

Minimal response in watershed nitrate export to severe soil frost raises questions about nutrient dynamics in the Hubbard Brook experimental forest

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Abstract Experimental and theoretical work emphasize the role of plant nutrient uptake in regulating ecosystem nutrient losses and predict that forest succession, ecosystem disturbance, and continued inputs of atmospheric nitrogen (N) will increase watershed N export. In ecosystems where snowpack insulates soils, soil-frost disturbances resulting from low or absent snowpack are thought to increase watershed N export and may become more common under climate-change scenarios. This study monitored watershed N export from the Hubbard Brook Experimental Forest (HBEF) in response to a widespread, severe soil-frost event in the winter of 2006. We predicted that nitrate (NO_3^-) export following the disturbance would be high compared to low background streamwater NO_3^- export in recent years. However, post-disturbance annual NO_3^- export was the lowest on record from both reference (undisturbed) and treated experimental harvest or CaSiO_3 addition

watersheds. These results are consistent with other studies finding greater than expected forest NO_3^- retention throughout the northeastern US and suggest that changes over the last five decades have reduced impacts of frost events on watershed NO_3^- export. While it is difficult to parse out causes from a complicated array of potential factors, based on long-term records and watershed-scale experiments conducted at the HBEF, we propose that reduced N losses in response to frost are due to a combination of factors including the long-term legacies of land use, process-level alterations in N pathways, climate-driven hydrologic changes, and depletion of base cations and/or reduced soil pH due to cumulative effects of acid deposition.

Keywords Experimental watersheds · Frost event · Long-term monitoring · Nitrogen cycling · Watershed stream export

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Introduction

The cycling of nitrogen (N) has been dramatically altered by human activity (e.g., Vitousek et al. 1997; Galloway et al. 2003) and a central focus of ecosystem ecology for decades. Nitrogen supply often controls productivity of terrestrial and aquatic ecosystems, and N cycling is coupled with other biogeochemically important elements (e.g., carbon and phosphorus). Nutrient losses from forest ecosystems depend on

factors such as the timing of nutrient availability, competitive uptake by roots and microbes, and hydrologic controls. Experimental and theoretical work emphasize the role of plant nutrient uptake in regulating ecosystem nutrient losses and predict that losses will increase with forest succession (Vitousek and Reiners 1975), disturbance (Bormann and Likens 1979), and continued inputs of atmospheric N (Aber 1992). Nitrate (NO_3^-), the most mobile form of N, is typically the focus of such nutrient losses from watershed-ecosystems. In Northern Temperate hardwood forests vegetation is largely dormant during winter months, and microbially-mediated soil processes are therefore the dominant controls on ecosystem N retention at this time (Judd et al. 2007). Soil processes occurring in winter set the stage for the spring snow-melt event, the period when the majority of annual N losses occur (e.g., Likens and Bormann 1995). Studies at the Hubbard Brook Experimental Forest (HBEF) and elsewhere indicate that soil frost events are followed by increased stream NO_3^- export (Likens et al. 1977; Mitchell et al. 1996; Groffman et al. 2001). Snowpack insulates soils from cold air temperatures, inhibiting soil freezing (Hart et al. 1962; Stadler et al. 1996), thus changes in the depth and timing of snowpack may alter winter soil dynamics with substantial effects on forest stream NO_3^- export and forest N budgets.

Like above-ground disturbances [e.g., tree harvesting (Likens et al. 1969), insect defoliation, drought (Murdoch et al. 2000), and crown damage (Houlton et al. 2003)], soil freezing disturbances are thought to result in a flux of N from forest soils, increasing stream NO_3^- concentrations and watershed N export. The mechanisms behind increased N losses from soil frost may include reduced N uptake due to fine root mortality (Tierney et al. 2001), increased N supply due to physical soil disturbances (Fitzhugh et al. 2001), enhanced microbial N mineralization following microbial death (DeLuca et al. 1992), inhibition of microbial N immobilization (Brooks et al. 1999), and physical changes in hydrologic pathways (Hall et al. 2002). Experimental studies indicate that NO_3^- is mobilized when soils freeze (e.g., Christiansen and Christensen 1991; DeLuca et al. 1992; Boutin and Robitaille 1995; Groffman et al. 2001), and positive relationships between stream NO_3^- export and variables related to soil freezing are frequently observed (Mitchell et al. 1996; Fitzhugh et al. 2003; Callesen

et al. 2007). For example, Mitchell et al. (1996) found that forest NO_3^- export from watersheds throughout the northeastern US (including the HBEF) was correlated with unusually cold winter temperatures, and Likens and Bormann (1995) suggested that high stream water NO_3^- concentrations at the HBEF in the winters of 1970 and 1974 were due to soil freezing induced by low snowfall in those years. Models also indicate that variables related to severity of soil freezing can predict streamwater NO_3^- loss, although these relationships are inconsistent over the long-term record, and appear to have weakened in the 1990s (Fitzhugh et al. 2003). However, effects of freeze/thaw manipulations on dissolved N pools in soils are sometimes subtle (e.g., Grogan et al. 2004), and the effects of such releases at the watershed scale are unclear (Herrmann and Witter 2002).

In the winter of 2005–2006, low snow fall and cold temperatures resulted in widespread and deep soil frost throughout the HBEF. We therefore expected large streamwater NO_3^- losses from the watersheds during the following year. We expected these losses to be at least comparable to other frost and disturbance events that have occurred throughout the long-term stream NO_3^- record at the HBEF, and we expected these losses to be particularly apparent because background NO_3^- export in stream water has been very low in recent years (Goodale et al. 2003) compared to the record since 1963 (Likens and Bormann 1995). To evaluate the effect of the soil frost event on NO_3^- export, we used long-term data to compare NO_3^- export from six, high-elevation, gauged watersheds and from the entire valley drained by Hubbard Brook. Several of the sub-catchments have received experimental treatments, (forest cutting and addition of CaSiO_3), which allowed us to compare the response of these past disturbances to the 2006 frost event, as well as three, major frost events in the past.

Methods

Study site

The HBEF is located in the White Mountains of New Hampshire, USA (43°56' N, 71°45' W). Vegetation is characteristic of a mature northern hardwood forest ecosystem and is dominated by American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*),

and yellow birch (*Betula allegheniensis*). Soils are acidic ($\text{pH} < 4.5$), well-drained spodosols of sandy loam texture with a thick (3–15 cm) surface organic layer (Likens and Bormann 1995). Annual precipitation averages about 1,400 mm and is evenly distributed on a monthly basis throughout the year. About one-third to one quarter of annual precipitation is snow, and snowpack generally persists from mid-December until mid-April, with a peak depth in March. However, occasional midwinter thaws result in elevated streamflow. The snowpack normally melts during March, April, and May, and about 54% of the annual streamflow and 68% of annual NO_3^- export occur during this period (Likens and Bormann 1995). Snow-covered soils typically do not freeze, but in the absence of snowpack, soil frost can occur (Likens and Bormann 1995). The study area receives moderate atmospheric N inputs (average bulk dissolved inorganic N (DIN) deposition of $\sim 6 \text{ kg N ha}^{-1} \text{ y}^{-1}$ from 1999–2008).

