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Spatial and temporal dynamics of stream chemistry in a forested watershed

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Abstract. Spatial dynamics of solute chemistry and natural abundance isotopes of nitrate (^{15}N and ^{18}O) were examined in seven locations and at the watershed outlet in 2001 and 2002 in a forest watershed in the Adirondack Mountains of New York State, USA. Temporal dynamics were examined during five discharge periods: winter, snowmelt, spring, summer, and fall, based on discharge levels at the watershed outlet. Solute concentrations were variable across space and time with significant ($p \leq 0.05$) interaction effects. Year*period was significant for pH, NH_4^+, NO_3^-, total N, DOC, and total Al suggesting that inter-annual variability in discharge levels was more important for these solutes than intra-annual variability. Period*sampling point was significant for pH, Mg^{2+}, Ca^{2+}, sum of base cations, Si, and total Al suggesting that the differences in concentration of these solutes among sampling points were moderated by discharge levels. In general, groundwater sources located in upper watershed controlled stream chemistry at higher elevations with highest pH, Ca^{2+}, sum of base cations, Si, and SO_4^{2-} concentrations, with higher values in summer, and dilution effects during snowmelt. Two low elevation wetlands had a substantial influence over stream chemistry at those locations contributing lowest NO_3^- and highest DOC. Snowmelt exhibited among the lowest pH, sum of base cations, and SO_4^{2-}, and highest NO_3^-, total N, and total Al; snowmelt appeared to dilute groundwater, and flush stored soil-derived solutes. Summer discharge, composed mainly of groundwater, exhibited the lowest flow, among the highest Mg^{2+}, Ca^{2+}, and lowest DON, DOC, and total Al concentrations. Isotopic analysis indicated that NO_3^- was microbial with primary source in upper watershed soil, from where it was flushed to stream under high discharge-conditions, or drained to groundwater which became its secondary source when discharge was low. Watershed outlet did not exhibit specific solute levels found at source-areas, but represented solute dynamics in the rest of the watershed well.

1 Introduction

Solute concentrations in streams draining forested watersheds are important indicators of ecosystem health. A notable example of that is the export of nitrate (NO_3^-) from forests impacted by elevated atmospheric deposition of nitrogen (N) (Stoddard, 1994; Aber et al., 1989, 1998, 2002). Nitrate and sulfate exports are associated with the losses of Ca^{2+} and Mg^{2+} with possible increases in soil acidity and potential decreases in forest productivity. Pristine forests exhibit more dissolved organic N (DON) than polluted forests (Perakis and Hedin, 2001), while more extreme hydrologic regimes that are predicted for a changing climate may impact transfer of dissolved organic C (DOC) between systems (Eimers et al., 2008; Harrison et al., 2008).

Spatial dynamics of stream chemistries seem to be mostly determined by topographic positions of sources (Creed et al., 1996; Boyer et al., 1997; Welsch et al., 2001; Inamdar et al., 2004). Surface water at the base of a watershed integrates the chemical response of the entire watershed; whether or not the base of the watershed provides sufficient resolution of the spatial variation of surface water chemistry within the watershed has not been confirmed (Ogawa et al., 2006; Ito et al., 2007).

Temporal dynamics of solute concentrations are a complex result of differing patterns of solute production and consumption integrated via hydrologic pathways. High solute concentrations in surface waters may be present when net generation is high and under soil moisture conditions conducive to transport of solutes from the source of generation to streams (Creed and Band, 1998; Buffam et al., 2001; Welsch et al., 2001; Inamdar et al., 2004; Piatek et al., 2005; Mitchell et al., 2006). Low solute concentrations may be due to low rates of production when microbial activity or weathering rates are low, relatively high rates of consumption, or lack of hydrological connection between source and stream.

