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Nitrate and dissolved organic carbon mobilization in response to soil freezing variability

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Abstract Reduced snowpack and associated increases in soil freezing severity resulting from winter climate change have the potential to disrupt carbon (C) and nitrogen (N) cycling in soils. We used a natural winter climate gradient based on elevation and aspect in a northern hardwood forest to examine the effects of variability in soil freezing depth, duration, and frequency on the mobilization of dissolved organic carbon (DOC) and nitrate (NO_3^-) in soils over the course of 2 years. During a winter with a relatively thin snowpack, soils at lower elevation sites experienced greater freezing and especially variable freeze/thaw cycles, which in turn led to greater leaching of DOC from the organic horizon during the following growing season. In contrast to several previous field manipulation studies, we did not find changes in soil solution NO_3^- concentrations related to soil freezing variables. Our results are consistent with a soil matrix disturbance from freezing and thawing which increases leachable C. These results build upon previous laboratory experiments and field manipulations that found differing responses of DOC

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and NO_3^- following soil freezing, suggesting that mobilization of labile C may suppress NO_3^- losses through microbial immobilization of N. This research highlights the importance of studying natural variation in winter climate and soil freezing and how they impact soil C and N retention, with implications for surface water runoff quality.

Keywords Climate change · Winter · Snow · Soil water · Northern hardwood forest · Soil frost

Introduction

In recent years the ecological and biogeochemical effects of winter climate change and soil freezing have received increased attention, stemming from a greater awareness of the importance of winter ecological processes (Campbell et al. 2005), and how winter conditions can influence biological processes during the growing season (Groffman et al. 2012; Durán et al. 2014; Campbell et al. 2014b; Ladwig et al. 2016). Across the northeastern United States and eastern Canada, increases in winter temperatures outpaced those of summer during the 20th century (1.2 vs. 0.7 °C, respectively), and are projected to increase another 2.1–5.3 °C during the 21st century (Hayhoe et al. 2007). Winter climate change is associated with decreased snowpack accumulation and duration, which in turn can lead to increased occurrence of soil freezing (Campbell et al. 2010; Brown and DeGaetano 2011).

The processes controlling soil carbon (C) and nitrogen (N) cycling may be particularly sensitive to winter climate change and soil freezing (Matzner and Borken 2008). Soil freezing effects are evident in a variety of C and N cycling processes, including respiration (Muhr et al. 2009), dissolved organic carbon (DOC) leaching (Hentschel et al. 2008), N mineralization and nitrification (Shibata et al. 2013), and denitrification (Mørkved et al. 2006). While considerable progress has been made recently in understanding how soil C and N cycling processes respond to soil freezing across varying environments, there is also considerable uncertainty due to ambiguous or sometimes seemingly contradictory results. Much research has focused on leaching losses of N, primarily nitrate (NO_3^-) from soils. Observational results from a variety of forest and alpine ecosystems have shown increased mobilization of NO_3^- associated with soil freezing, including across the northeastern U.S. (Mitchell et al. 1996), and in Colorado (Brooks et al. 1998), Ontario (Watmough et al. 2004), Germany (Callesen et al. 2007), and Japan (Christopher et al. 2008). Other observational studies have shown NO_3^- losses due to soil freezing occur inconsistently (Fitzhugh et al. 2003), or not when expected (Judd et al. 2011). Field manipulations and laboratory experiments have also produced contradictory results on NO_3^- losses in response to soil freezing. While most snow removal experiments designed to induce soil freezing at the plot scale have resulted in increased NO_3^- losses from forested soils (Boutin and Robitaille 1995; Fitzhugh et al. 2001; Hentschel et al. 2009; Shibata et al. 2013; Campbell et al. 2014b), laboratory studies have found that soil freezing can either increase (Nielsen et al. 2001; Elliott and Henry 2009), or decrease NO_3^- leaching (Hentschel et al. 2008; Austnes and Vestgarden 2008; Reinmann et al. 2012).

Much of the variation in NO_3^- leaching losses in response to soil freezing may arise from interactions between C and N cycling processes. In a Norwegian montane heathland, induced soil freezing by snow removal promoted increased DOC leaching, but had no effect on NO_3^- losses (Austnes et al. 2008; Kaste et al. 2008). At the Hubbard Brook Experimental Forest (HBEF) in the northeastern U.S., Groffman et al. (2011) also found that induced soil freezing in snow removal plots increased soil solution DOC concentrations, with no increase in NO_3^- leaching, while Fitzhugh et al. (2001) found opposite patterns in a similar study at the same site several years earlier. These results suggest that mobilization of labile C by soil freezing may suppress NO_3^- losses through stimulation of microbial immobilization.

