Regional Assessment of the Contribution of Rain-on-Snow Events to NO_3–N Export from a Forested Landscape

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ABSTRACT

Rain-on-snow (ROS) events have the potential to contribute significantly to nitrate (NO_3-N) export from forested catchments, but have received relatively little research attention. This study assesses the importance of ROS events for NO_3–N export across 18 catchments in South-Central Ontario that receive the same N deposition but encompass a range of physiographic characteristics. Winter (December to February) NO_3-N export was calculated from 1982 to 1987, a period of high sampling frequency across these catchments. Rain-on-snow events contributed a similar proportion of total winter NO_3-N export across all catchments, with a median proportion of 55% of winter NO_3-N export from ROS events. There was a considerable variation in the total magnitude of winter NO_3-N export from these catchments, ranging from 0.01 to 0.4 KG/KG/HA. Analysis of relationships between NO_3-N export and physiographic characteristics indicated that catchments with more till coverage, less wetland coverage and steeper slopes exported more NO_3-N than those with less till coverage, more wetland coverage and shallower slopes. This may be due to the capacity of catchments with the former characteristics to sustain hydrologic linkages with the stream channel during the winter. An analysis of one catchment over a longer time period (1976 to 2001) revealed that years with higher maximum winter temperatures had more ROS events than cooler winters ($p<0.001$, $r=0.69$). As climate projections for this region include increased winter temperatures and more winter precipitation falling as rain, ROS events may increase in the future, raising concerns about increased NO_3-N loading to surface water.

Keywords: rain-on-snow; nitrate; forested catchments; forest hydrology; winter

INTRODUCTION

Nitrate (NO_3–N) is generally considered to be the growth-limiting nutrient in temperate forests, and despite relatively high levels of NO_3–N deposition in eastern North America the majority of NO_3-N input is currently retained within forested catchments (Watmough and Dillon, 2004). There is concern, however, that the supply of NO_3–N will eventually exceed the demand of forests, resulting in increased NO_3–N leaching in discharge waters (Aber et al., 1989) and associated declines in pH and increases in aluminium concentrations (Driscoll, et al., 2003; Eimers, et al., 2007).

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Nitrate (NO_3N) is generally considered to be the growthlimiting nutrient in temperate forests and despite relatively high levels of NO_3N deposition in eastern North America the majority of NO_3N input is currently retained within forested catchments (Watmough and Dillon, 2004). There is concern, however, that the supply of NO_3N will eventually exceed the demand of forests, resulting in increased NO_3N leaching in discharge waters (Aber et al., 1989) and associated declines in pH and increases in aluminium concentrations (Driscoll, et al., 2003; Eimers, et al., 2007).

A number of studies have demonstrated that hydrology, climatic variation and physiography are important factors that help explain the often large spatial and temporal variability in $NO_{3-}N$ export among catchments within the same deposition zone. For instance, Christopher et al. (2008) reported that streamflow origin (primarily from shallow soil waters or from deeper till groundwater) accounted for differences in patterns of $NO_{3-}N$ export between catchments. Sebestyen et al. (2008) found that high $NO_{3-}N$ concentrations during winter storms could be attributed to a greater degree of hydrological connectivity between the riparian area and the stream. Schiff et al. (2002) found that differences in $NO_{3-}N$ export between two adjacent catchments in southcentral Ontario were due to groundwater patterns influenced by stratigraphy and hydraulic conductivity. Interannual differences in $NO_{3-}N$ export have been related to mean annual temperature, soil frost events and summer drought intensity (Mitchell et al., 1996; Murdoch, et al. 1998; Groffman et al., 2001; Watmough and Dillon, 2004)

Of the NO_3N that leaches from seasonally snowcovered forest catchments, the vast majority is lost during the spring melt period (Galloway et al., 1987; Mitchell, 2001). NO_3N concentrations in streams are also high during the winter months (December to February) and N cycling beneath the snow pack is receiving increased research attention as biotic retention of NO_3N is low during this season and projections for winter warming could affect precipitation patterns and snow cover (Campbell et al., 2004; Groffman et al., 2001). Specifically, winter rainonsnow (ROS) events have been shown to contribute to nutrient export in advance of spring melt (McLean et al., 1995). Eimers et al. (2007) found that ROS events accounted for up to 40% of annual $NO_{3-}N$ export and up to 90% of winter $NO_{3-}N$ export from a catchment in southcentral Ontario. They suggested that $NO_{3-}N$ in runoff from ROS events may be transported relatively conservatively to the stream due to fast runoff rates and limited interaction with subnivean soil. The importance of ROS events to $NO_{3-}N$ budgets may be especially pronounced in catchments where physiographic characteristics enhance this limited interaction.