Nitrate concentrations have been measured weekly in the gauged streams that drain into the main stem of Hubbard Brook in the HBEF since the mid-sixties (Likens & Bormann 1995; Buso et al. 2000; Fig. 1). Six south-facing watersheds (W1–W6) were included in this study, along with the main stem of Hubbard Brook, a fifth order stream. Two of the sub-catchments (W3 and W6) are long-term reference watersheds. The remaining sub-catchments have received experimental manipulations (Table 1), including various clear-cutting treatments (W2, W4, and W5) and a wollastonite (CaSiO_3) addition (W1).

Climate and soil data

Soil temperature, percent soil frost, and snow depth data were obtained from the U.S Forest Service database (www.hubbardbrook.edu). Soil temperature data have been collected approximately weekly at one location west of Weir 4 (Fig. 1b) since 1959. In 2002, this site was designated a Soil Climate Analysis Network (SCAN) site, and new instrumentation was installed to collect daily soil temperature. Measurements of depth of soil frost were taken approximately weekly at the HBEF snow monitoring area, Snow Course 2 (Fig. 1b), beginning in 1960.

In the spring of 2006, we documented the extent of a major soil frost event in the HBEF with field surveys. On 17 March, we surveyed for presence and

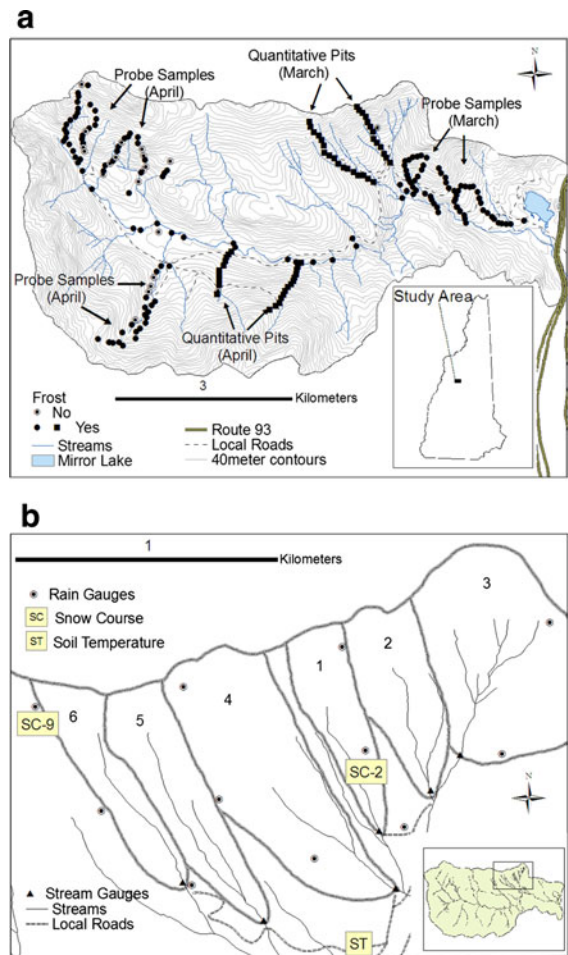


Fig. 1 **a** Map of the Hubbard Brook Valley indicating presence (black circles and squares) or absence (open symbols) of frost on four sample dates (Northeast cluster sampled in March, remainder sampled in April, 2006). **b** Inset of south-facing gauged watersheds and soil temperature and snow-depth measurement stations

depth of soil frost on the south-facing slopes near the experimental watersheds (Fig. 1a). Small soil pits (blocks about 10 cm^2) were dug every 100 m with an axe. We also recorded soil temperature and latitude and longitude with a GPS unit (Garmin). This procedure was repeated on 10 April near the gauged watersheds on the North-facing slopes (Fig. 1a), which typically accumulate greater snow depths. By this time, soils were beginning to thaw from the surface, and so a rapid method was established to determine presence or absence of soil frost and assess the extent of soil frost throughout the Valley. A steel-tipped, aluminum ski pole was used to probe frozen

Table 1 Characteristics of high elevation sub-catchments (W1–W6) and the entire Hubbard Brook Basin

Watershed	Size (ha)	Year	Treatment
W1	11.8	1999	CaSiO ₃ addition.
W2	15.6	1965–66	Deforested (no products removed) in winter
		1966–68	Treated with herbicides in the summer for 3 years.
W3	42.4		None (hydrologic reference).
W4	36.1	1970, 72, 74	Clear cut by strips in three phases. Timber products removed. Buffer of uncut trees along stream channel.
W5	21.9	1983–84	Whole-Tree harvest. Timber products removed.
W6	13.2		None (biogeochemical reference).
Hubbard Brook	2960		

soils approximately every 100 m along transects (position recorded with GPS unit). Soils were probed at 10 randomly selected sites at each location, and the presence or absence of soil frost was noted. These surveys were conducted on 11–12 April. While such Valley-wide surveys had not been conducted in the past, the 2006 soil frost event is anecdotally the most extensive in the past 30 years and perhaps since the long-term record began in 1956 (Personal observation Buso, D).

Hydrologic flux measurements

Stream discharge in the experimental watersheds is measured with v-notch weirs (Likens and Bormann 1995). The main stem of the Hubbard Brook was ungauged in 2006, so we estimated hydrologic flux using measured stream discharge from the south (W3; 42.4 ha) and north (W7; 76.4 ha) facing slopes to scale up to the entire Hubbard Brook Valley [2960 ha above gauge site (Bailey et al. 2003)]. Average water flux per unit area of north- and south-facing sub-watersheds was weighted by contribution of north (51%) and south (49%) slopes to the total watershed area. Previous work has shown a strong relationship between watershed area and stream discharge at the nine continuously gauged weirs (Likens and Bormann 1995). Annual fluxes were based on the water-year [June 1–May 31; Federer et al. 1990; referred to throughout in bimodal form (e.g., 2005–2006)], and winter (period spanning approximately December through March) therefore fall within one hydrologic period. Winters are referred to by the year in which they end (e.g., the spring 2006 frost event occurred in the winter of 2006), and effects of the event on

streamwater NO₃[−] export were measured in water-years 2005–2006 (which includes the winter 2006 spring melt) and water-year 2006–2007.

To analyze changes in winter (December through February) soil moisture over the long-term record, we estimated the percent of water retained in soils as precipitation minus streamflow (assuming evapotranspiration during winter was negligible).

Stream sampling and analysis

Routine weekly stream samples from the gauged watersheds were collected, as they have been since 1963, in clean, polyethylene bottles, shipped to the Rachel Carson Analytical Facility at the Cary Institute of Ecosystem Studies, and analyzed for NO₃[−] and other cations and anions on an ion chromatograph (Buso et al. 2000). Weekly samples of Hubbard Brook (Main stem) did not begin until January of 2003; monthly samples had been collected since June 1973. Weekly samples for dissolved organic carbon (DOC) and dissolved organic N (DON) have been taken from W6 beginning in 1995 (Likens et al. 2002). Total dissolved N (TDN) was measured by high-temperature catalytic oxidation (Buso et al. 2000), and dissolved organic N (DON) was calculated by subtracting NH₄⁺-N and NO₃-N from TDN.

