

Role of Soil Freezing Events in Interannual Patterns of Stream Chemistry at the Hubbard Brook Experimental Forest, New Hampshire

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Soil freezing is a disturbance of the below ground environment, potentially resulting in increased losses of NO_3^- and surface water acidification. Here, we report the effects of soil freezing on interannual variation in stream chemistry at the Hubbard Brook Experimental Forest, New Hampshire. Data from 1970 to 1997 of soil frost depth, snow cover, precipitation, air temperature, and stream discharge and chemistry were used in a stepwise linear regression model to select the variables that best predicted deviations of annual stream concentrations from 4-year running averages. Variables quantifying soil freezing severity were selected as significant predictors of short-term fluctuations in stream K^+ , NO_3^- , Ca^{2+} , and Mg^{2+} concentrations from 1970 to 1989, explaining 59 and 47% of the short-term variability in K^+ and NO_3^- , respectively. Fine-root mortality and disturbance of root–soil–microbe interactions, with subsequent effects on decomposition and nutrient uptake, likely contributed to the mobilization of K^+ and NO_3^- to streamwater following severe soil freezing events. The relationship between soil freezing and stream chemistry, however, weakened during the period 1990–1997. Because soil freezing has had inconsistent effects on stream chemistry during the period 1970–1997, it is

unclear whether future changes in the frequency, duration, and depth of soil freezing events as the result of changes in the snow cover regime under a warmer climate will have significant impacts on the losses of NO_3^- and nutrient-base cations from temperate northern ecosystems.

Introduction

The leaching of nitrate (NO_3^-) from soil to surface waters in forest watersheds can enhance the depletion of nutrient-base cations [calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+)] from available soil pools and influence the acid–base chemistry of soils and surface waters (1). Interannual variations in climate can significantly influence temporal patterns of stream NO_3^- concentration (2–4). In temperate northern ecosystems, changes in snow cover associated with climate change might be a major factor affecting the nature and extent of hydrological nutrient losses (5, 6).

Reductions in the depth and duration of snowpack under a warmer climate can result in enhanced nutrient losses by increasing the frequency, severity, and spatial extent of soil freezing events (7). Soil freezing is a climatic disturbance of the belowground environment, potentially disrupting nutrient cycling in the soil by altering the relationship between nutrient sources and sinks. A recent plot-scale manipulation of snow cover at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire demonstrated that soil freezing can result in the mortality of fine roots, causing the mobilization of NO_3^- from soil (8, 9). Other plot-scale work has also shown that reduced snow cover can lead to increased nitrogen losses (10, 11).

In addition to plot-scale work showing that soil freezing can affect nutrient losses, there is evidence that freezing events influence temporal patterns of stream chemistry at the watershed–ecosystem scale. In watersheds on the Colorado Front Range, stream NO_3^- losses were inversely related to the depth of snow cover, likely as the result of more severe soil freezing during years with low snowpack accumulation (12, 13). In four watersheds that spanned the northeastern U.S., including the HBEF, synchronous increases in stream NO_3^- during the snowmelt of 1990 were attributed to a regional-scale soil freezing event (14). Likens and Bormann (15) hypothesized that prominent increases in stream NO_3^- concentrations during the 1969–1970 and 1973–1974 water years were related to soil freezing events at the HBEF.

Although there is strong evidence that soil freezing can significantly influence stream NO_3^- dynamics, there are no previous reports quantitatively relating variables of soil freezing severity to interannual patterns of stream chemistry. The long-term stream chemistry dataset at the HBEF (15) provides an ideal opportunity to explore relationships between soil freezing and watershed-scale NO_3^- losses. Interest in understanding these relationships has increased in recent years with concerns about N saturation and puzzling declines in streamwater NO_3^- concentrations in the northeastern U.S. (3, 16, 17). In this study, our goal was to examine the relationship between soil freezing variables and interannual patterns of stream NO_3^- and nutrient cation concentrations at the HBEF during the period 1970–1997. Our approach was to focus on relationships between soil freezing events and annual deviations from 4-year running averages in streamwater chemistry, treating soil freezing events as stochastic short-term disturbances imposed on the long-term pattern of stream chemistry.