Changes in hydrology and resultant changes in surface water chemistry provide insights on solute sources. For example storm events often exhibit a shift in hydrologic flowpaths from ground water to soil horizons, and result in dilution of base cation and silica concentrations at peak flow (Harriman et al., 1990; Hill, 1993). On the other hand, solutes generated in mineral soil peak with increasing discharge (Hill, 1993). The largest NO_3^- fluxes from forested watersheds in the US occur with large runoff events, especially during early spring snowmelt when vegetation and microbial uptake of inorganic N is low (Mitchell et al., 1996; Baron and Campbell, 1997; Brooks and Williams, 1999; Park et al., 2003; Inamdar et al., 2004; Piatek et al., 2005). The presence of wetlands and changes in vegetative cover from coniferous to deciduous may be related to the generation and loss rates of organically-bound elements, such as DOC, DON, and Al (Campbell et al., 2002; Mitchell et al., 2003; Ito et al., 2005).

The Archer Creek watershed in the central Adirondack Mountains of New York State, USA, has been a site of extensive hydrobiogeochemical studies since the early 1990s. The area receives atmospheric N and S at rates of $10.1\,kg\,N\,ha^{-1}\,yr^{-1}$ and $6.3\,kg\,S\,ha^{-1}\,yr^{-1}$ (Park et al., 2003), and generates stream NO_3^- exports of $4.2\,kg\,N\,ha^{-1}\,yr^{-1}$ (Mitchell et al., 2001). Previous studies in this watershed increased our understanding of the regulation of solute fluxes during high-discharge hydrologic events. Snowmelt and storm activity, for example, flush NO_3^- to stream from sites of nitrification in upland soils (Ohrui et al., 1999; McHale et al., 2002; Inamdar et al., 2004; Piatek et al., 2005; Mitchell et al., 2006; Christopher et al., 2008). During these events, groundwater table rises to the upper soil horizons and establishes connectivity with the stream channel (Inamdar et al., 2004; Christopher et al., 2006). Post-event draining of NO_3^- to groundwater, facilitated by steep slopes, probably serves to recharge groundwater NO_3^- (Inamdar et al., 2004). In this system, groundwater appears to become the primary source of NO_3^- to stream during periods of high N demand by biota (summer), low rates of nitrification, or lack of water movement through the soil profile (under the snowpack) (McHale et al., 2002; Inamdar et al., 2004; Piatek et al., 2005; Mitchell et al., 2006).

Our understanding of the sources of DOC during high-discharge events of summer and fall is that near-surface soil water, and runoff from wetlands are the primary sources, with isolated saturated areas contributing when soil moisture conditions facilitate their connectivity with stream (Inamdar et al., 2004; Mitchell et al., 2006). Wetlands were a source of SO_4^{2-} during consecutive fall storms which followed an unusually dry summer; the processes responsible were decomposition and S mineralization of wetland organic matter in unusually dry conditions, followed by runoff (Mitchell et al., 2006).

Finally, high-flow events result in increases in acidity in stream water, with potential consequences for aquatic habitat. This is especially acute during snowmelt, but was also observed during consecutive fall storms that followed an unusually severe dry spell (Mitchell et al., 2006).

We now explore how these earlier observations focusing on the watershed outlet at high discharge periods extrapolate across the watershed and across different discharge volumes. This will shed light on the generality of the mechanisms described for high discharge events, and facilitate future modeling efforts to determine possible effects on solute generation during extreme weather predicted under climate change scenarios. Our primary objective was to identify the spatial and temporal dynamics of solute chemistry in a stream draining a forested watershed to better understand factors responsible for solute expression at the watershed outlet. We hypothesized that an extensive wetland present in the lower part of the watershed will have an important effect on stream chemistry. Our analysis included two years, one of which had a very high discharge at snowmelt, and one with a summer drought followed by several late summer/early fall storms; these hydrologically-distinct periods allowed us to test their particular effects on stream water chemistry.