Multiple experimental approaches have been used in previous studies to evaluate soil freezing effects on C and N cycling, including plot scale manipulations, controlled laboratory experiments, and retrospective analyses of long-term watershed data. While each approach has its advantages, our combined insight

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from application of these methods still leaves unanswered questions regarding the expected responses of C and N leaching to soil freezing and winter climate change. Rather than relying on field manipulations or laboratory studies which may have confounding effects on biogeochemical processes (Henry 2007), in this study we sought to evaluate NO_3^- and DOC mobilization in soil solutions in response to soil freezing across a natural gradient of winter climate in a northern hardwood forest. To achieve this objective, we established a series of 20 monitoring plots to measure soil solution chemistry along with snow depth, soil frost depth, and soil temperature variability for 2 years across a range of elevation and aspect that would capture the expected maximum winter climate variability across the valley of the HBEF in New Hampshire. This gradient provided us the opportunity to assess how variation in snow accumulation controls soil freezing variability and the consequences for solute losses of C and N from the soil. Specifically, we tested the hypothesis that soil frost depth varies inversely with snow depth, and that greater depths of soil frost promote leaching of NO_3^- and DOC during the subsequent growing season.

Methods

Site description

The HBEF is located in the White Mountains of New Hampshire, USA (43°56′N, 71°45′W). The forest composition is dominated by northern hardwood tree species, including sugar maple (*Acer saccharum* Marsh.), American beech (*Fagus grandifolia* Ehrh.), and yellow birch (*Betula alleghaniensis* Britt.). At higher elevations, balsam fir (*Abies balsamea* (L.) Mill), red spruce (*Picea rubens* Sarg.), and paper birch (*Betula papyrifera* var. cordifolia Marsh.) are common. The soils of the HBEF are largely Spodosols (Haplorthods) derived from glacial basal till and covered with a relatively thick (3–15 cm) organic horizon (Likens and Bormann 1995). The climate is cool and humid, with cold winters (mean January air temperature is −9 °C). Mean annual precipitation is 1.40 m, of which approximately 30 % falls as snow. The snowpack typically forms in December and reaches maximum depth in early March (Campbell et al. 2010).

Plot selection and characterization

Twenty individual plots were established during the fall of 2010 at the HBEF along an elevation gradient from 375 to 775 m to evaluate the role of climatic variation in controlling NO_3^- and DOC leaching in soil solutions. The plots were selected to capture the variability of winter climate across the HBEF and were located on both north and south-facing slopes throughout the elevation range (Fig. 1). This climate gradient encompasses a 2.0 °C range in winter air temperature, approximately the same as predicted to result from climate change across the northeastern U.S. during the next 50–100 years (Hayhoe et al. 2007). Plots were selected to have the same forest composition; specifically, canopy dominance by sugar maples was chosen because it is a common tree species and previous soil freezing manipulations have shown the most consistent biogeochemical responses in sugar maple stands (Fitzhugh et al. 2001; Groffman et al. 2001, 2011). The soils at each plot are well or moderately well-drained Typic Haplorthods with well-developed forest floors overlying the mineral horizons. The plots were each 10 m in diameter and located a minimum of 300 m from one another.

Monitoring of winter conditions

Snow depth and soil frost depth were measured approximately biweekly during the winters of 2010–2011 and 2011–2012. The snow depth was measured using Federal (Mt. Rose) snow tubes and recorded as the mean of three locations in each plot. Three replicate soil frost tubes were installed during the fall of 2010 at each plot according to the methods outlined by Hardy et al. (2001). These consisted of removable PVC tubes filled with methylene blue dye, which turns clear when frozen and thus allows personnel to visually measure the depth of frozen soils surrounding the frost tubes. Soil temperature and volumetric water content were continuously recorded at 5 cm depth with Decagon 5TM combination probes connected to Decagon EM50 dataloggers.

Soil solution sampling and chemical analysis

Of the 20 plots used in the gradient study, four had pre-existing zero tension lysimeters: one located west of Watershed 6 (Fuss et al. 2015), two in Watershed 1

