



Effects of soil freezing disturbance on soil solution nitrogen, phosphorus, and carbon chemistry in a northern hardwood ecosystem

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Abstract. Reductions in snow cover under a warmer climate may cause soil freezing events to become more common in northern temperate ecosystems. In this experiment, snow cover was manipulated to simulate the late development of snowpack and to induce soil freezing. This manipulation was used to examine the effects of soil freezing disturbance on soil solution nitrogen (N), phosphorus (P), and carbon (C) chemistry in four experimental stands (two sugar maple and two yellow birch) at the Hubbard Brook Experimental Forest (HBEF) in the White Mountains of New Hampshire. Soil freezing enhanced soil solution N concentrations and transport from the forest floor. Nitrate (NO_3^-) was the dominant N species mobilized in the forest floor of sugar maple stands after soil freezing, while ammonium (NH_4^+) and dissolved organic nitrogen (DON) were the dominant forms of N leaching from the forest floor of treated yellow birch stands. Rates of N leaching at stands subjected to soil freezing ranged from 490 to 4,600 $\text{mol ha}^{-1} \text{ yr}^{-1}$, significant in comparison to wet N deposition (530 $\text{mol ha}^{-1} \text{ yr}^{-1}$) and stream NO_3^- export (25 $\text{mol ha}^{-1} \text{ yr}^{-1}$) in this northern forest ecosystem. Soil solution fluxes of P_i from the forest floor of sugar maple stands after soil freezing ranged from 15 to 32 $\text{mol ha}^{-1} \text{ yr}^{-1}$; this elevated mobilization of P_i coincided with heightened NO_3^- leaching. Elevated leaching of P_i from the forest floor was coupled with enhanced retention of P_i in the mineral soil Bs horizon. The quantities of P_i mobilized from the forest floor were significant relative to the available P pool (22 mol ha^{-1}) as well as net P mineralization rates in the forest floor (180 $\text{mol ha}^{-1} \text{ yr}^{-1}$). Increased fine root mortality was likely an important source of mobile N and P_i from the forest floor, but other factors (decreased N and P uptake by roots and increased physical disruption of soil aggregates) may also have contributed to the enhanced leaching of nutrients. Microbial mortality did not contribute to the accelerated N and P leaching after soil freezing. Results suggest that soil freezing events may increase rates of N and P loss, with potential effects on soil N and P availability, ecosystem productivity, as well as surface water acidification and eutrophication.

Introduction

Traditionally, there have been few investigations of overwinter biogeochemical processes relative to studies during the growing season in temperate northern ecosystems because biological processes were largely thought to be insignificant under cold conditions. More recent studies, however, have shown that root and microbial processes are surprisingly active in cold (0 to 5 °C) and even frozen soils (e.g. Clein & Schimel 1995). Furthermore, a significant portion of ecosystem nutrient cycling and loss may occur during the overwinter period (Melloh & Crill 1995; Hobbie & Chapin 1996; Brooks et al. 1996, 1997; Saarnio et al. 1999). For example, ~69% of annual stream nitrate (NO_3^-) export occurs during snowmelt between the months of March and May at the biogeochemical reference watershed (W6) of the Hubbard Brook Experimental Forest (HBEF) in the White Mountains of New Hampshire (Likens & Bormann 1995). The controls on these overwinter biogeochemical processes, as well as their relationship to growing season processes, are not fully understood.

Climate change may significantly disturb biogeochemical processes by altering the overwinter snow cover and soil temperature regimes (Brooks et al. 1998; Brooks & Williams 1999). We hypothesize that reductions in the depth and annual duration of snow cover may be a regional scale effect of climate warming in northern hardwood forests of eastern North America. While there are no detailed predictions of snow depth changes with global warming, both field and modeling experiments suggest that snowpack dynamics are highly responsive to climate change (Cooley 1990; van Katwijk et al. 1993; Giorgi et al. 1994; Williams et al. 1996; Moore & McKendry 1996; Baron et al. 2000). In northern latitudes, the development of the seasonal snowpack may insulate the soil from freezing air temperatures. As the depth of soil freezing typically exhibits an inverse relationship with snow depth, a lack of snow, or a late accumulating snow pack, results in soil freezing that is deeper and of longer duration than when the snowpack is established in early winter (Stadler et al. 1996; Shanley & Chalmers 1999). Reduced snow cover under a warmer climate may therefore lead to increases in the frequency, severity, and spatial extent of soil freezing events.

Soil freezing may significantly disturb the belowground environment and the normally tight linkages between mineralization and uptake processes that are thought to be important to nutrient conservation in forest ecosystems (Bormann & Likens 1979). Rates of decomposition and mineralization of soil organic matter may be accelerated following soil freezing events as the result of inputs of labile organic matter via: (i) increased fine root and microbial mortality (Biederbeck & Campbell 1971; Meyer et al. 1975; Morley et al. 1983; Sakai & Larcher 1987; Skogland et al. 1988), (ii) physical disruption

of soil aggregates (Soulides & Allison 1961; Hinman & Frederick 1968; Bullock et al. 1988), and (iii) fragmentation of fresh litter. The formation and subsequent growth of ice lenses could shear roots and change the soil structure at the root-soil interface, potentially resulting in impaired root uptake. Soil freezing can therefore result in increased nitrogen (N), phosphorus (P), and carbon (C) concentrations in soil solutions, potentially resulting in enhanced nutrient loss, soil solution acidification, and base cation depletion from soils (e.g. Mitchell et al. 1996).

Boutin and Robitaille (1995) manipulated snow cover in Canadian sugar maple stands which induced soil freezing and resulted in significantly elevated soil solution concentrations of NO_3^- and ammonium (NH_4^+), with peaks in NO_3^- occurring from July through September. Pronounced increases in stream NO_3^- concentrations during 1970 and 1974 at the HBEF have been related to soil freezing events (Likens & Bormann 1995). Mitchell et al. (1996) suggested that a synchronous pulse of stream NO_3^- concentrations in four watersheds spanning the northeastern U.S. during the snowmelt of 1990 was related to a regional scale soil freezing event in December 1989. These studies indicated that soil freezing may significantly influence soil solution chemistry and N loss in northern hardwood forests.