2   Methods

2.1   Site description

The study was conducted in the 135-ha Archer Creek catchment of the Arbutus Lake Watershed near the town of Newcomb (43°58′ N, 74°14′ W) in the Adirondack Park of New York State, USA (Fig. 1). Elevation of the watershed extends from 550 to about 700 m a.s.l. The area includes ridges, rocky hillsides, and wetlands. The Arbutus Lake watershed is within the Anorthosite Massif, a large igneous intrusion composed of up to 90% calcium-rich feldspar. Upland soils are coarse loamy, isotic, frigid, oxyaquic Haplorthods of the Becket-Mundal association, and are generally less than 1 m thick. Wetlands consist of Greenwood mucky peats from 1 to 5 m thick (Somers, 1986; McHale, 1999). Boulders and stones dominate the soil profile, originating from glacial till deposits from the continental glaciation that retreated 10 000 to 15 000 years ago. High sand (75%) and low clay (<10%)

content of the parent material provide for good drainage. Climate is characterized as continental. Mean annual temperature is 4.4°C and mean annual precipitation is 1010 mm (mean from 1951 to 1980; Shepard et al., 1989).

Vegetation consists of mixed hardwood-conifer stands typical of the northern hardwood forest. *Fagus grandifolia* Ehrh. (American beech) and *Acer saccharum* Marsh. (sugar maple) dominate the overstory at mid- and higher elevations, while *Tsuga canadensis* (L.) Carr. (eastern hemlock) and *Picea rubens* Sarg. (red spruce) dominate at lower elevations. *Abies balsamea* (L.) Mill. (balsam fir) and *Pinus strobus* L. (eastern white pine) are scattered throughout the watershed. Some of the wetlands support *Alnus incana spp. rugosa* (Du Roi) Clausen (speckled alder), an N-fixing species (Bischoff et al., 2001; Hurd et al., 2001).

Archer Creek has several tributaries (Fig. 1). One of them, located at elevation of about 650 m (S14), exhibits unusually high NO_3^- concentrations throughout the year and is fed by deep groundwater (McHale et al., 2002; Christopher et al., 2006, 2008). At low elevations, another tributary forms an extensive conifer wetland (S11) before it resumes channelized flow into an open grassy field. Archer Creek also flows through a small alder wetland about 30 m before it empties into Arbutus Lake.

2.2 Stream discharge and water chemistry

Stream discharge was monitored on Archer Creek during 2001 and 2002 at an H-flume located 10 m away from the lake inlet. The flume was enclosed, and equipped with automated stage-height recording at 15-min intervals. In winter, a heater kept the water inside the flume enclosure above freezing point. Fifteen-minute data were averaged to obtain daily values. Discharge exhibits substantial variability over a course of a year, and we identified specific discharge periods. These periods were: winter, snowmelt, spring, summer, and fall. Specific dates which correspond to these periods are listed in Table 1. For comparison, the length of corresponding discharge periods in both years was adjusted to the same number of days (Table 1).

Stream water was sampled weekly at the H-flume by autosamplers, and every two hours during storms in fall 2002 by "grab" samples. Stream water elsewhere in the catchment was sampled monthly by grab samples. For that purpose, seven sampling locations, spanning the elevation range of the Archer Creek catchment, were established (S15, S14, S13, S12, S10, S11, S9) (Fig. 1). The difference in elevation between the highest- and lowest-lying stream sampling locations is about 61 m, stretching over about 6 km. All but two of the sampling locations are separate tributaries to the main stream channel (S15, S14, S13, S12, S11, S10), and their solute concentrations are thought to be spatially independent (Legendre and Fortin, 1989; Wagener et al., 1998; Dent and Grimm, 1999). Further, parts of the Archer Creek system are steep and fast-flowing. Watershed outlet (S2) and
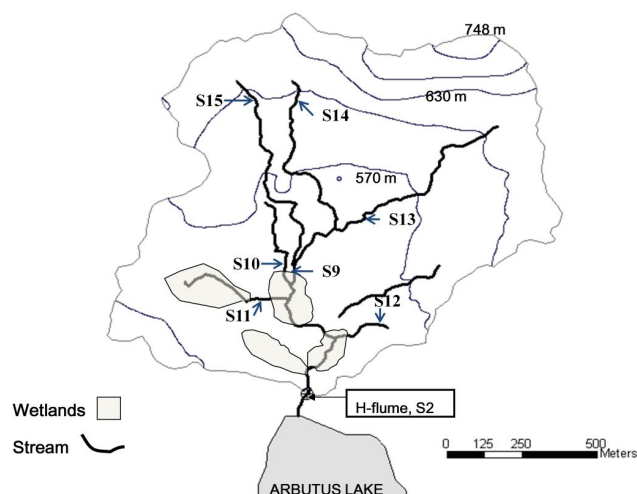

Fig. 1. Arbutus Lake Watershed in the Adirondack Mountains of New York, USA with locations of sampling points and elevations.

