Spatial patterns of soil nitrification and nitrate export from forested headwaters in the northeastern United States

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[1] Nitrogen export from small forested watersheds is known to be affected by N deposition but with high regional variability. We studied 10 headwater catchments in the northeastern United States across a gradient of N deposition ($5.4 - 9.4$ kg ha^{-1} yr^{-1}) to determine if soil nitrification rates could explain differences in stream water NO_3^- export. Average annual export of two years (October 2002 through September 2004) varied from 0.1 kg NO_3^--N ha^{-1} yr^{-1} at Cone Pond watershed in New Hampshire to 5.1 kg ha^{-1} yr^{-1} at Buck Creek South in the western Adirondack Mountains of New York. Potential net nitrification rates and relative nitrification (fraction of inorganic N as NO_3^-) were measured in Oa or A soil horizons at 21–130 sampling points throughout each watershed. Stream NO_3^- export was positively related to nitrification rates ($r^2 = 0.34$, $p = 0.04$) and the relative nitrification ($r^2 = 0.37$, $p = 0.04$). These relationships were much improved by restricting consideration to the 6 watersheds with a higher number of rate measurements (59–130) taken in transects parallel to the streams (r^2 of 0.84 and 0.70 for the nitrification rate and relative nitrification, respectively). Potential nitrification rates were also a better predictor of NO_3^- export when data were limited to either the 6 sampling points closest to the watershed outlet ($r^2 = 0.75$) or sampling points <250 m from the watershed outlet ($r^2 = 0.68$). The basal area of conifer species at the sampling plots was negatively related to NO_3^- export. These spatial relationships found here suggest a strong influence of near-stream and near-watershed-outlet soils on measured stream NO_3^- export.

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1. Introduction

[2] Forested headwater catchments in the northeastern United States are important contributors of both water and nitrogen (N) to higher-order rivers [*Alexander et al.*, 2007]. High stream water N export has been linked to anthropogenic sources [*Likens and Bormann*, 1974a, 1974b, 1995; *Vitousek et al.*, 1997; *Caraco and Cole*, 1999] and can be a symptom of excess N in the watershed, which can cause eutrophication downstream. Although anthropogenic N deposition may be a regional driver of stream N export [e.g., *Boyer et al.*, 2002; *Howarth et al.*, 2006], high variability is found among small watersheds. In eastern North America, adjacent watersheds can have drastically different N export patterns and rates [e.g., *Ross et al.*, 1994; *Schiff et al.*, 2002; *Hales et al.*, 2007; *Christopher et al.*, 2008]. The variability has been related to many watershed attributes including soil chemistry (as it affects N transformation rates), hydrology, topography, vegetation (primarily tree species and age), land use history and in-stream processes. All of these potential drivers are interrelated and their relative influence varies among watersheds. Quantifying the role of these factors with respect to stream N export remains a challenge.

[3] Two of the factors mentioned above, hydrology and in-stream processes, have received considerable attention in recent years. Watershed-specific characteristics such as hydrological flow paths [*Schiff et al.*, 2002; *Watmough et al.*, 2004] can alter seasonal variation in N export and annual flux. The hydrologic connectivity across the landscape is crucial in determining the movement of both water [*Jencso*

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et al., 2009] and solutes [*Covino and McGlynn*, 2007]. Different stream reaches may be gaining or losing water, which affects the relationship of soil nitrification rates to stream export. Recent work has also shown the importance of in-stream NO_3^- and especially NH_4^+ uptake, consuming as much as half of the inorganic N inputs to headwater streams [*Peterson et al.*, 2001; *Bernhardt et al.*, 2003]. *Mulholland et al.* [2008] further showed that in-stream NO_3^- uptake and denitrification were both important sinks for terrestrial NO_3^- inputs but that these processes were less efficient as N inputs increased. Thus, even accounting for in-stream NO_3^- consumption, greater terrestrial inputs of NO_3^- likely lead to greater stream NO_3^- export.

[4] Rates of N deposition have been much higher across Europe than northeastern North America and a clearer pattern of deposition effects has emerged there [*MacDonald et al.*, 2002; *Aber et al.*, 2003]. High NO_3^- leaching has invariably been observed when inorganic N deposition rates were higher than 30 kg ha^{-1} yr^{-1} and the soil pH was <4.5 [*MacDonald et al.*, 2002]. In the northeastern United States, total N deposition rates have usually been <12 kg ha^{-1} yr^{-1} [*Aber et al.*, 2003] and have decreased somewhat over the last decade [*Aleksic et al.*, 2009; *Butler et al.*, 2011]. Within this lower range, the effect of N deposition on N loss has not always been clear [*Aber et al.*, 2003]. *Gundersen et al.* [2006], compiling studies from both Europe and North America, showed that high concentrations of NO_3^- beneath the soil profile and in surface waters were associated with either increased N input (fertilization or deposition), reduced plant uptake (e.g., from harvest activity), or enhanced mineralization of soil N. Many studies have shown that additions of N will enhance soil mineralization rates and, so, the concept of using soil nitrification rates to predict NO_3^- export is reasonable. Inputs of N are processed in watershed soils and, as the system becomes saturated with N, soil nitrification and NO_3^- stream export should both increase [*Ågren and Bosatta*, 1988; *Aber et al.*, 1989]. However, this progression has not been routinely observed in the northeastern United States [*Lovett and Goodale*, 2011]. *Goodale et al.* [2003] found a decline in NO_3^- export in New Hampshire streams between the mid-1970s and the mid-1990s during a period when N deposition was relatively high. They hypothesized that climate variation could be increasing N retention and masking the above effects. The connection between watershed soil processes and NO_3^- export is not always clear [*Judd et al.*, 2011] with in-stream processing likely a factor in affecting watershed export [*Bernhardt et al.*, 2005]. With N deposition now decreasing in the region, it may be even more difficult to discern cause and effect [*Kothawala et al.*, 2011]. However, soil N transformation rates, specifically net nitrification, may still prove to be a good predictor of stream NO_3^- export among watersheds.

[5] In most northeastern U.S. watersheds, the large majority of nitrate export occurs during periods of high flow in the fall and spring, especially during snowmelt. During the growing season, plant uptake limits leaching of nitrate and overall downward water movement is also limited by evapotranspiration [*Driscoll et al.*, 2001]. Disease and defoliation can result in both greater net nitrification and nitrate leaching by altering the water cycle [*Townsend et al.*, 2004]. Production of nitrate occurs during the winter months and flushing of nitrate out of the watershed occurs during the spring [*Driscoll et al.*, 2003; *Sebestyen et al.*, 2008]. Similarly, any excess nitrate from the summer is mobilized when shallow hydrologic pathways are reactivated during fall storms. During these periods, the relative contribution of water flowing through upper soil horizons is greatest. Measurements of potential net nitrification in the upper soil should therefore relate to overall nitrate export, assuming connectivity of soil sampling locations to shallow flow paths and the stream network.

[6] In an earlier study, we measured soil net nitrification and ammonification rates at 10 small research watersheds in the mountains of New York, Vermont and New Hampshire [*Ross et al.*, 2009]. The goal was to determine if there were common factors controlling net nitrification rates across a number of sites with differing watershed characteristics, such as dominant tree species and topographical metrics. Similar to many other studies [e.g., *Dise et al.*, 1998; *Lovett et al.*, 2002; *Ross et al.*, 2004], the soil C/N ratio was related to net nitrification rates. The best overall single predictor, however, was the proportion of conifer species (basal area) in the sampling plots. Contrary to many previous studies [e.g., *Lovett et al.*, 2002, 2004; *Ross et al.*, 2004], *Ross et al.* [2009] found no positive effect of sugar maple (*Acer saccharum*) on net nitrification; plots dominated by yellow birch (*Betula alleghaniensis*) had rates that were just as high as plots dominated by sugar maple. The goal of the present study was to determine if watershed-wide measures of nitrification rates predict stream NO_3^- export. Our hypothesis was that potential net nitrification rates measured in the near-surface horizons would be proportional to the NO_3^- transported into the streams and exported from the watershed. Connectivity between soils with high potential nitrification rates and the stream should result in greater stream nitrate export.