Because weekly sampling can bias export calculations for solutes with strong flow-concentration relationships (Johnson et al. 1969), we sampled daily (and hourly during rain events) from the three sites (W6, W1, and Hubbard Brook) from 26 April through 3 November 2006 to ensure NO₃[−] export was not “missed.” These daily samples were analyzed using a spectrophotometric method (Crumpton et al. 1992)

due to cost and time limitations. Briefly, samples were refrigerated in the dark and analyzed usually within 2 weeks of collection. Duplicate analysis of a subset of samples indicated high method precision. Samples were rerun over time, with no significant change in concentrations after 4 months of storage. Samples run using both the IC and spectrophotometric methods were used to provide a regression ($R^2 = 0.9671$; $P < 0.01$) to adjust an offset in the spectroscopic method results ($y = 0.9972 \times -0.1623$). All values are reported as NO_3^- -N.

N fluxes

We calculated both annual water-year NO_3^- fluxes and volume-weighted mean (VWM) NO_3^- concentrations. Fluxes were calculated for both the weekly (ion chromatograph method; Buso et al. 2000) and intensive (daily + storm event; spectrophotometric method) streamwater NO_3^- concentrations. Using the weekly samples allowed us to compare annual fluxes throughout the long-term record. We calculated daily N exports (in kg ha^{-1}) from daily flow (L ha^{-1}) and routine, weekly N concentration measurements (in mg L^{-1}), using the average N concentration between discrete samples for days without chemical samples. Monthly and annual N exports (kg ha^{-1}) were summed from daily exports. Volume-weighted mean concentrations (in mg L^{-1}) were derived from dividing the monthly or annual exports by the total monthly or annual water flow (Likens and Bormann 1995). For water-years 2006–2007 and 2007–2008 we used average daily concentrations and total daily water flux during the intensive sampling period. During storm events, average daily concentrations were used.

Annual NO_3^- export calculations from W1, W6, and Hubbard Brook were slightly lower when intensive daily sampling was used compared to the standard weekly sampling (daily sampling resulted in annual export 1–10% lower than when weekly sampling was used because of dilution of NO_3^- during elevated flows in the recession period). We therefore used the weekly measurements for export calculations, which allowed us to compare more sites over longer times.

Regression analysis (SPSS) was used to detect trends in winter soil moisture and DOC and DON export.

Results

Climate and soil data

Soil temperature data indicated that extensive soil frost developed around 20 February 2006 and continued into April 2006. Overall, soil temperatures were slightly colder in 2005 and 2006 than in the previous three winters (Fig. 2d). Soil frost also occurred in the winter of 2007, but later in the season than in winter 2006. Data from the SCAN site at the HBEF indicated that during the winters of 1999 through 2007, soil frost was most severe (in frequency and depth) in 1999, and that the winter of 2006 had only slightly greater soil frost than the other years. Maximum snow depths throughout the winter of 2006 were among the lowest on record, similar to the winters of 1983, 1991, 1992, and 2004 (Fig. 3a). The maximum snowpack depth during March 2006 was the lowest recorded during the period of 1970–2007 (Fig. 3b).

Hydrologic fluxes

Stream flow in the reference watershed (W6) was about half the long-term average (1970–2009) during March and April as a result of low, accumulated snowpack (Table 2). There were slight increases in annual precipitation (0.55 mm yr^{-1} , $P = 0.09$) and streamflow (0.29 mm yr^{-1} , $P = 0.052$) since 1956 (Fig. 4a). The percent of water retained in soils during winter months decreased significantly during this time period (Fig. 4b; $P = 0.042$).

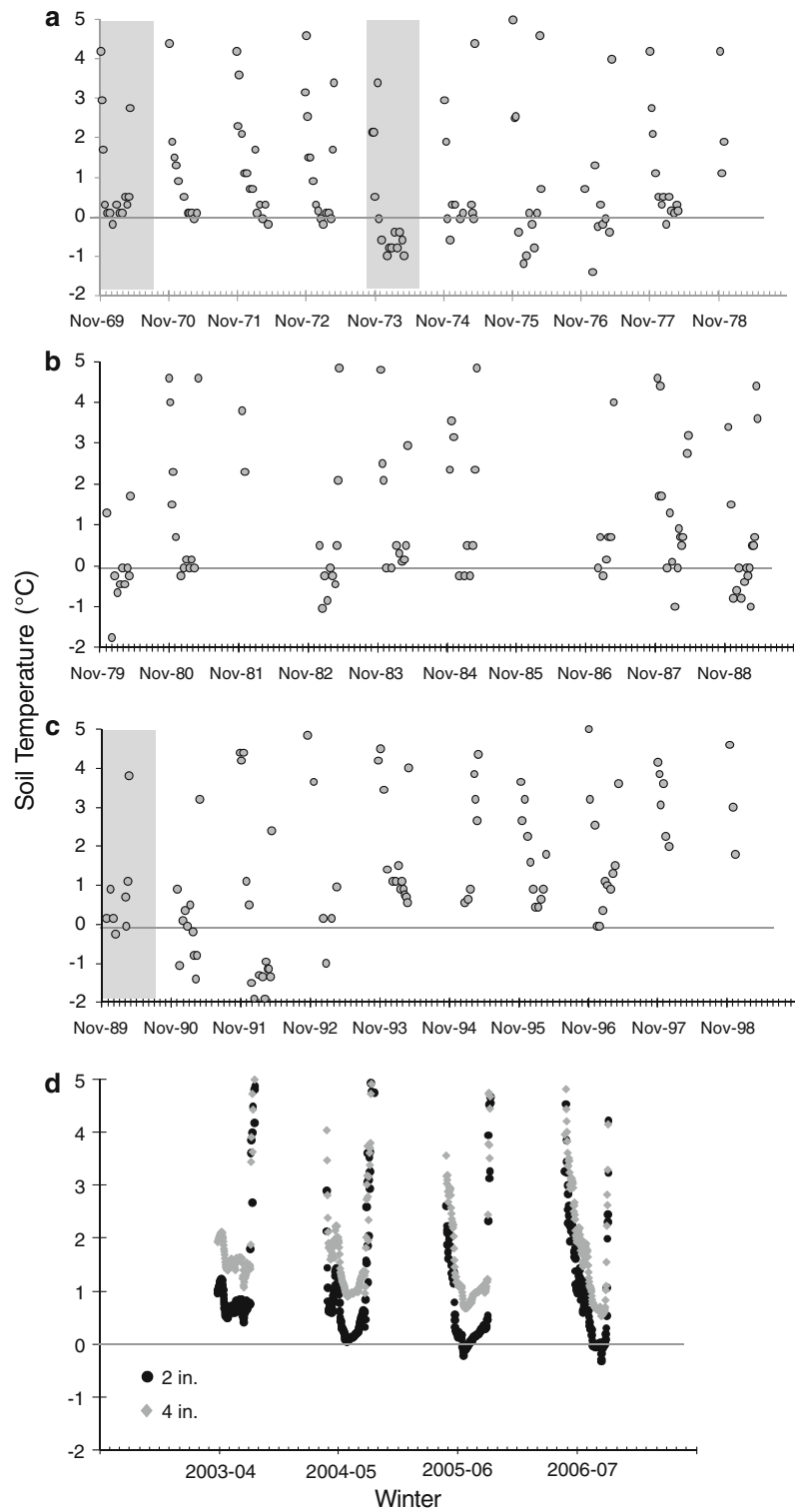
Frost surveys

The spring 2006 frost survey showed that soil frost was widespread throughout the Hubbard Brook Valley (Fig. 1). Frost surveys conducted on 17 March revealed that soil frost was widespread and deep (avg. depth 9 cm). Pits dug on 10 April indicated that soil frost was also widespread on north-facing slopes (avg. depth 7 cm). Overall, frost was found at 78% of sites during the three surveys.