S9 are nested mixing points. Due to their substantially different chemistry, stream points S11, S14, and S15 were sampled for parts of the year in 2002 with autosamplers approximately biweekly during baseflow, hourly during summer/fall storms, and daily during snowmelt. These more frequent data were also averaged to obtain daily values.

Silica concentration was first measured in January 2002. After collection, samples for chemical analyses were shipped on ice to the Biogeochemistry Laboratory at SUNY-ESF in Syracuse, NY, where they were analyzed as follows: NO_3^- and SO_4^{2-} on a Dionex IC, DOC on a Tekmar-Dohrmann Phoenix 8000 TOC analyzer, K^+, Na^+, Ca^{2+}, Mg^{2+}, total Al and dissolved Si on a Perkin-Elmer ICP-AEC Div 3300 instrument, NH_4^+ by continuous flow colorimetry, total dissolved N (TDN) by persulphate oxidation, pH by glass electrode potentiometry, and DON was calculated by subtracting dissolved inorganic N ($NH_4^+ + NO_3^-$) from TDN. All DOC samples were filtered with 0.5 μm glass fiber filter prior to analysis. Potassium and Na^+ are not reported here; however, they were included with Mg^{2+} and Ca^{2+} in the calculation of the sum of base cations C_b. The biogeochemistry laboratory is a participant in the US Geological Survey performance evaluation program to ensure data quality. A system of calibration QC, detection QC, analytical blanks and replicates is used with every set of samples (Mitchell et al., 2001).

2.3 Sample collection for natural abundance isotopes

Stream water was sampled at the H-flume for natural abundance isotopes of NO_3^- (^{15}N and ^{18}O) bi-weekly during the snowmelt of 2001 and 2002, every four hours during fall storms of 2002, and monthly the rest of the time. Stream water in all other locations was tested once a month during the study period, except when snow hindered access. Reported

Table 1. Discharge periods (based on flow level), discharge diagnostics, and corresponding dates for 2001 and 2002. Data adjusted to reflect equal number of days in both years (actual number of days given).

		2001		2002	
	Adjusted # of days	Adjusted cumulative discharge in mm (actual discharge; % of annual total)	Dates included (actual # days)	Adjusted cumulative discharge in mm (actual discharge; % of annual total)	Dates included (actual # days)
			1 Jan–3 Apr		1 Jan–28 Mar
Winter	120	142.3 (147; 25%)	1–31 Dec (124)	173.2 (170; 24%)	1–31 Dec (117)
Snowmelt	30	252.1 (269; 46%)	4 Apr–5 May (32)	191.3 (191; 26%)	29 Mar–27 Apr (30)
Spring	60	129.3 (121; 1%)	6 May–30 Jun (56)	121.3 (131; 18%)	28 Apr–30 Jun (65)
Summer	80	16.7 (17; 3%)	1 Jul–19 Sep (81)	3.0 (3; 0.4%)	1 Jul–21 Sep (83)
Fall	70	31.7 (33; 6%)	20 Sep–30 Nov (72)	64.8 (65; 31%)	22 Sep–30 Nov (70)
TOTAL		586		561	

isotopic values for $\delta^{18}O$ of NO_3^- of throughfall, bulk precipitation, and snow in this region (Northeastern US) have a seasonal variation of only 2–4‰ (Pardo et al., 2004); therefore, atmospheric NO_3^- values from this watershed reported earlier by Piatek et al. (2005) were used as comparisons.

