

Winter-Time Climatic Control on Dissolved Organic Carbon Export and Surface Water Chemistry in an Adirondack Forested Watershed

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Although most of forested watersheds in temperate and boreal regions are snow-covered for a substantial portion of the year, responses of biogeochemical processes under the snow pack to climatic fluctuations are poorly understood. We investigated responses of dissolved organic carbon (DOC) and surface water chemistry in stream and lake discharge waters draining the Arbutus Lake Watershed in the Adirondacks of New York State to climatic fluctuations during the snow-covered months from December through April. Interannual variability in stream discharge corresponded to changes in air temperature and snow pack depth across the winter months. Concentrations of DOC in stream water draining a subcatchment showed immediate positive responses to rising temperatures and subsequent increases in runoff during most snowmelt events. Increases in DOC concentrations usually coincided with decreases in pH and increases in total aluminum (Al) concentrations, while the correlations between concentrations of DOC and SO_4^{2-} or base cations were negative. Although changes in air temperature, snow pack depth, and runoff were all significantly correlated with stream water concentrations of major solutes, stepwise linear regression found that runoff was the best predictor of solute concentrations. Results of stepwise linear regression with long-term monthly monitoring data collected at the lake outlet showed weaker but still consistent climatic effects on interannual variations in concentrations of DOC and other solutes. Over the 17 winter periods from December 1983 through April 2000, changes in seasonal average concentrations of DOC, H^+ , and Al in lake discharge generally corresponded to interannual variations in temperature, precipitation, and runoff, while SO_4^{2-} and base cations displayed an opposite trend. The results suggest that snowmelt-mediated DOC responses to temperature fluctuations during the winter months might offset increases in the surface water pH caused by decreasing acidic

deposition and pose a potential hazard of Al toxicity in surface waters.

Introduction

Although dissolved organic carbon (DOC) export from terrestrial ecosystems is relatively small as compared to global pools and fluxes of C in plants and soils (1, 2), the DOC of terrestrial origin is believed to play an important role in surface water acidification (3), metal binding and transport (4), and C turnover processes due to its labile properties (5, 6) in aquatic environments. Some recent studies have linked long-term changes in DOC concentrations in surface waters to climatic warming (7, 8). While a declining trend in DOC export from some Canadian watersheds has been ascribed to decreased discharge caused by warming (7, 9, 10), warming-induced increase in DOC production has been suggested to have enhanced DOC export from British upland watersheds over the past decade (8). Significant increases in surface water DOC concentrations have also been observed for some Adirondack lakes that are part of the Long-Term Monitoring project over the last two decades (3).

Unlike patterns observed for the production and transport of DOC during the growing season, little is known about responses of watershed DOC export to interannual variations in winter-time climatic fluctuations. Considering the well-known hydrologic flushing of DOC during the spring snowmelt in alpine watersheds (11, 12), the interplay between changing air temperatures and runoff responses might be an important regulator of DOC export during episodic snowmelt events in winter months for watersheds in warmer temperate regions. To date, efforts for understanding climatic impacts on biogeochemical processes under the snow pack have largely been focused on the role of soil freeze/thaw cycles in element fluxes to streams (13–15). Our previous analyses on long-term trends in NO_3^- export from an Adirondack forested watershed showed that winter-time temperature fluctuations played a key role in interannual variations in NO_3^- export (16).

The Arbutus Lake Watershed in the Adirondack Mountains of New York State has been the site of long-term biogeochemical monitoring including micrometeorological measurements since 1940 and surface water chemistry monitoring since 1983 as part of Adirondack Long-Term Monitoring project (3, 17). We investigated short- and long-term responses of DOC concentrations in stream and lake discharge waters to climatic fluctuations during winter to obtain a better understanding of DOC responses to changing climate. We also examined implications of changing stream water DOC concentrations for surface water chemistry during episodic snowmelt events by analyzing concomitant responses of pH and major anions (NO_3^- and SO_4^{2-}) and cations (Al and base cations).

