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Climate Effects on Stream Nitrate Concentrations at 16 Forested Catchments in South Central Ontario

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Increased nitrate (NO_3) concentrations in streamwaters draining forested catchments are reportedly an early indicator of nitrogen (N) saturation. Nitrate concentrations in streams draining 16 forested catchments in south central Ontario were monitored over a 16-year period, during which time N bulk deposition was relatively constant ($\sim 9 \text{ kg ha}^{-1} \text{ yr}^{-1}$). Mean annual NO_3 concentrations in streams were both highly variable among catchments and among years, although patterns of annual concentration were similar among many catchments. Coherence analysis identified two stream groupings. Shallow soils, moderate slopes, low NO_3 concentration, and a large wetland component characterized the first group. The second group had primarily upland characteristics including deeper soils, steeper slopes, higher NO_3 concentrations, and a much smaller wetland component. Patterns in NO_3 concentration in wetland-influenced streams appeared to be related to summer drought and cumulative frost depth, whereas NO_3 concentrations in upland-draining streams appeared to be related to both mean annual air temperature and summer drought. Because a number of different climate parameters as well as the physical character of the catchments apparently influence NO_3 export, NO_3 concentrations in streams are not a good indicator of N saturation in this region.

Introduction

Sulfur (S) emissions have decreased substantially during the past two decades in eastern North America, while nitrogen (N) emissions have remained relatively unchanged. Concerns have been expressed over the potential for N saturation of forested catchments, which may occur when chronic N deposition increases ammonium (NH_4) and nitrate (NO_3) in excess of plant or microbial demand (1, 2). Potential effects of N saturation include increased NO_3 leaching and base cation losses from soil, altered fluxes of trace gases, increased N levels in trees and consequent nutrient imbalances, and greater tree sensitivity to freezing and pests (3). Increased NO_3 levels in streamwater have been related to elevated inputs of N (4, 5), and short-term N additions to soils have also led to enhanced NO_3 export (6). A rise in stream NO_3 levels has therefore been assumed to be an early indicator of N

saturation (3). However, a significant positive relationship between N deposition and stream NO_3 is only observed above a critical N deposition threshold of around $10 \text{ kg of N ha}^{-1} \text{ yr}^{-1}$ (4, 5, 7), a value typical of (or greater than) N deposition over much of eastern North America (8–10).

Nitrate export from forested catchments in eastern North America can vary greatly between adjacent catchments and appears to be influenced by both biotic (e.g., tree species composition) and abiotic (e.g., depth of till, slope) factors, the relative importance of which varies among regions (11–14). Furthermore, recent studies have shown that NO_3 concentration in streams draining forests can vary considerably between years, and inter-annual changes have been related to a number of different climate variables, which may explain synchronous patterns of NO_3 export in eastern North America (15). Mitchell et al. (8), for example, suggested that an increase in NO_3 export from four forested catchments in New England was related to an anomalous cold period in the winter of 1990 and proposed that subsequent soil freezing may have resulted in root damage causing greater NO_3 export. Murdoch et al. (9) reported that NO_3 concentration in streams draining a forested catchment in New York were positively related to mean annual air temperature but also noted that high NO_3 levels occurred in 1990. Fitzhugh et al. (16) similarly suggested that soil freezing led to increased NO_3 export but that the relationship between soil chemistry and NO_3 weakened during the 1990s. Van Miegroet et al. (17) suggested that both temperature control on N production and hydrologic control on NO_3 leaching were responsible for the inter-annual variation in NO_3 export observed at a high elevation red spruce forest in the southern Appalachians. Inclusion of climate variables and other disturbances into the PnET-CN model led to an improvement in the ability of the model to predict NO_3 concentration at the Hubbard Brook Experimental Forest (Watershed 6), New Hampshire (18). In the United Kingdom, synchronous patterns of NO_3 export from upland catchments were negatively correlated with winter values for the North Atlantic Oscillation Index and mean winter temperature (19).

In south central Ontario, N deposition is greater than for S, and current exceedance of the critical load for acidity is based largely on the assumption that NO_3 leaching will increase as N accumulates in soil (10, 20). Detection of the early stages of N saturation is clearly extremely important, and factors other than N deposition that may affect NO_3 export from forested catchments need to be considered. It has been previously documented that adjacent subcatchments in south central Ontario can exhibit large (up to 10-fold) differences in annual NO_3 export (11, 12), although the impact of climate variations on NO_3 export from forests in the region has not been previously investigated. Nitrate concentrations in streams draining 16 headwater catchments in south central Ontario have been continuously monitored for a period of 16 years between 1982/1983 and 1997/1998. In this study, patterns in annual NO_3 concentration among catchments were compared, and the potential relationship with selected climatic variables was examined.

Materials and Methods

Study Region. The 16 headwater catchments are located in the Muskoka–Haliburton region of south central Ontario. The climate of the study area is north temperate; annual precipitation ranges from 800 to 1100 mm, with 25–33% falling as snow. Average monthly temperature ranges from -4 to -10°C in the coldest winter months and between 16 and 18°C in the summer.