The objective of this study was to determine the importance of ROS events for $NO_{3-}N$ export from 18 forested headwater catchments in the same region of southcentral Ontario. Intercatchment differences in such properties as slope, wetland coverage and extent of minor till (>1 m in depth) coverage allowed us to assess whether relationships exist between catchment physiography and ROS $NO_{3-}N$ export.

METHODS

Study area

The 18 headwater catchments used in this study are located in the MuskokaHaliburton district of southcentral Ontario, within a 50 km radius of Dorset, Ontario (45°13’N, 78°56’W). Details regarding catchment location and physiography can be found in Dillon et al. (1991) and Buttle and Eimers (in press), and catchment areas are given in Table 1. Streamflow and water chemistry from the catchments have been monitored by the Ontario Ministry of the Environment (OMOE), Dorset Environmental Science Centre (DESC) since the mid 1970s. The catchments lie within the Great Lakes St. Lawrence forest region and are largely covered by mixed hardwood forests dominated by sugar maple (*Acer saccharum*), 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 are common throughout the region and are dominated by white cedar (*Thuja occidentalis*), black spruce (*Picea mariana*), and tamarack (*Larix laricina*) (Watmough et al., 2004).

Table 1: Catchment areas, discharge and NO_3N concentration characteristics (19821987).

Basin[+]	Area (ha),	Mean ROS, event discharge (mm)	Mean ROS, event discharge/ Mean total winter discharge (%)	Maximum event stream [NO_3N] (ug/L)	Mean annual stream [NO_3N] (ug/L)
HP3	26.0	48.0	41.1	730.0	26.9
HP3A	19.6	50.7	41.6	805.0	46.2
HP4	119.1	33.0	30.2	381.0	23.6
HP5	190.5	45.0	37.7	1545.0	30.6
HP6	10.0	37.0	32.8	875.0	54.6
HP6A	15.3	43.4	41.9	298.0	4.0
PC1	23.3	44.4	41.0	386.3	13.4
RC1	133.6	38.6	32.2	365.0	25.9
RC2	27.0	43.3	37.6	235.0	11.2
RC3	70.5	47.8	35.0	277.0	25.4
RC4	45.5	44.3	34.1	385.0	26.2
DE5	30.0	41.9	41.7	400.0	1.7
DE6	21.8	48.6	43.1	448.0	3.3
DE8	67.0	52.3	45.8	448.0 7.3	
DE10	78.9	51.1	45.5	360	.0 4.1
CB1	59.7	37.5	39.9	280.0	12.0
CB2	123.6	43.7	41.1	270.0 14.1	
BC1	20.4	38.7	45.8	375.0	12.0

[+]Basins are identified according to the lake to which they drain. BC – Blue Chalk Lake, CB – Chub Lake, DE – Dickie Lake, HP – Harp Lake, PC – Plastic Lake, RC – Red Chalk Lake

Bedrock in this region is largely granitized biotite and hornblende gneiss, with some amphibolite and schist (Watmough and Dillon, 2003). Surficial geology ranges from exposed bedrock, thin till (< 1m thick) interrupted by rock ridges, to plains with continuous till cover 1 > 10-m thick (Devito et al., 1999)**.** The latter category was termed “minor till” by Jeffries and Snyder (1983). Low lying areas are often mantled by peat (Watmough and Dillon, 2003). Acidic brunisols and podzols are found in upland areas (Jeffries and Snyder, 1983), while poorlydrained areas have gleysols and organic soils (Jeffries and Snyder, 1983).

Rainonsnow events were identified in the winters (December 1 – February 28) of 6 years (1982 1987) at all 18 catchments. These years were selected for study because water chemistry sampling was conducted at a relatively high frequency across all catchments during this period. Stream NO_3-N concentrations during each winter were measured on average every 3.3 days, thus facilitating the assessment of NO_3-N export during ROS events which can have a short duration (mean length of 11.8 days during this period).

The climate in this region is temperate, with mean daily winter (December, January and February) temperatures ranging from 10.0°C to 5.8°C and total winter precipitation ranging from 177 mm to 340 1 1 mm. The study area receives relative uniform N deposition ranging between 6.4

and 11.4 kg of N haa , with approximately half this deposition in the form of NO_3–N (Watmough et al., 2004).

Identifying rainonsnow events

Rainonsnow events were identified using daily streamflows at each catchment outflow together with daily temperature and precipitation data from three meteorological stations in the region operated by the OMOE. When data from these stations were missing or questionable, they were supplemented with data from the Meteorological Service of Canada (MSC) station at Dorset.