Stream NO_3^-

In water-year 2005–2006 (includes the 2006 frost event), NO_3^- export from the reference watersheds

Fig. 2 a–c Weekly winter soil temperature data at 8 cm depth and **d** daily winter soil temperatures at 2 (black circles) and 4 (grey diamonds) inches (5.1 and 10.2 cm) at SCAN site west of weir 4 in the HBEF. Only data from December through April is plotted. Grey bars in **a** indicate “frost” years. Temperatures below 0°C indicate soil frost



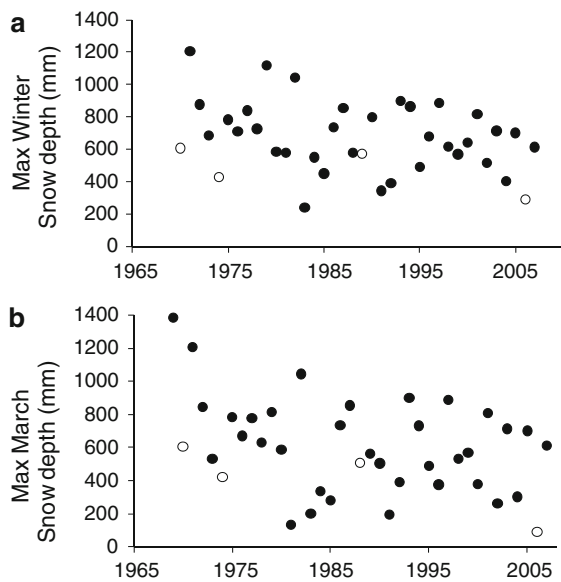


Fig. 3 **a** Maximum snow depth over the winter and **b** during March at Snow Course 2 (See Fig. 1). Open circles indicate “frost” years

(W3: $1.0 \text{ kg ha}^{-1} \text{ y}^{-1}$ and W6: $0.9 \text{ kg ha}^{-1} \text{ y}^{-1}$) and from two of the remaining four treatment watersheds was the lowest on record. Compared to the average NO_3^- export during the period between 1975 and 2004, these annual values were 58–96% lower (Table 2; VWM NO_3^- concentrations 69–97% lower; Fig. 5).

Nitrate export was 2 to 4.2 times greater in the following year (water-year 2006–2007; VWM

average concentrations 1.5 to 4 times greater). Compared to long-term average export (1975–2004), annual export from the reference watersheds (W3 and W6) was 36 and 54% lower in 2006–2007 (VWM concentration 41 and 60% lower); export from W2, W4, and W5 was 15, 51, and 87% lower (VWM concentration 21, 52, and 89% lower); annual export from W1 was 8% greater (VWM concentration 7% lower) than the long-term (1975–2004) average.

Compared to other years in which soil frost was suspected to be important (1969–1970, 1973–1974, and 1989–1990), NO_3^- export from the subcatchments was at least 88% lower in water-year 2005–2006, with only two exceptions: export from W5 was only 21% lower than in 1989, and export from W2 was 22% greater than in 1972 (Table 2). The following year (water-year 2006–2007), NO_3^- export was also generally less than other frost years, but the difference was not as great. Nitrate export from W3, W4, and W6 in 2006–2007 was at least 62% lower than previous frost events, with the following exceptions: export from W5 and W2 in 2006–2007 was two- and 1.5-times greater than export following the 1973–1974 and 1989–1990 frost events, respectively; export from W1 was 41% of export following the 1989 frost event. The NO_3^- concentration and export from W1 was greater in 2006–2007 than for any of the other treated Watersheds (Fig. 5b, 6a).

Even when compared to recent non-soil frost years (water-years 2000–2004), NO_3^- export from the

Table 2 Annual water-year, long-term (1974–2005; \pm SD) and frost-event NO_3^- export and volume-weighted mean (VWM) concentrations from treated and reference watersheds

Year	W1	W2	W3	W4	W5	W6
Export ($\text{kg ha}^{-1} \text{ y}^{-1}$)						
Long-term avg.	10.9 (9.5)	3.9 (5.6)	5.9 (5.1)	10.7 (11.7)	13.2 (32.7)	6.4 (6.0)
1969–70		414.7		31.2		28.2
1973–74	48.6	1.4	27.3	75.0	32.4	32.7
1989–90	18.8	12.5	10.4	21.4	0.6	16.8
2005–06	2.8	1.7	1.0	2.6	0.5	0.9
VWM NO_3^- (mg L^{-1})						
Long-term avg.	1.2 (0.9)	0.4 (0.6)	0.7 (0.5)	1.1 (1.2)	1.5 (3.8)	0.7 (0.6)
1969–70		37.6		3.6		3.2
1973–74	3.6	0.09	2.1	4.9	2.4	2.3
1989–90	2.0	1.2	1.0	2.1	0.05	1.6
2005–06	0.2	0.13	0.1	0.2	0.04	0.07

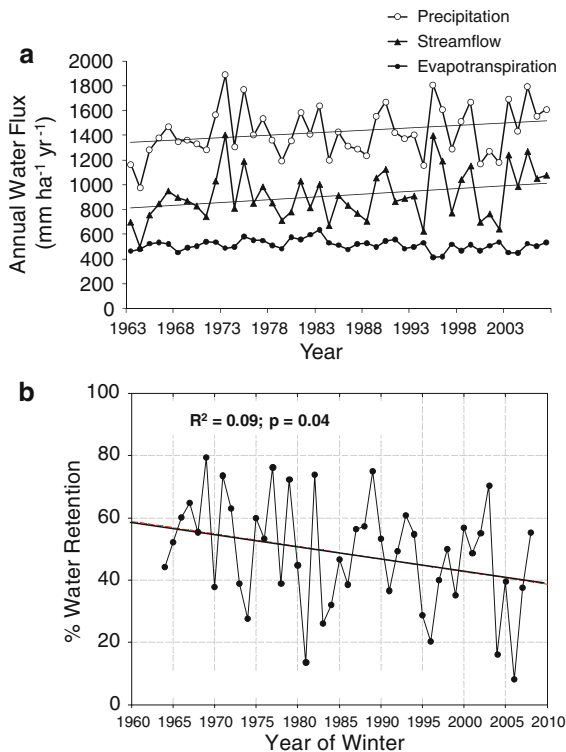


Fig. 4 **a** Annual waterflux of precipitation (P; $R^2 = 0.07$), streamflow (S; $R^2 = 0.08$) and evapotranspiration in W6, and **b** total percent water retention (precipitation minus streamflow; assumes transpiration was negligible; $R^2 = 0.09$) during December through February of each year

gauged watersheds was 42–57% lower (except for W5 which was only 15% lower) in 2005–2006. Fewer data are available for Hubbard Brook, but export in 2005–2006 was about half that of export in 2003–2004 and 2004–2005.