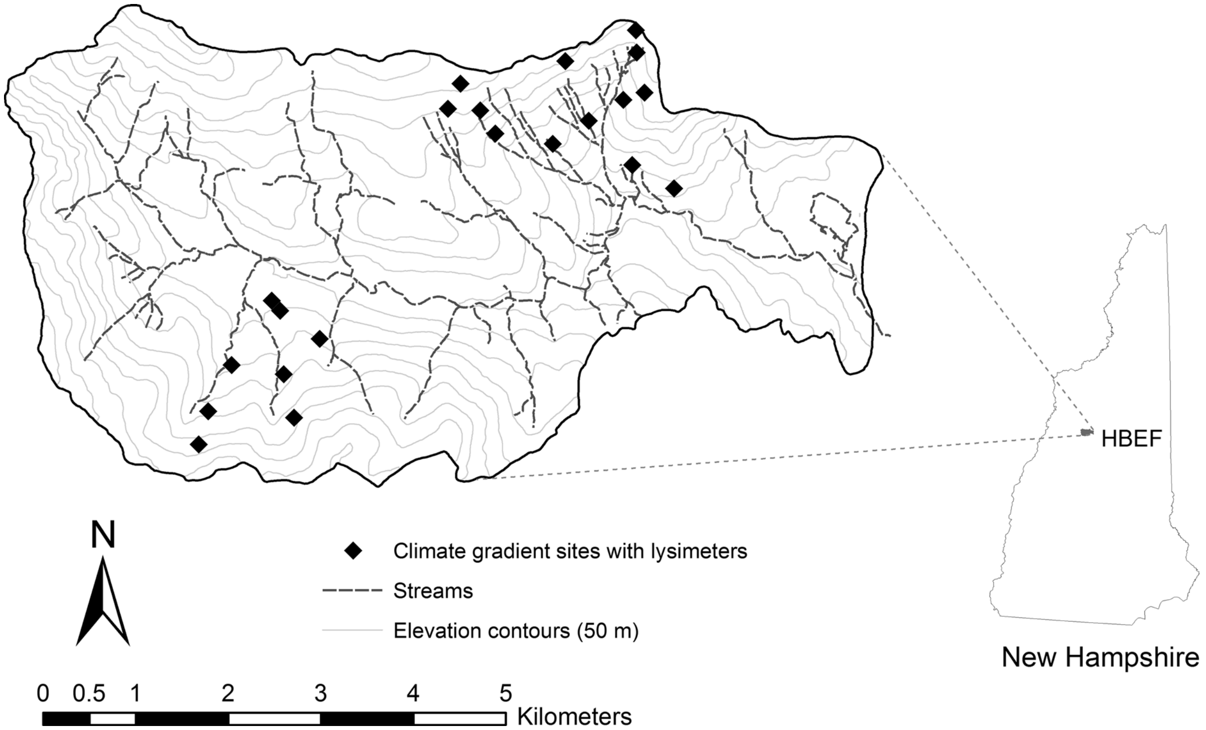

Fig. 1 Map of the HBEF with winter climate gradient lysimeter sites indicated

(Cho et al. 2010), and one on Mt. Kineo (Groffman et al. 2011). At each of the 16 other plots, tension-free lysimeters were installed during September and October of 2010. One plot was relocated following the spring of 2011 to improve accessibility and expand the elevational range on the south-facing slopes. Lysimeter collectors were constructed from angled cross sections of 4 inch diameter PVC pipes (effective dimensions of 20 × 7.5 cm), which drain via PVC tubing to 2-L polyethylene reservoirs. A soil pit was excavated at each site and the lysimeter collectors were inserted in the upslope face of the soil pit just beneath the forest floor (Oa horizon), and within the Bs horizon at depths of approximately 40 cm below the forest floor. The soil pits were backfilled to prevent water accumulation and to ensure thermal conditions of the soil were not disturbed.

The lysimeters collected soil water continuously and were emptied approximately monthly following installation. It took roughly 6 months for the installation disturbance effects on chemistry to subside; NO_3^- concentrations were used as an indicator of soil disturbance. Sampling for data collection commenced in March 2011 and continued through September 2012, providing 2 years of data for spring and summer.

Soil solution samples were measured for NO_3^- concentrations by ion chromatography (Dionex, Sunnyvale, CA). Dissolved organic carbon (DOC) was analyzed through persulfate oxidation followed by infrared CO_2 detection (Teledyne Tekmar, Mason, OH).

Computational methods and statistical analyses

We examined potential relationships between soil solution chemistry data and variables representative of the winter climate gradient encompassed by the 20 plots for each of the two winters. The maximum frost depth from the biweekly measurements was selected as an indicator of frost intensity variation among the sites. The standard deviation of log-transformed winter soil temperature observations (*SDL winter soil temperature*) was chosen as a measure of soil temperature variability and an indicator of frequency of freeze and thaw events during the winter (Durán et al. 2014). Snowpack variation among sites was characterized by creating a *‘snowpack’* variable, the area under the curve of snow depth plotted against time following Durán et al. (2014), which provides a measure that includes both depth and duration of winter snow.

Regression analysis was used to explore the relationship between concentrations of soil solution DOC and NO_3^- and winter climatic variables. Previous research on soil frost effects on soil solution chemistry have reported differing effects between early and late summer (Fitzhugh et al. 2001; Haei et al. 2010). Therefore, the soil solution chemistry data were grouped as mean concentrations for each plot for both the early growing season (May through July) or late growing season (August and September). Paired *t* tests were used to compare mean DOC and NO_3^- concentrations between the 2 years of the study.

Results

Characterization of winter climate gradient

Across the 20 monitoring plots, snowpack accumulation was markedly higher during the winter of 2010–2011 compared to 2011–2012 (Fig. 2). The deeper snowpack during the first winter was the combined result of lower air temperatures and higher precipitation. From December through February of 2010–2011 the mean air temperature was −8.1 °C and 326 mm of precipitation fell (at HBEF weather station #1), compared to −4.3 °C and 273 mm of precipitation during the same months of the following winter. Across the gradient of sites, *SDL winter soil temperature* were generally greater during the winter of 2011–2012, while maximum soil frost depths were similar between years (Fig. 2). Maximum soil frost depths in 2010–2011 generally occurred early in the winter and subsided once a deeper snowpack accumulated. The relationship between snow depth and soil frost was significantly negative during the second winter, but no significant relationship was observed during the first, snowier winter (Fig. 3).

Soil solution NO_3^- concentrations

Soil solution NO_3^- concentrations were consistently higher in the Oa compared to the Bs horizon. Nitrate concentrations varied seasonally in both horizons, with the highest concentrations found in the spring and winter, and a marked decrease during the summer months (Fig. 4).