The WINTER degreeday snowmelt model (Scheider et al., 1983) was used to estimate daily rainfall and snowmelt based on precipitation and temperature records for the study area. The model was calibrated against snow course data from the OMOE and tested against snow cover data from MSC stations in the study area. The model was found to provide realistic simulations of observed patterns of snow accumulation and loss in the region (see Buttle [submitted] for further details).

For each catchment, daily streamflow data for December 1 to February 28 were inspected for rapid increases in flow. When a peak in streamflow was observed, the rainfall, snowmelt and snow accumulation output from the WINTER model were consulted to determine if the peak was due to an ROS event. Additionally, daily snowfall/rainfall data from the Dorset MSC station and precipitation data from the nearest meteorological station were consulted to confirm the form of precipitation. Events in March were excluded because the major spring snowmelt usually begins at this time in this region, and our focus was on winter ROS events. Daily streamflow data were also used to determine the minimum daily flow for each of the study catchments during the winter period.

Stream water samples were analyzed for NO_3–N following standard methods (Ontario Ministry of the Environment 1983). Missing NO_3–N data were interpolated (e.g. Eimers et al., 2007) and NO_3–N export for each individual ROS event was calculated by summing daily NO_3N fluxes for the duration of each event hydrograph. Fluxes of NO_3–N were calculated for each winter season (December 1February 28) consistent with previous mass balance studies in the region (e.g. Watmough and Dillon, 2003).

One catchment (HP3) was selected to examine the relationship between winter temperature and ROS event frequency for 1976 – 2001, since it had the most continuous stream discharge record for this period. The streamflow record was separated into quickflow (QF) and delayed flow components using the Hewlett and Hibbert (1967) method. Quickflow is a measure of stormflow response to water inputs, and previous work has emphasized the importance of QF events for solute export from the DESC basins (e.g. Dillon et al., 1991, Hinton et al., 1997). Predicted depths of snowpack water equivalent, rainfall and snowmelt from the WINTER model were used to identify those QF events resulting from ROS inputs. The temperature record at the Harp Lake meteorological station was used to determine the maximum daily temperature for each winter during this time period.

Statistical analyses

Buttle and Eimers (in press) applied Principal Component Analysis (PCA) to physiographic characteristics of the DESC catchments, in order to derive Principal Components (PCs) which could be used as independent variables to explain intercatchment difference in streamflow metrics. PCA was applied with no rotation to the correlation matrix of physiographic variables (StatSoft 2000), and all PCs with an eigenvalue greater than 1 were retained. The first PC accounted for 40 % of the variation in the physiographic data, and was positively associated with the fractional coverage of thin till/rock ridges and peat in the catchments and negatively associated with mean catchment slope and fractional coverage of minor till (> 1 m in depth). Average winter NO_3–N export and average ROS NO_3–N export from each catchment for the 1982 – 1987 period were each regressed against each catchment's factor loading on PC1 (SysStat Software 2006), in order to examine whether export was related to catchment physiography. This approach was felt to be preferable to simple regression of export on individual catchment properties, since there was a significant association between many of the physiographic metrics for the DESC catchments (e.g. mean catchment slope and fraction of the catchment mantled by minor till cover).

RESULTS

Rainonsnow events, 1982 1987

ROS events occurred in each of the years from 19821987 at a frequency of 12/a (Table 2). The events ranged in size from 10.0 mm to 55.1 mm, with a median event size of 23.6 mm. The median temperature on days with ROS events was 3.3°C. Different catchments experienced slightly different frequencies and magnitudes of ROS due to variation in rainfall across the study region. The percentage of total winter precipitation attributable to ROS events ranged from 5.0 to 31.1% (Table 2), while the percentage of total winter runoff from ROS events ranged from 30.2 to 45.8% (Table 1). This agrees with the long term record (19762001) from one catchment (HP3) where ROS events accounted for between 0 and 34.2% of winter precipitation, and between 0 and 79.2% of winter runoff, suggesting that these study years were fairly typical.