[7] The inclusion of adjacent watersheds with differing patterns of NO_3^- export enabled further exploration of factors affecting export in headwater catchments receiving similar inputs of N deposition.

2. Methods

2.1. Sites

[8] The 10 study watersheds were located at seven research sites across three northeastern U.S. states and ranged in size from 7 to 217 ha (Figure 1 and Table 1). Each catchment contained one first- or second-order gauged stream. All watersheds were completely forested with vegetation ranging from mixed northern hardwoods to mixed conifers (Figure 2). All forests were closed canopy of mixed age but generally mature with no harvesting for at least 55 years. Leaf area index (LAI) measured in 2000 in the Hubbard Brook Experimental Forest (HBEF) watersheds 1 and 6 ranged from ~5–6 m^2/m^2, with lower values found at higher elevations [*Rhoads et al.*, 2002]. This range is likely representative of LAI in the other watersheds, where no such data exist. At three sites, 2 contrasting watersheds were studied (described further below). Sites were selected because of ongoing stream monitoring and to cover both a range in forest type and geographical location. A brief description of each watershed follows.

[9] The Winnisook drains the eastern slope of Slide Mountain, the highest peak in the Catskill Mountains of

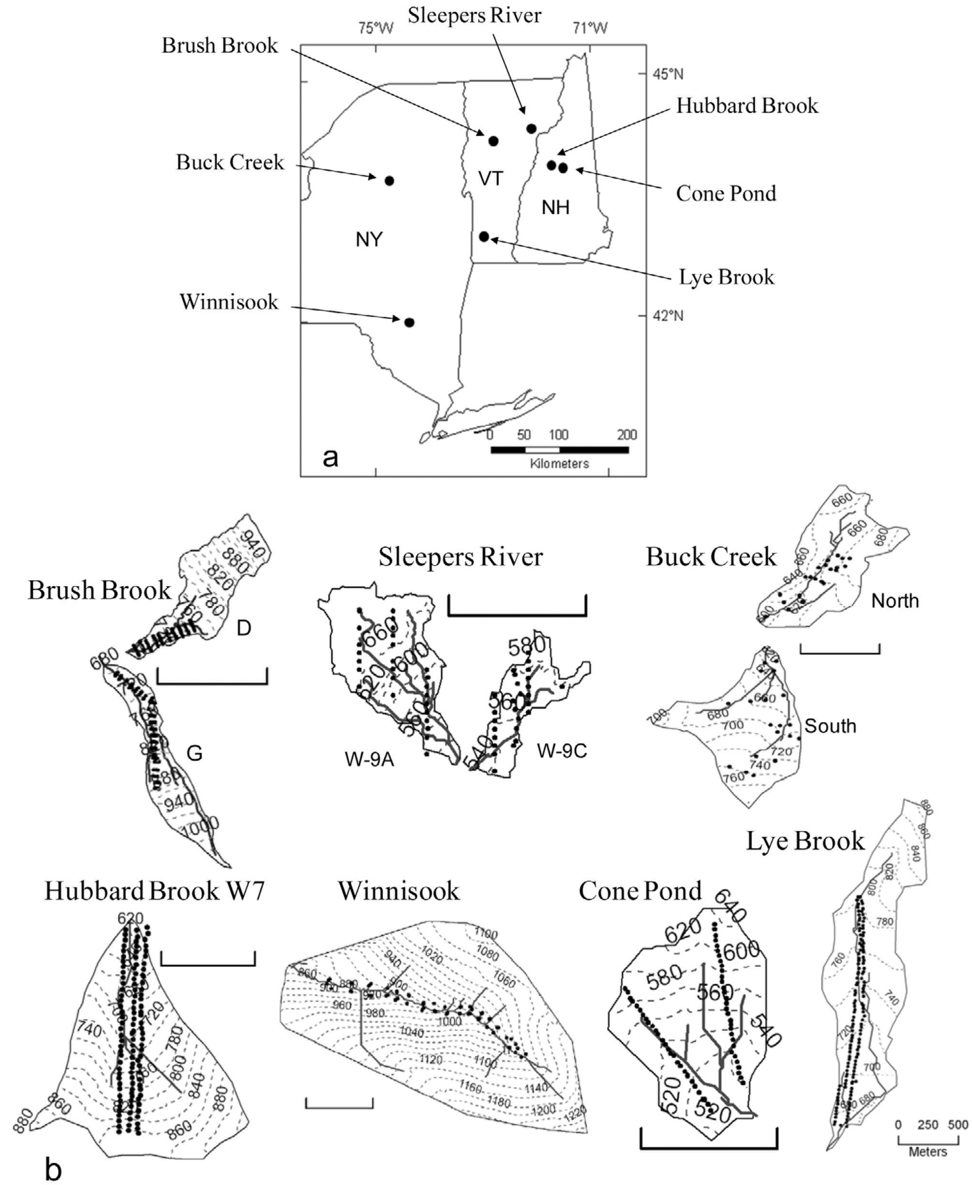

Figure 1. (a) Location of the watersheds in New York (NY), Vermont (VT), and New Hampshire (NH). (b) Watershed maps, giving location of sampling points (Winnisook shows only half of the sampling points), stream channels, and 30 m contours. The scale bar associated with each watershed is 500 m (watershed sizes are given in Table 1).

Table 1. Watershed Location, Size, Average Elevation and Slope (as Determined With a Digital Elevation Model), 2003/2004 N Deposition and Precipitation, and Bedrock Lithology

Watershed	Location	Area (ha)	Average Elevation (m)	Average Slope (deg)	Annual N Deposition[a] (kg ha^{-1})	Annual Precipitation[a] (cm)	Bedrock Lithology
Winnisook	Oliverea, NY	217	1038	17	9.41	173	quartz sandstone
Buck Creek South	Inlet, NY	52	692	8	7.03	130	granitic gneiss
Buck Creek North	Inlet, NY	33.7	649	8	6.86	127	granitic gneiss
Lye	Sunderland, VT	121	759	5	7.17	150	granitic gneiss
Brush Brook G	Huntington/Duxbury, VT	11.4	839	21	6.57	145	mica schist
Brush Brook D	Huntington/Duxbury, VT	15.4	841	22	6.57	145	mica schist
Sleepers W9-A	Walden, VT	16	636	10	5.58	132	calc-granulite/mica schist
Sleepers W9-C	Walden, VT	7	566	5	5.36	127	calc-granulite/mica schist
HBEF W7	Ellsworth, NH	76	772	14	6.15	149	sulfidic mica schist
Cone Pond	Thornton, NH	33	564	11	5.53	135	mica schist/quartzite

[a]Modeled for 2003 and 2004 with ClimCalc (updated from *Ollinger et al.* [1993]).