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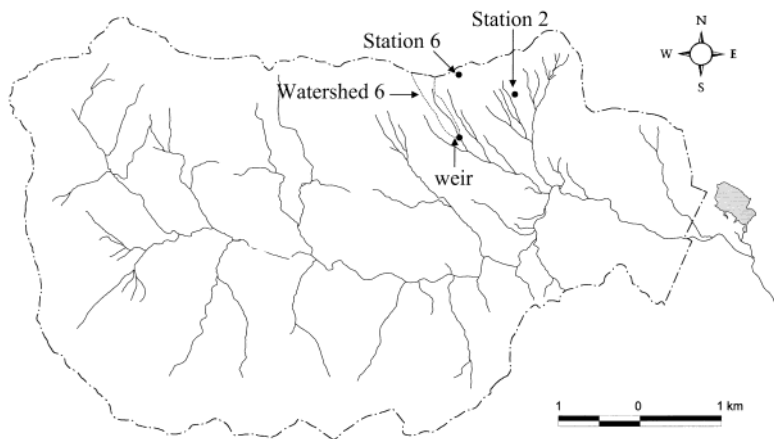


FIGURE 1. Map of the Hubbard Brook Experimental Forest showing the locations of stations 2 and 6, as well as the boundary of watershed 6.

Methods

The HBEF is located in the White Mountain National Forest in New Hampshire in the northeastern U.S. (43°56' N, 71°45' W). Vegetation at the HBEF is a mixed northern hardwoods-coniferous ecosystem. The forest was selectively cut during the 1880s and 1910s, and some of the older stands were damaged by a hurricane in 1938. Soils are shallow (75–100 cm), acidic (pH 3.9) typic Haplorthods developed from unsorted basal tills.

Soil frost data were collected at approximately weekly intervals during the winters from 1956 to 1997 at station 2, which is representative of middle-elevation south-facing slopes of the HBEF (Figure 1). During periods of soil frost, two holes were excavated, and the depth of soil frost was measured. Prior to 1970, soil frost measurements at the HBEF were sporadic, and the general impression was that soil frost did not occur. Soil frost data prior to 1970 were therefore not used in this analysis because they were considered unreliable. For this study, we determined two variables that quantified soil freezing severity for each winter: (i) the maximum winter soil frost depth and (ii) the sum of daily soil frost depths. We calculated the sum of daily snow depths for each winter at station 2 from measurements of snow depth made at approximately weekly intervals. The daily soil frost and snow depths were estimated by linear interpolation between the weekly measurements. Additionally, we calculated the mean air temperatures for December through January, the mean winter air temperature (December through April), and the mean annual temperature for station 6 which was the nearest station to watershed 6 (W6) that recorded air temperature (Figure 1). Air temperature was recorded using Belfort hygrothermographs housed in weather shelters approximately 2 m above ground level. Annual precipitation was measured for watershed 6 (W6). Our definition of winter (December through April) differs from the standard definition used for the HBEF (December through February) (15) because we are examining soil frost processes that might occur after February. All soil frost and climate data were downloaded from the HBEF Web page (<http://www.hubbardbrook.org/>).

Stream samples were collected at approximately weekly intervals since 1963 above the weir at the biogeochemical reference watershed of the HBEF (W6; Figure 1), a south-facing watershed (15), and analyzed for NO_3^- , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , total Al, NH_4^+ , pH, SO_4^{2-} , and Cl^- using the methods described by Buso et al. (18). Total Al was not analyzed from 1970 through 1976. Rates of nutrient loss via streamwater export were calculated by the period-weighted method (15). For this study, annual volume-weighted concentrations were calculated by dividing the annual solute flux by the annual streamflow. Annual fluxes were calculated by calendar year

rather than the HBEF water-year because the HBEF water-year begins on June 1, a time when streamwater might be responding to soil freezing that occurred the previous winter. For example, Fitzhugh et al. (9) observed that responses of soil solution concentrations of NO_3^- to soil freezing at the HBEF were greatest during the growing season beginning in June.

