foliar chemistry, and nitrogen cycling across a nitrogen deposition gradient in southern Appalachian deciduous forests. *Can J For Res* 35:1901–13.
- Boggs JL, McNulty SG, Pardo LH. 2007. Changes in conifer and deciduous forest foliar and forest floor chemistry and basal area tree growth across a nitrogen (N) deposition gradient in the northeastern US. *Environ Pollut* 149:303–14.
- Brady NC, Weil RR. 2001. *The nature and properties of soils*. Upper Saddle River, NJ: Prentice Hall.
- Braun S, Thomas VFD, Quiring R, Fluckiger W. 2010. Does nitrogen deposition increase forest production? The role of phosphorus. *Environ Pollut* 158:2043–52.
- Burnham KP, Anderson DR. 2002. *Model selection and multi-model inference: a practical information-theoretic approach*. New York: Springer-Verlag.
- Butler TJ, Likens GE, Vermeylen FM, Stunder BJB. 2003. The relation between NO<sub>x</sub> emissions and precipitation NO<sub>3</sub><sup>-</sup> in the eastern USA. *Atmos Environ* 37:2093–104.
- Compton JE, Cole DW. 1998. Phosphorus cycling and soil P fractions in Douglas-fir and red alder stands. *For Ecol Manage* 110:101–12.
- Craine JM. 2009. *Resource strategies of wild plants*. Princeton, NJ: Princeton University Press.
- Craine JM, Morrow C, Stock WD. 2008. Nutrient concentration ratios and co-limitation in South African grasslands. *New Phytol* 179:829–36.
- Davidson EA, Howarth RW. 2007. Environmental science—nutrients in synergy. *Nature* 449:1000–1.



- Dodds WK. 2003. Misuse of inorganic N and soluble reactive P concentrations to indicate nutrient status of surface waters. *J N Am Benthol Soc* 22:171–81.
- Driscoll CT, Whitall D, Aber J, Boyer E, Castro M, Cronan C, Goodale CL, Groffman P, Hopkinson C, Lambert K, Lawrence G, Ollinger S. 2003. Nitrogen pollution in the northeastern United States: sources, effects, and management options. *Bioscience* 53:357–74.
- Elser JJ, Bracken MES, Cleland EE, Gruner DS, Harpole WS, Hillebrand H, Ngai JT, Seabloom EW, Shurin JB, Smith JE. 2007. Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. *Ecol Lett* 10:1135–42.
- Elser JJ, Andersen T, Baron JS, Bergstrom AK, Jansson M, Kyle M, Nydick KR, Steger L, Hessen DO. 2009a. Shifts in lake N:P stoichiometry and nutrient limitation driven by atmospheric nitrogen deposition. *Science* 326:835–7.
- Elser JJ, Kyle M, Steger L, Nydick KR, Baron JS. 2009b. Nutrient availability and phytoplankton nutrient limitation across a gradient of atmospheric nitrogen deposition. *Ecology* 90:3062–73.
- Elser JJ, Peace AL, Kyle M, Wojewodzic M, McCrackin ML, Andersen T, Hessen DO. 2010. Atmospheric nitrogen deposition is associated with elevated phosphorus limitation of lake zooplankton. *Ecol Lett* 13:1256–61.
- Elvir JA, Rustad L, Wiersma GB, Fernandez I, White AS, White GJ. 2005. Eleven-year response of foliar chemistry to chronic nitrogen and sulfur additions at the Bear Brook Watershed in Maine. *Can J For Res* 35:1402–10.
- Fenn ME, Poth MA, Aber JD, Baron JS, Bormann BT, Johnson DW, Lemly AD, McNulty SG, Ryan DE, Stottlemeyer R. 1998. Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses, and management strategies. *Ecol Appl* 8:706–33.
- Finzi AC. 2009. Decades of atmospheric deposition have not resulted in widespread phosphorus limitation or saturation of tree demand for nitrogen in southern New England. *Biogeochemistry* 92:217–29.
- Galloway JN, Aber JD, Erisman JW, Seitzinger SP, Howarth RW, Cowling EB, Cosby BJ. 2003. The nitrogen cascade. *Bioscience* 53:341–56.
- Goffe WL, Ferrier GD, Rogers J. 1994. Global optimization of statistical functions with simulated annealing. *J Econom* 60:65–99.