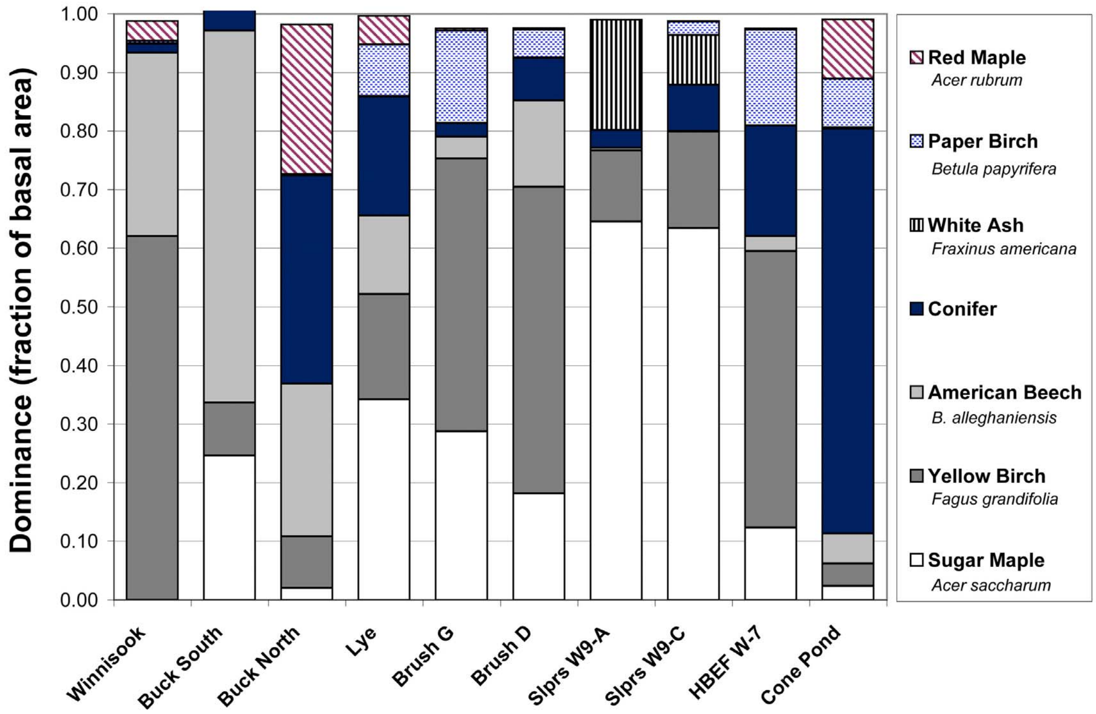

Figure 2. The relative dominance of tree species in the nitrification rate sampling plots at each watershed. Values represent the fraction of the total basal area (≥10 cm dbh) represented by each species. Conifer species consisted of red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), and eastern hemlock (*Tsuga canadensis*).

New York State. This was the largest watershed studied and has the highest average elevation (Table 1). Some selective harvesting has occurred over the last 100 years in the lower half of the watershed but none more recent than the 1960s.

[10] The Buck Creek watershed is located in the western Adirondack Mountains of NY and 2 subwatersheds with contrasting tree species were sampled. Buck South is dominated by American beech (*Fagus grandifolia*) whereas Buck North has a strong component of conifers (primarily red spruce, *Picea rubens*) and beech (Figure 2). The Buck North watershed is also smaller, narrower with more rugged terrain than Buck South (Table 1) and the Buck North stream is more acidic and has lower base flow under extended dry conditions compared to Buck South [*Lawrence et al.*, 2007, 2011]. Land use has been logging and recreation, but no logging has occurred for at least 50–60 years.

[11] The Lye stream is located in southern Vermont's Green Mountains just south of the Lye Brook Wilderness Area. The watershed has a low average slope (Table 1) and a minor component of wetlands; 4.7% is shown in the 2011 National Wetlands Inventory (http://www.fws.gov/wetlands), whereas none is mapped at the other sites (although Buck Creek does not appear to be included in the current database). The Lye area was logged approximately 85 years ago [*Campbell et al.*, 2000].

[12] Brush Brook D and G are located in Camels Hump State Forest in the central Green Mountains of Vermont. The 2 watersheds drain opposing slopes and have contrasting NO_3^- export patterns [*Ross et al.*, 2004; *Hales et al.*, 2007]. Brush Brook D has relatively shallow soils with dense basal till and the stream is intermittent and acidic (pH 5.0 average 1996–1999 [*Hales et al.*, 2007]). Brush Brook G has deeper soils without densipan, numerous high-pH (≥7.0) seeps, and the stream pH is near neutral [*Ross et al.*, 1994; *Hales et al.*, 2007]. Land use history is logging, and operations ceased in the early 1960s [*Whitney*, 1988].

[13] The Sleepers River Research Watershed in northeastern Vermont contains a forested headwater catchment, W9 [*Shanley et al.*, 2002, 2004; *Pellerin et al.*, 2011]. This 41 ha watershed has 3 subwatersheds, and we studied W-9A and W-9C. These 2 small watersheds differ mainly in topographic relief, with the average slope of W-9C much lower (Table 1). Land use history includes both agriculture and logging, with the last intensive logging in 1929 and selective cutting in 1960 [*Thorne et al.*, 1988; *Sebestyen et al.*, 2008].

[14] In HBEF, the 76 ha watershed 7 (W7) was last logged about 80 years ago [*Likens and Bormann*, 1995]. Compared to the south-facing watersheds at the HBEF, which are mostly composed of northern hardwoods, W7 has a greater spruce-fir component. W7 is at a higher elevation on a north-facing slope, and the difference in vegetation has been attributed to the colder climate [*Schwarz et al.*, 2003].

[15] The Cone Pond watershed [*Bailey et al.*, 1995, 1996] is conifer dominated (Figure 2) with a mixture of red spruce and eastern hemlock (*Tsuga canadensis*). It differs in land use history from the other watersheds in that there is no known forest harvest, but there was a large fire around 1820 [*Buso et al.*, 1984] and charcoal can still be found beneath the forest floor [*Ross et al.*, 2011].

[16] Bedrock type varies considerably among watersheds from low-Ca sandstones at Winnisook to a range of metamorphosed sedimentary rocks at most other sites (Table 1). Sleepers River is underlain with quartz-mica schist with beds of calcareous granulite [*Shanley et al.*, 2004] and W9-A contains numerous enriched seeps. Soils at all sites are fine sandy loams or silt loams and are classified as either Spodosols or Inceptisols. The Inceptisols usually display some podzolization and are generally found at wetter sites or sites with higher base cation status [*Ross*, 2007].

2.2. Nitrate Export

[17] Depending on the nature of the stream sampling, different methods were used to calculate annual NO_3^- export. At Cone Pond and HBEF W7, sampling for chemical analyses was performed weekly. At the other watersheds, sampling for chemical analyses was flow based using automated samplers but also included weekly to monthly grab samples. Stream stage was continuously monitored using V notch weirs at Cone Pond, HBEF W7, Brush Brook, Buck North and Sleepers River, and natural controls at the other sites. Stage was converted to discharge for sites with natural controls, using rating curves developed from manual flow measurements taken over a range of conditions. Daily water flux and weekly NO_3^- concentrations were used to calculate annual NO_3^- export at Cone Pond and HBEF W7. Nitrate flux at Sleepers River, Brush Brook and Lye was computed using concentration models based on instantaneous flow, antecedent flow, and seasonal terms [*Aulenbach and Hooper*, 2006; *Peters et al.*, 2006]. At Sleepers River, periods of missing flow record at W-9A and W-9C were reconstructed from well-established relations with flow at the main W-9 weir. At Winnisook and the two Buck Creek sites, daily concentrations of NO_3^- were estimated from daily flow for months in which a statistically significant relation between flow and concentration existed. Data collected from 1999 to 2004 were used to develop concentration-flow relationships. If a concentration-flow relation did not exist for a month, the monthly mean concentration was used for each day in that month. Daily concentrations were applied to daily flows to determine daily fluxes that were summed for the individual water years. Though water year (WY) periods used by individual sites varied, this investigation used a common WY beginning 1 October; for example, WY 2003 runs from 1 October 2002 through 30 September 2003. Nitrate in stream samples from Lye, Sleepers River and Cone Pond was analyzed at the USFS Northern Research Station analytical lab in Durham, NH. Samples from Winnisook and Buck Creek were analyzed at the U.S. Geological Survey Laboratory in Troy, NY; HBEF W7 samples were analyzed at the Cary Institute for Ecosystem Studies Rachel Carson Analytical Laboratory in Millbrook, NY and those from Brush Brook at the UVM Agricultural and Environmental Testing Lab. All labs employed ion chromatography using standard methods and all labs participated in internal and external quality assurance programs.