We determined 4-year running averages for annual stream concentrations and fluxes and calculated annual deviations from running averages. Annual deviations from the 4-year running averages were used to quantify the interannual variability in stream concentrations and flux. Given previous studies demonstrating that the response of soil solution chemistry to soil freezing disturbances can be greatest during the growing season (9, 11), rather than being confined exclusively to the spring snowmelt season, we calculated deviations of mean annual concentrations from running averages, rather than of mean spring concentrations from running averages.

We tested the hypothesis that interannual patterns in stream chemistry were related to interannual differences in soil freezing severity using stepwise least-squares linear regression (19). The independent variables were the maximum and cumulative winter soil frost depths, annual precipitation, and cumulative annual snow cover, as well as air temperatures for the December through January, winter, and annual periods. For the stepwise regression, the year of the soil frost was considered to be the year the winter ended. For example, for the winter of December 1979 through April 1980, the maximum and cumulative frost depths were coded as having occurred in 1980. The years for the mean December–January air temperatures and annual snow cover were treated similarly to the year of soil frost. Dependent variables were the annual deviations of stream concentrations and fluxes from 4-year running averages. Annual deviations from 4-year running averages were chosen as the response variable because soil freezing is not likely to influence the long-term (>5-year) pattern of stream chemistry; thus, we are viewing soil freezing as a stochastic, short-term disturbance superimposed on the long-term pattern of stream chemistry. Stepwise regression was conducted for the entire period (1970–1997), as well as for each decade (1970–1979, 1980–1989, 1990–1997). The significance level to enter the stepwise regression was 0.30, and the significance level to stay in the model was 0.10.

Results and Discussion

Streamwater Concentrations. Annual volume-weighted streamwater NO_3^- concentrations during the period 1970–1997 were greatest in 1970 and remained relatively high (>30

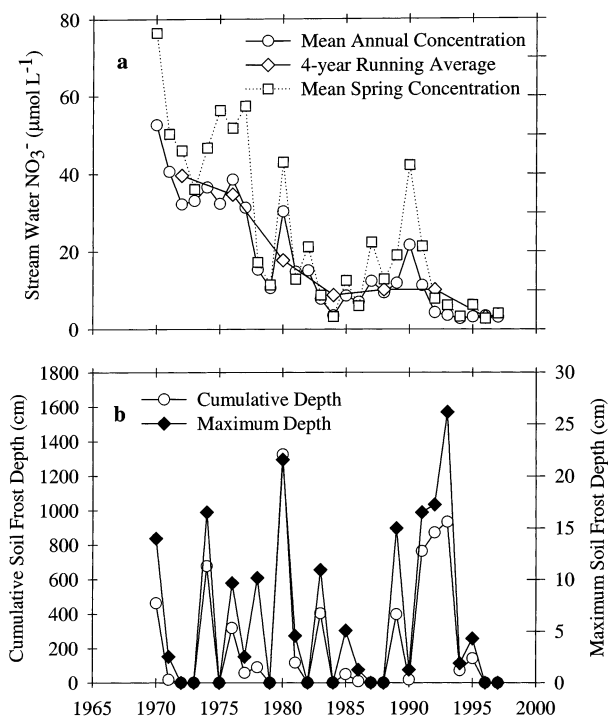


FIGURE 2. Time series of (a) mean annual streamwater NO_3^- concentration (circles), mean spring stream NO_3^- concentrations (squares), and the 4-year running average stream NO_3^- concentration (diamonds) at watershed 6 of the HBEF and (b) cumulative soil frost depth (circles) and maximum soil frost depth (diamonds) at station 2 of the HBEF.