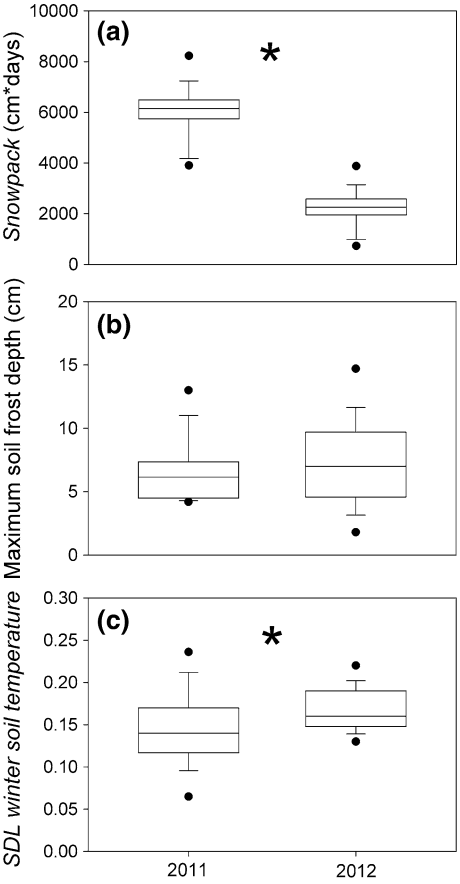

Fig. 2 Boxplots of 2011 and 2012 winter climate variables across all monitoring plots, **a** snowpack, **b** maximum soil frost depth, and **c** *SDL winter soil temperature*. *Boxes* represent median (*horizontal lines in the boxes*) and 25th and 75th percentiles (*box edges*) of the data. The *whiskers* are 10th and 90th percentiles and the *dots* are the lowest and highest values. Statistically significant differences ($P < 0.05$), as analyzed by paired *t* test, are marked by *

Across the gradient of plots, we found NO_3^- concentrations in soil solutions did not vary significantly with snow or soil freezing (Table 1) in either year. There was high variation in NO_3^- concentrations among our sites, with mean values in the Oa horizon ranging from approximately 6 to 245 μmol L^{-1}, and from almost zero up to nearly 30 μmol L^{-1} in the Bs horizon during the early growing season of 2011. Concentrations of NO_3^- were lower in the solution draining the Oa horizon during the early growing season of 2012 compared to 2011 ($P < 0.01$; Fig. 5).

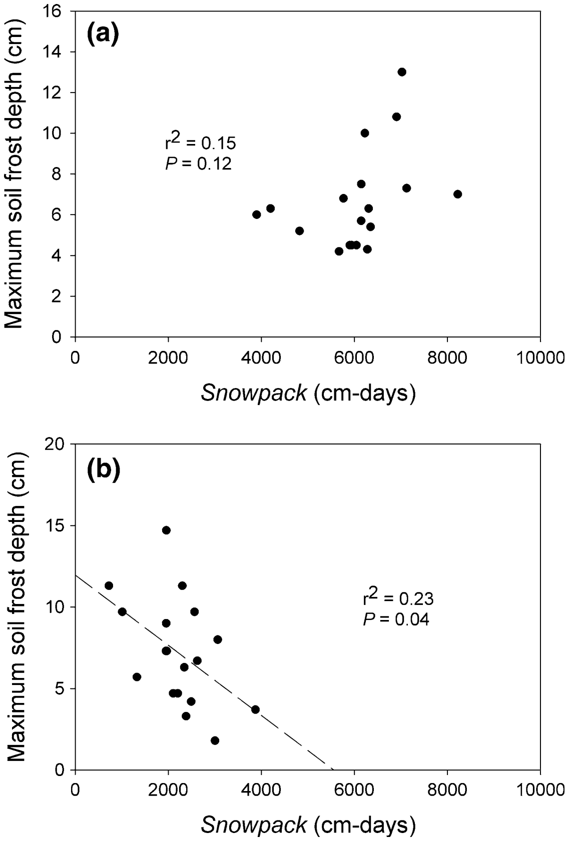

Fig. 3 Relationship between maximum soil frost depth and the *Snowpack* variable for the winter of **a** 2010-2011 and **b** 2011–2012 across 20 winter climate gradient monitoring plots

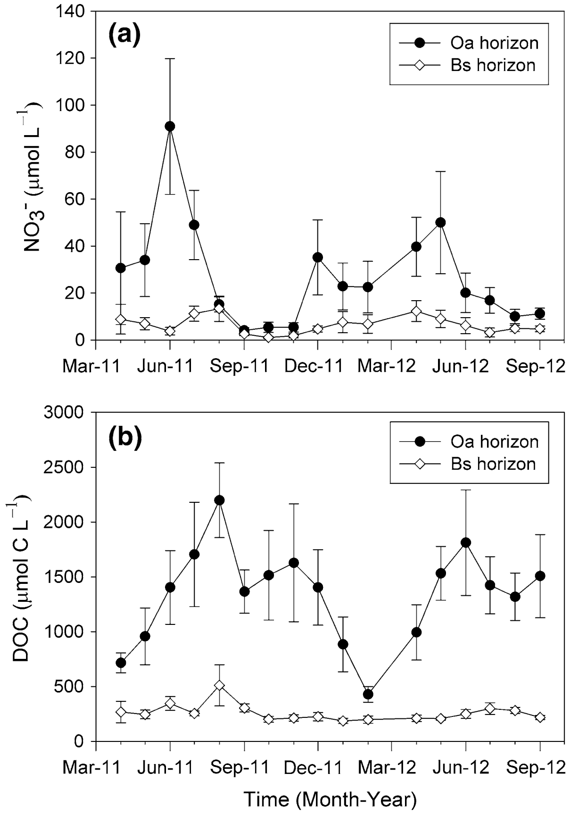

Fig. 4 Monthly mean concentrations of **a** NO_3^-, and **b** DOC in soil solutions. *Error bars* indicate standard errors