In this paper, data are presented from a snow manipulation study at the HBEF. The overwinter snow cover and soil temperature regimes were manipulated during two consecutive winters at four experimental stands (two sugar maple and two yellow birch). Snow cover was removed from the first snowfall through early February to depict the effects of a late accumulating snow cover on the overwinter soil temperature regime and on biogeochemical processes. Our objectives were: (i) to elucidate the effects of soil freezing on soil solution N, P, and C chemistry and (ii) to evaluate the responses of soil solution chemistry relative to measurements of soil freezing effects on fine root dynamics and soil N cycling reported in other articles in this series (Tierney et al. this issue; Groffman et al. this issue).

Methods

Study site

The HBEF is located in the White Mountains of New Hampshire, U.S.A. (43°56' N, 71°45' W). The climate of the HBEF is characterized by long, cold winters and short, cool summers; the growing season occurs from approximately June through September (Likens & Bormann 1995). Precipitation is distributed relatively evenly throughout the year (annual mean = 140 cm), with 25 to 33% of precipitation occurring as snow (Federer et al. 1990). Mean

air temperatures range from -10°C in January to 17°C in July. A continuous snowpack typically begins to develop in late autumn and soils usually do not freeze during the overwinter period because the snow insulates the soil from freezing air temperatures (Likens & Bormann 1995). Canopy vegetation is dominantly mixed northern hardwoods and conifers. Sugar maple (*Acer saccharum*) and yellow birch (*Betula alleghaniensis*) comprise ~ 36 and 28% , respectively, of the basal area of trees between 21 and 70 cm dbh at the biogeochemical reference catchment at the HBEF, watershed 6 (Bormann et al. 1970). Soils are predominantly well-drained, coarse-loamy, mixed frigid acidic Typic Haplorthods (pH ~ 3.9) developed in shallow glacial till (mean thickness = 2 m) overlying metamorphosed sedimentary and igneous rocks (Dahlgren & Driscoll 1994).

Experimental stands

Four experimental stands were established at the HBEF (Hardy et al. this issue), two in sugar maple ($\sim 80\%$ dominance) stands and two in yellow birch ($\sim 80\%$ dominance) stands. These species were chosen because the elevation range of yellow birch (YB) typically exceeds sugar maple (SM), and thus YB would be expected to be more frost-hardy. Two 10 m by 10 m plots (one reference, one treatment) were located in each experimental stand (Hardy et al. this issue). In the fall and winter of 1996, minor amounts of understory vegetation were cleared from both treatment and reference plots for plot installations and to facilitate shoveling. Snow was removed by shoveling through early February at the treatment plots to induce soil freezing and to simulate the biogeochemical effects of a late accumulating snowpack as may be expected under a warmer climate. Snow removal occurred during two consecutive winters (1997–1998 and 1998–1999). The treatment was initiated in November 1997. Between 5 to 10 cm of snow from early-winter storms was manually compacted at the treatment plots to protect plot installations and the forest floor from shovel damage and to increase the albedo of the forest floor, promoting soil freezing. The smooth backside of the shovels was used to carefully compact the snow and protect the soil from disruption prior to its freezing. This compacted snow layer was maintained throughout the entire treatment period and observations each spring confirmed that the protective compact layer of snow was effective in minimizing compaction of the forest floor. The reference plots accumulated snow at natural rates all winter, while the treatment plots accumulated snow at natural rates after snow removal ceased in early February.

Duplicate zero-tension (gravity) lysimeters, similar to the design of Driscoll et al. (1988), were installed both below the Oa and within the Bs soil horizons at each plot during the autumn of 1996, giving a total of 4

lysimeters per plot (Hardy et al. this issue). Lysimeters below the Oa horizon were installed between 3 and 8 cm below the surface of the forest floor, while lysimeters in the Bs horizon were installed between 10 and 22 cm below the forest floor surface. After installation, lysimeters were sampled at approximately monthly intervals until initiation of the snow cover manipulation. An additional set of lysimeters was installed at a YB treatment plot during the summer of 1998. Gravity lysimeters are believed to mostly sample macropore flow during hydrological events and while the soil is draining to field capacity (Litaor 1988) and thus provide a sample of water exported from the ecosystem. Soil solutions were collected on 37 dates at weekly to monthly intervals from December 1997 through November 1999 and shipped on ice to Syracuse University for chemical analyses.

Laboratory methods

Soil solutions were stored at $\sim 4^{\circ}\text{C}$ in a constant temperature room until analysis. Samples were analyzed for the following solutes (typically in the order listed): dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), ammonium (NH_4^+), nitrate (NO_3^-), soluble reactive phosphorus (SRP), and total nitrogen (TN). As concentrations of DIC, DOC, NH_4^+ , NO_3^- , and SRP may change during storage, these analyses were completed as soon as possible (typically within 2 weeks of sample collection). For soil solution samples with a collection volume less than 100 ml, DIC and SRP were not measured due to relatively large sample volume requirements for these analyses. Analyses of SRP were initiated in February 1998, while analyses of the other solutes were completed on all samples, sample volume permitting.

Analysis of DIC was via phosphoric acid addition to convert DIC to CO_2 , followed by infrared detection (Dohrmann 1984). Analysis of DOC occurred after filtration by persulfate and ultraviolet enhanced oxidation, followed by infrared detection of CO_2 (McDowell et al. 1987). Ammonium was analyzed with an autoanalyzer via phenate colorimetry (APHA 1981). Nitrate was analyzed by ion chromatography (Tabatabai & Dick 1983). Soluble reactive phosphorus was measured through the formation of a blue antimony-phospho-molybdate complex and measurement on a UV-VIS spectrophotometer at 880 nm. This technique was believed to primarily measure ortho-phosphate but due to hydrolysis, some polyphosphate, organic phosphate, and metal phosphates may have been detected. Inorganic P (P_i) was assumed to equal SRP. Total nitrogen (TN) was analyzed by persulfate oxidation and analysis of NO_3^- on an autoanalyzer via hydrazine reduction (Ameel et al. 1993). Dissolved organic N (DON) was calculated as the difference between TN and inorganic N ($\text{NH}_4^+ + \text{NO}_3^-$).