The great reduction in NO_3^- export during March and April following the frost event resulted in a greater proportion of annual export occurring during rain events in May and June, relative to other years (Fig. 6).

In 2006, NO_3^- export from the reference watershed (W6) during the March and April melt event was less than 10% of the long-term average during these months, while export following previous frost events was at least twice as great as average export (Table 3). Volume-weighted mean NO_3^- concentrations were lower during spring in 2006, whereas spring VWM concentrations from previous frost events were similar to long-term averages (Table 3).

Stream DOC and DON

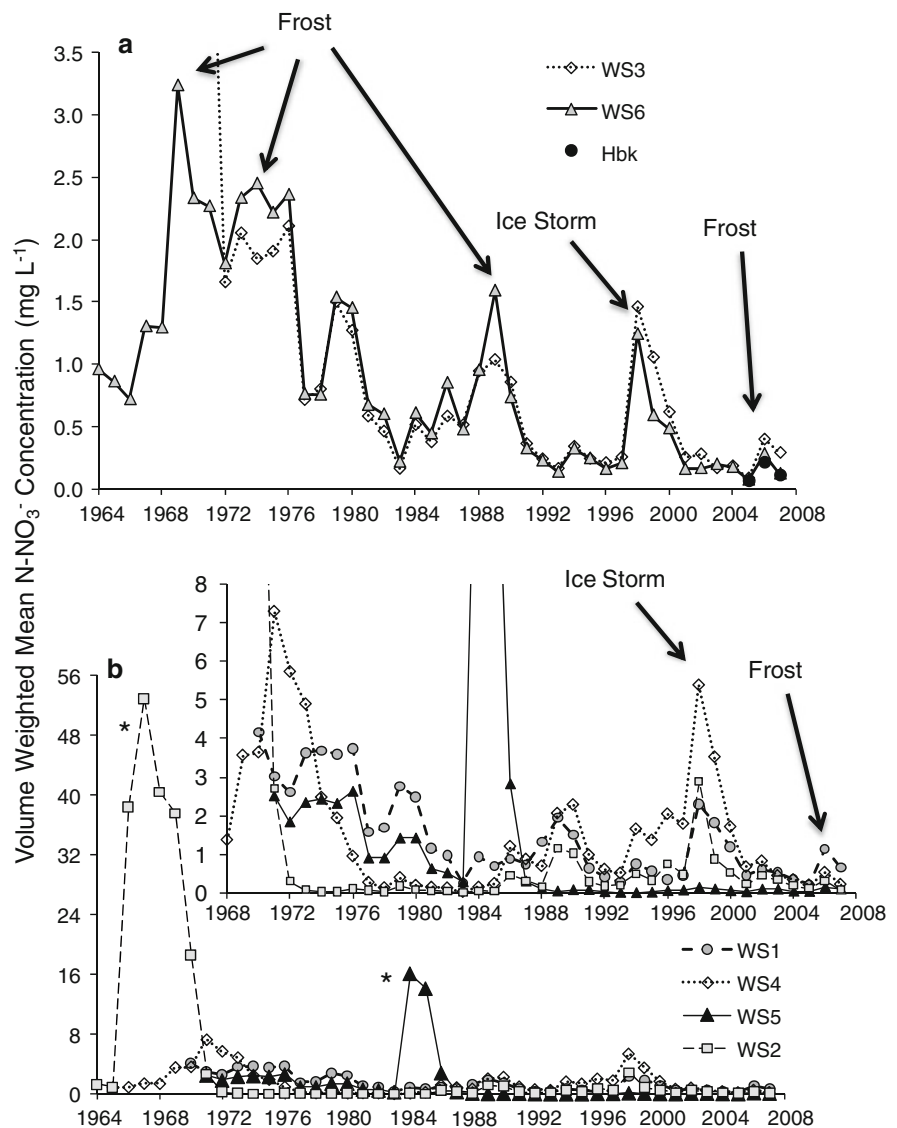
There was a slight decrease (not significant) in DON and the ratio of DOC to DON [Fig. 7; average DOC:DON = 24 (Std. Dev = 6.9)] from 1995 to 2007. During this period, DON export [average $1.04 \text{ kg ha}^{-1} \text{ y}^{-1}$ (Std. Dev. = 0.42)] was on average 48% lower than NO_3^- export; however, during 2005–2006, DON export ($1.27 \text{ kg ha}^{-1} \text{ y}^{-1}$) was 30% greater than NO_3^- export. Compared to the two years previous and the two years following the 2006 frost event, DON export in 2005–2006 was 61% higher, but it was not significantly different from earlier years during this time period (Fig. 7).

Discussion

Past correlations between soil frost and NO_3^- export at the watershed (Likens and Bormann 1995; Mitchell et al. 1996) and plot scale (Groffman et al. 2001) led us to expect a large response to the extensive soil-frost event of winter 2006. In contrast to our predictions, NO_3^- export was the lowest on record since 1963, indicating that winter frost had little immediate effect on NO_3^- export during the spring snow melt. This result continues the puzzling trend of reduced NO_3^- export from northeastern US forests receiving relatively high N loadings from atmospheric deposition (Likens and Bormann 1995; Goodale et al. 2003; Bernhardt et al. 2005). A slight response in NO_3^- export was observed in the following water-year (2006–2007), but the magnitude of the response was small compared to previous disturbances (Fig. 6). These somewhat surprising results highlight our lack of understanding of forest N cycling and response to disturbance, and suggest that either previous correlations derived for watershed NO_3^- export were wrong, our understanding of the factors that contribute to a frost response is incomplete, or that changes in the past decades have reduced watershed responses to soil freezing events.

Two central theories related to watershed nutrient retention predict that forested ecosystems will become “leakier” over time as plant biomass accumulation and nutrient uptake slows (maturation: Vitousek and Reiners 1975), and as nutrient inputs from atmospheric N deposition exceed nutrient demand (N saturation hypothesis: Aber et al. 1989).

Fig. 5 Annual (water-year) volume-weighted mean NO_3^- concentrations in **a** reference and **b** experimentally manipulated subcatchments. The main stem of Hubbard Brook is also shown in **a**. Arrows indicate years with severe frost and the 1998 ice storm. Asterisks indicate experimental watershed scale treatments (refer to Table 1)



However, despite the cessation of forest biomass increase since the early 1980s (Likens et al. 1994; Fahey et al. 2005; Siccama et al. 2007) and moderately elevated N deposition for at least the last four decades ($\sim 6 \text{ kg N ha}^{-1} \text{ y}^{-1}$ at the HBEF), NO_3^- export has unexpectedly declined in the HBEF and throughout the northeastern US (Likens et al. 2002; Driscoll et al. 2003; Goodale et al. 2003; Bernhardt et al. 2005). In fact, at the HBEF, NO_3^- export in water-years 2002 through 2005 was the lowest of any four-year period throughout the long-term record (begun in 1963). Furthermore, a shift from DIN to DON export cannot explain reduced watershed N export (Fig. 7).

While a number of mechanisms behind the reduced NO_3^- export have been proposed, the issue remains unresolved (Bernhardt et al. 2005; but see Bernal et al. submitted). Below we consider the challenges in detecting soil frost events, and how changes such as recovery from past logging, climatic variability or change, and cumulative effects of acid deposition might explain reduced effects of soil frost and reduced NO_3^- export in general.