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The study area lies within the Great Lakes St. Lawrence forest region and is dominated by semi-natural mixed hardwood forests. Sugar maple (*Acer saccharum*) dominates much of the landscape especially in the eastern section, although white pine (*Pinus strobus*) is dominant in some areas. Associated tree species include American beech (*Fagus grandifolia*), red maple (*Acer rubrum*), yellow birch (*Betula allegheniensis*), white ash (*Fraxinus americana*), basswood (*Tilia americana*), ironwood (*Ostrya virginiana*), red pine (*Pinus resinosa*), white spruce (*Picea glauca*), balsam fir (*Abies balsamea*), eastern hemlock (*Tsuga canadensis*), aspen (*Populus* sp.), and white birch (*Betula papyrifera*). Small wetlands dominated by white cedar (*Thuja occidentalis*), black spruce (*Picea mariana*), and tamarack (*Larix laricina*) are common throughout the region, covering an estimated 10% of the total area. Forests were heavily logged in the late 1800s, initially for white pine but later for other species. Forests are generally uneven aged; their composition and age structure are determined largely by forest management practices.

Nitrogen Deposition. Deposition data were obtained from collections of bulk deposition, which we define as that caught in a continuously open, 0.25 m² collector. The collectors were fitted with Teflon-coated funnels that are screened (80 μ m Nitex mesh) to prevent contamination by insects and debris. Precipitation samples were removed from collectors when there was sufficient volume for chemical analyses, typically weekly. All chemical analyses were performed at the Ontario Ministry of Environment (OME) laboratory with appropriate quality control procedures. Calibration was controlled, accuracy was checked, and among-run precision was measured by a minimum of two quality control standards and a long-term blank, which were prepared and maintained independently of the calibration standards. Deposition and volume-weighted concentrations for NO₃ and NH₄ were calculated for each water year (June 1–May 31) between 1982/1983 and 1998/1999. In this study, no attempt was made to estimate the relative contribution of N dry deposition, and we acknowledge that our measurements of bulk deposition may underestimate total inputs of N to the catchments (21).

Stream Sampling. Stream stage was recorded continuously at a V-notched or H-flume weir at each catchment outflow, and daily stream discharge (m³ d⁻¹) was computed using established stage–discharge relationships. Water samples for chemical analyses were collected at the weir at regular intervals (at least fortnightly) when there was flow, although sampling was more frequent during the spring melt period. Streamwater was analyzed for NH₄, NO₃, and Kjeldahl N (TKN) using standard methods (22). Total organic nitrogen was calculated as the difference between TKN and NH₄ (22). Data are presented as volume-weighted concentrations.

Climate Data. Climate data (temperature and precipitation) were collected along with bulk deposition at three or more monitoring stations in the Muskoka–Haliburton region over the period of study (23). Soil temperature data were not available, so data from the Ottawa region (~150 km east of the study sites) were used. Although these data are unlikely to exactly match conditions in the study region in terms of absolute temperature, year to year differences in the extent of soil freezing between regions were expected to be similar. Nevertheless, relationships between soil freezing and NO₃ concentration should be interpreted with this consideration in mind.

Laboratory Experiments with Soils. Drought can have a large impact on stream NO₃ concentration, particularly in wetland-draining streams (24), presumably because mineralization and nitrification processes are stimulated by fluctuating moisture conditions. To assess the effect of drying and re-wetting on NO₃ release in the study region, a laboratory

experiment was conducted on organic soils collected from representative upland and wetland sites. Forest floor material was collected from four sites in both a deciduous (sugar maple dominated) and a coniferous (white pine dominated) stand, and samples from individual collections were pooled. Similarly, peat was collected at a depth of 20–40 cm beneath the base of live *Sphagnum* plants from four sites in a conifer *Sphagnum* swamp.

In the laboratory, peat, deciduous and coniferous collections were divided in two; one-half was sealed in plastic bags to preserve field moisture content, while the other half was air-dried until the moisture content was $\leq 20\%$ of the initial value. Air-dried samples were subsequently re-wet with deionized H₂O until the moisture content was approximately equal to the initial value. At 24 h following re-wetting, water-extractable (1:5 soil:solution) NO₃ concentration in the dried/re-wet and continuously moist LFH (forest floor) and peat material was measured by ion chromatography (Dionex 6000).

Statistical Analysis. Monotonic (i.e., unidirectional) trends in annual N deposition and NO₃ concentrations in the 16 streams were examined using the Seasonal Mann-Kendall Test in the software package DETECT (25). To investigate similarities in stream NO₃ patterns among catchments, we used temporal coherence analysis following Brien et al. (26) and Rusak et al. (27). Nitrate concentrations were first transformed to z-scores (i.e., mean of 0 and standard deviation of 1), and between-lake relationships were tested by Pearson correlation. The resultant correlation matrix was then tested for homogeneity to identify subsets of catchments with similar temporal patterns. Catchments were grouped by first selecting the three-catchment subset with the highest mean correlation and then sequentially adding other catchments to this subset. As described in Arnott et al. (28), subsets of coherent catchments were identified if (a) their correlation matrix was homogeneous (i.e., all correlations are equal) and (b) if the grand mean of their correlation matrix was not equal to zero ($p < 0.05$).

We next investigated whether specific climate factors were related to patterns in annual average NO₃ concentration in each group, using stepwise multiple regression (SYSTAT). Climate parameters included in this analysis were based on previous reports and included the following: mean annual temperature, mean spring (March–May) temperature, mean March temperature, total spring precipitation, total March precipitation, cumulative frost depth (the sum of daily frost depths), minimum soil temperature, and summer drought (the number of days with zero streamflow, $Q = 0$). Streamflow is highly responsive to changes in summer precipitation and temperature in this region, and the number of continuous days with zero streamflow is a good indicator of summer dryness in catchments that are dominated by thin till and soils (29).