Soil solution DOC concentrations

In contrast to NO_3^- concentrations, soil solution DOC was highest in the summer and lowest in the winter. Markedly lower concentrations were measured in the Bs compared to the Oa horizon (Fig. 4). The DOC concentrations in soil solutions were similar overall between the growing seasons of 2011 and 2012. Mean concentrations in the Oa horizon were modestly greater during the early growing season in 2012 relative to 2011 ($P = 0.11$), but the Bs solutions showed no difference ($P = 0.93$).

There was a weak positive relationship ($P < 0.10$) between DOC concentrations in Oa horizon DOC and *SDL winter soil temperature* during May–July 2011. In 2012 there was a strong relationship between Oa horizon DOC and *SDL winter soil temperature* ($P < 0.01$) as well as a weak relationship with frost depth ($P = 0.07$; Table 1; Fig. 6). Generally these relationships were not found in the solutions of the Bs horizon, though a modest positive relationship between DOC and soil frost depth was observed in the Bs horizon during the early growing season of 2012 (Table 1). There was also a significant positive relationship between Oa soil water DOC and *SDL winter soil temperature* during snowmelt of 2012 ($P = 0.04$). By the late growing season (August–September) of both years, no relationship between DOC concentration in soil solution and the previous winters' climate variables was evident (Table 1).

Soil solution DOC concentrations were generally unrelated to corresponding NO_3^- concentrations. A weak positive relationship in the Oa horizon was noted for the early growing season of 2011 ($P = 0.25$), although less than 10 % of the variation in NO_3^- concentrations could be explained by DOC.

Table 1 Linear regression Pearson correlation coefficients and *P* values for NO_3^- and DOC concentrations as a function of maximum soil frost depth or *SDL winter soil temperature* during the preceding winter in soil solutions draining (a) the Oa horizon, and (b) the Bs horizon

	NO_3^-		DOC	
	Max frost depth	SDL winter soil temperature	Max frost depth	SDL winter soil temperature
(a) Oa horizon				
2011				
Early growing season				
R	−0.19	−0.08	0.00	0.45
P	0.50	0.77	0.99	**0.09**
Late growing season				
R	−0.05	−0.45	−0.10	0.32
P	0.86	**0.08**	0.71	0.23
2012				
Early growing season				
R	−0.01	−0.08	0.45	0.65
P	0.97	0.75	**0.07**	**<0.01**
Late growing season				
R	−0.12	−0.34	0.27	0.26
P	0.64	0.18	0.30	0.32
(b) Bs horizon				
2011				
Early growing season				
R	−0.15	−0.12	−0.26	0.13
P	0.54	0.89	0.28	0.89
Late growing season				
R	−0.27	−0.33	−0.23	0.09
P	0.32	0.21	0.40	0.74
2012				
Early growing season				
R	−0.05	−0.21	0.44	0.15
P	0.83	0.62	**0.08**	0.56
Late growing season				
R	0.41	0.30	−0.08	0.26
P	**0.09**	0.23	0.78	0.33

Early growing season is May through July; late growing season is August and September. *P* values in bold indicate statistically significant relationships ($P \leq 0.1$)

Discussion

Using a natural gradient of winter climate, as opposed to a snow removal manipulation in the field or laboratory experiment, has the advantage of capturing the dynamics of snow-soil frost interactions under actual ambient soil temperature variations. The positive relationship between maximum soil frost depth and the *SDL winter soil temperature* observed for the winter of 2011–2012, but not for 2010–2011, reflects the lower snowpack accumulation during the second winter, which exposed the soil to greater temperature variability. Our measure of winter temperature variability (*SDL winter soil temperature*) provided a good analog for freeze/thaw cycle differences between years. At 5 cm depth, there were nearly twice as

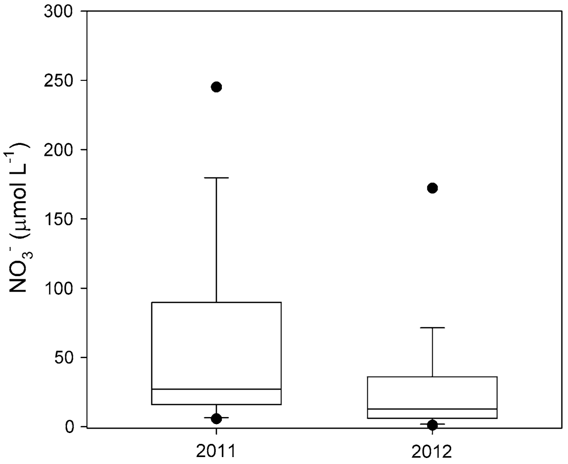

Fig. 5 Nitrate concentrations in soil solution draining the Oa horizon during the early growing season (May–July) of 2011 and 2012. *Boxes* represent median (*horizontal line in the box*) and 25th and 75th percentiles (*box edges*) of the data. The *whiskers* are 10th and 90th percentiles and the *dots* are the lowest and highest values. Concentrations in 2012 are lower ($P < 0.01$) based on a paired *t* test