Table 2: Characteristics of ROS events

	Median #of events	Median ROS rainfall (mm)	mm ROS/mm winter precipitation (%)	Average mean daily airtemperature (₀C)	Maximum mean daily air temperature (₀C)	MeanROS NO3Nexport (kg/ha)	Mean winter export (kg/ha)
1982	2	56.3	20.5	5.8	16.5	0.04	0.16
1983	2	57.9	21.2	9.0	12.5	0.19	0.23
1984	2	95.3	31.2	8.2	10.5	0.10	0.16
1985	1	11.8	5.0	10.0	9.5	0.01	0.07
1986	1	12.7	7.2	7.4	6.0	0.01	0.04
1987	1	17.9	5.3	8.1	7.5	0.04	0.13

NO_3 export during ROS events

The total magnitude of winter NO_3N export varied greatly across catchments, from 0.01 kg/ha/winter (DE5) to 0.4 kg/ha/winter (HP3A) (Figure 1a). There was also wide variation in NO_3– N export in ROS event runoff, from 0.01 kg/ha/winter (DE5) to 0.22 kg/ha/winter (HP3A) (Figure 1b).The contribution of ROS events to total winter NO_3–N export ranged from 36% to 86% (Figure 1c) greatly exceeding the proportion of winter precipitation from ROS. Despite the broad range of physiographic characteristics of these catchments, ROS events accounted for a similar proportion of total winter NO_3–N export, with all but one catchment falling within 1.5 standard deviations of a median proportion of export of 55% (Figure 1c).

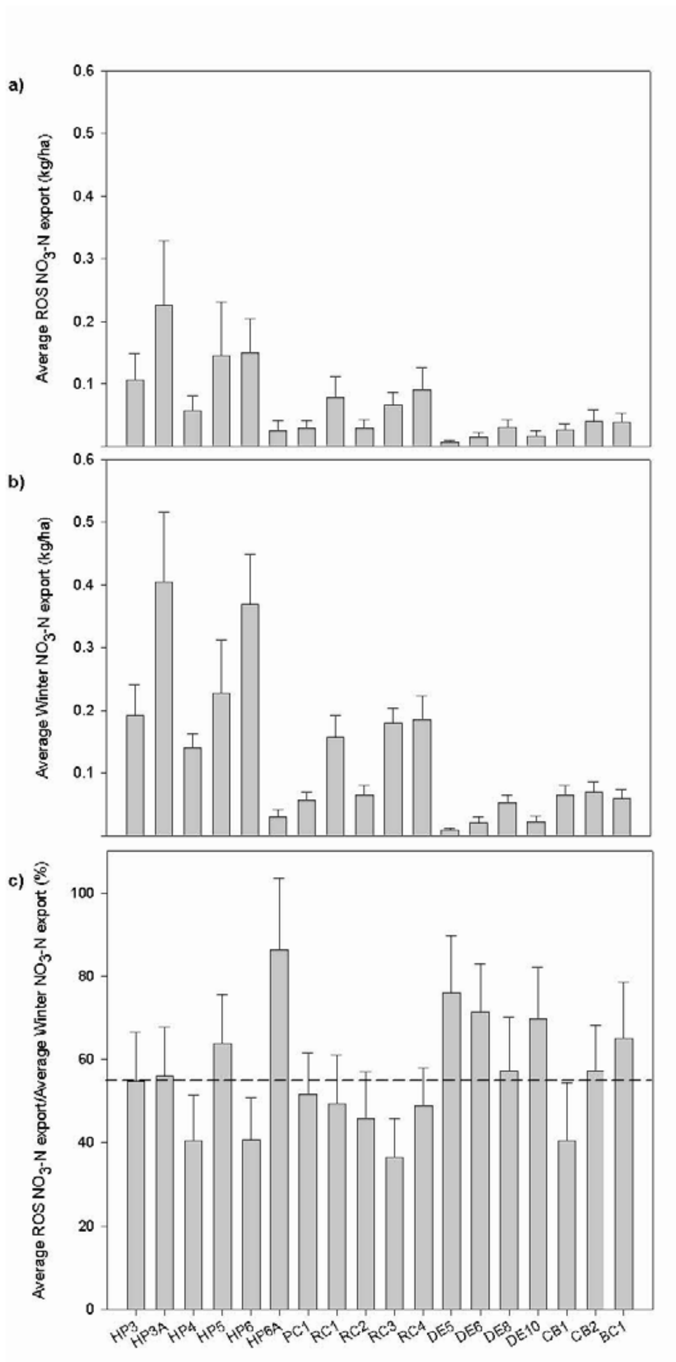

Figure 1. a) Mean (±SE) winter NO3N export from 19821987; b) Mean (±SE) ROS NO3N export from 19821987; c) Mean (±SE) proportion of winter NO3N export from ROS events from 1982 to 1987. The dashed line represents the median proportion of winter NO3N export from ROS events of 55%.