Results and Discussion

Deposition. Sulfate (SO₄) deposition in Muskoka–Haliburton declined by ~50%, in contrast N deposition was unchanged, and there was no significant trend in NO₃ or NH₄ concentration in bulk deposition during the study period (30). As a result, the SO₄/(NO₃ + NH₄) (equiv/equiv) ratio in bulk deposition decreased from around 1.0 at the start of the study period to ~0.6 by the late 1990s. Annual bulk N deposition ranged between 6.4 and 11.4 kg of N ha⁻¹, averaging ~9.0 kg of N ha⁻¹ yr⁻¹ during the 16-year period. However, bulk deposition typically underestimates total N input to forested catchments; therefore, N deposition in Muskoka–Haliburton is close to the deposition threshold (10 kg of N ha⁻¹ yr⁻¹) above which significant leaching of NO₃ has been reported to occur in European catchments (5, 31).

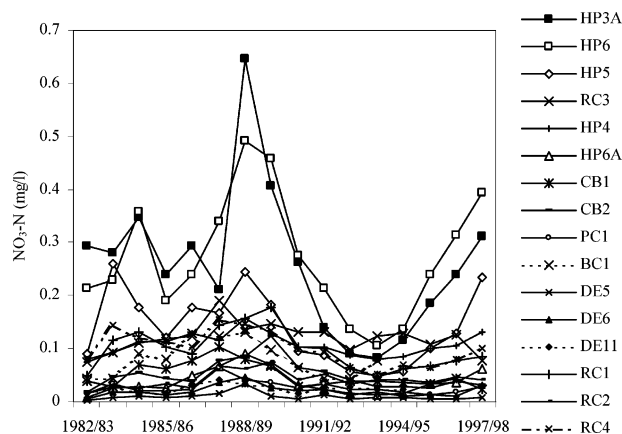


FIGURE 1. Mean annual NO_3 (mg of N L^{-1}) concentrations in streams draining 16 headwater catchments in south central Ontario.

Nitrate Leaching. Mean annual NO_3 concentration in streamwater was extremely variable among the 16 catchments (Figure 1), and average concentrations over the entire period of record ranged from 0.01 (DE5) to 0.29 mg of N L^{-1} (HP3A) (Tables 1 and 2). The majority (56–84%) of NO_3 export from catchments occurred during spring melt (February–March). Snowpack NO_3 concentrations measured during a 5-year period (1987–1991) at six locations at both a deciduous (HP5; 0.44 ± 0.08 mg of N L^{-1}) and a coniferous (PC1; 0.44 ± 0.09 mg of N L^{-1}) catchment were similar between years and catchments. Therefore internal catchment processes, rather than loss of NO_3 accumulated in the snowpack over winter, are likely responsible for the large differences observed between catchments and over time.

Temporal Patterns in Annual Nitrate Concentration. Temporal patterns in annual NO_3 concentration were similar among many but not all catchments. Coherence analysis identified two groups of streams (Figure 2). The first group, which contained nine streams, had predominantly lowland characteristics with shallow soils, moderate slopes, low NO_3 concentration, and a relatively large peat component (Table 1). Average topographic slopes in this group ranged from 1.0 to 5.9%, with an overall mean of 2.4%. Four of the nine catchments lacked deep (>1 m) till deposits, and peat coverage was between 2.8 and 25.4%. Mean annual organic N concentration was between 0.23 and 0.44 mg of N L^{-1} , with an overall average of 0.36 mg of N L^{-1} . Mean annual NO_3 concentration in group 1 streams was much lower than organic N concentrations and was between 0.02 and 0.12 mg of N L^{-1} , with an overall average of 0.06 mg of N L^{-1} . There was a small but significant increase in mean annual NO_3 in only one (RC2) of the nine streams over the period of study. The second group contained seven streams and had predominantly upland characteristics including deeper soils, steeper slopes, higher NO_3 concentration, and a much smaller wetland component (Table 2). Average topographic slope ranged from 1.0 to 8.5%, with an overall mean of 5.8%. Deep till deposits covered between 6.6 and 97.1% of the catchments, with an overall average of 55.2%. Four of the seven catchments had no notable peat component, and mean annual organic N concentration was between 0.13 and 0.37 mg of N L^{-1} , with an overall average of 0.24 mg of N L^{-1} . Mean annual NO_3 concentration in group 2 streams was generally greater than in group 1 and was between 0.04 and 0.29 mg of N L^{-1} , with an overall average of 0.15 mg of N L^{-1} . There was no significant change in mean annual NO_3 concentration in any of the seven streams over the period of study. Upland forest composition did not differ notably between the two groups. Hardwoods, primarily sugar maple, dominate upland forests at 15 of the catchments, whereas the forest at PC1 is primarily coniferous (Tables 1 and 2). Nitrate accounts for only 2.4–

25.8% (mean 11.6%) of total stream N in group 1 as compared with 12.1–54.3% (mean 32.2%) in group 2, although total annual N retention (inorganic N inputs in deposition minus total N export in stream) is similar in both groups because organic N export from group 1 catchments is greater (Table 1).