Materials and Methods

Study Site. The Arbutus Lake Watershed is located within the Huntington Wildlife Forest (43°59'N, 74°14'W) in the Adirondack Mountains of New York State, with elevations ranging from 513 to 748 m. The mean annual temperature and total annual precipitation averaged 4.8 °C and 1080 mm from 1981 to 2000, respectively. The watershed has an area of 352 ha including the Arbutus Lake, which has a surface area of 50 ha, a maximum depth of 8.4 m, and a hydrological retention time of 0.6 year (17, 18). The Archer Creek subcatchment (135 ha) represents the major inflow of water

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(≈40%) to the Arbutus Lake. The overstory vegetation in the upper slopes is comprised of mixed northern hardwoods consisting of American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*), red maple (*Acer rubrum*), yellow birch (*Betula alleghaniensis*), and white pine (*Pinus strobus*). Lower slopes adjacent to the lake margins are often dominated by conifer stands composed of eastern hemlock (*Tsuga canadensis*), red spruce (*Picea rubens*), and balsam fir (*Abies balsamea*). The surficial geology consists of thin to medium deposits of glacial till with a high sand content, while the bedrock geology is largely composed of igneous rocks with some calcium-rich minerals (18). The wetland located in valley bottom is a palustrine peatland (Greenwood Mucky peats) and comprises only 4% of the whole subcatchment area, which is typical in many watersheds in the Adirondacks (19).

Sampling and Laboratory Analysis. The Archer Creek subcatchment has been gauged since October 1994 for stream discharge near the lake inlet using an H-flume, which is a hybrid between a weir and a flume that forces water through a modified v-notch. Readings from a pressure transducer of water depth were converted to discharge based on a calibrated rating curve. Since the initiation of the monitoring, water samples have been taken weekly from the stream draining into the lake inlet and analyzed for pH, major anions and cations, and total dissolved N, while analysis of DOC started in May 1999. Following collection, water samples in opaque, brown polyethylene bottles were refrigerated in the field and during the transport until analyzed following storage at 1 °C at the Biogeochemistry Laboratory at SUNY–ESF. For DOC analysis, subsamples were filtered using a precombusted glassfiber filter (Whatman GF/F). Acidified filtrates were measured for DOC using UV-enhanced persulfate oxidation followed by infrared detection of CO₂ on a carbon analyzer (Phoenix 8000, Tekmar, Mason, OH). A potassium phthalate solution was used as a standard, and an external DOC standard (Organic Carbon Standard 1000 ppm, LabChem, Pittsburgh, PA) was used for QC purposes. Major anions including NO₃⁻, SO₄²⁻, and Cl⁻ were analyzed using ion chromatography (DX-120, Dionex, Sunnyvale, CA). Inductively coupled plasma (ICP) spectrometry (FMA-03, Spectro Analytical, Marlborough, MA) was used for analyzing Ca²⁺, Mg²⁺, and total Al. For all analytes, concentrations below the detection limits were replaced by half of each detection limit value.

The surface water chemistry of the Arbutus Lake has been monitored on a monthly basis by the Adirondack Long-Term Monitoring (ALTM) program since February 1983 (3, 18). For most analytes, similar analytical methods were used except that the ALTM program includes measurements of acid neutralizing capacity (ANC) and different species of Al (monomeric Al: Al_m; organic, monomeric Al: Al_{om}; and inorganic, monomeric Al: Al_{im}). Further details on analytical methods can be found elsewhere (18).

Data Processing and Statistical Analysis. Air temperature data were obtained from a National Weather Service station close (6 km) to the watershed (Newcomb, Essex County; elevation: 506 m). Since only minimum and maximum values were available, the mean daily air temperature was computed as the average of the maximum and minimum daily values (20). Measurements of precipitation and snow pack depths were obtained from the long-term meteorological monitoring at the Huntington Wildlife Forest site since the early 1940s on a daily basis by Adirondack Ecological Center staff.