Computation of water and solute fluxes

The water fluxes through the Oa and Bs soil horizons were calculated using a simple mass balance model. Assuming that the vertical distribution of evapotranspiration (ET) within a soil profile corresponded with the distribution of fine roots, then 44% of ET occurred from the Oa horizon and above (forest floor horizons) (Fahey & Hughes 1994). From June through November when ET was significant, the daily water flux through the Oa horizon was calculated based on this vertical distribution of ET and measured values of precipitation and stream flow at the biogeochemical reference watershed (W6) at the HBEF. From December through May when ET was less significant, the daily water flux through the Oa horizon was assumed to equal daily stream flow at W6. The daily water flux through the Bs horizon was assumed to equal daily stream flow throughout the year. Water fluxes through the Oa and Bs horizons were assumed to be zero when stream flow was zero. Water fluxes were assumed to be equal among stands. Measurements of soil hydrological variables (e.g. soil water tension, soil hydraulic conductivity) were beyond the scope of this project and therefore water fluxes could not be calculated separately for each stand.

The water fluxes predicted by the simple model were compared with those predicted by a more complex, process-based model of catchment hydrology developed for the HBEF, BROOK90 version 3.24 (Federer 1995). Catchment parameters for W6 of the HBEF were used in BROOK90 simulations. Input data (daily values of solar radiation, minimum and maximum air temperatures, vapor pressure, and wind speed) were obtained from the HBEF web page (www.hbrook.sr.unh.edu). Soil temperature and soil freezing processes are not considered in BROOK90. The BROOK90 model was run with data that began January 1996, allowing 23 months for soil water storage to 'equilibrate'. Model output from December 1997 through December 1998 was used to calculate water fluxes through the Oa and Bs soil horizons. BROOK90 predicted that 105 and 101 cm of water flowed through the Oa and Bs horizons, respectively, while the simple model predicted that 132 and 108 cm of flux occurred through the respective horizons. While estimates of the water flux through the Bs horizon were similar between BROOK90 and the simple model, the flux through the Oa from BROOK90 seemed unreasonably small (i.e. ET occurring below the Oa horizon was likely greater than 4 cm). Predictions of water flux were strongly correlated ($p < 0.005$) between the simple model and BROOK90, indicating that the temporal patterns of water flux were similar between the simple model and BROOK90. We therefore concluded that the simple mass balance model was a reasonable tool for calculating water fluxes through the soil horizons. Because we were unable to quantify the effects of soil freezing on infiltration, we assumed that water

fluxes were equal between treatment and reference plots. The potential effects of soil freezing on water fluxes are addressed below in the discussion.

Average solute concentrations for each pair of lysimeters on every sampling date were calculated using the volume of soil solution collected as a weighting variable. These volume-weighted average solute concentrations were multiplied by the daily water flux to calculate the solute fluxes through the Oa and Bs soil horizons for each experimental plot ($n = 8$).

Statistical analyses

All statistical analyses were performed using SAS software at the $\alpha = 0.05$ level of significance (SAS 1989). Monthly solute concentrations were calculated by dividing the monthly soil solution solute fluxes by the monthly water fluxes. One-way analysis of variance (ANOVA) was performed separately for each month to test for soil freezing treatment effects on soil solution NO_3^- , NH_4^+ , DON, P_i , DOC, and DIC concentrations by tree species (SM, YB) and soil horizon (Oa, Bs). The overall mean values of the monthly soil solution solute concentrations were compared between reference and treatment plots using repeated measures ANOVA separately for each species (SM, YB) and soil horizon (Oa, Bs) combination; the mean sum of squares of stands within a treatment was used as the error term in testing the null hypothesis for the soil freezing treatment effect. To test if the response of soil solution chemistry to soil freezing disturbance differed between SM and YB stands, a response variable was calculated for each experimental stand. The response variable was the monthly treatment solute concentration minus the monthly reference concentration. Positive values of the response variable therefore indicated greater treatment than reference concentrations. Mean values of the response variable were compared between stands of different tree species using repeated measures ANOVA separately for each soil horizon; the mean sum of squares of stands within a species was used as the error term in testing the null hypothesis. Pearson correlation coefficients were determined between soil solution solute concentrations separately for each tree species, soil horizon, and treatment. Linkages between solute concentrations were identified as statistically significant correlations and were compared between reference and treatment plots within single species. Statistical tests comparing mean solute fluxes between reference and treatment plots were not performed because water fluxes were not directly measured.

Results

Effects of snow cover manipulation on the overwinter soil temperature regime

The removal of snow cover through early February resulted in substantial changes in overwinter soil temperatures. Freezing temperatures ($<0^{\circ}\text{C}$) were observed at 10 cm or deeper in the soil profile at all treatment plots while soils remained thawed at 10 cm depth and deeper at all reference plots during the winters of 1997–1998 and 1998–1999 (Hardy et al. this issue). Soils at the treatment plots typically began to freeze in late December and remained frozen through early April (Hardy et al. this issue). Soil freezing was more severe during the winter of 1998–1999 than 1997–1998, likely as the result of colder winter air temperatures.

Soil solution nitrogen

Responses of soil solution NO_3^- concentrations to the soil freezing disturbance were evident to varying degrees for each tree species in both soil horizons (Figure 1). In the Oa horizon of SM stands, soil solution NO_3^- concentrations were initially similar between reference and treatment plots until early in the growing season of 1998 (May). Treatment concentrations then increased sharply relative to reference levels and remained elevated until late in the growing season of 1998 (October), after which treatment concentrations returned to reference levels. This seasonal pattern was repeated during the second year of the experiment (1999). The mean monthly soil solution NO_3^- concentration was significantly greater in treatment than reference plots during July and August of 1998 for soil water draining the forest floor of SM stands (Figure 1). The overall mean monthly soil solution NO_3^- concentration was significantly greater at the treatment than the reference plots for the Oa horizon leachate of SM stands (Table 1). A response was also evident in the Bs horizon solution during the growing season of both years, with the mean monthly treatment NO_3^- concentration being significantly greater than the reference level during June of 1999 (Figure 1).