2.3. Soil Nitrification Rates

[18] Potential net nitrification rates were determined by the 1 day method of *Ross et al.* [2006], which measures the NO_3^- concentration in the field and again after 1 day's incubation of a mixed horizon sample, i.e., not an intact core. All methods that measure N transformation rates in forest soils cause some degree of disturbance that can alter the rates [*Hart et al.*, 1994; *Ross and Hales*, 2003; *Kaur et al.*, 2010] and thus rates are necessarily termed "potential." The 1 day rates are relatively high but well correlated with both longer incubations of mixed soil samples [*Ross et al.*, 2006] and intact cores [*Ross et al.*, 2004]. These potential rate measurements are indices and should not be interpreted as actual rates, regardless of the method. The 1 day procedure provides a quick potential rate measurement with the advantage of also measuring the in situ NO_3^- concentration. We measured potential rates in the first horizon below the Oe that was >2 cm thick (i.e., thick enough to sample). This was either an Oa (≥20% C) or an A (<20% C) horizon using USDA Natural Resource Conservation Service criteria [*Natural Resources Conservation Service Soil Survey Staff*, 2006]. We chose this upper soil horizon for two primary reasons: (1) these high-organic surface horizons have the highest net nitrification rates in the soil profile and therefore should maximize differentiation among the watersheds and (2) this near-surface sampling is relatively rapid, enabling greater coverage of each watershed.

[19] Sites were sampled 2–4 times beginning in the fall of 2001 and ending in the spring of 2004, with the majority of the sampling (77%) performed between the fall of 2002 and the late spring of 2004, roughly corresponding with N export from water years 2003 and 2004. Two different approaches were used in the spatial distribution of sampling (Figure 1b). At all except the Buck Creek and Sleepers River sites, transects were oriented parallel to the mainstream channel, but well away from the riparian corridor, with sampling points established either 20 or 30 m apart. On each sampling date, alternate transect points were sampled (i.e., 40 or 60 m apart) or additional transects were laid out, usually 50 m distant, if previous ones were fully sampled. This approach provided spatial overlap in each sampling and allowed testing of seasonal variability.

[20] At all but one site, Brush G, no significant seasonal effect on nitrification rates was detected [*Ross et al.*, 2009]. Most sites were sampled four times but two were only sampled twice (Cone Pond and Winnisook); the number of sampling points ranged from 59 to 130 with a mean of 85 (Table 2). At the Buck Creek and Sleepers River research sites, we sampled at previously established transect points. Sleepers River W-9A and W-9C had north–south transects 122 m apart with 30.5 m between sampling points. We created an additional transect about halfway between the two already established in W-9C to provide more sampling points. Buck South and North both had seven transects, each with 2–5 sampling points, established approximately perpendicular to the stream. At both research sites, we performed repeated samplings in the neighborhood of each transect point [*Ross et al.*, 2009], resulting in fewer distinct sampling points (21–27) distributed throughout these 4 watersheds (Table 2).

2.4. Other Measurements

[21] Topographic and vegetation measurements were taken around each sampling point and a suite of chemical parameters were determined on the soil samples [*Ross et al.*, 2009]. Tree species (≥10 cm diameter breast height) were tallied in a circular plot (5 m radius at Brush Brook, 9 m radius

Table 2. Potential Net N Transformation Rates From the Oa or A Horizon, the C/N Ratio (Mass Basis) of the Horizon, Number of Sampling Points, and Their Density Averaged Over the Watershed[a]

	1 Day Nitrification (μmol kg^{-1} h^{-1})	1 Day N Mineralization (μmol kg^{-1} h^{-1})	Fraction of Inorganic N as NO_3^-	C/N Ratio	Number of Transect Points	Density Points/ha
			Winnisook Watershed			
Mean	19.2^{AB}	45.4	0.40	19.7	64	0.1
SE	1.7	3.2	0.03	0.5		
			Buck South Watershed			
Mean	11.8^{B}	37.9	0.33	20.3	21	0.4
SE	1.7	3.0	0.04	0.3		
			Buck North Watershed			
Mean	5.2^{C}	36.6	0.22	22.6	21	0.5
SE	1.1	2.2	0.03	0.6		
			Lye Watershed			
Mean	12.0^{B}	27.9	0.38	18.7	130	0.8
SE	0.8	1.7	0.02	0.2		
			Brush G Watershed			
Mean	19.5^{A}	23.7	0.59	16.8	66	6.0
SE	1.4	1.9	0.02	0.3		
			Brush D Watershed			
Mean	18.8^{AB}	30.1	0.46	17.5	80	6.0
SE	1.5	2.0	0.03	0.3		
			Sleepers W9-A Watershed			
Mean	22.1^{A}	29.2	0.44	15.0	27	1.7
SE	2.8	4.1	0.04	0.4		
			Sleepers W9-C Watershed			
Mean	7.7^{C}	31.6	0.14	17.7	27	3.9
SE	2.4	5.6	0.02	0.4		
			HBEF W-7 Watershed			
Mean	7.0^{C}	21.9	0.24	19.0	113	1.2
SE	0.7	1.7	0.02	0.2		
			Cone Pond Watershed			
Mean	1.3^{D}	3.4	0.11	27.4	59	1.8
SE	0.7	2.3	0.02	0.9		

[a]Significant differences (p-value < 0.05) among watershed nitrification rates are indicated by different superscript capitals; SE, standard error.

at Buck Creek and 10 m at all other sites) around each point and dominance calculated as the proportion of total basal area of any species or combination of species (Figure 2).

[22] Topographic metrics for each sampling location were also derived using 10 m digital elevation models (DEMs) from the national elevation data set (NED) of the U.S. Geological Survey [*Gesch et al.*, 2009]. Slope and aspect were derived using standard algorithms in ArcGIS v. 9.3.1 [*Environmental Systems Resource Institute*, 2009]. DEMs were processed using the *flowdirection* and *flowlength* algorithms of ArcGIS to estimate flow path distance from each sampling site to the location of the gage site for each watershed.

[23] The N deposition and precipitation estimates (Table 1) were derived from an updated version of ClimCalc [*Ollinger et al.*, 1993], generously provided by Danielle Haddad (personal communication, 2010). ClimCalc is a simple model for estimating atmospheric deposition in areas where it is not measured. The model was developed for the northeastern U.S. and uses a linear regression approach based on data from precipitation and chemical monitoring networks to generate spatial coverages. Wet deposition is estimated from precipitation volume and chemical measurements, whereas dry deposition is obtained by combining atmospheric concentrations of dry-deposited species with estimates of deposition velocities. Deposition velocities are difficult to measure and may be off by as much as a factor of 2 [*Ollinger et al.*, 1993]. The model provides annual estimates of wet and dry NH_4^+ and NO_3^- deposition on a calendar year basis.

[24] Linear regression analysis was performed using SAS 9.1 [*SAS Institute*, 2003] on NO_3^- export using a subset of independent variables from the watershed averages for nitrification rates and tree species from *Ross et al.* [2009]. The normality and variance of residuals were examined graphically to ensure all assumptions were met, especially with the small sample size.