$\mu\text{mol L}^{-1}$) through 1977 (Figure 2). From 1978 to 1991, annual volume-weighted NO_3^- concentrations decreased from previous values but were moderate and exhibited relatively little variation, ranging from 7 to 15 $\mu\text{mol L}^{-1}$, with the exception of two peaks (1980 and 1990). Nitrate concentrations were low and generally decreased from 1992 to 1997. The relatively high cumulative and maximum soil frost depths during 1970 and 1974 at station 2 indicated that these years had relatively severe soil freezing events (Figure 2), as observed by Likens and Bormann (15). The low cumulative soil frost depth during 1990 contrasts with the suggestion of Mitchell et al. (14) that 1990 was a winter with exceptionally severe soil freezing at the HBEF. In addition, cumulative soil frost depths were relatively high during 1980, as well as from 1991 to 1993.

For data during the entire period 1970–1997, the stepwise linear regression model selected the cumulative soil frost depth as a significant ($p < 0.10$) predictor of annual deviations of stream K^+ concentrations from 4-year running averages (Table 1). This relatively weak relationship between cumulative soil frost depth and stream K^+ concentration was the only model selected by stepwise regression that incorporated a soil freezing variable during the period 1970–1997. Annual precipitation was selected as a significant predictor of interannual fluctuations in stream Ca^{2+} , Mg^{2+} , total Al, and H^+ concentrations, cumulative snow cover depth was a significant predictor of interannual variations in stream Na^+ , total Al, NH_4^+ , and Cl^- concentrations, whereas mean annual air temperature was selected for stream Cl^- concentrations. Mean December through January and winter air temperatures were never selected during stepwise regression for the period 1970–1997. According to these results, soil freezing would not appear to be a strong influence on interannual fluctuations in streamwater concentrations between 1970 and 1997.

A markedly different conclusion, however, emerged when stepwise linear regression was performed on streamwater concentration data from 1970 to 1979 and from 1980 to 1989.

TABLE 1. Results^{a,b} of Stepwise Regression with Soil Freezing and Climate as Explanatory Variables and Annual Deviations of Stream Concentrations from 4-Year Running Averages as the Dependent Variables for the Period 1970–1997

dependent variable ($\mu\text{mol L}^{-1}$)	independent variable			
	annual precipitation (mm)	cumulative soil frost depth (cm)	cumulative snow cover (mm)	mean annual air temperature ($^{\circ}\text{C}$)
Ca^{2+}	0.15 (–)**	ns	ns	ns
Mg^{2+}	0.30 (–)***	ns	ns	ns
K^+	ns	0.22 (+)**	ns	ns
Na^+	ns	ns	0.13 (–)*	ns
total Al	0.24 (+)**	ns	0.30 (+)****	ns
NH_4^+	ns	ns	0.13 (–)*	ns
H^+	0.44 (+)****	ns	ns	ns
SO_4^{2-}	ns	ns	ns	ns
NO_3^-	ns	ns	ns	ns
Cl^-	ns	ns	0.20 (–)**	0.10 (+)*

^a Results are partial r^2 values; (+) or (–) denotes positive or negative relationship. ^b Significance levels: * = $p < 0.10$, ** = $p < 0.05$, *** = $p < 0.01$, **** = $p < 0.001$, ns = nonsignificant ($p > 0.10$).

TABLE 2. Results^{a,b} of Stepwise Regression with Soil Freezing and Climate as Explanatory Variables and Annual Deviations of Stream Concentrations from 4-Year Running Averages as the Dependent Variables for the Period 1970–1979

dependent variable ($\mu\text{mol L}^{-1}$)	independent variable			
	maximum soil frost depth (cm)	cumulative soil frost depth (cm)	mean annual air temperature ($^{\circ}\text{C}$)	mean winter air temperature ($^{\circ}\text{C}$)
Ca^{2+}	0.37 (+)*	ns	ns	ns
Mg^{2+}	ns	0.38 (+)*	ns	ns
K^+	ns	0.49 (+)**	ns	ns
Na^+	ns	ns	ns	ns
total Al	ns	ns	ns	ns
NH_4^+	0.58 (+)****	ns	0.28 (+)***	ns
H^+	ns	0.21 (–)**	ns	0.54 (+)***
SO_4^{2-}	ns	ns	ns	ns
NO_3^-	0.57 (+)**	ns	ns	ns
Cl^-	ns	ns	0.35 (+)*	ns

^a Results are partial r^2 values; (+) or (–) denotes positive or negative relationship. ^b Significance levels: * = $p < 0.10$, ** = $p < 0.05$, *** = $p < 0.01$, **** = $p < 0.001$, ns = nonsignificant ($p > 0.10$).