Unlike the SM stands, a seasonal pattern of NO_3^- response was not detected at the YB stands (Figure 1). Mean monthly treatment NO_3^- concentrations were significantly greater than reference values during June of 1999 for solutions draining the forest floor of YB stands and during July 1998 as well as April and May of 1999 for Bs horizon leachates (Figure 1). Although the overall mean monthly NO_3^- concentrations were not significantly different between treatment and reference plots of YB stands (Table 2), NO_3^- concentrations of Oa and Bs horizon solutions tended to be greater in the treatment

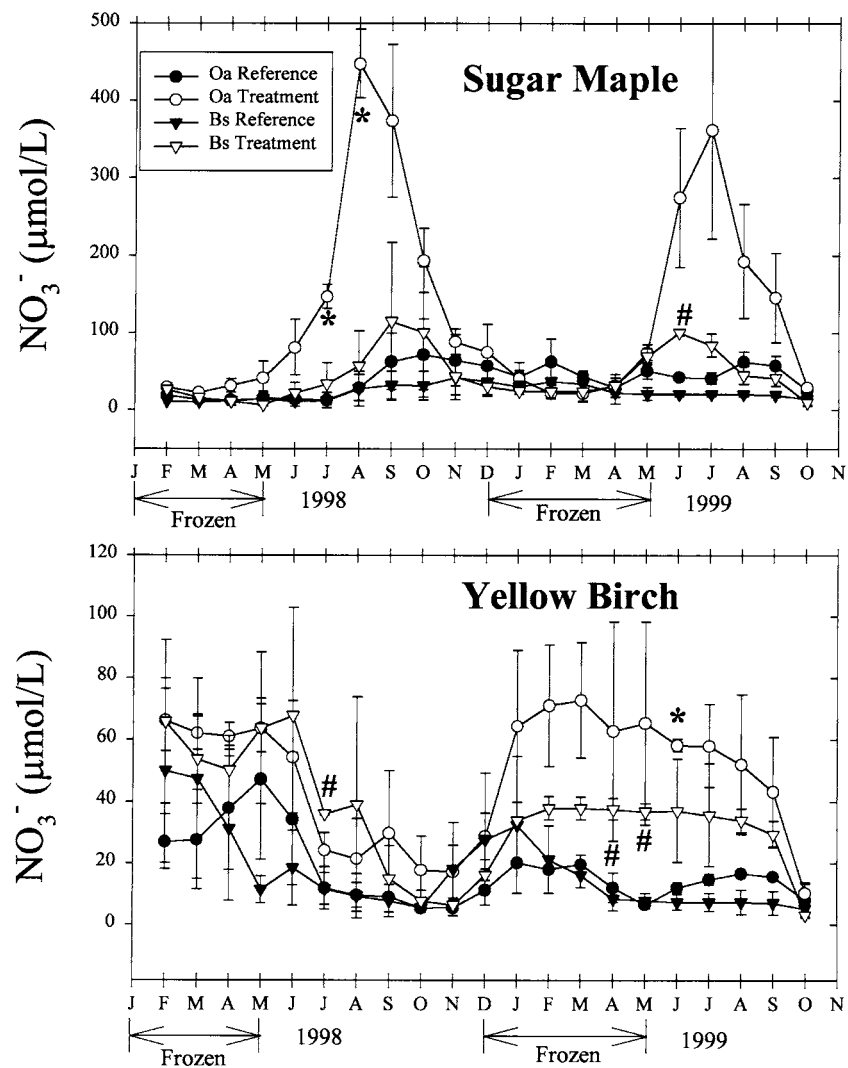


Figure 1. Mean monthly nitrate (NO_3^-) concentrations for soil solutions draining the Oa and Bs horizons of reference and treatment plots in sugar maple and yellow birch stands. As indicated on the x axes, soils were frozen from ~ December through April. Error bars are standard errors of the mean concentration between plots ($n = 2$). The symbols “*” and “#” denote a statistically significant ($p < 0.05$) soil freezing treatment effect for the Oa and Bs horizons, respectively, during the given month.

Table 1. Comparison of overall mean concentrations between reference and treatment plots for soil solutions draining the Oa and Bs horizons of sugar maple stands. Standard errors are in parentheses. The *p*-values of repeated measures ANOVA testing the effects of the soil freezing treatment and treatment-time interactions are indicated in the 'Freezing' and 'Freezing*Time' columns, respectively. All mean values are in $\mu\text{mol L}^{-1}$

	Reference	Treatment	Freezing	Freezing*Time
Oa Horizon				
NO_3^-	39 (4.2)	130 (21)	0.0495	<0.0001
NH_4^+	24 (3.9)	18 (2.3)	0.70	0.59
DON	30 (4.0)	36 (5.7)	0.80	<0.0001
P_i	0.36 (0.096)	2.3 (0.46)	0.19	0.022
DOC	970 (130)	1000 (120)	0.97	0.056
DIC	270 (12)	350 (28)	0.56	0.77
Bs Horizon				
NO_3^-	23 (2.4)	43 (6.9)	0.24	0.65
NH_4^+	6.5 (1.3)	21 (7.0)	0.45	0.71
DON	16 (2.0)	20 (2.6)	0.60	0.0088
P_i	0.094 (0.011)	0.13 (0.025)	0.66	0.0054
DOC	390 (46)	480 (46)	0.78	0.023
DIC	260 (14)	340 (35)	0.62	0.70

than the reference plots during the entire experiment, most notably during the second year (1999).

The soil freezing disturbance accelerated NO_3^- fluxes from each horizon of both species (Table 3). Treatment NO_3^- fluxes were 290 and 150% of reference fluxes from the Oa and Bs horizons, respectively, of SM stands, while treatment fluxes were 250 and 200% of reference fluxes from the Oa and Bs horizons, respectively, of YB stands. The proportion of annual soil solution NO_3^- flux during the summer and fall (June through November) was much higher in the treatment than the reference plots in the SM stands.

Soil freezing resulted in significantly elevated concentrations of NH_4^+ in the Oa horizon solutions of YB stands (Table 2), with the treatment NH_4^+ flux being 470% of the reference flux from the Oa horizons of YB stands (Table 3).

