Climatic Controls on the Dissolved Organic Carbon and Nitrate Export during Spring Snowmelt from Forested Catchments in South-Central Ontario

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ABSTRACT

Spring snowmelt is a major period of water and nutrient flux from forested catchments; the climatic conditions during the preceding winter can determine the chemistry and magnitude of that melt. The objective of this study was to determine the climatic controls on spring snowmelt dissolved organic carbon (DOC) and nitrate (NO_3-N) export. Low DOC concentrations were observed in years with increased spring runoff due to high winter snow accumulation and heavy spring rains ($p=0.01$, $r^2=0.25$). Spring NO_3-N concentrations were lower following winters with high maximum temperatures ($p<0.001$, $r^2=0.31$). Warm winters were also associated with a greater frequency of rain-on-snow events, which may successively deplete the snowpack pool of NO_3-N. Changes in climate are projected to be especially dramatic during the winter in this region, and therefore a thorough understanding of controls on biogeochemical and hydrological activity are important to project impacts on downstream surface water quality and quantity.

INTRODUCTION

The conditions during the preceding winter are critical for determining the timing and magnitude of the spring snowmelt (Brooks et al. 1999), the major period of water and nutrient export from seasonally snow-covered areas (Eimers et al. 2007; Eimers et al. 2009; Laudon et al. 2004). Over the winter, a combination of low biological activity and the accumulation of a snowpack result in a net seasonal retention of water and nutrients in the landscape (Jones 1999). Winter energy and precipitation inputs will determine the depth and persistence of the snowpack, which is both a pool of water and nutrients itself as well as a key determinant of soil temperature and moisture (Campbell et al. 2010). The melting of the snowpack in the spring causes high flows of water and large fluxes of nutrients in streams which drain from forests. The flowpaths and chemistry of this runoff are mediated by the topography of the catchment (Schiff et al. 2002; Christopher et al. 2008).

Climate projections for Ontario suggest that winter may be the time of year most impacted by warming trends with average winter temperatures in south-central Ontario increasing by 4–5°C by 2071–2100 compared with 1971–2000 (Colombo et al. 2007). Projections for changes in precipitation suggest that there may be a slight decrease in winter precipitation of less than 10% (Colombo

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et al. 2007). Temperature is perhaps a more critical determinant of winter hydrology and biogeochemistry compared with precipitation; Burns et al. (2007) found that warmer winter and spring temperatures helped to explain trends towards earlier snowmelt dates in the Catskill Mountains.

Winter-spring nitrate (NO_3-N) and dissolved organic carbon (DOC) may be particularly sensitive to perturbations in climate. For instance, mid-winter rain-on-snow (ROS) events have been shown to cause significant export of NO_3-N from forested catchments which can cause episodic acidification of surface waters and contribute significantly to seasonal and annual nutrient budgets (Casson et al. 2010; Eimers et al. 2007; Fitzhugh et al. 2001; Mitchell et al. 1996). Warmer winters tend to have more ROS events, likely because higher temperatures result in a higher proportion of winter precipitation to fall as rain compared with snow (Leung et al. 2004; Ye et al. 2008).

Dynamics of DOC export can be strongly influenced by the conditions of the spring snowmelt. Eimers et al. (2008) reported that annual average DOC concentrations were lower in years with higher spring runoff from wetland-dominated catchments due to a dilution effect. In upland-dominated catchments, DOC concentrations increase during spring melt due to flushing of surficial soils as the water table rises (Eimers et al. 2008; Sebestyn et al. 2008). Changes in spring snowmelt volume are primarily associated with changes in precipitation (Adams et al. 2009), thus it may be reasonable to expect changes in precipitation to affect DOC dynamics. Understanding the climatic controls on DOC and NO_3-N export is important for forecasting changes to nutrient dynamics under future climate change scenarios.