Pearson correlation coefficients and stepwise linear regression were used to evaluate significant relationships between surface water chemistry and climatic variables (SYSTAT, version 9). Statistical analyses were conducted with measured concentration data and daily weather data from each sampling day for the subcatchment study, while mean

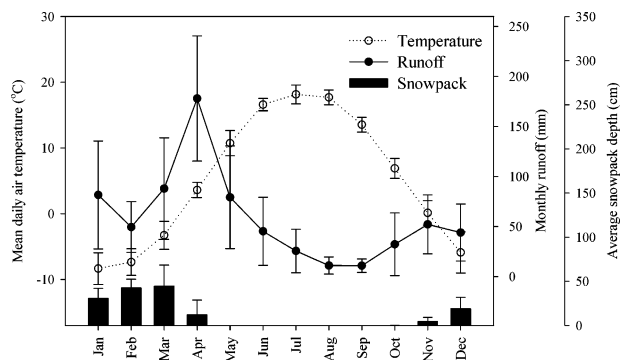


FIGURE 1. Monthly patterns in air temperature, runoff, and snowpack depth over the years 1995 through 2002 (mean ± SD, n = 8).

seasonal values of climatic, hydrological, and solute variables were used in the analyses of long-term monitoring data collected at the lake outlet. To compare interannual variations in solute concentrations at the lake outlet with those of climatic and hydrological variables at the same scale, we also transformed winter averages of each variable to Z-scores so that the transformed values have the mean of 0 and the standard deviation of 1. At the study site, snow usually starts to accumulate on the ground between late November and early December and the spring snowmelt continues until late April. We define winter months as being the snow-covered period from December to April. We did not consider the early winter in November in our definition of the snow-covered period because during this period, small amounts of snow, in combination with frequent melting events, do not allow stable snow packs to form. In addition, DOC leaching from freshly fallen litter often peaks between late autumn and early winter in temperate deciduous forests (21), which might confound our analysis of DOC relationships during the winter.

Results and Discussion

Winter Climatic Control on Hydrologic DOC Transport.

Over the eight years from 1995 through 2002, in which an intensive monitoring program was conducted in the Archer Creek subcatchment, stream discharge during the winter months spanning December through April represented on average 63% of annual discharge (Figure 1). As compared to other months, the winter months displayed large interannual variations in stream discharge, corresponding to a large variability in air temperature and snow pack depth. For the winter months over the same period, monthly averages of mean daily air temperature (T_{av}) showed a strong positive correlation with monthly runoff ($r = 0.65$, $p < 0.001$) and an inverse correlation with average snow pack depth ($r = -0.45$, $p < 0.01$), indicating a coupling between temperature fluctuations and snowmelt responses.

DOC concentrations in stream water draining the subcatchment generally showed a synchronized response to fluctuations of temperature and runoff during winter months (Figure 2). Although the weekly sampling scheme did not allow us to capture the fine scale temporal dynamics of the snowmelt response of DOC, DOC concentrations significantly increased on the several consecutive days with above-freezing temperatures and increased runoff, even before major spring snowmelt events. DOC concentrations in stream water showed a positive correlation with T_{av} for the entire study period (May 1999 to April 2002), largely due to generally higher DOC concentrations in the growing season than in the colder seasons (Table 1). However, stronger correlations with temperature (positive), runoff (positive), and snow depth (negative) were found for winter months. Stepwise multiple regression selected runoff, snow pack depth, and minimum