Effect of Climate on Stream Nitrate Concentration. Coherence analysis indicated two general patterns in stream NO_3 concentration; catchments which had a larger wetland component (and/or wetlands located near the outflow; group 1) tended to cluster together and exhibited a different pattern from catchments that had predominately upland characteristics (group 2). Stepwise multiple regression analysis selected summer drought duration and cumulative frost depth as significant predictors of NO_3 concentration in group 1 streams (Table 3; Figure 3). Summer drought duration and mean annual air temperature were predictors of mean annual NO_3 concentration in group 2 streams (Table 3, Figure 3).

Climate Effects on Wetland-Influenced Catchments. The pattern of NO_3 concentration in wetland-influenced catchments, such as PC1, was remarkably similar to the pattern of SO_4 concentration and is characterized by a dramatic increase in NO_3 concentration immediately following prolonged summer droughts (Figure 4).

Temporal variations in SO_4 export from wetlands have previously been attributed to the exposure and reoxidation of S stored in peat during drought-related water table declines and the subsequent release in fall runoff (29, 32, 33). Drought has been shown to inhibit mineralization and nitrification in soils leading to a decrease in NO_3 concentration (34), although drying may also stimulate mineralization upon subsequent re-wetting (35–37). The potential net release of NO_3 from peat following drying was demonstrated in a laboratory study. Within 24 h of re-wetting, extractable NO_3 concentration in dried peat increased approximately 7-fold as compared to continuously moist peat (Figure 5). The effects of drought on stream NO_3 concentration have been documented in lowland catchments in the U.K., and elevated NO_3 concentration persisted into the year following the drought (24). The positive relationship between cumulative frost depth and mean annual NO_3 concentration may be due to fine root mortality and/or microbial mortality, resulting in increased NO_3 leaching (8, 16, 38).

Climate Effects on Upland-Dominated Catchments. The positive relationship between NO_3 and summer drought in group 2 streams may indicate the presence of small wetlands within the catchments or processes that are drought-sensitive in streambed soil. Drying and subsequent re-wetting of deciduous LFH material in the laboratory resulted in a 2-fold increase in water-extractable NO_3 concentration within 24 h of re-wetting (Figure 5). This suggests that increases in NO_3 in group 2 streams following drought may in part be due to enhanced mineralization and nitrification conditions in organic surface soil resulting from alternating moisture conditions. Indeed, elevated NO_3 concentration has been observed in lysimeter leachate collected beneath the LFH horizon, immediately following summer dry periods at two of the study catchments (PC1 and HP4) (39). A positive relationship between stream NO_3 concentration and mean annual temperature has also been reported by Murdoch et al. (9) and was thought to be due to higher rates of N mineralization and nitrification in warmer years.

In contrast to other studies in eastern North America, estimates of soil freezing (minimum soil temperature or cumulative frost depth) were not significantly correlated with mean annual NO_3 concentration in the upland catchments (Table 3). Because soil temperature data were obtained from a site ~150 km east of the study region, differences between sites may have obscured any relationship between soil freezing and stream NO_3 . Notably, however, the lowest soil

TABLE 1. Group 1: Selected Catchment Characteristics^a

name (area, ha)	peat (%)	grade (%)	deep till (% > 1 m)	upland forest sp. ^b	annual NO ₃ (mg of N L ⁻¹)	annual TON (mg of N L ⁻¹)	N retention (%) ^c	NO ₃ (%) of total N	trend slope (mg of N L ⁻¹ yr ⁻¹)
RC2 (26.7)	10.5	1.5	0.0	SM, YB, HE	0.04	0.40	72.6	8.7	+0.0007*
RC3 (70.5)	9.9	3.5	81.7	SM, YB, RO	0.12	0.31	67.1	25.8	ns
RC4 (45.5)	2.9	2.5	76.3	SM, RO, RM	0.10	0.33	69.8	21.7	ns
CB1 (59.7)	2.8	3.0	24.2	RM, RO, SM	0.05	0.23	87.0	17.4	ns
CB2 (126.0)	8.0	2.0	16.7	SM, RM, RO	0.05	0.42	71.5	10.2	ns
PC1 (23.3)	7.0	5.9	9.6	WP, HE, RO	0.03	0.27	81.3	9.4	ns
DE5 (30.0)	25.4	1.0	0.0	RM, SM, YB	0.01	0.39	72.5	2.4	ns
DE6 (21.8)	22.0	1.6	0.0	RM, SM, YB	0.02	0.44	67.1	3.9	ns
DE11 (76.3)	20.9	1.0	0.0	RM, SM, YB	0.03	0.42	72.4	5.6	ns
mean	12.2	2.4	23.2		0.06	0.36	73.5	11.6	

^a Key: *, $p < 0.05$; ns, nonsignificant ($p > 0.05$); SM, sugar maple; YB, yellow birch; HE, eastern hemlock; RO, red oak; RM, red maple; WP, white pine; TON, total organic N (see ref 13 for full details). ^b Dominant tree species in upland parts of each catchment. ^c Annual retention defined as inorganic N input in bulk deposition – total N export in stream.