This study tested the hypothesis that variability in DOC and NO_3-N dynamics during spring snowmelt in forested catchments of south-central Ontario is related to variability in winter-spring climate. As such, the two objectives of this study were to a) determine patterns in winter-spring climate over the period of record for this area and b) examine the relationship between these climatic patterns and spring snowmelt DOC and NO_3-N concentrations and export.

METHODS

Study area

The six headwater catchments used in this study are located in the Muskoka-Haliburton district of south-central Ontario, within a 50 km radius of Dorset, Ontario (45°13'N, 78°56'W). These catchments within this region have been monitored for streamflow and water chemistry by the Ontario Ministry of the Environment (OMOE), Dorset Environmental Science Centre (DESC), since the mid 1970s (Figure 2). Details regarding catchment physiography can be found in Table 1. The catchments are part of the Great Lakes St. Lawrence forest region and are predominantly covered by mixed hardwood forests dominated by sugar maple (*Acer saccharum*), although white pine (*Pinus strobus*) is dominant in some areas. 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).

Bedrock in this region consists of granitic 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). 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 poorly-drained areas have gleysols and organic soils (Jeffries and Snyder 1983).

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 mm. The region is seasonally snow-covered, with the largest flux of water and nutrients in streams occurring during the spring snowmelt period (Eimers et al. 2007; Eimers et al. 2009). Annual runoff ranges from 0.2 to 0.9 m a-1 (Eimers unpublished data).
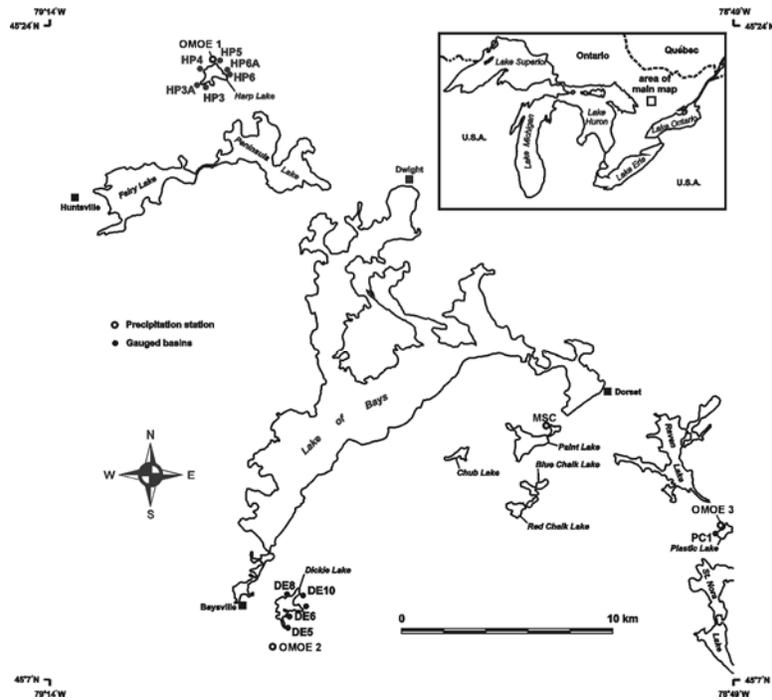
Figure 1. Study area.

Table 1 Characteristics of study catchments

Basin	Area (ha)*	Minor till (>1m deep) (%)*	Thin till, rock ridges (%)*	Peat (%)*	Pond (%)*
Harp (HP) 3	26	80	11	9	0
HP3A	19.6	97	0	3	0
HP4	119.1	52	36	8	3
HP6	10	45	45	10	0
HP6A	15.3	7	85	9	0
Plastic (PC) 1	23.3	11	79	10	0

* Adapted from Casson et al. (2010) with physiographic data from Buttle and Eimers (2009).

Meteorological data

Daily temperature (maximum, minimum and average) and precipitation data for the period from 1980–2002 were obtained from three meteorological stations in the region operated by the OMOE or from the Meteorological Service of Canada (MSC) station at Dorset when OMOE data were missing or questionable. For the period from 1950−1980, data were obtained from the MSC Haliburton station, located 50km south-west of Dorset. The data from Haliburton showed good agreement with the Dorset station for the period of overlap (1980−1992).