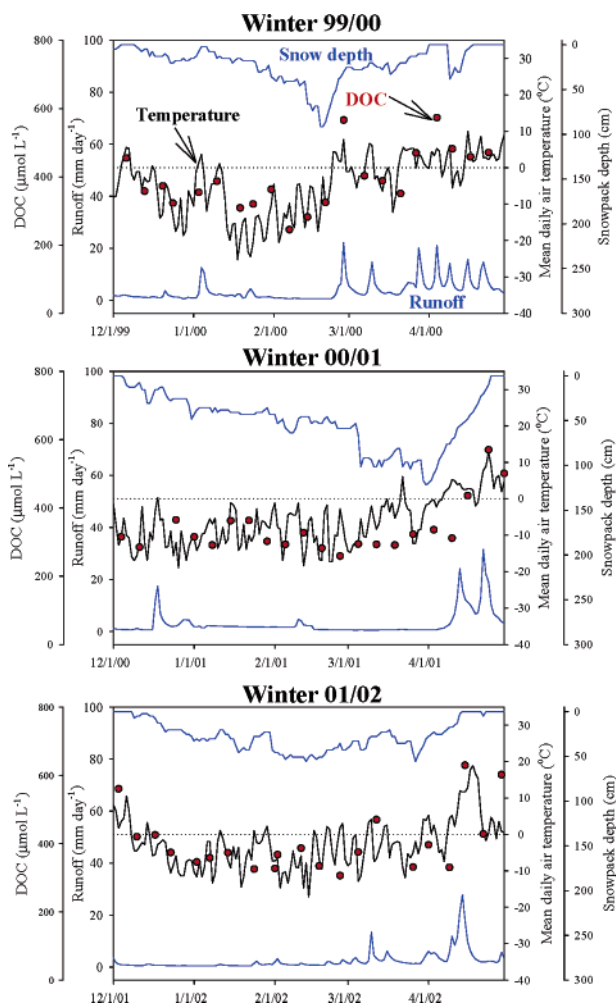


FIGURE 2. Responses of DOC concentrations in stream water draining the Archer Creek subcatchment to changes in average daily air temperatures, snow pack depth, and runoff during the winter months from December 1999 through April 2002. Dotted line indicates reference temperature (0 °C) for snowmelt. Note that the axis of snow pack depth has an inverted scale.

daily temperature (T_{\min}) as significant predictors of DOC concentrations (Table 2), implying a link between snowmelt response to temperature fluctuations and hydrologic DOC transport.

Seasonal variations in DOC concentrations in soils and streams have been linked either to seasonality in production at terrestrial source areas (21–23) or to the intensity and frequency of hydrological events such as storms and snowmelts (12, 24, 25). Past studies on watershed DOC export during spring snowmelt found that this period accounted for substantial portions of annual DOC export in many watersheds of temperate regions (11, 12, 26). Our results suggest that DOC export in winter months, even prior to spring snowmelt, can also be explained by hydrologic flushing during episodic melting events.

Since we used temperature data from sampling days in the regression analysis, day-to-day fluctuations in temperature might have dampened the relationship between air temperatures and solute concentrations, resulting in an overwhelming significance of runoff in explaining solute concentrations (Table 2). However, the general correspondence of both runoff and stream DOC concentrations to elevated temperatures over several consecutive days (Figure 2) suggests the significance of winter-time warming events as a trigger of hydrologic DOC flushing during the snow-covered period. Although sporadic increases in temperature

can also influence the subtle balance between microbial production and consumption of DOC in the soil under the snow pack, the synchrony between temperature, runoff, and DOC concentrations indicates the dominance of hydrological controls over soil microbial processes. Since soil temperature data were not available, it remains unclear how soil freeze/thaw cycles impacted the production of DOC in the soil under varying depths of snow pack. A more comprehensive monitoring program including measurements of soil temperature and freezing depth will improve our capacity to predict the response of soil biogeochemical processes to future climate change.