TABLE 2. Group 2: Selected Catchment Characteristics^a

name (area, ha)	peat (%)	grade (%)	deep till (% > 1 m)	upland forest sp. ^b	annual NO ₃ (mg of N L ⁻¹)	annual TON (mg of N L ⁻¹)	N retention (%) ^c	NO ₃ (%) of total N	trend slope (mg of N L ⁻¹ yr ⁻¹)
HP3A (19.7)	2.9	8.0	97.1	SM, YB, RM	0.29	0.18	71.4	54.3	ns
HP4 (119.5)	0.0	5.0	56.1	SM, RM, YB	0.11	0.27	75.9	26.4	ns
HP5 (190.5)	13.3	3.0	34.5	SM, YB, RM	0.14	0.37	63.9	24.8	ns
HP6 (9.97)	0.0	8.0	45.2	SM, HE, YB	0.27	0.27	62.9	46.1	ns
HP6A (15.3)	10.0	8.5	6.6	SM, HE, YB	0.04	0.26	84.0	12.1	ns
RC1 (133.6)	0.0	1.0	53.2	SM, YB, HE	0.10	0.22	78.8	26.4	ns
BC1 (20.4)	0.0	7.0	94.0	SM, YB, BE	0.08	0.13	89.5	35.1	ns
mean	3.7	5.8	55.2		0.15	0.24	75.2	32.2	

^a Key: *, $p < 0.05$; ns, nonsignificant ($p > 0.05$); SM, sugar maple; YB, yellow birch; RM, red maple; HE, eastern hemlock; BE, American beech; TON, total organic N (see ref 13 for full details). ^b Dominant tree species in upland parts of each catchment. ^c Annual retention defined as inorganic N input in bulk deposition – total N export in stream.

temperature in Ottawa was recorded in the winter of 1989 (Figure 6), which is the same year in which the highest NO₃ concentration was measured in upland draining streams (Figure 2). This may imply that soil temperature has a threshold rather than a linear effect on NO₃ export, such that soils must reach a minimum temperature before the effect is notable in stream chemistry.

Local and Global Factors Affecting Nitrate Concentrations in Wetland and Upland Dominated Streams. Nitrate concentrations in wetland-influenced (group 1) streams were generally low, implying that NO₃ retention was high in wetland systems. Efficient NO₃ retention may be a result of denitrification, which is favored by anoxic conditions that exist in wetlands during much of the year. Low NO₃ concentration in streams draining through wetlands may also be due to generally low rates of N mineralization and nitrification in wetland soil (12). This does not necessarily imply that N export from wetlands is low, because organic N compounds constitute the majority of N in wetland outflows (Table 1). For example, Devito and Dillon (40) estimated that annual net N retention (excluding denitrification) was approximately 10% for the wetland at PC1. The combined effect of lower NO₃ concentration and higher organic N export from wetlands is that wetland and upland draining catchments retain approximately the same amount of atmospheric N (excluding denitrification). However, NO₃ concentration in group 1 streams increased in years with prolonged summer drought, probably due to increased nitrification of N mineralized during summer dry periods. Summer droughts in south central Ontario have been associated with strong El Niño events (32), implying that global climate phenomena may influence NO₃ export from wetlands, and these effects are noticeable in catchments with either a significant wetland component or with wetlands located near the catchment outflow.

Nitrate concentrations in upland-draining (group 2) streams were generally higher than in wetland-influenced streams, although there was considerable variation in mean annual NO₃ concentrations among upland-draining catchments. While part of the difference may be due to variable wetland coverage in the predominantly upland catchments, previous studies have clearly shown that pronounced differences in stream NO₃ concentration can occur in adjacent catchments (11, 12, 41). Tree species composition has been shown to exert a strong influence on NO₃ export and higher observed NO₃ concentrations in streams draining sugar maple as compared to American beech or hemlock dominated catchments are believed to be due to the higher N-to-lignin content of sugar maple litter (42). Although more than 20 tree species are present in the catchments considered in this study, with the exception of PC1, upland areas in all catchments are dominated by hardwoods with sugar maple a major component. Therefore, species composition was unlikely to be the main determinant of differences in mean annual NO₃ concentration among catchments. This is not to say, however, that tree species composition does not impact stream NO₃, Devito et al. (12) for example, demonstrated that mineralization and nitrification rates are considerably higher in deciduous forest floor material as compared with coniferous or wetland soil in this region. Similarly, in the present study, net NO₃ release from deciduous LFH was far greater than for coniferous LFH or peat both under field-moist conditions and after drying and re-wetting (Figure 5). However, as only PC1 (Table 1) is not dominated by hardwood forest, tree species composition can only be partly responsible for differences observed between catchments. In this region, it is more likely that physical differences such as topography and stratigraphy play a larger role in controlling differences in mean annual NO₃ among catchments (11, 13, 41).