Hydrological data

Streamflow has been monitored continuously at each catchment outflow at a V-notch or H-flume weir since the late 1970s, and flow data were available for the six study catchments from 1980 to 2002. Seasonal discharge was calculated for winter (December–February) and spring (March–May); annual discharge was calculated from June-May. The streamflow data were extended back in time by developing relationships between catchment flow and Water Survey of Canada data from the North Magnetawan monitoring station. The relationships were used to model discharge for the period from 1950−1980.

Rain-on-snow events were identified in the winters (December 1–February 28) from 1980−2002 at all 6 catchments 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 or from the Meteorological Service of Canada (MSC) station at Dorset when OMOE data were missing or questionable. For the period from 1950−1980 where catchment discharge was not available, ROS events were conservatively defined as days during January and February (by which time there likely would be a developed snowpack) with precipitation greater than 3mm where the maximum temperature was greater than $0^{\circ}C$.

Chemistry data

Grab stream water samples for chemical analysis were typically taken weekly to biweekly at the catchment outlet, and streams were sampled more frequently during periods of high discharge. DOC and NO_3-N in stream water samples were determined colourimeterically (Ontario Ministry of the Environment 1983). DOC and NO_3-N export were calculated using the 'mid-point method' (Scheider et al. 1979; Jeffries et al. 1988), where the nutrient concentration on days with no measurement is estimated as being the same as the concentration on the closest sampling day. The nutrient concentration is then multiplied by the daily stream flow to estimate daily nutrient export. Fluxes of DOC and NO_3-N were calculated annually and for winter and spring consistent with previous mass balance studies in the region (e.g., Watmough and Dillon 2003).

Climate projections

Climate projections based on the CRCM V4.2 monthly data (aet run), generated and supplied by the Ouranos Climate Simulation Team via CCCma's data distribution Web page (Music and Caya 2007), were used to calculate trends in precipitation, temperature and runoff from 2000 to 2099. The values are downscaled to a $45m^2$ grid; the grid cell which encompasses the Dorset area was used. Monthly data were summed up to seasonal and annual values.

Data analysis

Time trends in seasonal and annual temperature, precipitation, runoff and volume-weighted DOC and NO_3-N concentrations were evaluated using the Mann-Kendall test. Relationships between climatic variables, runoff and DOC concentrations and NO_3-N fluxes were evaluated using linear regression at a significance level of $\alpha=0.05$ (SigmaStat, SYSTAT; Systat Software Inc.).

RESULTS

Temporal trends

Winter minimum and average temperatures as well as annual minimum and average temperatures increased significantly between 1950 and 2006 (Table 2). The minimum annual temperature occurred during the winter in all but two years, so these trends in temperature minima are equivalent. There were no significant trends in spring temperature; however there was a slight decreasing trend in spring precipitation. There were no significant trends in discharge over time (Table 2).