many instances where soil temperature crossed 0 °C—a mean of 4.1 per site in the second winter versus 2.1 per site in the first. During the winter of 2010–2011 the snowpack was relatively deep across all sites. This deep snowpack insulated the soil well throughout most of the winter, though early in the winter soils were exposed to freezing at some sites. The soil frost produced during the early freezing event declined steadily over the following weeks as the snowpack accumulated (Fuss et al. 2016). Overall these results indicate that a more pronounced soil frost gradient would occur during years with lower overall snowpack accumulation, ranging from reasonably well-insulated soils with little frost at higher elevations and on north-facing slopes to more exposed soils with deeper frost at the lower elevations and the south-facing slopes.

For studying nutrient cycling under varying snow and soil frost conditions, our climate gradient approach provides an alternative to the field and laboratory manipulations used in the past. The

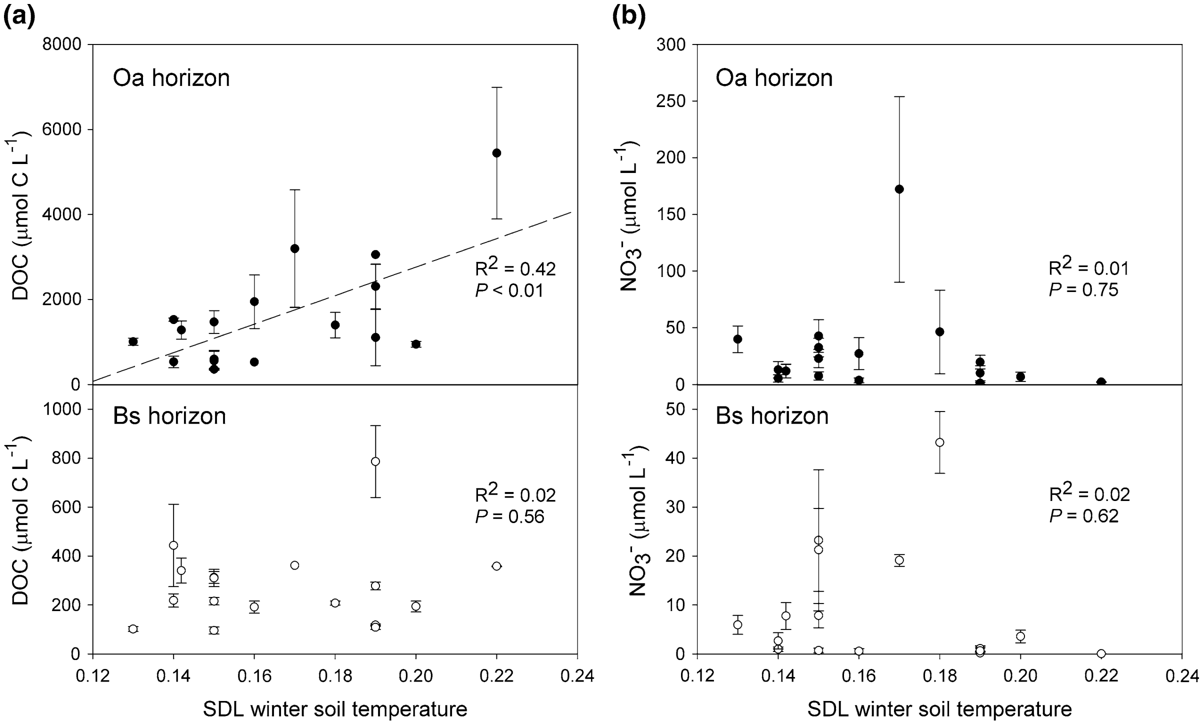

Fig. 6 Mean 2012 early growing season **a** DOC and **b** NO_3^- concentrations in soil solutions as a function of winter soil temperature variability (and likely freeze/thaw cycles). *Error bars* indicate standard errors

manipulation approaches provide information on how ecosystems respond in the short term to an abrupt climate change, while the gradient approach provides information on how ecosystem function is likely to change in response to long-term changes in climate. The manipulation studies often produce experimental artifacts associated with soil and vegetation disturbance and/or the sudden nature of the imposed climate change (Henry 2007). On the other hand, there are concerns that variation in soils and vegetation across the gradient are affected by factors other than climate, e.g., soil depth (Gillin et al. 2015). Researching the effects of climate change on ecosystems is inherently challenging because of limitations in any given approach. We argue that the combined insight from multiple approaches enhances our ability to identify patterns and draw conclusions.