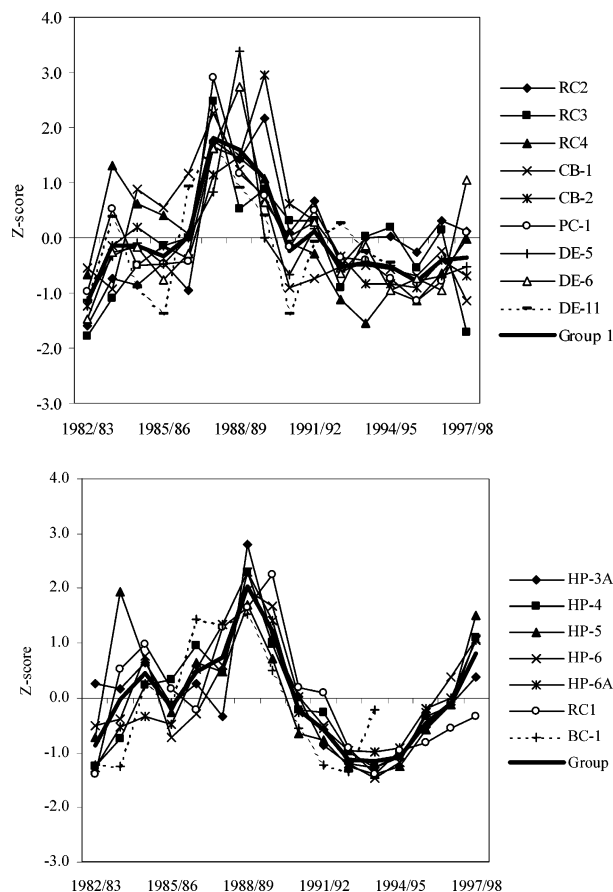


FIGURE 2. Standardized (z-score) mean annual NO_3 (mg of N L^{-1}) concentrations in two groups of streams, identified through coherence analysis.

TABLE 3. Results of Stepwise Linear Regression between Selected Climate Variables and Mean Annual Stream NO_3 Concentrations in Group 1 (Wetland-Influenced) and Group 2 (Upland-Dominated) Catchments for the Period 1982–1998^a

annual temp	spring temp	March temp	spring precip	March precip	summer drought	cumulative frost	min soil temp
Group 1							
ns	ns	ns	ns	ns	0.55 (0.001)	0.23 (0.12)	ns
Group 2							
0.35 (0.10)	ns	ns	ns	ns	0.44 (0.03)	ns	ns

^a Values are regression coefficients (r^2); significance levels (p) are in parentheses. ns, nonsignificant ($p > 0.15$).

The highest stream NO_3 levels in upland-draining streams were measured during 1989, which was also the year with the maximum depth of soil freezing and minimum recorded soil temperature. It is interesting to note that 1989 was the only year during the 16-year study period in which a strong La Niña episode (positive SOI) was recorded (Figure 6). Additionally, high NO_3 levels observed in 1989–1990 may reflect a delayed response to droughts that occurred during the late 1980s (18). This implies that global climate phenomena may influence NO_3 export from upland catchments in Muskoka–Haliburton. A similar suggestion has been made for upland catchments in Europe (19).

Nitrogen Saturation and the Role of Climate. Increasing NO_3 levels in surface waters during the 1980s caused considerable concern that forests were becoming N saturated

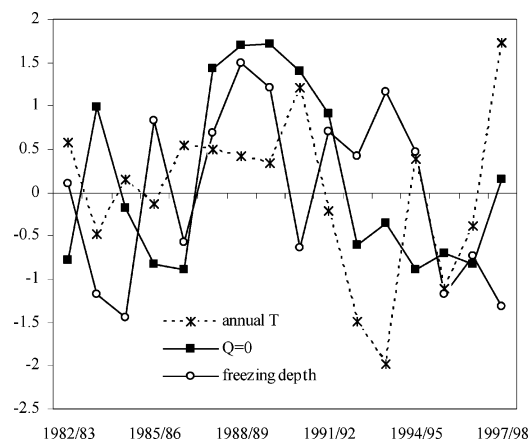


FIGURE 3. Standardized (z-score) mean annual air temperature, cumulative depth of soil freezing, and number of days with zero streamflow ($Q = 0$).

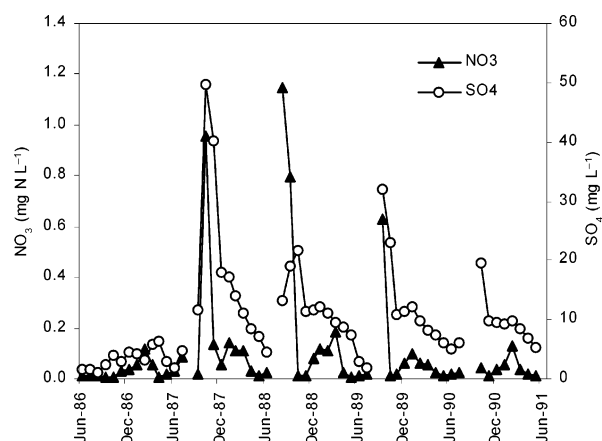


FIGURE 4. Mean volume-weighted monthly NO_3 (mg of N L^{-1}) and SO_4 ($\text{mg of SO}_4 \text{ L}^{-1}$) concentrations in PC1: June 1986–May 1991.

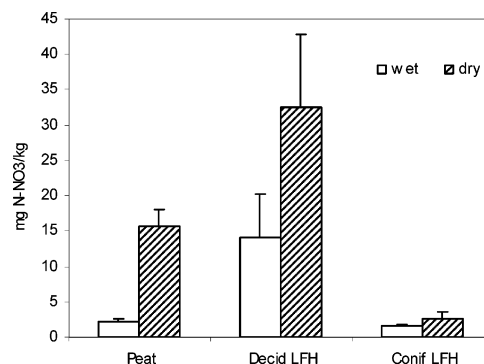


FIGURE 5. Water-extractable NO_3 (mg of N L^{-1}) concentration in peat, deciduous LFH, and coniferous LFH that were air-dried and subsequently re-wet (dry) or maintained at field-moist conditions (wet). Values are mean \pm standard deviation.