Climate projections suggest significant increasing trends in temperature over the next century, and that these increases will be of approximately the same magnitude in the winter, spring and annually (Table 2). Precipitation was also projected to increase in the winter and spring as well as
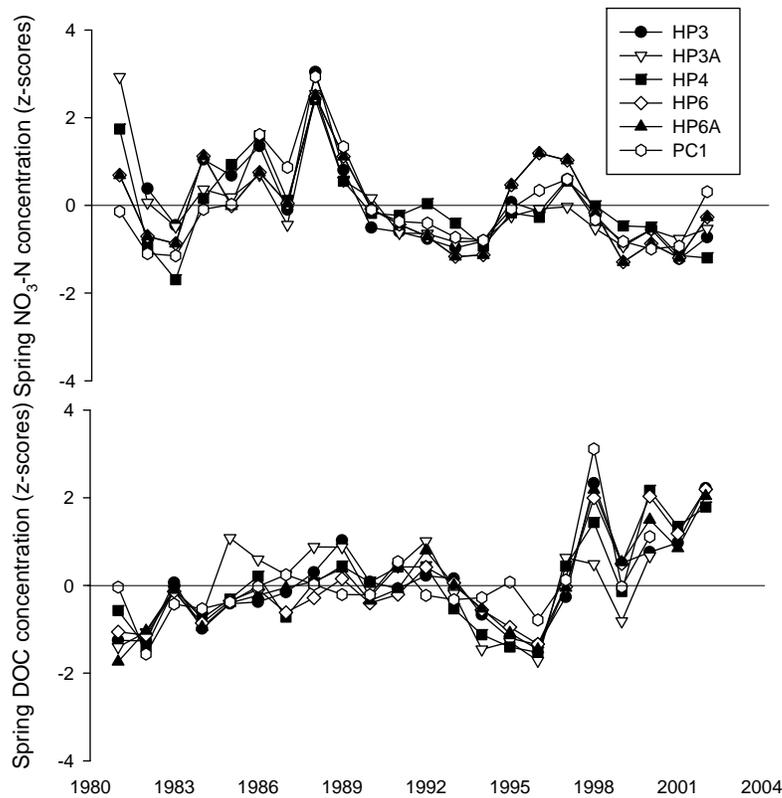
Figure 2. Spring volume-weighted a) NO$_3$-N concentrations and b) DOC concentrations at six study catchments.

annually, and winter runoff is projected to increase, but there were no projected changes in spring or annual runoff (Table 2).

Patterns in spring NO$_3$-N concentrations were relatively coherent across the study catchments, and there were no trends between 1980 and 2002 (Figure 2a). Patterns in spring DOC concentrations were not as coherent across catchments as NO$_3$-N, and similarly did not change significantly over time; although there was some suggestion that the DOC concentrations may be increasing at sites with high DOC, especially over the last 15 years of the record (Figure 2b).

Table 2 Annual rate of change (unit year^{-1}) of climate and runoff metrics obtained by the Mann-Kendall test. One asterisk indicates the slope is significant at α=0.05; Three asterisks indicate the slope is significant at α=0.001

	Historical data				Climate projections			
	Period	Winter	Spring	Annual	Period	Winter	Spring	Annual
Minimum Temperature (^{o}C)	1950-2006	+ 0.12 ***	+ 0.05	+ 0.13 ***	2000-2099	+ 0.07 ***	+ 0.07 ***	+ 0.07 ***
Average Temperature (^{o}C)	1950-2006	+ 0.03 *	+ 0.02	+ 0.02 ***	2000-2099	+ 0.06 ***	+ 0.05 ***	+ 0.06 ***
Maximum Temperature (^{o}C)	1950-2006	- 0.01	+ 0.05	+ 0.01	2000-2099	+ 0.05 ***	+ 0.04 ***	+ 0.04 ***
Precipitation (mm)	1950-2006	+ 0.30	- 0.17 *	+ 1.32	2000-2099	+ 0.94 ***	+ 0.84 ***	+ 1.83 ***
Discharge (mm)	1976-2002	+ 0.55	+ 0.21	+ 0.73	2000-2099	+ 0.85 ***	+ 0.08	+ 0.17
% annual discharge	1976-2002	+ 0.86	+ 0.00		2000-2099	+ 0.16 ***	+ 0.32 ***	