Samples for natural abundance isotopic analysis of nitrate were prepared using the microbial denitrifier method (Sigman et al., 2001; Casciotti et al., 2002) at the USGS Isotopic Laboratory in Menlo Park, CA, USA, and analyzed on a Micromass IsoPrime stable isotope mass spectrometer. The reported values are defined as:

$$\delta^{15}N=(^{15}N/^{14}N_{sample})/(^{15}N/^{14}N_{standard}-1)*1000[\text{‰}]$$

$$\delta^{18}O=(^{18}O/^{16}O_{sample})/(^{18}O/^{16}O_{standard}-1)*1000[\text{‰}]$$

Procedural quality was controlled. First, most of the samples collected at the H-flume were collected, processed, and analyzed in duplicate, except in very few cases where nitrate levels were too low. Duplicate isotopic determinations on each sample were averaged. Second, USGS Isotopic Laboratory uses internationally accepted standards for $\delta^{18}O-NO_3^-$, with $\delta^{15}N$ of 15.96‰ relative to air nitrogen, and with $\delta^{18}O$ of 19.6‰ relative to SMOW. Analytical precision for our samples was ±0.6‰ for $\delta^{15}N$ and ±0.7‰ for $\delta^{18}O$.

2.4   Statistical analysis

We tested differences in the concentration of solutes among years (2001, 2002), stream sampling locations (S2 to S15), and discharge periods (winter, snowmelt, spring, summer, and fall) with analysis of variance in SAS (SAS Institute®). We used the "weight" statement to adjust for unequal sample number across locations. Our model was:

$$[C]_{ijk}=\mu+Y_i+S_j+(YS)_{ij}+P_k+(YP)_{ik}+(SP)_{jk}$$
$$+(YSP)_{ijk}+e_{ijk},$$

where
$[C]$=observed solute concentration
μ=overall mean observation
Y_i=fixed effect of year (i=1, 2)
S_j=fixed effect of stream sampling points (j=2–15)
YS_{ij}=fixed effect of interaction of year and location of sampling point
P_k=fixed effect of discharge period (k=1–5)
YP_{ik}=fixed effect of interaction of year and discharge period
SP_{jk}=fixed effect of interaction of sampling point and discharge period
YSP_{ijk}=fixed effect of a three-way interaction of year, location, and period, and
e_{ijk}=random error term.

2.5   Relationships among solutes across space and time

We performed linear regression analyses of solute concentrations at their individual locations and at different discharge periods against key source indicators of groundwater (Si), mineral soil (Total Al), and forest floor or wetland (DOC) to better understand sources of the solutes. Further, relationships of specific solute with NO_3^- concentrations were also explored. Nitrate could be thought of as an indicator of N saturation in the system; with a decreasing capacity of ecosystem to retain atmospheric N inputs, watersheds leak more NO_3^- (Stoddard, 1994).

2.6   Relationships of solutes to discharge

We performed linear regression analyses of solute concentrations at each location against daily, current-period cumulative, and previous-period cumulative discharge to better understand how these relationships change across space. Daily discharge was discharge on a given day in mm per day, current-period cumulative discharge was total discharge added for adjusted number of days per period in mm per

Table 2. Anova table for all solute concentrations (Type III SS). All values are weighted on the frequency of observations. DON and δ^{18}O-NO$_3^-$ were not significant for any effect in the model. Blank cells indicate non-significant effects at $p \leq 0.05$. n.a.=data not available to evaluate effect.

	pH	NH$_4$	Mg	Ca	C$_b^1$	Si	SO$_4^{2-}$	NO$_3^-$	Total N	DOC	Total Al	δ^{15}N$-$NO$_3^-$
Year						n.a.						
Sampling point (S)	0.000		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Period			0.006	0.001	0.000	0.000		0.000		0.000	0.003	0.040
Year*S						n.a.						
Year*Period	0.004	0.000				n.a.		0.000	0.000	0.000	0.040	
Period*S	0.004		0.000	0.000	0.000	0.000					0.032	

^{1}C$_b$ is the sum of basic cations: K$^+$, Na$^+$, Mg^{2+}, and Ca^{2+}.

period, and previous-period cumulative discharge was cumulative discharge for the period immediately preceding the one tested, in mm per period.