(43). However, positive trends of the 1980s were generally reversed in the 1990s (18, 44, 45). Aber et al. (18) reported that the decline in NO_3 at the W6 watershed at Hubbard Brook could be explained by climate and disturbance variables using the PnET-CN model. In the present study, there was no consistent trend in stream NO_3 concentration during the period 1982–1998. Climate appears to have played a significant role in altering temporal trends in surface water NO_3 levels due to a number of extreme climate events that occurred during the late 1980s. Higher NO_3 levels in streams and lakes during the late 1980s resulted in an apparent increasing trend in NO_3 during the first half of the study

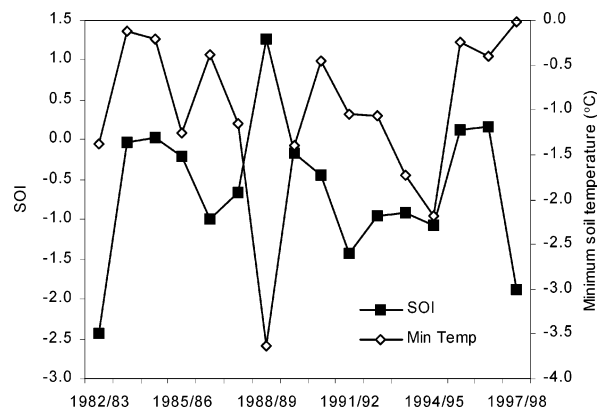


FIGURE 6. Standardized annual (June–May) Southern Oscillation Index (SOI) (<http://www.cpc.noaa.gov>) and minimum soil temperature at Ottawa, 1982–1998.

period, whereas these same high NO_3 levels give the impression of a decline through more recent years. Even so, mass budget estimates indicate that forested catchments in Muskoka–Haliburton and other parts of eastern North America are retaining significant amounts of atmospheric N (10). In the present study, a simple N budget excluding dry deposition, denitrification, and N fixation shows that 63% (HP6) to 87% (BC1) of the annual N in bulk deposition was retained within the catchments (Table 1). This amounts to an annual net retention of between 5.6 and 7.7 kg of N ha^{-1} .

Nitrate concentrations in streamwater draining forested catchments in Muskoka–Haliburton are extremely variable, between both catchments and years. Differences in NO_3 export among catchments are likely controlled by physical variations such as the areal extent and location of wetlands and the proportion of deep till and topographic slope, although tree species composition may also play a part. Inter-annual variations in NO_3 concentration were similar among many but not all catchments, with wetland-influenced catchments generally following one pattern and upland-dominated catchments exhibiting a different trend. Patterns in wetland-influenced catchments appeared to be related to summer drought, with increased NO_3 concentration occurring in the fall of years with prolonged droughts. In contrast, NO_3 concentration in streams draining predominately upland forests appeared to be affected by both mean annual temperature and summer drought. Because a number of different climate parameters as well as the physical character of catchments apparently influence NO_3 export, NO_3 concentrations in streams are not a good indicator of N saturation in this region.