Spring runoff and DOC trends

There were significant positive relationships with the maximum monthly spring runoff and both the sum of January-February precipitation from the preceding winter (p=0.01, r^2=26) as well as the sum of March-April precipitation (p<0.001, r^2=0.57). The best predictive relationship was with the sum of precipitation from January to April (p<0.001, r^2=0.73, Figure 3a). For both a representative upland-dominated catchment (HP3A) and a representative wetland-dominated catchment (HP6A), there were significant negative relationships between the sum of precipitation from January to April and spring DOC concentrations, although the relationship was stronger at HP6A (HP3A: p=0.04, r^2=0.18, Figure 3b; HP6A: p=0.01, r^2=0.25, Figure 3c).
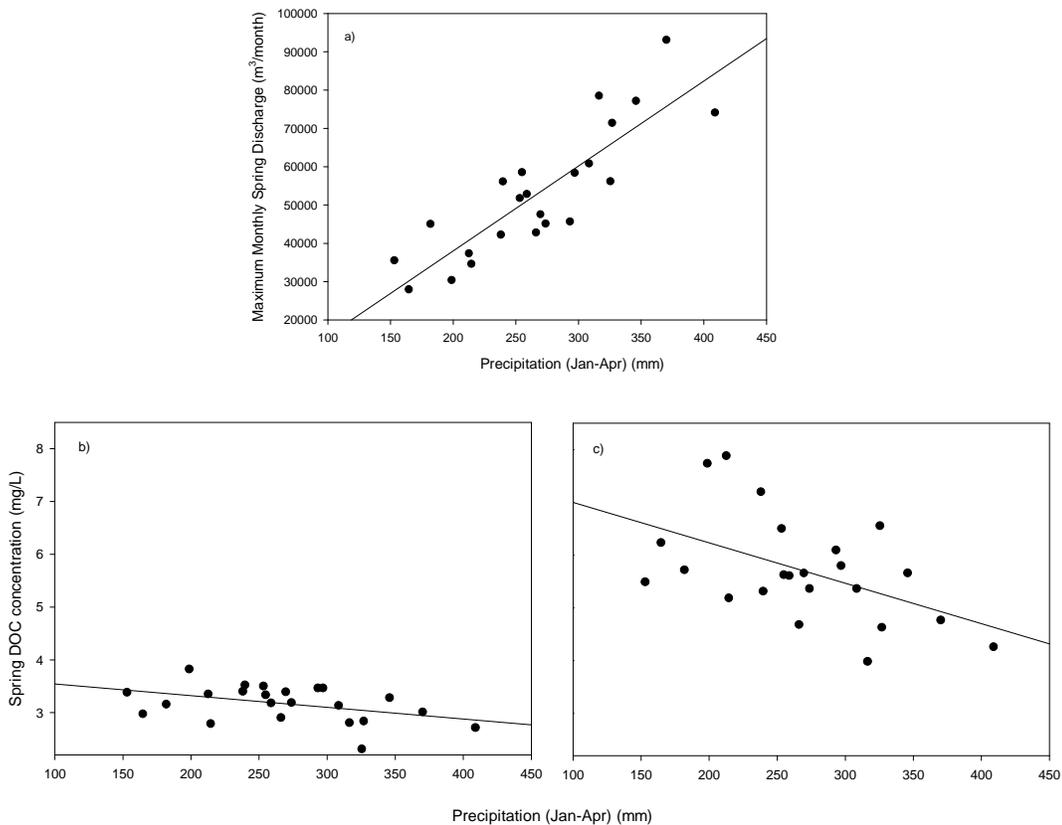
Figure 3. a) Sum of precipitation from January to April vs. maximum monthly spring discharge from eight study catchments from 1980 to 2002; b) Sum of precipitation from January to April vs. spring DOC concentrations from an upland-dominated catchment (Harp 3A) from 1980 to 2002; c) Sum of precipitation from January to April vs. spring DOC concentrations from a wetland-dominated catchment (Harp 6A) .from 1980 to 2002.