Implications of DOC for Surface Water Chemistry. From December through April, DOC concentrations in stream water had strong, negative correlations with pH and concentrations of SO_4^{2-} and sum of base cations ($C_B = K + Na + Ca + Mg$) but a positive correlation with concentrations of total Al (Table 1). However, significant correlations were not found for the whole observation period, except for Al, which showed a positive correlation with DOC. Although pH and Al showed significant correlations with C_B and NO_3^- , they had the strongest relationships with DOC or SO_4^{2-} . Previous studies on episodic acidification during spring snowmelt also found concurrent increases in NO_3^- , DOC, H^+ , and Al and decreases in SO_4^{2-} and base cations in some Adirondack streams and ascribed differences among these solutes to changes in hydrologic flow paths during snowmelt (26, 27). On the basis of the relative importance of NO_3^- , DOC, and H^+ in forest floor leachates, Rascher et al. (24) suggested that changed water flow paths from deep groundwater to upper soil water determined the chemical composition and acidity of stream water during snowmelts. While shallow soil water in watersheds with thin deposits of glacial till usually contains low concentrations of SO_4^{2-} as well as base cations (27), the inverse relationship between DOC and SO_4^{2-} can also be explained in part by the ability of SO_4^{2-} to displace DOC from sorption sites (28).

Since Krug and Frink (29) hypothesized that acidic deposition shifts major agents of surface water acidification from natural organic acids to strong inorganic acids, substantial attention has been given to the role of acid anions in watershed acidification. For Adirondack lakes, it has been suggested that the role of NO_3^- will be increasingly important not only for episodic acidification during the spring snowmelt but also for chronic acidification due to declining S deposition (27, 30). Our correlation analysis, however, showed a relatively weak correlation ($r = -0.33$) between NO_3^- concentrations and pH in discharge water from the subcatchment during the winter months, as compared to the strong negative correlation between DOC and pH ($r = -0.73$; Table 1). Considering the high proportion of organic acids in dissolved organic matter (31), increasing DOC concentrations might play a major role in the reduction in stream water pH during episodic melting events. This result is consistent with other experimental and monitoring studies that demonstrated the importance of organic acids in modifying surface water acidity in response to changes in strong acid inputs (32–35). Driscoll et al. (3) recently suggested that increases in surface water DOC concentrations would offset some portions of increases in pH and ANC that are occurring in many Adirondack surface waters largely due to decreases in acidic deposition in this area.

Soil acidification leads to increased leaching of inorganic aluminum (Al^{3+}) that may be toxic to aquatic biota (36, 37). As a result of recovery from acidification, however, declines in surface water concentrations of inorganic Al have been observed in many watersheds across Europe and North America (3, 38), although some watersheds have shown no change or even slight increases in total Al concentration, in part due to increases in concentrations of the organic fraction

TABLE 1. Correlation Coefficients (*r*) between Concentrations of DOC and Total Al and pH in Stream Water Draining the Archer Creek Subcatchment and Either Climatic and Hydrological Variables or Major Solutes for the Whole Study Period (May 1999 to April 2002; *n* = 155) or Winter Months (December to April; *n* = 63)^a

		climatic and hydrological variables						chemical variables				
		<i>T</i> _{max}	<i>T</i> _{min}	<i>T</i> _{av}	ppt	snow depth	runoff	pH	Al	NO ₃ ⁻	SO ₄ ²⁻	C _B
whole period	DOC	0.30 (***)	0.43 (***)	0.38 (***)	0.02	NA	0.12	-0.14	0.56 (***)	-0.21 (**)	0.07	-0.04
	pH	0.37 (***)	0.30 (***)	0.34 (***)	0.02	NA	-0.62 (***)	NA	-0.47 (***)	-0.54 (***)	0.18 (*)	0.59 (***)
	Al	0.20 (*)	0.32 (***)	0.26 (**)	0.02	NA	0.45 (***)	NA	NA	0.00	-0.35 (***)	-0.40 (***)
winter	DOC	0.58 (***)	0.63 (***)	0.64 (***)	0.04	-0.54 (***)	0.77 (***)	-0.73 (***)	0.85 (***)	0.20	-0.77 (***)	-0.66 (***)
	pH	-0.41 (***)	-0.43 (***)	-0.45 (***)	0.03	0.27 (*)	-0.64 (***)	NA	-0.77 (***)	-0.33 (**)	0.82 (***)	0.56 (***)
	Al	0.56 (***)	0.60 (***)	0.61 (***)	-0.01	-0.50 (***)	0.77 (***)	NA	NA	0.35 (**)	-0.84 (***)	-0.68 (***)