Although not statistically significant, the overall mean monthly DON concentration was greater in treatment than reference plots in the Oa horizon

Table 2. Comparison of overall mean concentrations between reference and treatment plots for soil solutions draining the Oa and Bs horizons of yellow birch stands. Standard errors are in parentheses. The *p*-values of repeated measures ANOVA testing the effects of the soil freezing treatment and treatment-time interactions are indicated in the 'Freezing' and 'Freezing*Time' columns, respectively. All mean values are in $\mu\text{mol L}^{-1}$

	Reference	Treatment	Freezing	Freezing*Time
Oa Horizon				
NO_3^-	18 (2.3)	48 (4.1)	0.10	0.51
NH_4^+	23 (1.7)	100 (13)	0.034	0.95
DON	49 (2.4)	130 (45)	0.29	0.56
P_i	1.2 (0.12)	1.8 (0.29)	0.29	0.66
DOC	2100 (87)	3700 (950)	0.31	0.47
DIC	190 (10)	420 (29)	0.042	<0.0001
Bs Horizon				
NO_3^-	17 (3.0)	36 (3.7)	0.20	0.66
NH_4^+	69 (20)	25 (4.1)	0.15	<0.0001
DON	45 (4.5)	35 (4.2)	0.69	0.57
P_i	2.4 (0.69)	0.52 (0.12)	0.46	0.33
DOC	1500 (110)	1100 (140)	0.76	0.48
DIC	280 (23)	300 (16)	0.80	0.066

of YB stands (Table 2). The treatment DON flux was 300% of the reference flux from the Oa horizon of YB stands (Table 3).

Soil solution inorganic phosphorus

Responses of P_i to soil freezing were found in the Oa horizon leachates of SM and YB stands (Figure 2). In the Oa horizon leachates of SM stands, treatment P_i concentrations were elevated relative to reference levels from June through October of 1998 as well as from April through July of 1999, with the mean monthly P_i concentration being significantly greater in treatment than reference plots during May 1999 (Figure 2). Although the soil freezing treatment effect was not statistically significant, the treatment-time interaction was significant (Table 2), reflecting the seasonal response of soil solution P_i concentrations to the soil freezing disturbance in the Oa horizon leachates of SM stands (Figure 2). In the Oa horizon solutions of YB stands, treatment concentrations were greater than reference levels from June through

Table 3. Comparison of mean monthly soil solution solute fluxes between reference and treatment plots for the Oa and Bs soil horizons of sugar maple and yellow birch stands. Standard errors are in parentheses. All units are in $\text{mol ha}^{-1} \text{ month}^{-1}$

	Oa Horizon		Bs Horizon	
	Reference	Treatment	Reference	Treatment
Sugar Maple Stands				
NO_3^-	40 (5.8)	120 (18)	18 (2.7)	27 (4.3)
NH_4^+	24 (5.5)	17 (2.3)	4.3 (0.89)	9.3 (2.0)
DON	34 (7.6)	36 (6.1)	13 (3.2)	17 (3.6)
P_i	0.43 (0.18)	2.1 (0.47)	0.068 (0.013)	0.094 (0.030)
DOC	1000 (200)	1000 (180)	310 (57)	340 (59)
DIC	290 (31)	390 (62)	220 (32)	310 (63)
Yellow Birch Stands				
NO_3^-	22 (4.5)	55 (7.9)	18 (4.9)	35 (6.9)
NH_4^+	25 (3.1)	110 (21)	30 (7.0)	22 (5.4)
DON	53 (6.9)	160 (64)	37 (5.3)	30 (6.1)
P_i	1.2 (0.12)	1.9 (0.38)	1.3 (0.46)	0.28 (0.064)
DOC	2200 (240)	4100 (1400)	1200 (170)	1000 (200)
DIC	200 (21)	450 (66)	200 (25)	260 (37)

August of 1999. Treatment P_i fluxes were 480 and 160% of reference fluxes in the Oa horizon leachates of SM and YB stands, respectively (Table 3).

Soil solution carbon

The overall mean monthly soil solution DIC concentration was significantly greater in the treatment than the reference plots of Oa horizon leachate for YB stands (Table 2). The treatment DIC flux was 200% of the reference flux from the Oa horizon of YB stands (Table 3).

A response of DOC concentrations to the soil freezing disturbance was not apparent at either the SM or YB stands (Tables 1 and 2).

Comparison of soil solution responses between sugar maple and yellow birch stands

The responses of soil solution NO_3^- and NH_4^+ concentrations to the soil freezing disturbance tended to differ between SM and YB stands, with NO_3^- and NH_4^+ tending to exhibit greater responses in SM and YB stands, respectively. Although not statistically significant, the p -values for the stand