Frost in the long-term record

The effects of frost on forest N fluxes have received more attention in recent years because climate change

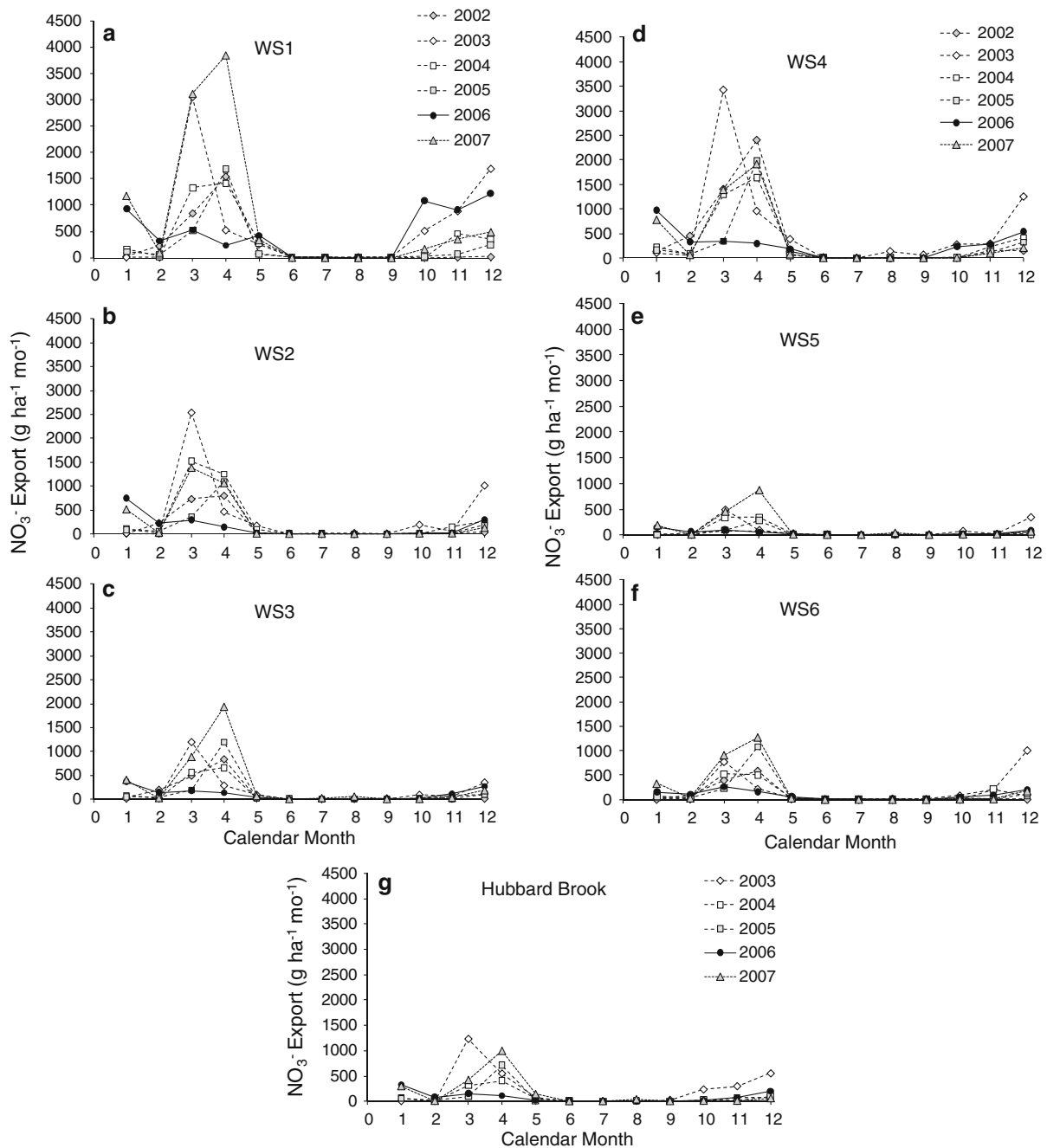


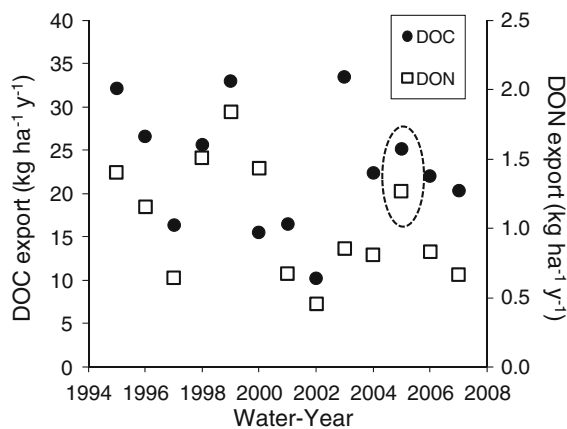
Fig. 6 Seasonal pattern in NO_3^- export over recent years in sub-catchments (a–f) and the entire Hubbard Brook Valley (g). Refer to Table 1 for watershed-scale treatments done in W1, W2, W4, and W5. Note that the frost event occurred in winter 2006

may increase the frequency and severity of soil frost if the timing of snowpack were altered and the amount of snow were diminished (Groffman et al. 2001). While soil frost events appear to be somewhat more common in the latter half of the long-term

record at the HBEF, large export of NO_3^- following frost events is less common, suggesting that changes have occurred whereby frost events no longer result in increased NO_3^- export. Fitzhugh et al. (2003) found a significant positive relationship between soil

Table 3 Comparison of long-term averages (1970–2008; \pm SD) and frost-event monthly stream-flow, NO_3^- export, and volume-weighted mean concentrations (VWM) from W6 (reference watershed)

	March	April	May
Flow ($\text{mm ha}^{-1} \text{mo}^{-1}$)			
Long-term avg.	118.8 (69.7)	210.1 (79.8)	107.0 (53.3)
1970	28.0	266.7	81.6
1974	98.1	265.4	147.4
1990	207.9	141.4	132.6
2006	75.1	81.8	206.3
Export ($\text{g ha}^{-1} \text{mo}^{-1}$)			
Long-term avg.	2069 (2602)	2689 (3166)	725 (1262)
1970	1073	14205	2551
1974	3729	8616	2443
1990	7650	3532	1921
2006	262	159	56
VWM NO_3^- (mg L^{-1})			
Long-term avg.	1.57 (1.36)	1.27 (1.31)	0.59 (0.84)
1970	3.84	5.33	3.13
1974	3.80	3.25	1.66
1990	3.68	2.50	1.45
2006	0.35	0.20	0.03

**Fig. 7** Annual export of dissolved organic carbon and nitrogen (DOC and DON) from W6. Water-year 2005–06 is circled

frost variables and stream NO_3^- export from W6 during the period 1970–1989, but the relationship disappeared in more recent years (1990–1997). However, linking soil frost to NO_3^- export is a challenge because documenting soil frost itself is difficult and impacts of frost are likely to depend on a myriad of factors.