^a C_B: sum of K⁺, Na⁺, Ca²⁺, and Mg²⁺; *T*_{max}, *T*_{min}, and *T*_{av} denote maximum, minimum, and average daily air temperatures of the sampling day, respectively; ppt denotes total precipitation of the sampling day; asterisks indicate statistical significance at **P* < 0.05, ***P* < 0.01, or ****P* < 0.001; and NA indicates analysis not done.

TABLE 2. Results of Stepwise Linear Regression between Stream Concentrations of Major Solutes and Selected Climatic and Hydrological Variables over the Winter Months from December 1999 through April 2002^a

solute		climatic and hydrological variables					
		<i>T</i> _{max}	<i>T</i> _{min}	<i>T</i> _{av}	ppt	snow depth	runoff
DOC	ns	0.04 (+)***	ns	ns	0.13 (-)****	0.51 (+)****	
pH	ns	ns	ns	ns	ns	0.41 (-)****	
Al	ns	0.03 (+)**	ns	ns	0.08 (-)***	0.58 (+)****	
NO ₃ ⁻	ns	ns	ns	ns	0.09 (+)***	0.20 (+)****	
SO ₄ ²⁻	ns	0.05 (-)***	ns	ns	ns	0.57 (-)****	
C _B	ns	ns	ns	ns	0.06 (+)**	0.35 (-)****	

^a Values are partial coefficients of determination (*r*²); *T*_{max}, *T*_{min}, and *T*_{av} denote maximum, minimum, and average daily air temperatures of the sampling day, respectively; ppt denotes total precipitation of the sampling day; positive or negative relationships are indicated by (+) or (-), respectively; and asterisks indicate significance levels (**p* < 0.10, ***p* < 0.05, ****p* < 0.01, *****p* < 0.001; *n* = 63), while ns is for not significant.

of Al (3, 39). The strong correlation between DOC and total Al observed during snowmelt events (Table 1) suggests that leaching of total Al might have been enhanced by complex building between DOC and inorganic Al (35), although we cannot rule out the possibility that decreased pH following snowmelt could have enhanced solubility of inorganic Al. Elevated Al concentrations during snowmelt have been well-documented, and some studies linked increases in Al with depressed pH that occurred concurrently with increasing discharge (26, 27, 40, 41).

Climatic Control on Interannual Variations in DOC and Surface Water Chemistry. To look at whether climatic controls observed for the subcatchment can also explain long-term interannual variations in DOC and related surface water chemistry of discharge water from the whole watershed, we analyzed long-term (1983–2000) monthly water chemistry data collected at the lake outlet. For the winter months, stepwise linear regression between seasonal averages of solute concentrations and climatic variables selected *T*_{min}, precipitation, or runoff as a significant predictor of interannual variations in specific solute concentrations (Table 3). While runoff was the best predictor for changes in concentrations of all analyzed solutes in the intensive monitoring data set from the Archer Creek subcatchment (Table 2), precipitation was the only significant factor for explaining interannual variations in average concentrations of DOC, pH, and Al_{om} during the winter. While runoff was the significant predictor for concentration variations in Al_m and NO₃⁻, portions of