For both the decades 1970–1979 and 1980–1989, stepwise regression selected soil freezing variables as significant predictors of annual deviations of stream Ca^{2+} , Mg^{2+} , K^+ , and NO_3^- concentrations from 4-year running averages (Tables 2 and 3). While soil freezing explained a relatively modest proportion (13–38%) of the interannual variability in stream Ca^{2+} and Mg^{2+} concentrations during 1970–1989, large percentages of the interannual variations in stream K^+ (49–63%) and NO_3^- (54–57%) concentrations were explained by soil freezing severity (Tables 2 and 3). These results strongly suggest that interannual variability in the depth and duration of soil freezing contributed to temporal fluctuations in stream K^+ and NO_3^- concentrations at the HBEF during 1970–1989.

Mortality of fine roots is a likely mechanism explaining the enhanced stream K^+ and NO_3^- concentrations during years with severe soil freezing. Soil freezing increases fine-root mortality at the HBEF (8) and decomposition, and leaching of dead fine roots releases significant quantities of K^+ (20). Disruption of interactions among roots, microbes, and soil likely contributed to increased stream NO_3^- and K^+ concentrations during years with severe soil freezing at the HBEF as the result of decomposition of fine-root necromass and decreased root uptake. For the decade 1980–1989, the year 1980 had a significant influence in determining the

TABLE 3. Results^{a,b} of Stepwise Regression with Soil Freezing and Climate as Explanatory Variables and Annual Deviations of Stream Concentrations from 4-Year Running Averages as the Dependent Variables for the Period 1980–1989

dependent variable ($\mu\text{mol L}^{-1}$)	independent variable				
	maximum soil frost depth (cm)	cumulative soil frost depth (cm)	annual precipitation (mm)	mean December–January air temperature ($^{\circ}\text{C}$)	cumulative snow cover (mm)
Ca^{2+}	0.28 (+)***	ns	0.60 (–)****	ns	ns
Mg^{2+}	ns	0.13 (+)*	0.65 (–)***	ns	ns
K^{+}	ns	0.63 (+)***	ns	ns	ns
Na^{+}	ns	ns	ns	ns	ns
total Al	ns	ns	ns	ns	ns
NH_4^{+}	ns	ns	ns	ns	ns
H^{+}	ns	ns	ns	0.40 (–)*	ns
SO_4^{2-}	ns	ns	ns	ns	ns
NO_3^{-}	ns	0.54 (+)****	0.04 (–)*	ns	0.36 (+)***
Cl^{-}	ns	ns	ns	ns	0.52 (–)**

^a Results are partial r^2 values; (+) or (–) denotes positive or negative relationship. ^b Significance levels: * = $p < 0.10$, ** = $p < 0.05$, *** = $p < 0.01$, **** = $p < 0.001$, ns = nonsignificant ($p > 0.10$).

TABLE 4. Results^{a,b} of Stepwise Regression with Soil Freezing and Climate as Explanatory Variables and Annual Deviations of Stream Concentrations from 4-Year Running Averages as the Dependent Variables for the Period 1990–1997

dependent variable ($\mu\text{mol L}^{-1}$)	independent variables				
	maximum soil frost depth (cm)	cumulative soil frost depth (cm)	annual precipitation (mm)	mean annual air temperature ($^{\circ}\text{C}$)	mean December–January air temperature ($^{\circ}\text{C}$)
Ca^{2+}	ns	ns	ns	ns	ns
Mg^{2+}	ns	ns	ns	ns	ns
K^{+}	ns	ns	ns	ns	ns
Na^{+}	ns	ns	ns	ns	ns
total Al	ns	0.20 (–)***	0.05 (–)*	0.72 (+)***	ns
NH_4^{+}	ns	ns	ns	ns	ns
H^{+}	ns	ns	0.62 (+)***	ns	0.22 (+)**
SO_4^{2-}	ns	ns	ns	ns	ns
NO_3^{-}	0.25 (–)**	ns	ns	0.58 (+)**	ns
Cl^{-}	ns	ns	0.48 (+)*	ns	ns