Soil frost was considered extremely rare prior to 1970 in the HBEF (Hart et al. 1962). The first occurrences of widespread soil frost due to late

accumulation of snowpack were observed in the winters of 1969–1970 and 1973–1974 (Likens and Bormann 1995). It was noted that annual stream NO_3^- concentrations and export increased abruptly in the following years (Fig. 5). Likewise, extreme cold in December of 1989 at HBEF and throughout the Northeastern US resulted in frozen soil beneath snowpack (Mitchell et al. 1996), although the extent and depth of soil frost were not known. Elevated NO_3^- export during the spring of 1990 was attributed to this soil frost event (Mitchell et al. 1996). Curiously, NO_3^- export remained elevated for at least two years after each of these events, suggesting that mechanisms other than short-term nitrification responses to the soil disturbance from soil frost may have been responsible for elevated NO_3^- export. One explanation may be that root die back due to soil frost reduced vegetative uptake and increased NO_3^- losses, and that such damage persists for two to three years following these disturbances (Tierney et al. 2001).

Challenges in linking soil frost and N dynamics

Linking soil frost and watershed NO_3^- export is difficult for several reasons. First, accurate data on watershed-scale soil frost are scarce. Documenting

soil frost events is difficult because soil data are typically limited spatially and long-term records are sparse. Most studies rely on soil temperature data collected at relatively few stations (e.g., 1, Fitzhugh et al. 2003; 8–10, Callesen et al. 2007), from air temperature data (Mitchell et al. 1996), or from soil probes, which may be located some distance from the study watershed (Watmough et al. 2004). Soil conditions can be highly variable depending on topography, aspect, and hydrology, and a limited number of point measurements are not likely to reflect accurately the conditions throughout the watershed. The available long-term soil temperature data at the HBEF show evidence of moderate to significant soil frost in at least 17 of the past 58 years. However, while our frost survey in March and April of 2006 clearly showed that soil frost was widespread (Fig. 1) and deep throughout the HBEF that winter, the USFS soil frost data (from the same site used in the Fitzhugh et al. (2003) study) showed that soil temperatures were not extreme when compared to other recent years (Fig. 2). In fact, data from Station 2 indicated that the winters of 1999 and 2007 had greater maximum depth and % soil frost than 2006. Therefore, it appears that without better spatial information on soil frost, temporal patterns based on one or a few points are of limited use for correlating meaningful frost information with NO_3^- export.

Snow depth data do not clearly relate to soil frost either. For example, snow depth in winter 2006 was smaller than average, but similar, shallow snow depths were also observed in winters of 1983, 1991, 1992, and 2004 (Fig. 3a–c). The winters of 1970 and 1974 had relatively low snowpack and were considered frost events (Likens and Bormann 1995). However, other years with shallow snowpack were not followed by the high NO_3^- export that occurred in 1970 and 1974. These data suggest that factors other than just low snowpack and cold soils contribute to a frost event.

Therefore, it is not at all clear what constitutes a “frost event,” and a second difficulty in relating soil frost to watershed NO_3^- export is that the overall impact of a frost event and the magnitude of watershed N losses are likely to depend on the interactions of a number of factors. The depth, spatial extent, timing of onset, antecedent soil moisture, freeze/thaw cycles and frequency of frost occurrence

will vary from year-to-year and spatially, and are all likely to play a role in the impact of frost on ecosystem N loss. Experimental freeze/thaw cycles generally result in increased NO_3^- export (review by Henry 2007). However, many of these experiments use changes in temperature exceeding what is usually found in the field, and more realistic amplitudes of temperature cycles produced only minimal responses (Henry 2007). The development of a “frost metric” that characterizes the degree and intensity of soil frost by incorporating several of the important aspects of soil frost might help elucidate effects of frost on soil N processing. The use of such metrics would require data on soil moisture and temperature from multiple locations throughout a catchment.

A third difficulty in establishing relationships between soil frost and watershed NO_3^- export is that numerous watershed-scale processes may alter the impact of soil frost on the amount of NO_3^- that makes it to streams for export. Comparing frost responses among the sub-catchments suggests that disturbance history may play a large role in the magnitude of response to frost events. For example, in 1974, watersheds that had recently received clear cut treatments (W2 and W4) did not respond to the frost event, while other watersheds, treated and untreated (e.g., W1, W5, W6), showed at least a small increase in export (Table 2; it is difficult to interpret effects on W3 because of the high export value in water-year 1972). Likewise, following the 1989 frost event, all watersheds, showed a clear increase in NO_3^- export except for W5, which had been clear cut in 1983–1984. Response to frost disturbance may be minimized if it were to occur during early stages of forest successional development following a previous disturbance (e.g., clear cutting), because plant nutrient uptake would be high. Watersheds clear cut in the late sixties and early seventies (W2 and W4) appeared to be unresponsive to frost for a period of 3–8 years, but after 19 to 24 years, these watersheds were again responsive to the 1989 frost event. Watershed 5, which was clear cut later (1983–1984), was highly retentive of NO_3^- during the 1989 frost event and was the only watershed to show no response to the ice storm (10 years post-clear cutting). The 1998 ice storm disturbance may have prolonged the period of insensitivity to frost, as W5 was also the least responsive to the 2006 frost event. These results

suggest that mechanisms other than damage to plant roots are responsible for enhanced N releases in response to soil frost, since nutrient uptake is still strong. However, frost has been shown to induce fine root mortality (Tierney et al. 2001), and the increase in DON export in water-year 2005–06 compared to years prior to and following the frost event (Fig. 7) could be due to exudates from root mortality.

Soil frost and watershed N export

A reduced response to soil freezing events over time at the HBEF could be due to either (1) reduced release (nitrification) of NO_3^- from soils, (2) increased uptake of soil-released NO_3^- prior to it entering streams, or (3) increased in-stream uptake of released NO_3^- . Most studies measuring effects of soil frost on soil N losses have used plot-level manipulations or controlled laboratory incubations, but fewer data are available for watershed-scale effects. While most of these studies document moderate to substantial increases in soil NO_3^- following soil freezing, some indicate that effects can be more subtle (Grogan et al. 2004). Soil NO_3^- released by soil freezing could either reduce forest productivity if N were limiting, through long-term ecosystem leaching (i.e., stream export), or could enhance productivity by reducing soil compaction and enhancing nutrient release from organic matter (Schmidt and Lipson 2004). Soil frost may be unimportant for ecosystem N budgets at the watershed scale if effects on soil NO_3^- releases were either subtle or releases were retained by soils or stream sediments.

Mechanisms behind NO_3^- mobilization from frozen soils include lysis of microbial cells (Soulides and Allison 1961), increased rates of nitrification, fine root mortality (Tierney et al. 2001; but see above), and physical disturbance (Groffman et al. 2001). Groffman et al. (2001) found that experimentally induced soil freezing mobilized NO_3^- , and fine root mortality and physical disruption of soil aggregates, but neither stimulation of nitrification or cell lysis appeared to be the cause. Although no data exist from the early period of the record at HBEF on frost effects on soil processes, it is unlikely that reductions in soil microbial biomass over the past decades account for reduced NO_3^- mobilization, since changes in microbial biomass are thought to occur mainly in the first

two decades of secondary forest succession (e.g., Jia et al. 2005).