TABLE 3. Results of Stepwise Linear Regression between Winter Average Concentrations of Major Solutes in Lake Discharge and Selected Climatic and Hydrological Variables over 17 Winter Periods from December 1983 through April 2000^a

solute		climatic and hydrological variables					
		<i>T</i> _{max}	<i>T</i> _{min}	<i>T</i> _{av}	ppt	snow depth	runoff
DOC	ns	ns	ns	0.22 (+)*	ns	ns	
pH	ns	ns	ns	0.40 (-)***	ns	ns	
Al _m	ns	ns	ns	ns	ns	0.33 (+)**	
Al _{om}	ns	ns	ns	0.39 (+)***	ns	ns	
NO ₃ ⁻	ns	ns	ns	ns	ns	0.24 (+)**	
SO ₄ ²⁻	ns	0.38 (-)***	ns	ns	ns	ns	
C _B	ns	0.52 (-)***	ns	ns	ns	ns	

^a Values are partial coefficients of determination (*r*²); *T*_{max}, *T*_{min}, and *T*_{av} denote seasonal averages of maximum, minimum, and average daily air temperatures, respectively; ppt denotes seasonal total precipitation; Al_m and Al_{om} denote total monomeric and organic and monomeric components of Al, respectively; positive or negative relationships are indicated by (+) or (-), respectively; and asterisks indicate significance levels (**p* < 0.10, ***p* < 0.05, ****p* < 0.01; *n* = 17), while ns is for not significant.

variations in SO₄²⁻ and C_B were explained by *T*_{min}. In addition to precipitation, air temperature and runoff showed significant correlations with other climatic and chemical variables (data not shown). Among three temperature variables, *T*_{min} had the highest correlation with precipitation (*r* = 0.83, *p* < 0.001), runoff (*r* = 0.65, *p* < 0.01), DOC (*r* = 0.35), pH (*r* = -0.56, *p* < 0.05), and Al_{om} (*r* = 0.54, *p* < 0.05).

Considering that stream DOC concentrations during snowmelt usually peak before maximum discharge and then decrease rapidly as melting continues (12), the monthly sampling scheme is assumed to miss many cases of concentration increases following episodic melting events. In-lake biogeochemical processes might also have dampened climatic signals in DOC concentrations at the lake outlet (17, 42). In the analysis of elemental input/output budgets for 52 Adirondack lakes, Ito et al. (42) suggested a possible increase in degradation of allochthonous DOC of terrestrial origin with increasing hydraulic retention time, based on an inverse relationship found between DOC output and hydraulic retention time. However, the degree of chemical transformation or stability of DOC in lake water during the cold winter season is largely unknown. Given these constraints, along with the fact that snow represented approximately 75% of precipitation during winter months over the entire study period, it seems plausible that the seasonal total precipitation,

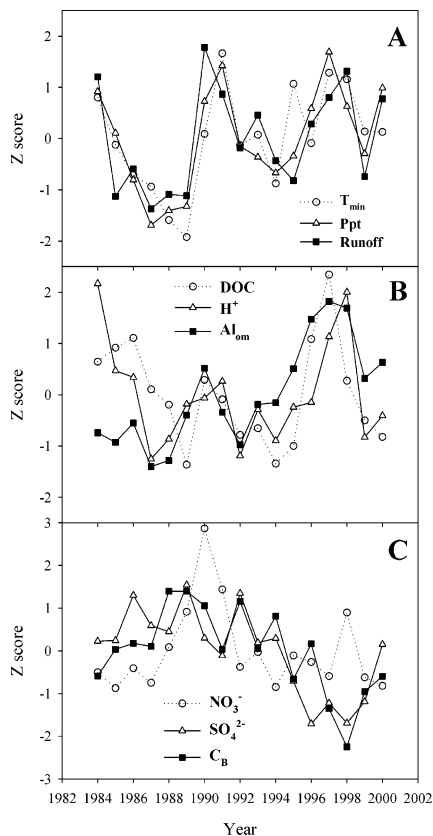


FIGURE 3. Interannual variations in standardized (*Z*-score) seasonal averages of climatic and hydrological variables (A) and solute concentrations (B and C) in discharge water from the Arbutus Lake during the winter months from December 1983 through April 2000. *T*_{min}: minimum daily air temperature; ppt: precipitation; *Al*_{om}: organic, monomeric Al; and *C*_B: sum of base cations (*K*⁺, *Na*⁺, *Ca*²⁺, and *Mg*²⁺).

as the ultimate source of meltwater, might have played a more direct role in explaining interannual variations in DOC concentrations than air temperature or runoff.