^a Results are partial r^2 values; (+) or (–) denotes positive or negative relationship. ^b Significance levels: * = $p < 0.10$, ** = $p < 0.05$, *** = $p < 0.01$, **** = $p < 0.001$, ns = nonsignificant ($p > 0.10$).

relationship between soil freezing and interannual variations of stream K^{+} and NO_3^{-} (Figure 3). When 1980 is excluded from the regression, deviations of stream K^{+} are no longer significantly related to soil freezing during the period 1981–1989, whereas the partial r^2 drops from 0.54 to 0.21 and the p value increases from 0.0003 to 0.066 when 1980 is eliminated from the relationship between deviations of stream NO_3^{-} and the cumulative soil frost depth. However, we are aware of no disturbance during 1980, other than soil freezing, to which the marked increase in stream NO_3^{-} could be attributed. We therefore believe that the leverage of 1980 in driving the relationship between soil freezing and interannual variations of stream NO_3^{-} and K^{+} during the decade 1980–1989 is real. There are no leverage points evident in the significant relationship between soil freezing and interannual variations of stream NO_3^{-} and K^{+} during 1970–1979 (Figure 3).

In contrast with the period 1970–1989, soil freezing variables were not significantly related to annual deviations of stream Ca^{2+} , Mg^{2+} , and K^{+} from 4-year running averages during the period 1990–1997 (Table 4). Whereas soil freezing variables exhibited significant positive relations with annual deviations of stream NO_3^{-} during 1970–1979 (Table 2) and 1980–1989 (Table 3), a negative relationship was evident during 1990–1997 (Table 4). Several severe soil freezing events during the early 1990s had a negligible effect on stream NO_3^{-} (Figure 2). It remains unclear why the relationship between soil freezing and interannual patterns of stream K^{+} and NO_3^{-} concentrations differed dramatically between the periods

1970–1989 and 1990–1997. Stream NO_3^{-} concentrations tended to decrease after 1990 and remained relatively low from 1993 through 1997 (Figure 2). This decline in stream NO_3^{-} from the 1970s to the 1990s is also evident in the Bowl Natural Area (16) and at Mt. Moosilauke (17), indicating that this long-term pattern at the HBEF is apparent at the regional scale within the White Mountains of New Hampshire. Using the PnET series of models, Aber et al. (3) were unable to replicate the overall low rate of stream inorganic nitrogen loss during the 1990s or the pattern of decreasing stream NO_3^{-} loss since 1990 at the HBEF. If the decreases in stream NO_3^{-} from 1991 through 1997 were driven by biotic processes (i.e., microbial and/or plant immobilization), then it would be possible that the mechanism(s) causing this decline might also have decoupled the previously extant relationship between soil freezing and stream NO_3^{-} .

Mitchell et al. (14) hypothesized that synchronous increases in stream NO_3^{-} during the snowmelt of 1990 in four watersheds across the northeastern U.S. were caused by a regional-scale soil freezing event in December 1989. Results of this study, however, suggest that the marked increase in stream NO_3^{-} concentration during 1990 at the HBEF did not result from soil freezing. Interestingly, mean annual temperature was not significantly related to annual deviations of stream NO_3^{-} during 1970–1989 (Tables 2 and 3), but a strong relationship was evident between these variables during 1990–1997 (Table 4). Of the years 1970–1997, 1990 had the greatest mean annual air temperature (5.5°C). A positive effect of temperature on net N mineralization (21),