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Literature Cited

- Driscoll, C. T.; Whitall, D.; Aber, J. D.; Boyer, E.; Castro, M.; Cronan, C.; Goodale, C. L.; Groffman, P.; Hopkinson, K.; Labert, K.; Lawrence, G.; Ollinger, S. *Bioscience* **2003**, *53*, 357–374.
- Aber, J. D.; Goodale, C. L.; Ollinger, S. V.; Smith, M. L.; Magill, A. H.; Martin, M. E.; Hallett, R. A.; Stoddard, J. L. *Bioscience* **2003**, *53*, 375–389.
- Aber, J. D.; Nadelhoffer, K. J.; Steudler, P.; Melillo, J. M. *Bioscience* **1989**, *39*, 378–386.
- Dise, N. B.; Matzner, E.; Forsius, M. *Environ. Pollut.* **1998**, *102*, 453–456.
- Stoddard, J. L.; Traaen, T. S.; Skjelkvale, B. L. *Water Air Soil Pollut.* **2001**, *130*, 781–786.
- Kahl, J. S.; Norton, S. A.; Fernandez, I. J.; Nadelhoffer, K. N.; Driscoll, C. T.; Aber, J. D. *Environ. Sci. Technol.* **1993**, *27*, 565–568.
- Wright, R. F.; Roelofs, J. G. M.; Bredemeier, M.; Blanck, K.; Boxman, A. W.; Emmett, B. A.; Gundersen, P.; Hultberg, H.; Kjonaas, O. J.; Moldan, F.; Tietema, A.; van Breeman, N.; van Dijk, H. F. G. *For. Ecol. Manage.* **1995**, *71*, 163–169.
- Mitchell, M. J.; Driscoll, C. T.; Kahl, J. S.; Likens, G. E.; Murdoch, P. S.; Pardo, L. H. *Environ. Sci. Technol.* **1996**, *30*, 2609–2612.
- Murdoch, P. M.; Burns, D. A.; Lawrence, G. B. *Environ. Sci. Technol.* **1998**, *32*, 1642–1647.
- Watmough, S. A.; Dillon, P. J. *For. Ecol. Manage.* **2003**, *177*, 155–177.
- Schiff, S. L.; Devito, K. J.; Elgood, R. J.; McCrindle, P. M.; Spoelstra, J.; Dillon, P. J. *Water Resour. Res.* **2003**, *1292*; DOI: 10.129/2000WR00170.
- Devito, K. D.; Westbrook, C. J.; Schiff, S. L. *Can. J. For. Res.* **1999**, *29*, 1793–1804.
- Dillon, P. J.; Molot, L. A. *Biogeochemistry* **1990**, *11*, 23–43.
- Creed, I. F.; Band, L. E. *Water Resour. Res.* **1998**, *34*, 3079–3093.
- Park, J.; Mitchell, M. J.; McHale, P. J.; Christopher, S. F.; Meyers, T. P. *Global Change Biol.* **2003**, *9*, 1602–1619.
- Fitzhugh, R. D.; Likens, G. E.; Driscoll, C. T.; Mitchell, M. J.; Groffman, P. M.; Fahey, T. J.; Hardy, J. P. *Environ. Sci. Technol.* **2003**, *37*, 1575–1580.
- van Miegroot, H.; Creed, I. F.; Nicholas, N. S.; Tarboten, D. G.; Webster, K. L.; Shubzda, J.; Robinson, B.; Smoot, J.; Johnson, D. W.; Lindberg, S. E.; Lovett, G. M.; Novdin, S.; Moore, S. *Sci. World* **2001**, *1*, 480–492.
- Aber, J. D.; Ollinger, S. V.; Driscoll, C. T.; Likens, G. E.; Holmes, R. T.; Freuder, R. J.; Goodale, C. L. *Ecosystems* **2002**, *5*, 648–658.
- Monteith, D. T.; Evans, C. D.; Reynolds, B. *Hydrol. Process.* **2000**, *14*, 1745–1749.
- Arp, P.; Oja, T.; Marsh, M. *Can. J. For. Res.* **1996**, *26*, 696–709.
- Neary, A. J.; Gizyn, W. I. *Can. J. For. Res.* **1994**, *24*, 1089–1100.
- Ontario Ministry of Environment. *Handbook of analytical methods for environmental samples*; 1983.
- Dillon, P. J.; Dillon, P. J.; Lusis, M.; Reid, R.; Yap, D. *Atmos. Environ.* **1988**, *22*, 901–905.
- Reynolds, B.; Edwards, A. *Agric. Water Manage.* **1995**, *27*, 181–202.
- Cluis, D. A.; Langlois, C.; Van Coille, R.; Laberge, C. *Environ. Monit. Assess.* **1989**, *12*, 429–441.
- Brien, C. J.; Venables, W. N.; James, A. T.; Mayo, O. *Biometrika* **1984**, *71*, 545–554.
- Rusak, J. A.; Yan, N. D.; Somers, K. M.; McQueen, D. J. *Am. Nat.* **1999**, *153*, 46–58.
- Arnott, S. E.; Keller, B.; Dillon, P. J.; Yan, N.; Paterson, M.; Findlay, D. *Environ. Monit. Assess.* **2003**, *88*, 365–388.
- Eimers, M. C.; Dillon, P. J. *Biogeochemistry* **2002**, *61*, 337–355.
- Watmough, S. A.; Dillon, P. J. *Biogeochemistry* **2004**, *67*, 369–398.
- Dise, N. B.; Wright, R. F. *For. Ecol. Manage.* **1995**, *71*, 153–161.
- Dillon, P. J.; Molot, L. A.; Futter, M. *Environ. Monit. Assess.* **1997**, *46*, 105–111.
- Devito, K. D.; Hill, A. R.; Dillon, P. J. *Biogeochemistry* **1999**, *44*, 187–203.
- Foster, N. W.; Morrison, I. K.; Yin, X.; Arp, P. A. *Can. J. For. Res.* **1992**, *22*, 1753–1760.
- Birch, H. F. *Plant Soil* **1960**, *12*, 81–96.
- Kieft, T.; Srooker, E.; Firestone, M. *Soil Biol. Biochem.* **1987**, *119*, 119–126.
- Venterink, H. O.; Davidsson, T. E.; Kiehl, K.; Leonardson, L. *Plant Soil* **2002**, *243*, 119–130.
- Fitzhugh, R. D.; Groffman, P. M.; Tierney, G. L. *Biogeochemistry* **2001**, *56*, 215–238.
- LaZerte, B. D.; Scott, L. *Can. J. For. Res.* **1996**, *26*, 1353–1365.
- Devito, K. D.; Dillon, P. J. *Water Resour. Res.* **1993**, *29*, 2675–2685.
- Creed, I. F.; Band, L. E. *Water Resour. Res.* **1998**, *34*, 3105–3120.
- Lovett, G. M.; Rueth, H. *Ecol. Appl.* **1999**, *9*, 1330–1344.
- Driscoll, C. T.; Postek, K. M.; Kretser, W.; Raynal, D. J. *Water Air Soil Pollut.* **1995**, *85*, 583–588.
- Driscoll, C. T.; Driscoll, K. M.; Mitchell, M. J.; Raynal, D. J. *Environ. Pollut.* **2003**, *123*, 327–336.
- Goodale, C. L.; Aber, J. D.; Vitousek, P. M. *Ecosystems* **2003**, *6*, 75–86.

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