Interannual variations in standardized (*Z*-score) seasonal averages of solute concentrations in lake discharge and selected climatic variables exhibited distinct patterns of response to climatic variability (Figure 3). Changing patterns in winter precipitation and lake discharge well matched those of *T*_{min} throughout the 1980s and 1990s with only a few exceptions (Figure 3A). Standardized winter average concentrations of DOC, *H*⁺, and *Al*_{om} generally corresponded to climatic fluctuations over the last two decades (Figure 3B). While changing patterns of *NO*₃⁻ appeared similar to those of DOC, *H*⁺, and *Al*_{om}, *SO*₄²⁻ and *C*_B displayed an opposite trend to climatic fluctuations, showing a general decline in concentrations throughout the 1990s (Figure 3C). Although DOC had weaker correlations with pH (*r* = -0.55, *p* < 0.05) and *Al*_{om} (*r* = 0.32), as compared to the strong relationships found for short-term stream water data (Table 1), the interplay between changing temperature, precipitation, and runoff appears to exert a great influence on the long-term patterns of concentration of *H*⁺ and *Al* as well as DOC.

While inorganic Al dominates the toxicity of Al in acidified soils and surface waters, enhanced complexation between organic acids and inorganic Al species has been found in watersheds recovering from acidification (3, 43). Some modeling results have suggested that the complexation between organic acids and inorganic Al is most prominent in the pH range between 5 and 6 (35), although Driscoll and Postek (44) observed a decline in the ratio of organic Al to DOC as the pH increased from 4.1 to 7.5 in some Adirondack

lakes. The pH range from 5 to 6 was typical for stream and lake waters during snowmelt events. Although inorganic Al can be more available due to increased dissolution and/or cationic exchange as the pH decreases, only a weak correlation was found between pH and inorganic fraction of Al (*Al*_{im}; *r* = 0.19). Driscoll et al. (3) observed similar trends of shift in Al speciation from toxic inorganic forms to less toxic organic forms in 13 of the 16 Adirondack lakes. Despite the less toxic properties as compared to the inorganic counterpart, Al organic complexes might pose a potential threat to aquatic organisms because physicochemical changes can any time alter the equilibrium between organic and inorganic Al species (35).

In most areas of Europe and North America, declines in acidic deposition have led to substantial recovery of surface waters from decades of watershed acidification (38, 45). Several recent studies have suggested that watershed biogeochemical responses to declining acidic deposition can exhibit unpredictable patterns, possibly due to the confounding effects of climatic variability (16, 20, 46). Increasing DOC, as observed in some European surface waters through the 1990s (8, 47), has also been suggested as a confounding agent that can influence chemical recovery of acidified waters through the acidifying or buffering capacity of organic acids (43, 48). In addition to some past studies showing the importance of snowmelt in regulating stream water chemistry in major spring snowmelt events, our results highlight that snowmelt responses to temperature fluctuations are crucial in hydrologic transport of DOC and related compounds throughout the entire snow-covered period. Diverging long-term trends observed for DOC, *H*⁺, and *Al* on one hand and *SO*₄²⁻ and *C*_B on the other hand (Figure 3) suggest that DOC responses to winter-time climatic variability can play a pivotal role in understanding complex patterns associated with surface water recovery from acidification. Considering these environmental implications of DOC and the intensifying climatic variability in recent decades, DOC responses to changing climate warrant further detailed study.

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