- Gradowski T, Thomas SC. 2006. Phosphorus limitation of sugar maple growth in central Ontario. *For Ecol Manage* 226:104–9.
- Gradowski T, Thomas SC. 2008. Responses of *Acer saccharum* canopy trees and saplings to P, K and lime additions under high N deposition. *Tree Physiol* 28:173–85.
- Gress SE, Nichols TD, Northcraft CC, Peterjohn WT. 2007. Nutrient limitation in soils exhibiting differing nitrogen availabilities: what lies beyond nitrogen saturation? *Ecology* 88:119–30.
- Gundersen P, Emmett BA, Kjonaas OJ, Koopmans CJ, Tietema A. 1998. Impact of nitrogen deposition on nitrogen cycling in forests: a synthesis of NITREX data. *For Ecol Manage* 101:37–55.
- Güsewell S. 2004. N:P ratios in terrestrial plants: variation and functional significance. *New Phytol* 164:243–66.
- Houlton BZ, Wang YP, Vitousek PM, Field CB. 2008. A unifying framework for dinitrogen fixation in the terrestrial biosphere. *Nature* 454:U327–34.
- Hoyle MC. 1971. Effects of the chemical environment on yellow-birch root development and top growth. *Plant Soil* 35:623–33.
- Ito M, Mitchell MJ, Driscoll CT. 2002. Spatial patterns of precipitation quantity and chemistry and air temperature in the Adirondack region of New York. *Atmos Environ* 36:1051–62.
- Ito M, Mitchell MJ, Driscoll CT, Roy KM. 2005. Nitrogen input-output budgets for lake-containing watersheds in the Adirondack region of New York. *Biogeochemistry* 72:283–314.
- Koerselman W, Meuleman AFM. 1996. The vegetation N:P ratio: a new tool to detect the nature of nutrient limitation. *J Appl Ecol* 33:1441–50.
- Long RP, Horsley SB, Hallett RA, Bailey SW. 2009. Sugar maple growth in relation to nutrition and stress in the northeastern United States. *Ecol Appl* 19:1454–66.
- Lovett GM, Goodale CL. 2011. A new conceptual model of nitrogen saturation based on experimental nitrogen addition to an oak forest. *Ecosystems* 14:615–31.
- Lovett GM, Weathers KC, Sobczak WV. 2000. Nitrogen saturation and retention in forested watersheds of the Catskill Mountains, New York. *Ecol Appl* 10:73–84.
- Magill AH, Aber JD, Berntson GM, McDowell WH, Nadelhoffer KJ, Melillo JM, Steudler P. 2000. Long-term nitrogen additions and nitrogen saturation in two temperate forests. *Ecosystems* 3:238–53.
- Magill AH, Aber JD, Currie WS, Nadelhoffer KJ, Martin ME, McDowell WH, Melillo JM, Steudler P. 2004. Ecosystem response to 15 years of chronic nitrogen additions at the Harvard Forest LTER, Massachusetts, USA. *For Ecol Manage* 196:7–28.
- Marklein AR, Houlton BZ. 2012. Nitrogen inputs accelerate phosphorus cycling rates across a wide variety of terrestrial ecosystems. *New Phytol* 193:696–704.
- McNeil BE, Read JM, Driscoll CT. 2007. Foliar nitrogen responses to elevated atmospheric nitrogen deposition in nine temperate forest canopy species. *Environ Sci Technol* 41:5191–7.
- McNeil BE, Read JM, Sullivan TJ, McDonnell TC, Fernandez IJ, Driscoll CT. 2008. The spatial pattern of nitrogen cycling in the Adirondack Park, New York. *Ecol Appl* 18:438–52.
- McNeil BE, Read JM, Driscoll CT. 2012. Foliar nitrogen responses to the environmental gradient matrix of the Adirondack Park, New York. *Ann Assoc Am Geogr* 102:1–15.
- McNulty SG, Aber JD, Boone RD. 1991. Spatial changes in forest floor and foliar chemistry of spruce-fir forests across New England. *Biogeochemistry* 14:13–29.
- McNulty SG, Boggs J, Aber JD, Rustad L, Magill A. 2005. Red spruce ecosystem level changes following 14 years of chronic N fertilization. *For Ecol Manage* 219:279–91.