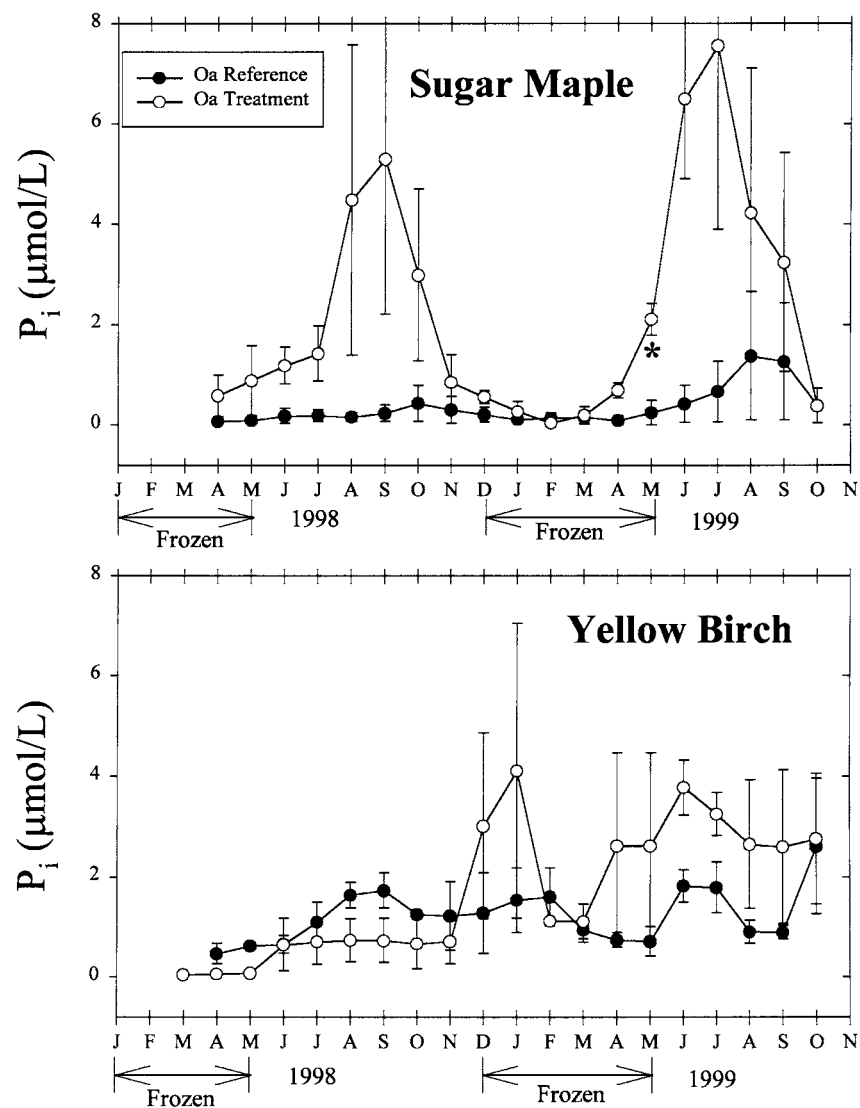


Figure 2. Mean monthly inorganic phosphorus (P_i) concentrations for soil solutions draining the Oa horizon of reference and treatment plots in sugar maple and yellow birch stands. As indicated on the x axes, soils were frozen from ~ December through April. Error bars are standard errors of the mean concentration between plots ($n = 2$). The symbol * denotes a statistically significant ($p < 0.05$) soil freezing treatment effect during the given month.

Table 4. Comparison of the mean values of the response variable in Oa horizon solutions between sugar maple and yellow birch stands. The response variable ($\mu\text{mol L}^{-1}$) is the monthly treatment minus reference concentration. Standard errors are indicated in parentheses. The p -values of repeated measures ANOVA testing the effects of stand and stand-time interactions are indicated

	Sugar Maple	Yellow Birch	Stand	Stand*Time
DIC	79 (28)	210 (34)	0.43	0.92
DOC	42 (110)	1600 (970)	0.48	0.37
NH_4^+	-6.6 (3.6)	79 (13)	0.060	0.93
NO_3^-	90 (21)	30 (3.8)	0.084	<0.0001
SRP	1.9 (0.48)	0.62 (0.29)	0.45	0.19
DON	5.2 (5.1)	84 (45)	0.33	0.49

effects were relatively low for the mean NO_3^- ($p = 0.084$) and NH_4^+ response ($p = 0.060$; Table 4). Additionally, the stand-time interaction was statistically significant for NO_3^- (Table 4).

Correlations between soil solution solutes

Patterns of correlations between solutes exhibited differences between reference and treatment plots within single species. Both NO_3^- and P_i responded strongly to the soil freezing disturbance in the Oa horizon of SM stands. These solutes exhibited stronger correlations at treatment plots ($r = 0.85$) than at reference plots ($r = 0.24$) in the Oa horizon waters of SM stands (Table 5). Concentrations of DIC, NO_3^- , NH_4^+ , and DON exhibited treatment responses in the Oa horizon solution of YB stands. Treatment NO_3^- concentrations were significantly correlated with NH_4^+ but this relationship was not evident in Oa horizon solutions draining reference plots of YB stands (Table 6). Correlations between DOC and NH_4^+ , between DOC and DON, and between NH_4^+ and DON were stronger at treatment than reference plots in the Oa horizon solution of YB stands.

Discussion

Soil freezing accelerates nitrogen leaching

Soil freezing disturbance appears to have accelerated the leaching of total nitrogen ($\text{TN} = \text{NO}_3^- + \text{NH}_4^+ + \text{DON}$) from the forest floor at all experimental

Table 5. Pearson correlation coefficients (r), significance levels (p), and number of observations (N) for concentrations of selected soil solution solutes at reference and treatment plots collected from the Oa horizon of sugar maple stands. Only significant ($p < 0.05$) correlations are shown

	DOC			NH ₄ ⁺			NO ₃ ⁻			P _i			DON		
	r	p	N	r	p	N	r	p	N	r	p	N	r	p	N
Sugar Maple Reference Plots Oa Horizon															
DIC	0.51	0.0001	91	0.39	0.0001	91			0.28	0.011	81	0.34	0.0009	91	
DOC				0.71	0.0001	105			0.58	0.0001	86	0.74	0.0001	105	
NH ₄ ⁺							0.25	0.0092	110	0.29	0.0077	86	0.68	0.0001	108
NO ₃ ⁻									0.24	0.029	86				
P _i												0.48	0.0001	86	
Sugar Maple Treatment Plots Oa Horizon															
DIC															
DOC				0.61	0.0001	102	0.67	0.0001	102	0.51	0.0001	88	0.44	0.0001	101
NH ₄ ⁺							0.53	0.0001	107	0.49	0.0001	89	0.53	0.0001	106
NO ₃ ⁻										0.85	0.0001	89	0.62	0.0001	106
P _i													0.33	0.0018	89

Table 6. Pearson correlation coefficients (r), significance levels (p), and number of observations (N) for concentrations of selected soil solution solutes at reference and treatment plots collected from the Oa horizon of yellow birch stands. Only significant ($p < 0.05$) correlations are shown

	DOC			NH ₄ ⁺			NO ₃ ⁻			P _i			DON		
	r	p	N	r	p	N	r	p	N	r	p	N	r	p	N
Yellow Birch Reference Plots Oa Horizon															
DIC				0.49	0.0001	61	-0.31	0.015	61						
DOC				0.35	0.0011	85	-0.28	0.010	85				0.55	0.0001	82
NH ₄ ⁺										0.44	0.0001	71	0.23	0.032	85
NO ₃ ⁻															
P _i															
Yellow Birch Treatment Plots Oa Horizon															
DIC				0.39	0.014	39									
DOC				0.67	0.0001	66							0.97	0.0001	64
NH ₄ ⁺							0.31	0.0026	90				0.54	0.0001	81
NO ₃ ⁻															
P _i															

stands. Soil solution losses of N could be increased via enhanced supply and/or decreased biotic assimilation. The supply of N could increase after soil freezing via: (i) fine root mortality, (ii) physical disruption of soil aggregates, (iii) microbial death, and (iv) fragmentation of fresh litter. Biotic assimilation of N could decrease after soil freezing due to reduced fine root uptake. The absence of treatment responses for net N mineralization and microbial biomass suggests that neither of these mechanisms contributed to accelerated N losses from the forest floor subsequent to soil freezing disturbance (Groffman et al. this issue). The lack of a treatment response for N mineralization, coupled with the relatively mild soil freezing events induced by our snow manipulation (soil temperatures never decreased below -5°C at the treatment plots), were consistent with the results of Nielsen et al. (submitted) who found that N mineralization only increased when soils from our experimental plots were subjected to severe soil freezing in the laboratory (-13°C). Similarly, previous studies have suggested that soil temperatures may need to decrease below -5°C for significant mortality of microbes (e.g. Edwards & Cresser 1992). The accelerated leaching of NO₃⁻ observed at all treatment plots was consistent with the significant increases in extractable soil NO₃⁻ and net nitrification at the treatment plots (Groffman et al. this issue).