[25] Canonical correspondence analysis (CCA) was used to explore the relationship between tree species distribution and three watershed measurements: average annual nitrate export, potential net nitrification rates and surface soil C/N ratio. This multivariate approach ordinates species distribution relative to the independent variables [*Peck*, 2010]. Watershed plot averages of basal area were used for the 11 species found; resulting in a matrix of 110 numbers with 21 zero values. Analysis was performed using PC-ORD [*McCune and*

Table 3. Nitrate Export for the 10 Watersheds for Water Years (WY) 2003 and 2004 (1 October–30 September) and, Where Available, Average Export for the Previous 4 Years

Watershed	Nitrate Export WY03 (kg N ha^{-1} yr^{-1})	Nitrate Export WY04 (kg N ha^{-1} yr^{-1})	Nitrate Export Average WY03–04 (kg N ha^{-1} yr^{-1})	Nitrate Export Average WY99–02 (kg N ha^{-1} yr^{-1})
Winnisook	3.68	5.90	4.79	2.14
Buck Creek South	4.75	5.38	5.07	5.13
Buck Creek North	1.15	1.38	1.27	1.13
Lye	2.50	5.05	3.78	nd
Brush Brook G	5.54	4.03	4.78	nd
Brush Brook D	4.91	1.85	3.38	nd
Sleepers W9-A	1.87	1.40	1.63	nd
Sleepers W9-C	0.60	0.45	0.52	nd
HBEF W7	0.90	0.92	0.91	1.07
Cone Pond	0.15	0.00	0.08	0.12

Mefford, 2011] with axis scores centered and standardized to unit variance. A randomization test was used to reject the null hypothesis of no structure in the matrix of tree species data (p = 0.001). Similar axis scores were obtained when using dominance values (fraction of basal area) rather than basal area and when three minor tree species (*Acer pensylvanicum, Acer rubrum* and *Tilia americana*) were eliminated from the analysis.

3. Results and Discussion

[26] The watersheds were located along a northeast trajectory (Figure 1) with total N deposition decreasing from 9.4 kg ha^{-1} yr^{-1} at Winnisook in the Catskills of New York to between 5.4 and 6.2 kg ha^{-1} yr^{-1} in eastern Vermont and central New Hampshire (Table 1). Average annual precipitation varied from 1270 to 1730 mm, with the highest amount in the Catskills (Table 1). These long-term averages (1970–2000) adjusted for elevation by ClimCalc, are overall 10% higher than those reported by *Ross et al.* [2009]. Most of the latter were 2002–2004 averages from the nearest NADP site, which was usually at a lower elevation. All watersheds were completely forested and tree species varied from mixed northern hardwood, with one of the three species (sugar maple, American beech (*Fagus grandifolia*) or yellow birch) usually dominant, to mixed conifers (red spruce, eastern hemlock and some balsam fir (*Abies balsamea*)) at Cone Pond (Figure 2). Average carbon (C) in the surface soils sampled (Oa or A horizon) ranged between 187 g kg^{-1} at Sleepers River W-9A to 441 g kg^{-1} at Buck Creek North [*Ross et al.*, 2009]. In all but the Sleepers River watersheds, Oa/A soil pH (3.1–3.7) was typical of the region. Sleepers River soils had higher pH (4.5–4.9) and high exchangeable calcium (Ca), reflecting the calcareous bedrock, but neither pH nor exchangeable Ca was found to be a good predictor of net nitrification rates across the 10 watersheds [*Ross et al.*, 2009].

3.1. Nitrate Export

[27] There was a broad range in NO_3^- export among watersheds during the 2003 and 2004 water years (Table 3), from 0.1 at Cone Pond to over 5 kg NO_3^-–N ha^{-1} yr^{-1} at Buck Creek South. These 2 water years were the only ones with data available for all watersheds but, for watersheds that had additional years of measurements, the longer-term averages were close to the 2003/04 average (Table 3), with the notable exception of Winnisook, where 2003/04 NO_3^- export was more than two times greater than in the period 1999–2002. The range in NO_3^- export was similar to that reported by *Campbell et al.* [2004] for 24 small watersheds that spanned a broader geographical range in the northeastern United States (West Virginia to Maine). Export of NO_3^- was highest in all watersheds during the spring snowmelt period, typical of most high-elevation watersheds in this region This spring flush may be common only in those northeastern watersheds with large snowpacks; *Goodale et al.* [2009] recently found a different pattern in lower-elevation forested headwaters in New York. Other forms of N export, specifically NH_4^+ and dissolved organic nitrogen (DON), were not measured in all watersheds. In streams where NH_4^+ was determined, it was typically low (<0.01 mg L^{-1}). In the watersheds where DON was analyzed, the annual values during this period were around 1 kg N ha^{-1} yr^{-1}, consistent with earlier findings in the same and similar watersheds by *Campbell et al.* [2000]. Although watershed retention of N deposition was not quantifiable at all sites because the total N export was not determined, N retention appeared to vary considerably, from quite high at Cone Pond (DON export averaged 0.7 kg ha^{-1} yr^{-1}, making total N export <1 kg ha^{-1} yr^{-1}) to less than 30% retention at Brush G. The large differences in export between geographically close watersheds (i.e., the 2 each at Buck Creek, Brush Brook and Sleepers River and HBEF W-7 versus Cone Pond) demonstrate that regional variation in drivers such as climate and anthropogenic N deposition was not the primary control on stream N export.

3.2. Potential Net Nitrification Rates and Export

[28] Potential net nitrification rates also ranged widely (Table 2 [see also *Ross et al.*, 2009]). There were significant differences among the watersheds, resulting in four groupings of rates (Table 2) which could be classified as high (Brush D and G, Sleepers W-9A and Winnisook), medium (Lye and Buck South), low (HBEF-W7, Buck North and Sleepers W9-C) and very low (Cone). Overall, nitrification rates were significantly related to NO_3^- export (Figure 3a) but with considerable variability at high rates. If we include only the watersheds in which we sampled transects parallel to the stream channel, the relationship is much improved (Figure 3b), however the sample n of 6 is quite low and limits statistical power. The NO_3^- fraction of inorganic N (NO_3^- + NH_4^+) mineralized (relative or percent nitrification) has been used in comparing different rate measurement methods [*Aber et al.*, 2003] and as an indicator of the dominant N transformation pathway within a watershed [*Gilliam et al.*, 2001]. In