- Mohren GMJ, Vandenburg J, Burger FW. 1986. Phosphorus deficiency induced by nitrogen input in Douglas-fir in the Netherlands. *Plant Soil* 95:191–200.
- Moldan B, Cerny J. 1994. *Biogeochemistry of small catchments: a tool for environmental research*. SCOPE 51. Chichester: John Wiley & Sons.
- Morris DP, Lewis WM. 1988. Phytoplankton nutrient limitation in Colorado mountain lakes. *Freshw Biol* 20:315–27.
- Nadelhoffer KJ. 2000. The potential effects of nitrogen deposition on fine-root production in forest ecosystems. *New Phytol* 147:131–9.
- Nanus L, Williams MW, Campbell DH, Elliott EM, Kendall C. 2008. Evaluating regional patterns in nitrate sources to watersheds in national parks of the Rocky Mountains using nitrate isotopes. *Environ Sci Technol* 42:6487–93.
- NERC. 2010a. *Northeastern Ecosystem Research Cooperative (NERC) compilation of foliar chemistry data for the north-*

- eastern United States and southeastern Canada. NERC 12.6. <http://www.nercscience.org>. Accessed 22 Nov 2010.
- NERC. 2010b. Northeastern Ecosystem Research Cooperative (NERC) compilation of surface water chemistry data for the northeastern United States and southeastern Canada. NERC 14.4. <http://www.nercscience.org>. Accessed 22 Nov 2010.
- Nilsson LO, Wallander H. 2003. Production of external mycelium by ectomycorrhizal fungi in a Norway spruce forest was reduced in response to nitrogen fertilization. *New Phytol* 158:409–16.
- Ollinger SV, Aber JD, Lovett GM, Millham SE, Lathrop RG, Ellis JM. 1993. A spatial model of atmospheric deposition for the northeastern United States. *Ecol Appl* 3:459–72.
- Ollinger S, Aber J, Federer C, Lovett G, Ellis J. 1995. Modeling physical and chemical climate of the northeastern United States for a geographical information system. USDA Forest Service General Technical Report NE-191, Radnor, PA.
- Ollinger SV, Smith ML, Martin ME, Hallett RA, Goodale CL, Aber JD. 2002. Regional variation in foliar chemistry and N cycling among forests of diverse history and composition. *Ecology* 83:339–55.
- Pardo LH, Templer PH, Goodale CL, Duke S, Groffman PM, Adams MB, Boeckx P, Boggs J, Campbell J, Colman B, Compton J, Emmett B, Gundersen P, Kjonaas J, Lovett G, Mack M, Magill A, Mbila M, Mitchell MJ, McGee G, McNulty S, Nadelhoffer K, Ollinger S, Ross D, Rueth H, Rustad L, Schaberg P, Schiff S, Schlei P, Spoelstra J, Wessel W. 2006. Regional assessment of N saturation using foliar and root delta N-15. *Biogeochemistry* 80:143–71.
- Pardo LH, McNulty SG, Boggs JL, Duke S. 2007. Regional patterns in foliar N-15 across a gradient of nitrogen deposition in the northeastern US. *Environ Pollut* 149:293–302.
- Pardo LH, Fenn M, Goodale CL, Geiser LH, Driscoll CT, Allen EB, Baron J, Bobbink R, Bowman WD, Clark C, Emmett B, Gilliam FS, Greaver T, Hall SJ, Lilleskov EA, Liu L, Lynch J, Nadelhoffer K, Perakis S, Robin-Abbott MJ, Stoddard J, Weathers K, Dennis RL. 2011. Effects of nitrogen deposition and empirical nitrogen critical loads for ecoregions of the United States. *Ecol Appl* 21:3049–82.
- Perring MP, Hedin LO, Levin SA, McGroddy M, de Mazancourt C. 2008. Increased plant growth from nitrogen addition should conserve phosphorus in terrestrial ecosystems. *Proc Nat Acad Sci USA* 105:1971–6.
- Pettersson R, McDonald AJS, Stadenberg I. 1993. Response of small birch plants (*Betula pendula*—Roth) to elevated CO<sub>2</sub> and nitrogen supply. *Plant, Cell Environ* 16:1115–21.
- Redfield AC. 1958. The biological control of chemical factors in the environment. *Am Sci* 46:205–21.