Temperature and NO_3-N trends

   In winters with higher maximum temperatures, there were a greater number of ROS events (p=0.001, r^2=0.40, Figure 4a). Higher winter maximum temperatures were also significantly related to higher proportions of annual NO_3-N flux occurring during the winter (p<0.01, r^2=0.39, Figure 4c) and lower proportions of NO_3-N during the spring (p<0.01, r^2=0.31, Figure 4b). These patterns were coherent across all catchments, regardless of topography. The higher temperatures were associated with higher winter discharge (p<0.001, r^2=0.42), but there was no significant relationship between temperature and spring discharge (p=0.63).
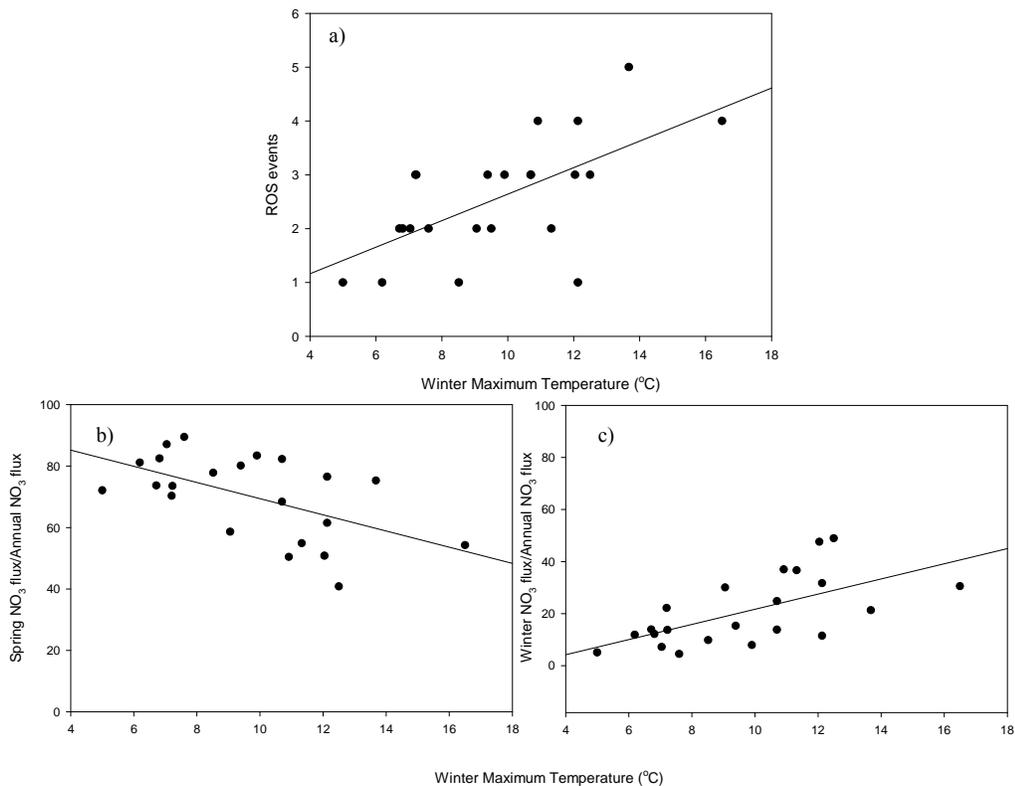
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Figure 4: a) Winter maximum temperature vs. number of rain-on-snow events from eight study catchments from 1980 to 2002; b) Winter maximum temperature vs. proportion of annual NO_3-N flux occurring during the spring from a representative catchment (Harp 3A) from 1980 to 2002; c) Winter maximum temperature vs. proportion of annual NO_3-N flux occurring during the winter from a representative catchment (Harp 3A) from 1980 to 2002

Climate controls on spring DOC concentrations

The magnitude of spring runoff is a function of both winter and spring precipitation (Figure 3). In January and February, most of the precipitation occurs in the form of snow, while March and April have mostly rainfall. Therefore, higher spring melt volumes occur in years when there is high snow accumulation over the year followed by lots of spring rainfall. There were no significant relationships between temperature metrics and spring runoff; however, higher winter temperatures may lead to reduced snow accumulation in forested catchments, which would ultimately lead to lower spring runoff (Campbell et al. 2010).