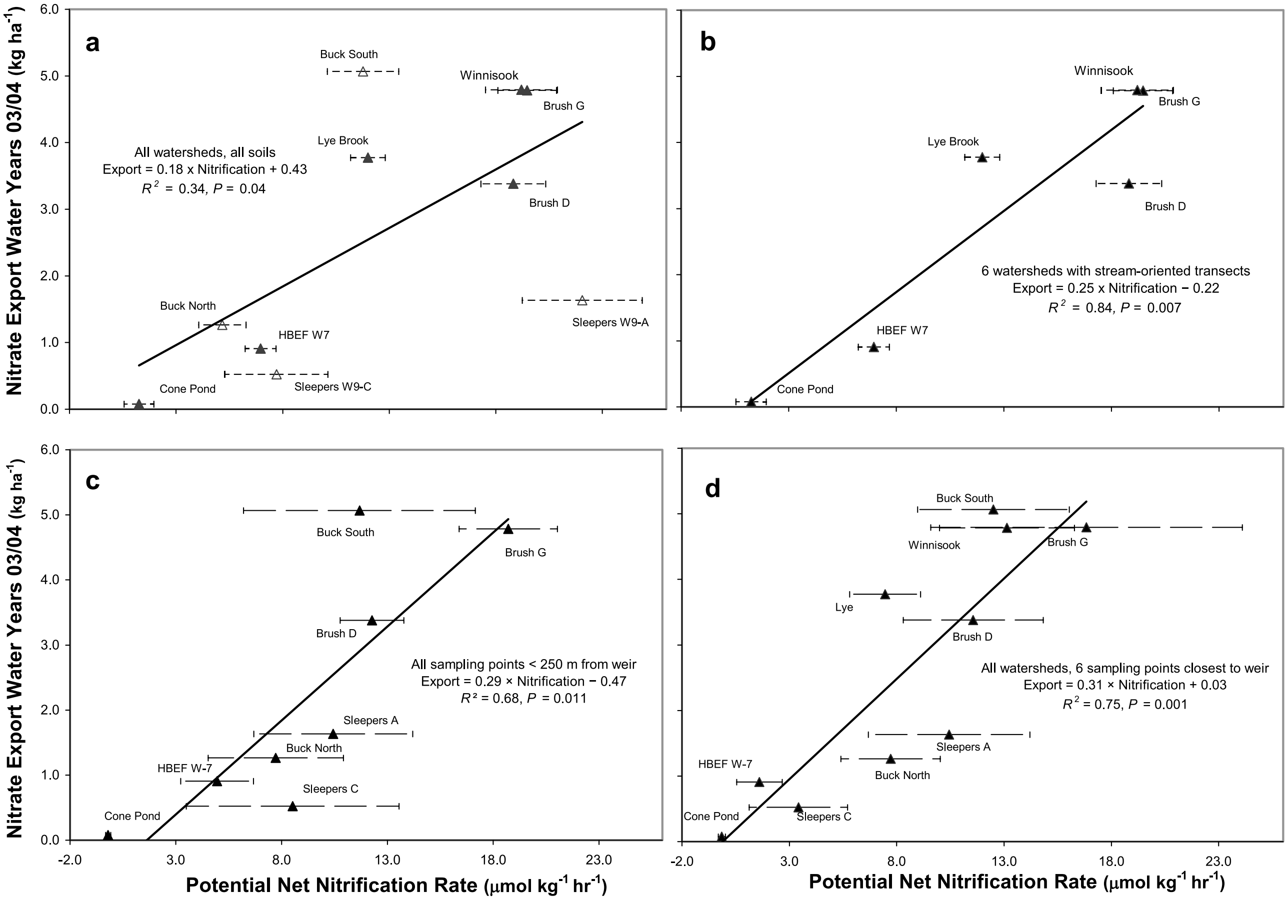

Figure 3. (a) Nitrate export from the 10 watersheds as a function of 1 day potential net nitrification rates measured in the Oa or A horizon. Closed triangles represent the 6 watersheds with higher sample numbers and transects oriented along the streams. (b) Nitrate export versus potential net nitrification rates for all samples from the 6 watersheds with higher sample numbers (closed triangles in Figure 3a). (c) Nitrate export versus potential net nitrification rates for only those samples within 250 m of the watershed outlet. Only 8 watersheds are included because Winnisook and Lye had no such sampling points. (d) Nitrate export versus the mean of the 6 sampling points closest to the watershed outlet.

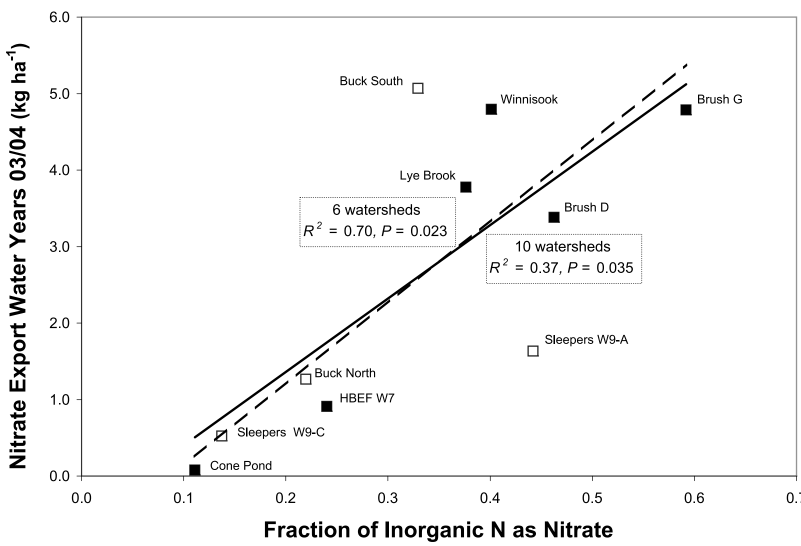

Figure 4. Nitrate export from the 10 watersheds as a function of relative nitrification or the fraction of inorganic N measured as NO_3^-. Closed squares represent the 6 watersheds with higher sample numbers and transects oriented along the streams.

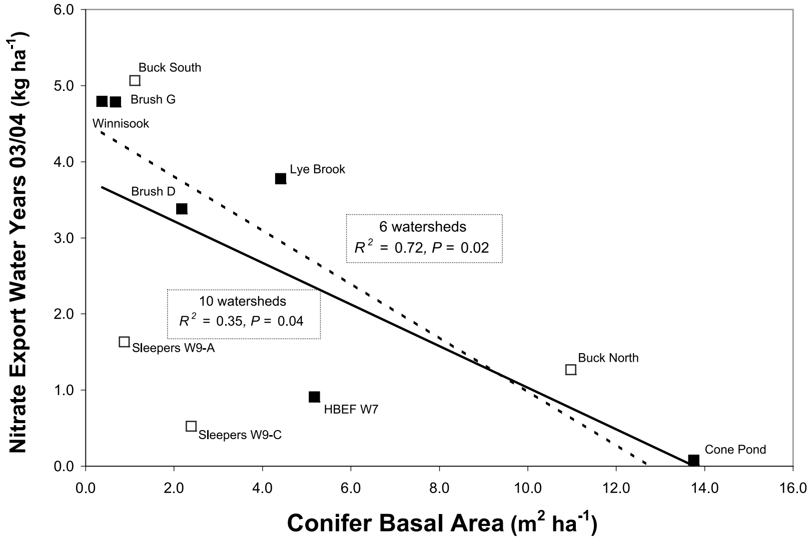

Figure 5. Nitrate export from the 10 watersheds as a function of the conifer basal area of plots around the nitrification rate sampling points. Closed squares represent the 6 watersheds with higher sample numbers and transects oriented along the streams.

our study, it was a slightly better predictor of NO_3^- export than nitrification rate for all the watersheds (Figure 4). In addition, the slopes were similar using either the 6 watersheds discussed above or all 10 watersheds, suggesting this may be a superior predictor. The soil concentration of NO_3^- in the field (time 0 in the net rate measurement) had the same explanatory power as relative nitrification for both sets of watersheds. Thus, a number of soil nitrification metrics were significantly related to stream NO_3^- export.

[29] The rationale for examining the subset of 6 watersheds separately (Figure 3b) is that these were the watersheds with the highest numbers of samples taken (Table 2) and had the sampling transects oriented parallel to the streams, in some cases, toward the bottom of the watershed (Figure 1b). The contrasting sampling schemes at Sleepers River and Buck Creek were utilized to take advantage of existing data collected at these points but the orientation and limited number of sites may not have represented nitrification rates in the watersheds adequately. The transects oriented parallel to the streams likely captured the potential for NO_3^- to move from the soil to the stream at periods of high flow such as during snowmelt, when most NO_3^- export occurred. The importance of the spatial relationship of the soil sampling points is further illustrated by examining only those points within 250 m flow path length of the watershed outlet (Figure 3c) or only the 6 sampling points closest to the watershed outlet in each watershed (Figure 3d). Both these subgroups explain much more of the variability in export (r^2 = 0.68 and 0.75, respectively) than using all points (Figure 3a, r^2 = 0.34). Two watersheds (Lye and Winnisook) did not have points within 250 m of the watershed outlet, while the remaining watersheds had an average of 14 points each (range 4–41). The improvement in the relationship (<250 m, Figure 3c) was not because of the absence of the Lye and Winnisook data (whose overall watershed averages lie close to the linear fit) but was strongly influenced by the lower nitrification rates in Sleepers W-9A and Brush D closer to the watershed outlet. Similarly, the strong relationship found when using only the 6 closest sampling points (Figure 3d) was the result of lower rates in the some of the watersheds having the highest overall net nitrification rates. The sampling scheme was not designed with this analytical approach in mind but our results are supported by recent work showing the importance of near-outlet stream solute inputs in determining the measured export [e.g., *Spoelstra et al.*, 2010] and the fact that stream reaches may both gain and lose water and solutes [e.g., *Covino and McGlynn*, 2007]. Along with in-stream processes, these factors may explain much of the apparent disconnect between overall watershed net nitrification rates and NO_3^- export measured at the watershed outlet.