Potential mechanisms of reduced N losses

Over the past decades, Northeastern US forests have experienced a number of changes, such as recovery from severe logging, climate change, and cumulative effects of acidic deposition, each of which could potentially affect nutrient cycling and soil-frost responses. One hypothesis explaining why forests have become less “leaky” to NO_3^- in recent decades is that they have only recently begun to recover from the effects of severe logging in the 1800s (McLauchlan et al. 2007). There is evidence from tree cores and lake sediments that forest N availability has been steadily decreasing for the past 80 years, perhaps due to recovery of soil immobilization potential, which may occur over much longer timescales than recovery of uptake potential (mainly by vegetation) (McLauchlan et al. 2007). However, NO_3^- export also appears to be declining in old-growth forests (Martin et al. 2000; Goodale et al. 2003), indicating that recovery from chronic disturbance may only partially explain current trends.

Climate change has the potential to impact N cycling through mechanisms such as changes in soil moisture, the amount, timing, and pathways of hydrological flow, or the lengthening of the growing season. If these more recent (i.e., decadal scale) changes also were to act to reduce soil N availability or delivery to streams, they would accentuate effects of recovery from chronic disturbance. For example, there is some evidence that soils have become wetter at the HBEF over the past decades. The first several years of the study (1963–1965) were the driest in the long-term record, and subsequent re-wetting of the soils might have played a role, that as yet cannot be ascertained, in the response to frost and release of NO_3^- in the 1970s. Our calculations of soil moisture suggest that soils have become wetter in winter in recent years (Fig. 4b). These moister soil conditions may be more favorable for denitrification (e.g., Davidson and Swank 1986), resulting in less available soil NO_3^- for export in the spring. However, isotopic analysis of archived streamwater samples provides no evidence of increased denitrification at HBEF (Bernal et al. submitted).

One factor that clearly plays a strong role in determining the fate of soil NO_3^- generated by frost is the amount and timing of snow-melt. For example, NO_3^- export may be greater from frost events that occur early in the winter, not only because damage to plant roots may be more severe at the end of the growing season, but also because the spring snow-melt event provides a strong hydrological connection between frost-affected soils and streams. In contrast, when frost events occur later in the winter, after much of the snow has melted, or when snowpack is small, the lack of hydrological connection between soils and streams may limit NO_3^- export. In all three previous frost events (1970, 1974 and 1990), stream-flow during March and April were similar to the long-term average, while in 2006 stream-flow was less than half the average value during these months (Table 3). Without a large snow melt-event, export of soil NO_3^- was delayed, allowing more time for soil processing and plant uptake of NO_3^- released from the frost event or increased in-stream retention at warmer temperatures. The frost events of 1970 and 1974, on the other hand, were followed by the accumulation of snow-pack, and snow remained until mid- April, providing an hydrological vehicle for transport of released NO_3^- to streams (Fig. 2a). A trend of reduced snowpack or more frequent melt events during the winter (Bernal et al. submitted), could explain reduced impacts of soil frost on NO_3^- export. However, it is not clear that a reduced hydrological connection during spring completely explains low NO_3^- export in 2006. Volume-weighted mean NO_3^- concentrations have declined over the long-term record, and were also reduced more than stream flow during the 2006 spring melt event (Table 2). This result could be explained by either increased uptake opportunity with reduced flow or less release of soil NO_3^- .

There does not appear to be strong evidence that a lengthening of the growing season (e.g., Schwartz and Reiter 2000) is responsible for increased N retention at HBEF (Bernal et al. submitted), since plant growth and biomass accumulation has decreased at HBEF (Likens et al. 1994; Fahey et al. 2005; Siccama et al. 2007). It is possible, however, that the breaking of plant dormancy earlier in the spring may have shifted the balance in competition for NH_4^+ between microbes and plants, potentially influencing the fate of this N during spring months.

A third hypothesis explaining reduced NO_3^- export from forested ecosystems of the northeastern US is that the cumulative effects of chronic acidic deposition has reduced nitrification in soil or otherwise made soils less responsive to frost disturbances. While deposition of HNO_3 can theoretically increase nutrient release from forests through N saturation (Aber et al. 1989), such effects have not been documented in forests of the northeastern US. Other effects of acid deposition, such as shifts in tree species or reduction in soil pH and accompanying reduction in Ca^{2+} availability and increase in Al^{3+} , could act to reduce soil microbial nitrification rates (e.g., Finzi et al. 1998; Christ et al. 2002,) and NO_3^- export. For example, models indicate that the decline in sugar maple and increase in American beech at HBEF could account for 18% of the decline in N export because of changes in decomposition and nitrification rates in soils (Bernal et al. submitted). At least some of the factors that may reduce nitrification rates (e.g., increased dissolved Al^{3+}) could also reduce plant uptake, which would act to increase NO_3^- export. This relation may explain why some studies find correlations between soil pH and calcium availability (e.g., Finzi et al. 1998; Christ et al. 2002), while others have not (Ross et al. 2009). In addition, detecting changes in soil pH (or any soil property, for that matter), particularly at the watershed-scale, is difficult because soils are highly heterogeneous. Soil Ca^{2+} availability (Peters et al. 2004) and pH (Groffman, P. Presonal cimmunication) in W1 are higher than in the other watersheds as a result of a large-scale experimental wollastonite ($1189 \text{ kg Ca ha}^{-1}$ as CaSiO_3) addition conducted in 1999 (www.hubbardbrook.org). Indeed, W1 showed the strongest response in NO_3^- export to the frost event (Figs. 5, 6), most closely matching our predictions, and suggesting that alleviating base cation depletion (and increasing soil pH) may have impacted the N cycle. However, as of 2003, there was no evidence of increases in soil nitrification potential in W1 (Groffman et al. 2006). In fact, there were declines in N pools (soil microbial biomass and inorganic N) and processes (potential net and gross mineralization rates) that could act as a sink for N, but no increase in stream N export, again suggesting a missing N sink. Groffman et al. (2006) suggest three possibilities for this sink: plant uptake, especially by saplings, storage in soil organic matter (SOM), or increased rates of denitrification. It seems plausible

that these N in sapling roots or in SOM could be released by a frost disturbance, either releasing NO_3^- directly or stimulating nitrification.

Clearly, the effects of acid rain and climate change, including air temperature, snow depth, soil frost, and hydrologic timing, could have a myriad of impacts on an already complex N cycle. Determining the relative magnitude of such factors and whether other factors are contributing to the reduced N export from northeastern US forests will require a combination of long-term monitoring, modeling, experimental manipulations at watershed and plot-level scales.

Conclusions

While the dynamic nature of ecosystems is acknowledged and borne out in model simulations, it is generally assumed that the ecosystem response to a particular disturbance is consistent over time. Our findings, however, show that the response to soil frost may have changed substantially over the past four decades in forests of the Northeastern US. Controls on N retention operate at time scales from seasonal to centuries, and our ability to understand current trends in ecosystem N export may be limited by a lack of understanding of how these various controls interact. The importance of land-use history has been acknowledged, but disentangling its effects from interannual climate variability, climate change, cumulative effects of acidic deposition, and other periodic disturbances such as ice-storms, insect infestations and disease remains a challenge. We propose that the combined effects of recovery from logging, increases in soil moisture, particularly in winter months, reduced spring snowpack, and cumulative effects of acid deposition have reduced N losses from forests in response to frost disturbance, and perhaps are contributing to the more general trend of reduced NO_3^- export from streams in the Northern Forest Ecoregion.

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