The accumulation of snow over the winter can also have biogeochemical effects on spring DOC concentrations. Previous work in this area has established a relationship between higher spring runoff and lower DOC concentrations in wetland-dominated catchments, due to a limited pool of flushable DOC from the peatlands and a subsequent dilution effect (Schiff et al. 1998; Eimers et al. 2008). This relationship does not exist as strongly at upland-dominated catchments, perhaps because DOC concentrations do not demonstrate this dilution effect (Laudon et al. 2004; Eimers et al. 2008; Sebestyn et al. 2008). Rather, DOC concentrations peak during peak spring flow, as there are pools of DOC in upper layers of mineral soil, derived from over-winter decomposition, which are continually flushed as snowmelt progresses and the contributing area increases (Sebestyn et al. 2008). In this study, a relationship between spring runoff and spring DOC concentrations was

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shown in both wetland- (HP6A) and upland-dominated (HP3A) catchments (Figure 3). The pattern in HP6A is consistent with a dilution mechanism explanation. The increased DOC concentration in HP3A with increased spring runoff may be due to increased rates of over-wintering microbial processes (e.g. decomposition) and therefore larger pools of flushable carbon in the soil.

Climate controls on spring NO_3-N fluxes

The proportion of precipitation falling as rain during the winter is a function of temperature (Ye et al. 2008). Warmer winters will also have thinner snowpacks (Campbell et al. 2010); however in this region, neither historical snowpack data (Buttle 2009) nor climate projections (Table 2) suggest that snowpacks of sufficient depth to decouple soil and air temperatures occur in every winter. Thus, higher winter temperatures are associated with an increased frequency of ROS events

Rain-on-snow events are responsible for both increased winter NO_3-N flux and increased winter discharge. However, these events account for only up to ~40% of winter discharge, but up to ~90% of winter NO_3-N flux (Eimers et al. 2007; Casson et al. 2010). This may be because storm runoff is composed of a high proportion of snowpack meltwater or rain which reaches the catchment outlet without much interaction with forest soils. As these two sources of water are high in NO_3-N in this region due to high rates of deposition (Watmough et al. 2004), the resulting storm runoff can have a high concentration of NO_3-N (Eimers et al. 2007; Casson et al. 2010). In addition, NO3-N is preferentially eluted from the snowpack during the early stages of melt (such as during mid-winter melts), which may also contribute to high NO_3-N concentrations during these events (Sickman et al. 2003) These events do not contribute as significantly to DOC export, perhaps because the concentrations of DOC in the rain and snowpack are relatively low (Casson, unpublished data).

This study suggests that warmer temperatures, associated with in more ROS events are related to increased winter NO_3-N flux, but decreased spring NO_3-N flux. Winter rain events deplete the accumulated snowpack stores of NO_3-N resulting in lower fluxes of the nutrient in the following spring. Although part of this is due to simply increased winter discharge from these events, warmer winters were not significantly related to decreased spring snowmelt volumes. This, combined with the high concentrations of NO_3-N in storm runoff, suggest that depletion of the NO_3-N pool during a warmer winter is a likely mechanism for decreased spring NO_3-N flux.

Climate projections

Climate projections for south-central Ontario indicate that winter temperature and precipitation will increase over the next century. This could have important implications for spring snowmelt chemistry. Warmer winters may result an increased frequency of ROS events, with more winter pulses of NO_3-N and ultimately lower spring NO_3-N fluxes. There is no projected change in spring runoff volume, likely because snow accumulation is projected to decrease with winter warming, despite projected increases in both winter and spring precipitation (Campbell et al. 2010). This may mean that the climate effects on spring snowmelt DOC dynamics will not be as acute as the effects on snowmelt NO_3-N dynamics. Changes in snowpack dynamics and the relative proportion of winter precipitation occurring as rain vs. snow will affect future spring snowmelt chemistry; a thorough mechanistic understanding of how climatic changes affect NO_3-N and DOC dynamics is important for predicting these changes.

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