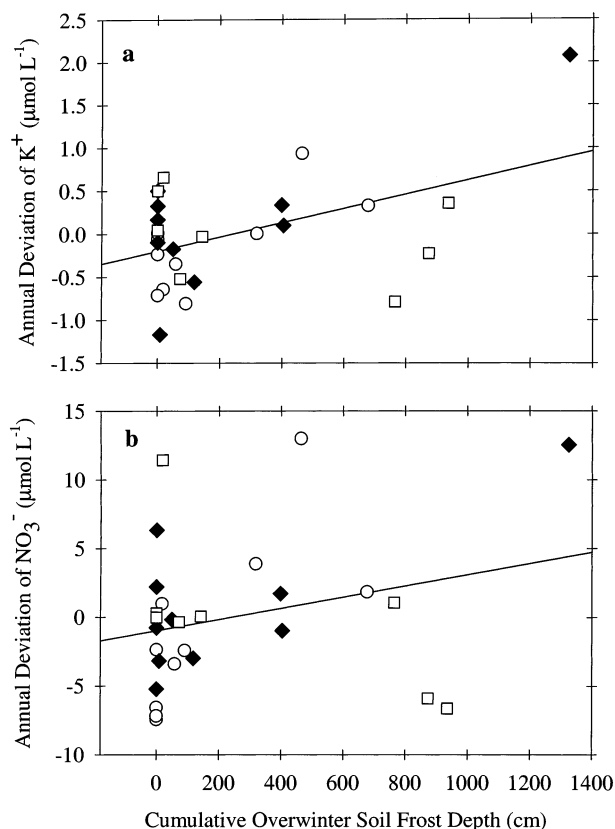


FIGURE 3. Linear regressions of annual deviations of stream (a) K^+ and (b) NO_3^- concentrations from 4-year running averages as functions of the cumulative winter soil frost depth at the HBEF. Symbols are coded by decade: 1970–1979 (circles), 1980–1989 (diamonds), 1990–1997 (squares). Regression lines are for the entire period (1970–1997).

and hence potentially on net nitrification, could link air temperature with stream NO_3^- concentration. Murdoch et al. (4) observed a significant positive relationship between mean annual temperature and annual stream NO_3^- concentration at Biscuit Brook in the Catskill Mountains of New York between 1984 and 1995. In contrast to the HBEF, the year 1990 at Biscuit Brook had moderate annual mean air temperatures and the greatest annual mean stream nitrate concentrations and was an outlier from the relationship between air temperature and stream NO_3^- . These results suggest that the processes contributing to the increase in stream NO_3^- during 1990 at the HBEF differed from those at Biscuit Brook.

The temporal pattern of mean streamwater NO_3^- concentrations during the spring season (March through May) was very similar to the pattern of mean annual stream NO_3^- concentration (Figure 2). Using mean spring concentration, rather than mean annual concentration, did not significantly improve the relationship between soil freezing variables and deviations of stream NO_3^- and K^+ concentrations from running averages for 1970–1997 or for any of the decades (results not shown).

Streamwater Fluxes. Stepwise regression did not select soil freezing variables as predictors of annual deviations of stream NO_3^- or nutrient-base cation fluxes from 4-year running averages (results not shown). Rather, precipitation was consistently selected as the best predictor of short-term fluctuations in stream flux, explaining between 25 and 78% of the variability. This result was not surprising, as interannual differences in stream discharge are driven largely by variability in precipitation inputs and variability in streamflow strongly influences rates of stream flux (15).

Future Research. Our results point to the need to develop models that depict the effects of soil freezing on ecosystem biogeochemistry. Such models will need to consider the effects of air temperature, snowpack depth, and other variables (e.g., solar radiation, aspect, soil properties, vegetation density) on the spatial and temporal variability of soil frost depth and severity within and among ecosystems. Future field studies at the process level will be necessary to identify the mechanisms (e.g., root and microbial mortality, plant uptake, soil aggregate disruption) that contribute to enhanced nutrient loss following soil freezing and to incorporate these mechanisms into biogeochemical models. Important goals of future research will also be to determine: (i) the length of time that ecosystems respond to soil freezing, (ii) whether the length of response is related to the severity of the freezing event, and (iii) whether the spatial distribution of soil frost within watersheds affects the response of stream chemistry (e.g., frost that occurs in riparian areas might result in greater responses of stream chemistry than frost that is confined exclusively to upper elevations of a catchment). We have initiated an experiment at the HBEF to examine these processes in more detail via snowpack manipulation. Such studies will be critical for predicting the effects of soil freezing on the acidification of watersheds, as well as on the availability and loss of nutrients in temperate northern ecosystems under a warmer climate with lower snow cover. Our results emphasize the utility of long-term monitoring in identifying temporal changes in ecosystem nutrient cycling and loss.