Spatial patterns in NO_3 export

Both winter total NO3–N export and ROS NO3–N export were significantly related to PC1 from Buttle and Eimers (in press) (r2=0.87, p<0.0001; r2=0.93, p<0.0001) (Figure 2a; Figure 2b). Catchments with greater till coverage, lower wetland coverage and steeper slopes exported greater

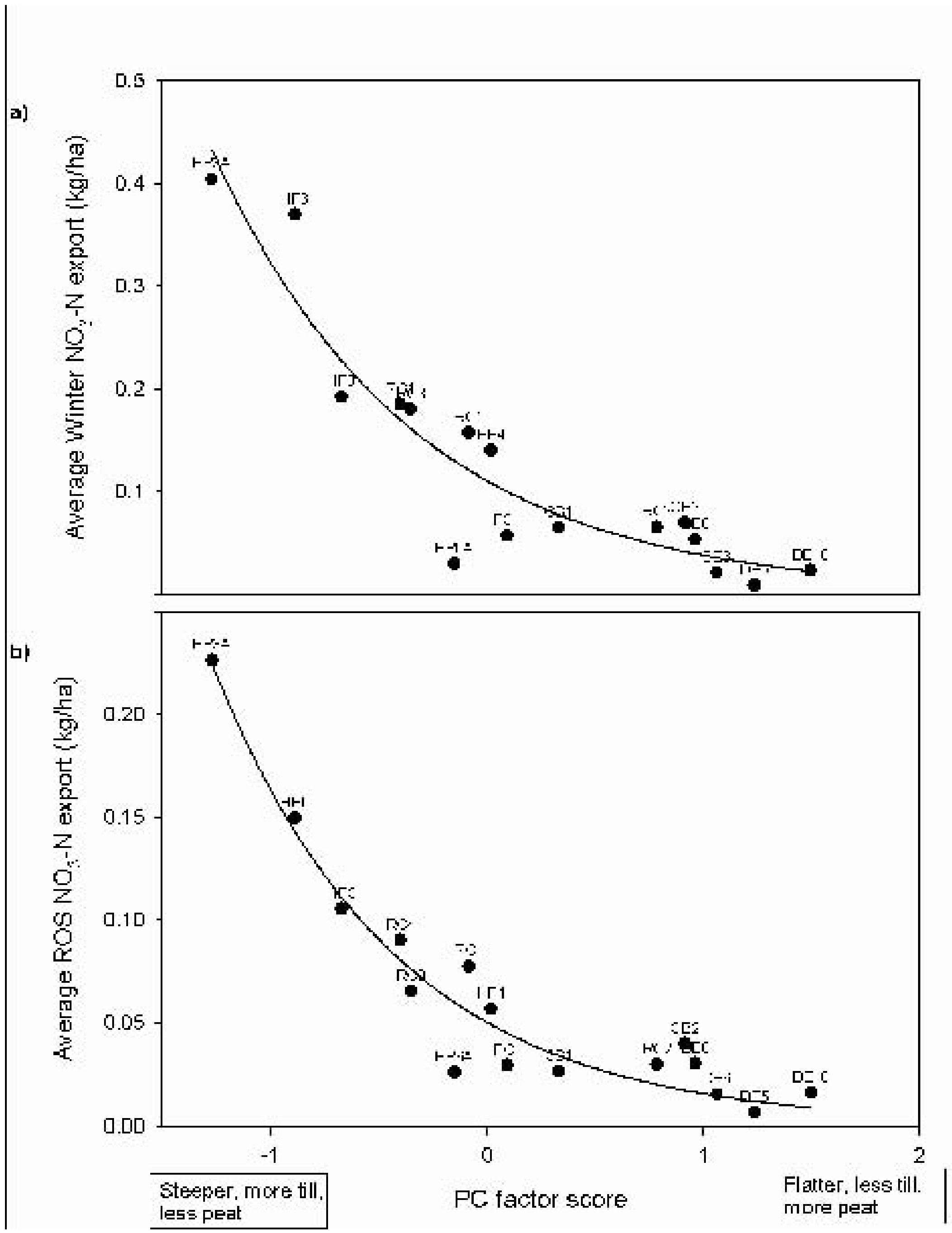

Figure 2: a) Average winter NO3N export (kg/ha) from 19821987 vs. PC factor score from Buttle and Eimers (2009) (r^2=0.87, p<0.0001, y=0.1105*exp(1.0739*x); b) average ROS NO3N export (kg/ha) from 19821987 vs. PC factor score from Buttle and Eimers (2009) (r^2=0.93, p<0.0001, y=0.0503*exp(1.1796*x). A more positive PC score indicates that the catchment is flatter, has less till and more peat, while a more negative PC score indicates that the catchment is steeper, has more till and less peat.

magnitudes of NO_3-N compared to those with less till, greater wetland coverage and shallower slopes. Two catchments (BC1 and HP5) were not included in this regression analysis. The PCA was based on catchment average values for the physiographic characteristics and supplementary data suggested that these values were not appropriate for these catchments. In the case of BC1, analysis of surficial geology maps and annual Ca export data suggest that the minor till fraction of this basin used in the PCA was an overestimate. In the case of HP5, the PC1 factor score was influenced by a high percentage of wetland cover. However, the wetlands in this large catchment are predominantly located in the headwaters, and thus may exert less of an influence over chemistry measured at the outflow than the total catchment fractional coverage of wetlands suggests.