3.3. Other Explanatory Variables

[30] In analyzing controls on the soil nitrification rates presented here, *Ross et al.* [2009] found that the most robust predictors were either the conifer or the red spruce basal area (strongly related to each other). Similar to many other studies, the soil C/N ratio was also a good curvilinear predictor of both soil nitrification rates and the abundance of conifers. In predicting watershed NO_3^- export, conifer basal area showed a significant relationship similar to nitrification metrics, with higher NO_3^- export found only in watersheds relatively low in conifer basal area (Figure 5). The tree species compositions are from the transect points (Figure 1b) and, thus, the species data may not represent the entire watershed but, on the other hand, may be representative of the portion of the watershed contributing more directly to streamflow generation. The soil C/N ratio (range 15.0–27.4) was not significant as a linear predictor of NO_3^- export, likely because the C/N ratio has a threshold (~23–25) above which net nitrification is usually negligible and it has not often been reported as a linear predictor of rates [*Gundersen et al.*, 2006]. Multivariate analysis (CCA, Figure 6) confirmed these findings, with net nitrification and C/N ratio both correlated with the first axis, which explained 37% of the species variance. Nitrate export was well correlated (r = −0.949) with the second axis, which explained an additional 19% of the variance. Northern hardwood species commonly found in

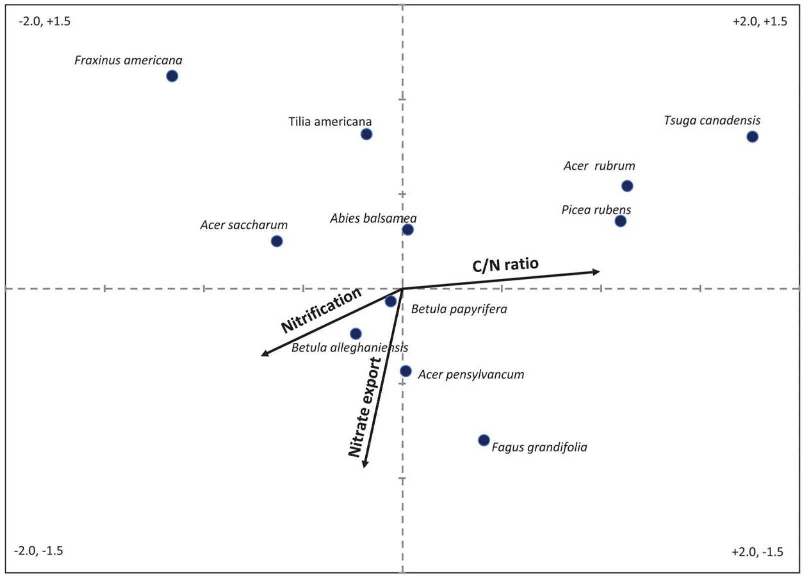

Figure 6. Biplot representation of canonical correspondence analysis using final species scores for the first 2 axes. The eigenvalues for axes 1 and 2 were 0.454 and 0.233, respectively, and together explained 55.8% of the species variance. All data are watershed plot averages.

sites with high base cation status appear in the upper left quadrant, red spruce and eastern hemlock are found in the upper right, while the other dominant hardwoods (yellow birch and American beech) are below axis 1. Nitrate export appears to be negatively associated with the two dominant conifer species, similar to the results of the linear analysis. Two variables, not found to be related to soil nitrification rates in the work by *Ross et al.* [2009], were somewhat weakly related to NO_3^- export in the 10 watersheds: beech density (r^2 = 0.40, p = 0.03) and the topographical index (tangent of upslope area/slope, r^2 = 0.48, p = 0.015). Both had a positive influence in their respective regression equations; however neither was significant in the subset of 6 watersheds shown in Figure 3b. The negative influence of conifer species appears to be the only common significant predictor for both net nitrification rates and NO_3^- export.

3.4. Adjacent Watersheds

[31] Three pairs of adjacent watersheds were studied, each with contrasting characteristics. In the plots sampled, Buck Creek South had the highest dominance of American beech (61%) of any watershed, 23% sugar maple and low (6%) conifer (Figure 2). Buck Creek North had moderate beech, low sugar maple and 34% conifer dominance, along with 19% red maple (*Acer rubrum*).

[32] Streamflow and chemistry in Buck North appears to reflect shallow flow paths in that it is acidic and intermittent [*Lawrence et al.*, 2007]. Both watersheds, similar to all we studied, had highest NO_3^- concentrations and export during spring snowmelt and after extended summer drought. However, Buck North was much lower than Buck South in both potential net nitrification and stream NO_3^- export. Despite our caveat about sampling design, Buck North fits well in the overall relationships between NO_3^- export and soil N transformations (Figures 3 and 4). Buck South had the highest NO_3^- export of any watershed (Table 3) but had only moderately high net nitrification rates (Table 2). An alternate explanation for the high NO_3^- export for Buck South is that N cycling was affected by severe beech bark disease (a complex of beech scale insects and *Nectria* fungi) that affected all of the beech trees in this beech-dominated watershed. As a result, canopy dieback was prevalent, and assimilatory uptake of N was likely to be less than in the other watersheds. Under conditions of lower plant uptake, the difference between actual and potential nitrification (which removes the factor of plant uptake and adds a stimulating disturbance effect) may have been less than in other watersheds with relatively healthy canopies that utilize more of the ecosystem N. This condition is consistent with lower potential nitrification rates in South Buck in relation to the high NO_3^- export shown when compared to the other watersheds in Figure 3. Nitrate concentrations in stream water at HBEF increased in watersheds with canopy damage from an ice storm without measurable increases in soil nitrification [*Houlton et al.*, 2003], demonstrating that this type of ecosystem effect occurs. These phenomena fit with the concept of N sink strength proposed by *Lovett and Goodale* [2011] in which decreases in the rate of NO_3^- removal by the plant sink are reflected in greater NO_3^- export without changing potential net nitrification rate measurements. Without further research, it is difficult to tell whether the apparent disconnect between watershed nitrification rates and NO_3^- export at Buck South was a function of disease or sampling design. Nonetheless the two adjacent Buck Creek watersheds fit the overall trend of greater export with higher nitrification rates in that their NO_3^- export differed by a factor of 4.0 and net nitrification differed by a factor of 2.3.

[33] The 2 Sleepers River W-9 watersheds also showed the trend of increasing NO_3^- export with higher net nitrification, both ~3 times higher in W-9A than W-9C, although both had lower export than would be predicted by the general relationship with rate measurements (Figure 3a). These watersheds are dominated by sugar maple and the high nitrification rates in W-9A were not unusual, while those in

W-9C were unexpectedly low [*Ross et al.*, 2009]. The lower average slope at W-9C may help explain its relatively lower NO_3^- export. This watershed has a small component of riparian wetlands, much of which are near its outlet into the larger W-9 stream, and denitrification may play a role in limiting NO_3^- export. However, there is no apparent explanation for both watersheds having such low NO_3^- export relative to the general relationship found at other sites, other than an artifact of the sampling design.

[34] The 2 Brush Brook watersheds differed in their NO_3^- export patterns in that the Brush G stream had relatively high growing season NO_3^- concentration while, during the same period, the Brush D stream was intermittent and quite low in NO_3^- export [*Ross et al.*, 1994; *Hales et al.*, 2007]. However, differences were not as pronounced during snowmelt and overall NO_3^- export was only 1.4 times higher in G compared to D. Net nitrification rates were similar but relative nitrification was 1.3 times higher in G. Soils of Watershed D were shallower to bedrock or dense basal till while Brush G had no densipan and numerous high-pH, high-Ca seeps [*Ross et al.*, 2004]. The temporal differences in stream NO_3^- concentration were likely a function of these high NO_3^- groundwater seeps, similar to those reported by *Burns et al.* [1998] in the Catskill Mts. of New York. Contrasting NO_3^- export from adjacent watersheds has also been reported by *Schiff et al.* [2002] in southern Ontario and *Christopher et al.* [2008] in the Adirondack Mts. of New York. In all these cases, hydrological flow paths appear to account for the differences.