DOC mobilization after soil freezing

Our results suggest a positive relationship between soil freezing (and freeze/thaw cycles, as indicated by *SDL winter soil temperature*) and the concentration of DOC in soil solutions, especially those draining the Oa horizon (Fig. 6). The relationship was much more distinct during the second year of our study when soil frost at the lower elevations was more pronounced. These results corroborate other field and laboratory studies that link soil frost, or freeze/thaw cycles, to increased DOC leaching in soil solutions (e.g. Hentschel et al. 2008; Haei et al. 2010; Campbell et al. 2014a). Kalbitz et al. (2000) noted that previous studies have shown freeze/thaw cycles increase DOC release from soils and speculated that a physical disruption of the soil matrix could make previously stabilized soil organic matter more available for leaching. Campbell et al. (2014a) observed a pulse of DOC in leachate from HBEF soils treated under severe frost (−15 °C) conditions in the laboratory and noted changes in the quality of DOC (as indicated by lower SUVA_{254}). They speculated that the pulse of labile DOC could have originated from microbial cells lysed during the severe frost treatment. Haei et al. (2012) also found increased lability of DOC leached from laboratory freeze experiments with boreal soils and also hypothesized a microbial origin. However, in a laboratory experiment with spruce forest soils, Hentschel et al. (2008) found a pulse of DOC following initial freezing and thawing, but they noted that the DOC quality did not change and suggested that soil freezing had mobilized DOC with lignin content too high to be derived from microbial lysis.

Our results are consistent with soil frost causing a physical disruption of the soil matrix that resulted in the prolonged release of DOC for several months during and after snowmelt rather than as a single pronounced pulse. Similarly, in their long-term soil frost manipulation experiment in northern Sweden, Haei et al. (2010) found that soil solution DOC concentrations during the spring and summer were positively related to the duration of soil frost during the previous winter. We also observed a stronger relationship between DOC mobilization and winter soil temperature variability compared to the maximum frost depth, suggesting that greater frequency of freezing and thawing of the forest floor is more disruptive to the soil matrix than a deep frost. It is possible, however, that our biweekly monitoring of frost depth may have missed the true maximum soil frost depths. The effect of the previous winter's soil freezing and temperature variability on DOC mobilization did not persist to the later sampling dates (August–September), suggesting that the soils had stabilized after several months or the most readily leachable DOC had been depleted. This pattern also emphasizes that elevated DOC leaching early in the growing season is more likely driven by the previous winter soil conditions, rather than inherent site characteristics. That is, without elevated DOC due to soil freeze/thaw cycles at our lower elevation plots, we would expect soil solution DOC to increase with increasing elevation (Dittman et al. 2007).

Variable response of $\mathrm{NO_3}^-$ to soil freezing

We found no clear relationship between winter climate variables and the concentrations of $\mathrm{NO_3}^-$ in soil solutions in either year, but we did find higher concentrations of $\mathrm{NO_3}^-$ in the Oa horizon during the early growing season of 2011 compared to 2012. Previous investigations into the response of $\mathrm{NO_3}^-$ leaching to soil freezing events have shown varying results. Snowpack manipulation (reduction by shoveling) studies at the HBEF during the winters of 1997–1998 and 1998–1999, and again in 2008–2009 and 2009–2010, showed a strong $\mathrm{NO_3}^-$ leaching response to induced soil frost (Fitzhugh et al. 2001; Campbell et al. 2014b). Fitzhugh et al. (2001) found

NO_3^- concentrations in soil solutions greater than 400 μmol L^{-1} during the growing season in the Oa horizon of treatment plots with sugar maple, compared to less than 100 μmol L^{-1} in the non-manipulated reference plots. Boutin and Robitaille (1995) found similar results following a snow removal experiment in a sugar maple stand in Québec. However, Groffman et al. (2011) found little treatment effect on NO_3^- in soil solution during a second snow manipulation study conducted in sugar maple stands at the HBEF during the winters of 2002–2003 and 2003–2004. Laboratory studies have also produced variable results. Freeze treatments of soil cores from a Norwegian heathland produced increased leaching of NH_4^+ and decreased leaching of NO_3^- (Austnes and Vestgarden 2008), while severe frost treatment of HBEF soil cores by Reinmann et al. (2012) led to lower losses of both NO_3^- and NH_4^+.

Differing results have also been noted in streamwater export of NO_3^- following widespread soil freezing events. High concentrations of streamwater NO_3^- occurred during snowmelt in 1990 across the northeastern U.S., following severe and widespread soil frost during the preceding winter (Mitchell et al. 1996). Fitzhugh et al. (2003) investigated deviations in the long-term streamwater chemistry record for W6 at the HBEF and found significant increases in annual fluxes of stream NO_3^- following soil freezing events only during the earliest years of the record, in the 1970s. The later years (1990s) of the record showed no conclusive relationship between soil freezing and NO_3^- response at the watershed level. Similarly, widespread soil freezing during the winter of 2005–2006 failed to result in increased NO_3^- runoff (Judd et al. 2011).

These variable and apparently contradictory results suggest that the response of NO_3^- leaching to soil freezing is subject to controls that are more complex than simply the presence of soil frost. The marked increases in soil solution NO_3^- reported by Fitzhugh et al. (2001) and (Campbell et al. 2014b) were attributed to reduced growing season N uptake by sugar maple fine roots, which had been damaged by the soil freezing. Tierney et al. (2001) observed significantly increased fine-root mortality resulting from those soil freeze treatments. Comerford et al. (2012) found increased root damage associated with soil freeze treatments. The response of NO_3^- leaching to soil freezing events may be regulated by the degree to which fine roots are damaged, but the exact causes of root damage by soil freezing remain uncertain. The soil temperatures experienced during soil freezing events are typically not cold enough to directly kill roots (>-4 °C), so a physical disruption of the soil matrix, such as frost heaving, may contribute to fine-root mortality. Cleavitt et al. (2008) however found no relationship between measured frost heaving and fine-root damage at the HBEF snow manipulation plots and suggested that cellular damage impaired fine root function. The rate, timing, and intensity of soil freezing also could contribute to root damage.