There was a relationship between minimum daily winter flow and percent coverage of minor till greater than 1 m in depth ($r=0.62$, $p<0.001$) (Figure 3**)**. Minimum daily winter flow ranged from 0 mm (indicating that the stream dried up during the winter) to 0.4 mm. Catchments with greater minor till coverage had higher minimum daily winter flows

ROS event frequency

The discharge record for catchment HP3 (19762001) indicated there were between 0 and 5 winter ROS QF events/a. There was no significant temporal trend in the frequency of QF events produced by during this period ($p=0.09$) (Figure 4a); however, there was a significant relationship between the number of winter QF events produced by ROS in this catchment and maximum daily winter temperature at the HP meteorological station ($r=0.69$, $p<0.001$) (Figure 4b).

DISCUSSION

NO_3 export during ROS events

The proportion of winter NO_3-N export occurring during ROS events is relatively consistent across the catchments despite wide ranges in physical characteristics (Figure 1c). These results suggest that the findings of Eimers et al. (2007) can be generalized across this area and that ROS

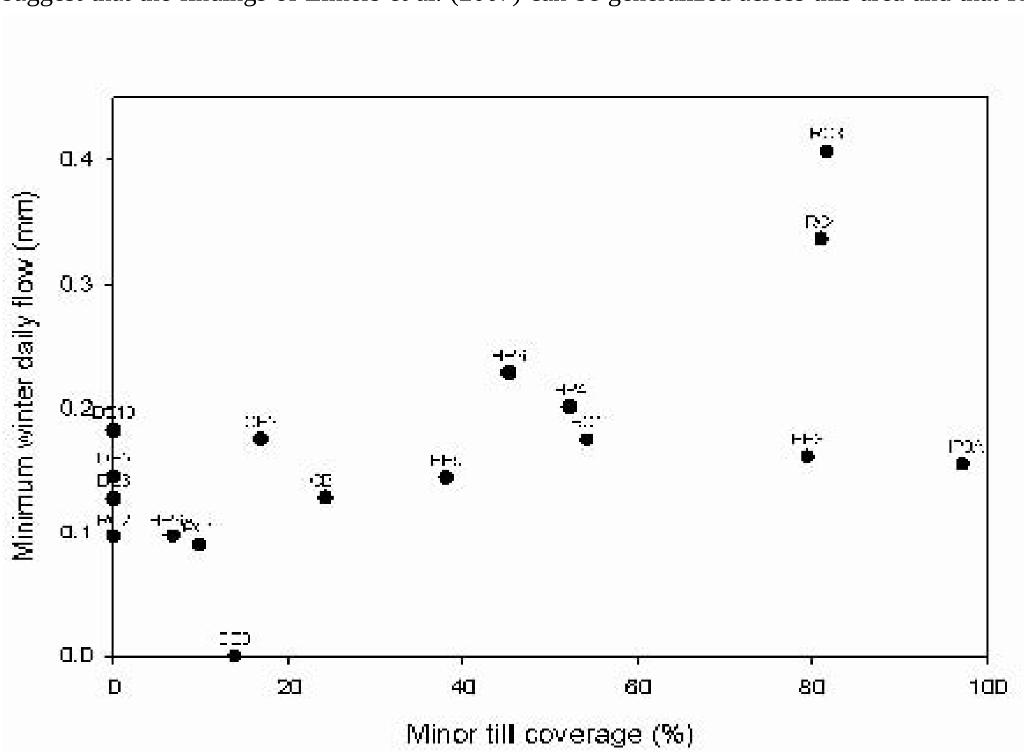

Figure 3**:** Minimum daily winter flow during the 1982 – 1987 period vs. minor till coverage in the study catchments ($r=0.62$; $p<0.01$).