- Reich PB, Oleksyn J. 2004. Global patterns of plant leaf N and P in relation to temperature and latitude. *Proc Nat Acad Sci USA* 101:11001–6.
- Schaberg PG, Perkins TD, McNulty SG. 1997. Effects of chronic low-level N additions on foliar elemental concentrations, morphology, and gas exchange of mature montane red spruce. *Can J For Res* 27:1622–9.
- Schaberg PG, DeHayes DH, Hawley GJ, Murakami PF, Strimbeck GR, McNulty SG. 2002. Effects of chronic N fertilization on foliar membranes, cold tolerance, and carbon storage in montane red spruce. *Can J For Res* 32:1351–9.
- Schindler DE. 1977. Evolution of phosphorus limitation in lakes. *Science* 195:260–2.
- Schindler DW, Hecky RE, Findlay DL, Stainton MP, Parker BR, Paterson MJ, Beaty KG, Lyng M, Kasian SEM. 2008. Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. *Proc Nat Acad Sci USA* 105:11254–8.
- Sherman J, Fernandez IJ, Norton SA, Ohno T, Rustad LE. 2006. Soil aluminum, iron, and phosphorus dynamics in response to long-term experimental nitrogen and sulfur additions at the Bear Brook Watershed in Maine, USA. *Environ Monit Assess* 121:421–9.
- Tessier JT, Raynal DJ. 2003. Use of nitrogen to phosphorus ratios in plant tissue as an indicator of nutrient limitation and nitrogen saturation. *J Appl Ecol* 40:523–34.
- Thomas RQ, Canham CD, Weathers KC, Goodale CL. 2010. Increased tree carbon storage in response to nitrogen deposition in the US. *Nat Geosci* 3:13–17.
- Townsend AR, Cleveland CC, Asner GP, Bustamante MMC. 2007. Controls over foliar N:P ratios in tropical rain forests. *Ecology* 88:107–18.
- Treseder KK. 2004. A meta-analysis of mycorrhizal responses to nitrogen, phosphorus, and atmospheric CO<sub>2</sub> in field studies. *New Phytol* 164:347–55.
- Vadeboncoeur MA. 2010. Meta-analysis of fertilization experiments indicates multiple limiting nutrients in northeastern deciduous forests. *Can J For Res* 40:1766–80.
- Vitousek PM, Porder S, Houlton BZ, Chadwick OA. 2010. Terrestrial phosphorus limitation: mechanisms, implications, and nitrogen–phosphorus interactions. *Ecol Appl* 20:5–15.
- Wallenda T, Kottke I. 1998. Nitrogen deposition and ectomycorrhizas. *New Phytol* 139:169–87.
- Weand MP, Arthur MA, Lovett GM, McCulley RL, Weathers KC. 2010a. Effects of tree species and N additions on forest floor microbial communities and extracellular enzyme activities. *Soil Biol Biochem* 42:2161–73.
- Weand MP, Arthur MA, Lovett GM, Sikora F, Weathers KC. 2010b. The phosphorus status of northern hardwoods differs by species but is unaffected by nitrogen fertilization. *Biogeochemistry* 97:159–81.
- Weathers KC, Lovett GM, Likens GE, Lathrop R. 2000. The effect of landscape features on deposition to Hunter Mountain, Catskill Mountains, New York. *Ecol Appl* 10:528–40.
- Weathers KC, Simkin SM, Lovett GM, Lindberg SE. 2006. Empirical modeling of atmospheric deposition in mountainous landscapes. *Ecol Appl* 16:1590–607.
- Yanai RD. 1992. Phosphorus budget of a 70-year-old northern hardwood forest. *Biogeochemistry* 17:1–22.
- Yin XW. 1993. Variation in foliar nitrogen concentration by forest type and climatic gradients in North America. *Can J For Res* 23:1587–602.
- Yu X, Driscoll CT, Montesdeoca M, Evers D, Duron M, Williams K, Schoch N, Kamman NC. 2011. Spatial patterns of mercury in biota of Adirondack, New York lakes. *Ecotoxicology* 20:1543–54.
- Zhu XB, Cox RM, Arp PA. 2000. Effects of xylem cavitation and freezing injury on dieback of yellow birch (*Betula alleghaniensis*) in relation to a simulated winter thaw. *Tree Physiol* 20:541–7.