3.5. Influence of N Deposition

[35] Total N deposition (both as NH_4^+ and NO_3^-) was highest at Winnisook, the southern and westernmost site with the highest average elevation. This area (Catskill Mountains) generally receives the highest precipitation and N deposition in the northeastern United States. Watersheds east of Vermont's central Green Mountains had the lowest N deposition, but the overall range (5.4–9.4 kg ha^{-1} yr^{-1}) was small compared to that found in Europe, e.g., 1–70 kg ha^{-1} yr^{-1} reported by *Gundersen et al.* [2006]. *Aber et al.* [2003] evaluated 83 northeastern U.S. watersheds and found that when N deposition exceeded a threshold of 6.8 kg ha^{-1} yr^{-1}, NO_3^- export increased with increasing N deposition. The geographical range in that study was from West Virginia to Maine, wider than ours, and the deposition amounts were higher, up to 12 kg N ha^{-1} yr^{-1}, because the measurements were mostly from the 1990s when atmospheric inputs were higher. It is interesting to note that the range of 0.3–5.0 kg N ha^{-1} yr^{-1} in NO_3^- export reported by *Aber et al.* [2003] was quite similar to the 0.1–5.1 kg ha^{-1} yr^{-1} range found in this study, even with our lower range in N deposition. *Aber et al.* [2003] also found considerable variation in N export within different regions within the northeast United States. In their study, the number of sampling points used to measure soil nitrification rates was not thought sufficient to overcome the spatial variability within each watershed. With our more intensive sampling, we hoped to address this issue. Our nitrification rates explain differences among our study watersheds, but the number of watersheds (10) is not sufficient to explain any regional trends in NO_3^- export relative to N deposition patterns.

3.6. Other Factors Affecting Nitrate Export

[36] Nitrate export from the Winnisook watershed was much higher in water years 2003 and 2004 (mean of 4.8 kg ha^{-1} yr^{-1}) compared with water years 1999 through 2002 (mean 2.1 kg ha^{-1} yr^{-1}). Soil nitrification rates measured in the late spring of 2003 and 2004 were also high and, based on our other data, high NO_3^- export rates would be expected. The abrupt increase in export was likely related to moderate insect defoliation observed during these years that led to a possible increase in nitrification from decreased plant N uptake, and from inputs of insect frass, which in turn, led to greater NO_3^- leaching to the stream. This response has been documented in other watersheds in the eastern United States. [*Webb et al.*, 1995; *Lewis and Likens*, 2007]. An increase in net nitrification rates has often been found after an increase in N supply [*Nave et al.*, 2009]. The impact of insect-induced defoliation, or other exogenous factors such as freezing injury, likely affects both soil processes and stream export. However, the connection is not always clear. *Fitzhugh et al.* [2001] showed that soil freezing increased net nitrification in a plot study at HBEF, yet *Judd et al.* [2011] found no major increases in NO_3^- export from HBEF streams in response to watershed-wide severe soil freezing. In the Winnisook watershed, we are hypothesizing that insect-induced defoliation led to both increased net nitrification and stream NO_3^- export. This scenario contrasts with the possible scenario in Buck South in which stream NO_3^- export was increased by the occurrence of beech bark disease more than net nitrification. Both scenarios are possible depending on the influence of the disturbance on net nitrification rates, plant uptake and water relations. However, more work is needed to substantiate these mechanisms.

[37] Land use history, including fire, may also be a factor in determining net nitrification rates [*Likens and Bormann*, 1974a; *Goodale and Aber*, 2001; *Ollinger et al.*, 2002]. Land use history usually determines the age and often the species of trees found in a watershed. Most of our study watersheds had mixed northern hardwoods of a similar age with no documented history of fire. Cone Pond was dominated by older conifer species and had an intense fire in 1820 that left visible charcoal remnants beneath the current forest floor [*Buso et al.*, 1984; *Ross et al.*, 2011]. The soils at Cone Pond had very low nitrification and ammonification rates [*Ross et al.*, 2009] and the stream had very low NO_3^- export (Table 2). The soils also had the highest C/N ratio (Table 3) with a mean of 27.4, the only watershed in our study above the nitrification threshold of 23–25 found by many others [*Aber et al.*, 2003; *Ross et al.*, 2004, 2009; *Gundersen et al.*, 2006]. The fire, the conifers and the soil C/N ratio all complement each other as factors leading to low net nitrification rates and N export. However, Cone Pond was one of the easternmost watersheds in our study and, thus, was on the low end of N deposition (Table 1), which could be a contributing factor to low N export. This low export is likely the result of watershed processes that would still create low export under higher N deposition. Buck Creek North may be a better example of low export driven by conifer species and low nitrification rates. It has a lower basal area of conifers than Cone Pond but received higher N deposition.

[38] Hydrology may explain differences in NO_3^- export at the Brush Brook watersheds as discussed above. Bedrock chemistry and hydrology may also be factors at Sleepers River. Both Sleepers River watersheds had soils with relatively high pH, unusual for forest soils of this region but presumably from the influence of underlying calcareous bedrock (average pH of 4.7 in the surface horizons sampled compared to an average pH of 3.4 in the other 8 watersheds [*Ross et al.*, 2009]). Subsurface structure creates lateral flow, resulting in nutrient-rich seeps, often on hillslopes. The low NO_3^- export at Sleepers River relative to its nitrification rates may stem from these pH differences. Perhaps higher riparian or in-stream processing occurred. However, *Williard et al.* [2005] found the highest baseline stream NO_3^- concentrations in a grouping of watersheds that included those with limestone bedrock and soils with relatively higher N content and lower C/N ratios, consistent with higher nitrification. Again, the lack of higher NO_3^- export from Sleepers W9-A may simply be due to a lack of direct connectivity between the high nitrifying soils and the stream.

4. Conclusions

[39] Stream NO_3^- export from these northeastern U.S. watersheds could be predicted by soil potential net nitrification rates if the spatial pattern of sampling was oriented toward the stream outlet. This sampling design encompasses both soil processes (nitrification) as affected by tree species and hydrologic flow paths as affected by topography and subsurface structure. This study did not identify explicit flow paths but it suggested the importance of down-gradient landscape positions in controlling stream NO_3^- export. Connectivity between soils with high potential nitrification rates and the stream will result in greater stream nitrate export. Future work needs to explicitly examine these spatial relationships that determine NO_3^- movement from the landscape to the stream.

[40] While it appears that a recent downward trend in N deposition in the northeastern United States could lead to lower NO_3^- export, uncertainty associated with a changing climate and political regulations makes it difficult to predict future trends. *Kothawala et al.* [2011] suggested that lower NO_3^- stream export in nearby Ontario was in response to decreased N deposition, *Sebestyen et al.* [2009] predicted lower annual NO_3^- export at Sleepers River in response to predicted climate change, due mainly to the effect of a longer growing season. On the other hand, *Campbell et al.* [2009] predicted higher NO_3^- export as the mineralization and nitrification rates increase with a warmer, wetter climate in the future. Changes in tree species composition will also be important. Our results suggest that soil nitrification rates, as influenced by conifer dominance, can help explain regional variation in stream NO_3^- export. Anecdotal evidence suggests red spruce is increasing in many of these watersheds, and future increases in conifer density should lead to lower NO_3^- export. So, both the uncertainty and ecological importance are high. There is a great need to monitor and study these complicated interactions in the future.

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