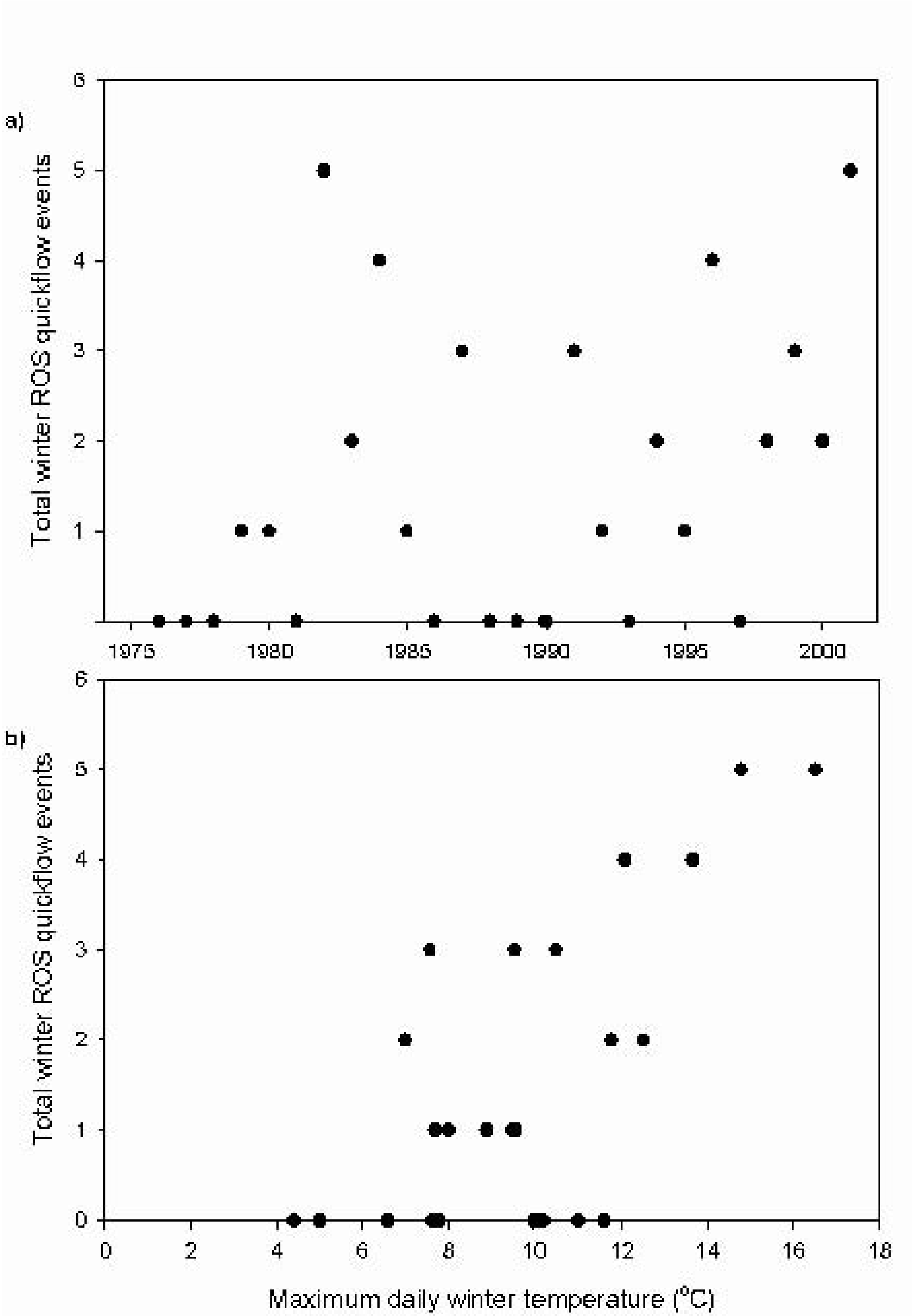

Figure 4: a) Time series of number of winter ROS quickflow events from HP3, 19762001 (p=0.09); b) number of winter ROS quickflow events from HP3 vs. maximum daily winter temperature (o C), 19762001 (r=0.69, p<0.001).

of ROS events, which constitute a modest proportion of total winter precipitation, cause a large proportion of total winter NO_3–N export.

There is also a large degree of synchronicity in the response of catchments to ROS events at the landscape scale. Years with high ROS rainfall tend to have both high ROS NO_3–N export and a high proportion of total winter NO_3–N from ROS events across catchments (Table 2). This suggests that physiographic characteristics do not influence the proportion of NO_3–N export contributed by ROS events. Rather, the landscape behaves in a similar manner despite differences in physiographic properties in response to climactic factors, suggesting that ROS events are important mechanism of NO_3–N export in this region.