Fluxes of dissolved inorganic N ($\text{DIN} = \text{NO}_3^- + \text{NH}_4^+$) from the forest floor of treated plots (range: $1400 \text{ mol ha}^{-1} \text{ yr}^{-1}$ to $2400 \text{ mol ha}^{-1} \text{ yr}^{-1}$) were substantially greater than throughfall DIN fluxes entering the forest floor at W6 of the HBEF between 1989 and 1992 (range: 420 to $630 \text{ mol ha}^{-1} \text{ yr}^{-1}$; Lovett et al. 1996). This comparison of fluxes entering and leaving the forest floor indicates that most of the increase in DIN subsequent to soil freezing was derived from sources internal to the forest floor, rather than reduced plant uptake of throughfall N.

Hardy et al. (this issue) found that the reduction in soil infiltration caused by the soil freezing treatment was proportional to the decrease in snow water equivalence, approximately a 13 to 16% reduction in the annual water flux. As treatment soil solution solute fluxes from the Oa horizon were greater than 200% of reference fluxes for NO_3^- in SM stands and for NO_3^- , NH_4^+ , and DON in YB stands (Table 3), a 16% reduction in solute flux at the treatment plots caused by the decrease in infiltration still resulted in treatment solute fluxes substantially greater than reference fluxes.

Decomposition, mineralization, and nitrification of fine roots killed during the overwinter period likely contributed significantly to accelerated N leaching from the treatment plots. Tierney et al. (this issue) estimated that elevated fine root necromass could have potentially contributed an excess flux (treatment minus reference flux) of about $360 \text{ mol N ha}^{-1} \text{ yr}^{-1}$, approximately 20% of the average excess soil solution N flux from the Oa horizon ($1800 \text{ mol ha}^{-1} \text{ yr}^{-1}$). Greater soil solution N fluxes than the N potentially derived from fine root mortality and decomposition suggest that N source(s) in addition to fine root mortality must have contributed to the excess N leaching from the forest floor. In addition to fine root mortality, hydrological N losses after soil freezing may have increased due to an enhanced supply of N via physical disruption of soil aggregates and fragmentation of fresh litter, as well as decreased plant uptake of N generated within the forest floor.

Soil solution NH_4^+ did not respond to soil freezing at the SM stands; the pronounced response of soil solution NO_3^- , therefore, suggests that decreased competition for available NH_4^+ between nitrifiers and heterotrophs and/or between nitrifiers and root-mycorrhizal complexes stimulated nitrification and enhanced NO_3^- losses from SM stands. Our results indicate that the reduction in root N uptake may have been important as a regulator of hydrological N loss. Physical disturbance of root-soil-microbial interactions by soil freezing may have affected hydrological N losses by reducing the synchrony between mineralization and uptake processes.

Our original hypothesis was that soil solution responses would be greater in SM than YB stands as the result of the greater cold hardiness of YB. Fine root mortality, however, was similar between SM and YB treatment plots

(Tierney et al. this issue). The greater soil solution NO_3^- response in SM than YB stands was consistent with the higher extractable soil NO_3^- concentrations and greater potential net nitrification rates in SM than YB stands (Groffman et al. this issue). Nielsen et al. (submitted) also observed that nitrification was greater in SM than YB in response to laboratory soil freezing for soils from our experimental stands. The greater soil solution NH_4^+ response for YB than SM stands was consistent with the results of Nielsen et al. (submitted) who observed greater extractable soil NH_4^+ concentrations and greater N mineralization rates in YB than SM for soils subjected to laboratory soil freezing from our experimental stands. An additional factor that may have contributed to the differing soil solution N responses between stands was the difference in mycorrhizal associations, as SM has endomycorrhizal while YB has ectomycorrhizal associations. Ectomycorrhizal hyphae may extend into the soil for much greater distances than endomycorrhizal hyphae (Marschner & Dell 1994); physical disruption of the soil aggregates may therefore have disturbed the root-mycorrhizal complex of YB more than SM, resulting in more impaired uptake of NH_4^+ by YB than SM. Endomycorrhizal fungi are believed to increase P uptake more than ectomycorrhizal fungi (Aber & Melillo 1991). Although not statistically significant, the greater P_i response in SM than YB stands in the Oa horizon (Table 4), is consistent with the hypothesis that soil freezing disturbed the root-mycorrhizal complex differently between stands. We emphasize that these explanations of the differing soil solution N response between tree stands are not conclusive and that more mechanistic comparisons are needed. Similarly, it was unknown why soil solution responses were most pronounced at SM stands during the summer and autumn, whereas no clear seasonal response occurred at YB stands.

The responses of soil solution N were greater in the forest floor than in the Bs soil horizon, with the ratio of TN fluxes in the Bs to the Oa averaging 0.29. Root uptake, microbial immobilization, NH_4^+ adsorption onto cation exchange sites, as well as the sorption of DON to mineral soil were potential mechanisms immobilizing N from the soil solution during percolation from the Oa towards the Bs soil horizon. Lateral flow of soil solutions leaching below the forest floor could also have contributed to the differences in N fluxes observed between the soil horizons. Root uptake of DIN was considered to be an unlikely retention mechanism because most roots occur in the forest floor (Fahey & Hughes 1994) and root mortality was not different between depths (T.J. Fahey, unpublished data).

Enhanced loss of TN from the Bs horizon (treatment minus reference fluxes) averaged $160 \text{ mol ha}^{-1} \text{ yr}^{-1}$. This quantity of N loss from the soil profile was significant, as indicated by comparison with rates of wet N deposition to the HBEF ($530 \text{ mol ha}^{-1} \text{ yr}^{-1}$ during 1992–1993; Mitchell et al.