Groffman et al. (2011) hypothesized that the differing responses of NO_3^- leaching to soil freezing events could be driven by interactions between C and N responses or interannual variability of C and N dynamics in the forest. Indeed, our results indicated moderate DOC mobilization following soil freezing (and especially freezing and thawing cycles) but no NO_3^- response. Furthermore, we found that Oa horizon NO_3^- concentrations during the early growing season of 2012 were lower than in 2011 (Fig. 5), opposite of what might be expected as a response to the more intense soil freezing and thawing during the previous winter. This pattern is consistent with the hypothesis that when soil freezing mobilizes DOC, the increased DOC availability can enhance microbial immobilization of NO_3^- and suppress losses (Groffman et al. 2011). Durán et al. (2014) found lower N transformation rates at the lower elevation sites of our climate gradient (those with more freeze/thaw cycles), but insignificantly elevated soil respiration rates, indicating that increased C supplies potentially increased the uptake of inorganic N. Our results are also consistent with soil-freezing manipulation studies that found opposing or dissimilar responses of DOC and NO_3^-. The earliest freeze treatment study at the HBEF produced marked increases in NO_3^- leaching and no significant effect on DOC concentrations (Fitzhugh et al. 2001). In contrast, a field snow manipulation in Norway resulted in increased DOC leaching but no increases in NO_3^- (Austnes et al. 2008; Kaste et al. 2008). In laboratory treatments, Austnes and Vestgarden (2008) found increased DOC and decreased NO_3^- mobilization following freezing of soil cores.

The often opposing responses from various studies are consistent with the hypothesis that when DOC is mobilized in response to soil freezing disturbance, a corresponding response of NO_3^- may be limited by increased microbial N immobilization or denitrification as freshly mobilized DOC becomes available as a labile carbon source. Experimental additions of labile DOC to streamwater have been shown to dramatically reduce NO_3^- runoff losses through increased microbial N immobilization or denitrification (e.g. Bernhardt and Likens 2002; Sobczak et al. 2003). Increased DOC availability has also been hypothesized to underlie the widespread trend of decreasing NO_3^- concentrations in streams across the northeastern U.S. (Goodale et al. 2005). Mørkved et al. (2006) noted pulses of N_2O following soil freezing and thawing and attributed them to increases in denitrification resulting from increased availability of DOC to fuel denitrifiers. In soils from several of our climate gradient sites at the HBEF, Morse et al. (2015) found increased fluxes of N_2O and N_2 during or shortly after snowmelt that were correlated with higher NO_3^- concentrations. However, those gas fluxes decreased to low levels soon after snowmelt, indicating that increased DOC leaching during the summer was more likely increasing immobilization rather than denitrification.

Winter climate change implications

The contrasting winter conditions in the 2 years of this study, and the gradients of winter variables within the HBEF, illustrate that changes in snowpack accumulation can have marked effects on soil freezing intensity and frequency. Campbell et al. (2010) have shown that the winter climate at the HBEF has been warming and the snowpack has been decreasing, especially at lower elevations and on the south-facing side of the valley. We expect continued warming to decrease winter snowpack accumulation further (Pourmokhtarian et al. 2012, 2016) and in more widespread areas, exposing soils to greater temperature variability and frost development. Our results show that the sites with the thinnest snow cover and greatest soil freezing are the most likely to respond with higher leaching of DOC during the months following winter. This finding has implications for the C balance of soils and nutrient cycling under future climate scenarios, suggesting a potential for increased loss of soil organic carbon following soil freezing events. It also underscores the need to investigate how climate-driven changes in DOC mobilization may affect trends in surface water DOC and NO_3^- concentrations over the long term.

Summary and conclusions

Our results demonstrate that reduced insulation of soil associated with decreased winter snowpack accumulation can lead to increased soil frost formation and greater susceptibility to midwinter freeze and thaw cycles. Increases in soil frost intensity and soil freeze/thaw events can, in turn, lead to changes in soil solution chemistry. Mobilization of DOC was greater in soils most affected by freezing. Elevated DOC leaching persisted for several months into the growing season before stabilizing, indicating a likely soil matrix disruption which exposed more readily leachable DOC. We observed the strongest response in solutions draining the Oa horizon, consistent with the greater exposure of the upper soil horizons to freeze disturbance and greater concentrations of organic matter. We found no relationship between soil freezing measures and soil solution NO_3^- concentrations following either of the two winters. Other studies have shown conflicting responses of NO_3^- leaching that vary from decreases to large increases, and the results presented here are consistent with the hypothesis that mobilization of labile DOC in soils may limit a NO_3^- increase by stimulating microbial N immobilization. These results are important to evaluations of future C and N dynamics in forest ecosystems which are likely to experience more frequent or severe soil freezing events as climate change continues to diminish snowpack accumulation.

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