Spatial patterns in NO_3 export

Although the proportion of winter NO_3–N due to ROS events is consistent across the landscape, the magnitude of total winter NO_3–N export and NO_3–N export during ROS events ranges widely between catchments. Differences in NO_3–N export from catchments receiving similar nitrogen (N) inputs have been observed in other studies (Schiff et al., 2002), and our results indicate that winter NO_3–N export can be explained in terms of catchment physiography. Catchments with steeper slopes, more till coverage and less wetland coverage have greater winter NO_3–N export. Eimers et al. (2007) argued that the similarity in NO_3–N concentrations in streamflow and incident rainfall or the accumulated snowpack in HP3A suggested that some NO_3–N in input water may be transported rapidly and conservatively into the stream channel with little interaction with catchment soil or biota. This is supported by isotopic analyses by Sebestyen et al., (2008), which indicate that some NO_3N seen in stream water is contained in snowmelt and ROS inputs to hillslopes that are rapidly routed to the stream channel. This conservative transport would likely be greatest in catchments with steep slopes such as HP3A, particularly near the catchment outflow. Catchments with greater proportions of till have been shown to maintain a more continuous hydrological linkage between upland areas and outflow streams (Devito et al., 1996). This is consistent with the association between winter minimum daily flows and the extent of minor till coverage in the DESC catchments (Figure 3). Catchments with little or no sustained flow during winter will export less NO_3–N overall. Thus, the Dickie (DE) catchments have less till coverage, low winter minimum flows and low total NO_3–N export (Figure 1; Figure 3). These catchments have relatively high proportions of total winter NO_3–N produced by ROS events (Figure 1c), since streamflow generation during the winter period and consequent opportunities for NO_3–N export are confined to ROS events. Conversely, catchments with higher minimum flows, such as the majority of the Harp (HP) catchments, not only export more NO_3–N during the winter but will establish hydrologic connectivity between slopes and streams more readily during periods of water input and thus have greater NO_3–N export during ROS events. Other studies have found that catchments with high proportions of wetland coverage tend to export less NO_3–N (Inamdar and Mitchell, 2006). Wetlands attenuate NO_3–N through biotic uptake by plants or microbes (Cirmo and McDonnell, 1997). Our results indicate that this behaviour may occur in the DESC catchments, since PC1 is positively associated with peat coverage in the catchments and NO_3–N export is negatively associated with PC1 (Figure 2). However, reduced biotic activity during winter relative to other seasons (Campbell et al., 2004) suggest that this factor is less significant than the role of catchment slope and till depth in controlling hydrologic connectivity and NO_3–N export.

These results also highlight the limitations of using catchment average physiographic characteristics for predicting nutrient effluxes in streams. Other studies have emphasized the importance of conditions close to the catchment outflow in determining NO_3–N export, especially during high flow events (Hill, 1990; Cirmo and McDonnell, 1998). In the present study, cases where a landscape element covered a high proportion of the catchment but was not dominant immediately upstream of the catchment outflow showed

anomalous NO_3–N export values and were excluded from the regression analyses. Predictions of nutrient export from the DESC catchments would benefit from data on the spatial patterns of physiographic properties within each catchment.

Climatic influences on ROS event frequency

One of the projected changes in climate in Central and Eastern Canada over the next 50 years is an increase in winter air temperatures (Barnett et al., 2005). Based on the past meteorological record, it is reasonable to expect that an increase in winter temperatures may result in more ROS events (Figure 4). Ye et al. (2008) also suggested that an increase in winter temperatures in Eurasia may cause an increase in the number of rain on snow events. An increase in precipitation falling as rain in the winter may lead to an increase in NO_3–N export, with the associated problem of episodic acidification of lakes and streams. NO_3–N, either from the snowpack, rainfall or catchment sources may be exported at high rates during these events since mechanisms involved in NO_3–N retention are likely at a minimum during winter compared with other seasons (Campbell et al., 2004). This issue deserves further study, since these results suggest that catchments with a range of physiographic characteristics in the DESC region are all prone to high NO_3–N export during ROS events and that the frequency of these events is related to winter temperature.

CONCLUSIONS

The proportion of winter NO_3–N export attributable to ROS events is consistent across basins with a range of physiographic characteristics. This suggests that despite the relatively dormant biological conditions during winter, interaction between ROS runoff and subnivean soil and/or biota leads to NO_3–N export from the catchments.

Marked differences in winter NO_3–N export exist between catchments despite similar N deposition patterns. This discrepancy may be due to physiographic and hydrologic factors within catchments such as slope and till depth. In addition, biogeochemical factors such as attenuation of NO_3–N by wetlands near catchment outflows may play a secondary role.

Warmer temperatures may cause more winter precipitation to fall as rain. The longterm record suggests that the frequency of ROS events increases with higher winter temperatures. This could lead to an increase in ROS NO_3–N export in the future, with associated episodic declines in stream pH.

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