1996) as well as rates of stream N export at W6 of the HBEF in 1997 (25 mol ha⁻¹ yr⁻¹; G. Likens, personal communication).

Our results were consistent with previous studies showing responses of DIN to soil freezing. Soil freezing induced by season-long removal of snow cover in Canadian SM stands resulted in pronounced increases in soil solution NH₄⁺ and NO₃⁻ concentrations (Boutin & Robitaille 1995). Minimum soil temperatures (-4 to -6 °C) induced by the snow cover manipulation by Boutin and Robitaille (1995) tended to be lower than the minimum soil temperatures observed during the current study. Nitrate loss during snowmelt was significantly greater at plots with inconsistent snow cover that experienced more severe soil freezing relative to plots with a deep and continuous snow cover at Niwot Ridge, Colorado; this pattern was attributed to a greater capacity of microorganisms to immobilize N at consistent snow cover plots (Brooks et al. 1998). Brooks et al. (1999) observed that N retention in the catchments of the Colorado Front Range was strongly and positively related to winter snow cover, consistent with subnivean controls on N cycling observed at the plot scale. During years with low snow cover and likely soil freezing at a high elevation catchment in Colorado, stream NO₃⁻ fluxes were significantly greater than years with normal snowpack accumulation (Lewis & Grant 1980). Brooks et al. (1998) hypothesized that observations of Lewis and Grant (1980) were due to a greater capacity of microorganisms to immobilize N in years with normal snow cover, rather than an increase in soil N pools during low snow years. Studies have linked marked increases in stream NO₃⁻ concentrations in the northeastern U.S. with natural soil freezing events (Likens & Bormann 1995; Mitchell et al. 1996).

Enhanced loss of DIN subsequent to soil freezing could have a variety of consequences for receiving waters, including eutrophication and acidification (Vitousek et al. 1997). Additionally, enhanced loss of N over the long-term (i.e. decades) could reduce the pool of N available for plant uptake. As N is generally believed to be the nutrient most limiting for plant growth in northern hardwood ecosystems (Aber et al. 1998), reductions in available N could reduce forest productivity as well as alter competitive relationships among tree species.

Effects of soil freezing on soil solution inorganic phosphorus

Soil solution P_i concentrations and fluxes responded to the soil freezing treatment in the Oa horizons of SM stands (Figure 2). The P_i mobilized from the forest floor was largely removed from solution before reaching lysimeters in the Bs horizon. The P_i mobilized from the forest floor at SM stands (25 mol ha⁻¹ yr⁻¹) was large relative to the available P pool (22 mol ha⁻¹) as well as

net P mineralization in the forest floor ($180 \text{ mol ha}^{-1} \text{ year}^{-1}$) estimated for the HBEF by Yanai (1992).

Overwinter fine root mortality was likely an important mechanism contributing to accelerated soil solution P_i mobilization from the forest floor. Multiplying the potential excess N flux from fine root mortality (Tierney et al. this issue) by the P:N ratio in fine root biomass and by the ratio of P:N released during the first year of incubation in mesh bags (Fahey et al. 1988), the potential excess P flux derived from fine root mortality was $6.1 \text{ mol ha}^{-1} \text{ yr}^{-1}$ which was about 31% of the average excess soil solution P_i flux from the forest floor of SM stands. Thus, at SM stands, mechanisms in addition to fine root mortality likely contributed to P_i mobilization (i.e. decreased plant P uptake and/or increased mineralization of organic P).

One previous study has demonstrated that release of P may be enhanced following soil freezing disturbance (Lewis & Grant 1980). They found that stream fluxes of orthophosphate were significantly greater during years with low snow cover and likely soil freezing relative to years with normal snow cover at a Colorado watershed.

Effects of soil freezing on soil solution dissolved inorganic carbon

A response of DIC to soil freezing was evident in the Oa horizon solution of YB stands (Table 2). Enhanced soil solution DIC concentrations likely resulted from restriction of CO_2 exchange between the soil and the atmosphere by ice lenses in the soil as well as compacted snow and ice at the soil surface. The absence of a soil CO_2 evolution response (Tierney et al. this issue) suggests that enhanced microbial respiration was unlikely to be a mechanism contributing to elevated soil solution DIC concentrations.

Linkages among solutes responding to soil freezing disturbance

The synchronous responses to the soil freezing treatment and strong correlations observed between solutes, most notably draining the Oa horizons, suggests that the mechanisms contributing to their enhanced concentrations may be linked. Nitrate and P_i responded to the soil freezing disturbance in SM stands (Figures 1 and 2). Variations in soil solution NO_3^- and P_i were strongly related in the Oa horizons of the SM plots (Table 5); mineralization of soil organic matter and/or decreased tree uptake were the likely mechanisms linking mobilization of these solutes from the forest floor.

At YB stands in the Oa horizon, the significant correlation between DOC and DON suggests that the responses of these solutes were linked by enhanced mobilization of soil organic matter (Table 6). The correlations between NH_4^+ and DOC, as well as between NH_4^+ and DON, suggests that

enhanced N mineralization and dissolution of soil organic matter may have been linked, although we were unable to reconcile these results with the lack of net N mineralization response observed by Groffman et al. (this issue). The relatively weak but significant correlation between NH_4^+ and NO_3^- in the Oa horizon of YB plots suggests that losses of these solutes were linked by N mineralization and nitrification.

Conclusions

This study demonstrated that mild soil freezing events can significantly influence soil solution chemistry and loss of N and P in a northern hardwood forest. However, critical gaps in our knowledge remain. While it was clear that fine root mortality was a potential mechanism contributing to enhanced nutrient loss, we were unable to quantify the contributions from physical disruption of soil aggregates, decreased root uptake, and fragmentation of fresh litter to enhanced soil solution fluxes. Future experiments utilizing stable isotopes may be valuable in quantifying these mechanisms. The differences in soil solution N and P responses between SM and YB stands were intriguing and merit more mechanistic investigation. Our results suggest that if soil freezing events become more frequent under a warmer climate, the availability and loss of N and P may be significantly altered, with potential consequent effects on terrestrial and aquatic ecosystems.

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