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Literature Cited

- Vitousek, P. M.; Aber, J. D.; Howarth, R. W.; Likens, G. E.; Matson, P. A.; Schindler, D. W.; Schlesinger, W. H.; Tilman, D. G. *Ecol. Appl.* **1997**, *7*, 737.
- Aber, J. D.; Driscoll, C. T. *Global Biogeochem. Cycles* **1997**, *11*, 639.
- Aber, J. D.; Ollinger, S. V.; Driscoll, C. T.; Likens, G. E.; Holmes, R. T.; Freuder, R. J.; Goodale, C. L. *Ecosystems* **2002**, *5*, 648.
- Murdoch, P. S.; Burns, D. A.; Lawrence, G. B. *Environ. Sci. Technol.* **1998**, *32*, 1642.
- Williams, M. W.; Losleben, M.; Caine, N.; Greenland, D. *Limnol. Oceanogr.* **1996**, *41*, 939.
- Stottlemyer, R.; Toczydlowski, D. *Hydrol. Process.* **1999**, *13*, 2215.
- Hardy, J. P.; Groffman, P. M.; Fitzhugh, R. D.; Henry, K. S.; Welman, A. T.; Demers, J. D.; Fahey, T. J.; Driscoll, C. T.; Tierney, G. L.; Nolan, S. *Biogeochemistry* **2001**, *56*, 151.
- Tierney, G. L.; Fahey, T. J.; Groffman, P. M.; Hardy, J. P.; Fitzhugh, R. D.; Driscoll, C. T. *Biogeochemistry* **2001**, *56*, 175.
- Fitzhugh, R. D.; Driscoll, C. T.; Groffman, P. M.; Tierney, G. L.; Fahey, T. J.; Hardy, J. P. *Biogeochemistry* **2001**, *56*, 215.
- Brooks, P. D.; Williams, M. W.; Schmidt, S. K. *Biogeochemistry* **1998**, *43*, 1.
- Boutin, R.; Robitaille, G. *Can. J. For. Res.* **1995**, *25*, 588.
- Brooks, P. D.; Campbell, D. H.; Tonnessen, K. A.; Heuer, K. *Hydrol. Process.* **1999**, *13*, 2191.
- Lewis, W. M., Jr.; Grant, M. C. *Arct. Alp. Res.* **1980**, *12*, 11.
- Mitchell, M. J.; Driscoll, C. T.; Kahl, J. S.; Likens, G. E.; Murdoch, P. S.; Pardo, L. H. *Environ. Sci. Technol.* **1996**, *30*, 2609.
- Likens, G. E.; Bormann, F. H. *Biogeochemistry of a Forested Ecosystem*, 2nd ed.; Springer-Verlag: New York, 1995.
- Martin, C. W.; Driscoll, C. T.; Fahey, T. J. *Can. J. For. Res.* **2000**, *30*, 1206.
- Goodale, C. L.; Aber, J. D.; Vitousek, P. M. *Ecosystems* **2002**, in press.

- (18) Buso, D. C.; Likens, G. E.; Eaton, J. S. *Chemistry of Precipitation, Streamwater, and Lakewater from the Hubbard Brook Ecosystem Study: A Record of Sampling Protocols and Analytical Procedures*; USDA Forest Service General Technical Report NE-275; USDA Forest Service: Newtown Square, PA, 2000.
- (19) Rawlings, J. O.; Pantula, S. G.; Dickey, D. A. *Applied Regression Analysis: A Research Tool*, 2nd ed.; Springer: New York, 1998.
- (20) Fahey, T. J.; Arthur, M. A. *For. Sci.* **1994**, *40*, 618.
- (21) Knoepp, J. D.; Swank, W. T. *Biol. Fertil. Soils* **2002**, *36*, 177.

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