3 Results

3.1 Stream discharge

The adjusted length of discharge periods ranged from 30 days for snowmelt to 120 days for winter (Table 1). Adjusted cumulative discharge ranged from 3 mm in summer of 2002 to 252 mm during snowmelt of 2001 (Table 1).

3.2 Spatial dynamics in solute concentrations and isotopic composition

There were no statistically significant differences in concentrations between sampling year 2001 and 2002 ($p \geq 0.05$). There were no statistical differences for DON or δ^{18}O$-$NO$_3^-$ (Table 2). The average concentration of DON for the period of study was 8.0 μmol L^{-1} (SE±3.0). The average value of δ^{18}O$-$NO$_3^-$ for the period of study was 2.7‰ (SE±2.9).

The main effect of stream sampling location was significant for SO$_4^{2-}$, NO$_3^-$, total N, and DOC (Table 2, Fig. 2); interactions, significant for other solutes, are discussed below. At an average of 213 μmol L^{-1}, SO$_4^{2-}$ concentrations were significantly higher at S14 and S15 than at S2, S10, and S11, at an average for these three locations of 130 μmol L^{-1}. Other locations were comparable to each other (Fig. 2). Nitrate concentrations were highest at S14 at 70.5 μmol L^{-1}, and lowest at S11 at 14 μmol L^{-1} (Fig. 2). Total N followed the trend for NO$_3^-$ with highest concentrations at S14. Dissolved OC had substantial variability at S12 and S13, probably due to a low sample size. At 878 μmol L^{-1}, S11 generated 290 μmol L^{-1} more DOC than the next highest at S2, and both S11 and S2 discharged significantly more DOC than any other sampling location (Fig. 2).

The interaction effect of sampling location and period was significant for NH$_4^+$, Mg^{2+}, Ca^{2+}, C$_b$, Si, and total Al con-
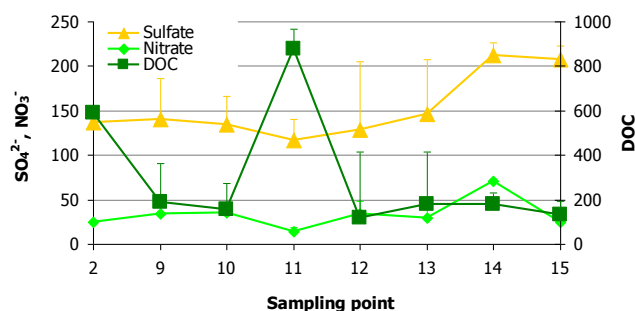

Fig. 2. Average concentrations (μmol L^{-1}) of NO$_3^-$, SO$_4^{2-}$ and DOC (+ standard error) at individual sampling locations within the Archer Creek watershed.

centrations, and for pH (Table 2). These interactions indicate that period had a moderating effect on stream sampling location. Ammonium did not exhibit a significant pair-wise comparison, despite an overall significance of the interaction. The largest across-period variation in Mg^{2+} was observed at S15 (Fig. 3); snowmelt and spring exhibited among the lowest levels of Mg^{2+}, and summer and fall among the highest. Calcium had a similar concentration pattern to Mg^{2+}. At S2 to S11, snowmelt had among the lowest and summer among the highest Ca^{2+} concentrations. Highest Ca^{2+} levels were observed at S14 regardless of period, and in summer and fall at S15; winter, spring, and snowmelt Ca^{2+} levels at S15 were comparable to those elsewhere in the watershed (Fig. 3). Sum of base cations followed dynamics observed for Mg^{2+} and Ca^{2+} (Fig. 3).

Some of the highest pHs were consistently detected at S14 and S15, and among the lowest at S11 during snowmelt and spring. However, S14 in summer had somewhat lower pH than it did at snowmelt, and that was opposite of all other locations (Fig. 4). Due to insufficient data, interactions for Si could not be evaluated to the same degree as for the rest of the elements (Fig. 4). Total Al exhibited a large variability among sampling locations and periods. In general, S2, S11, and S13 exhibited the highest Al concentrations during
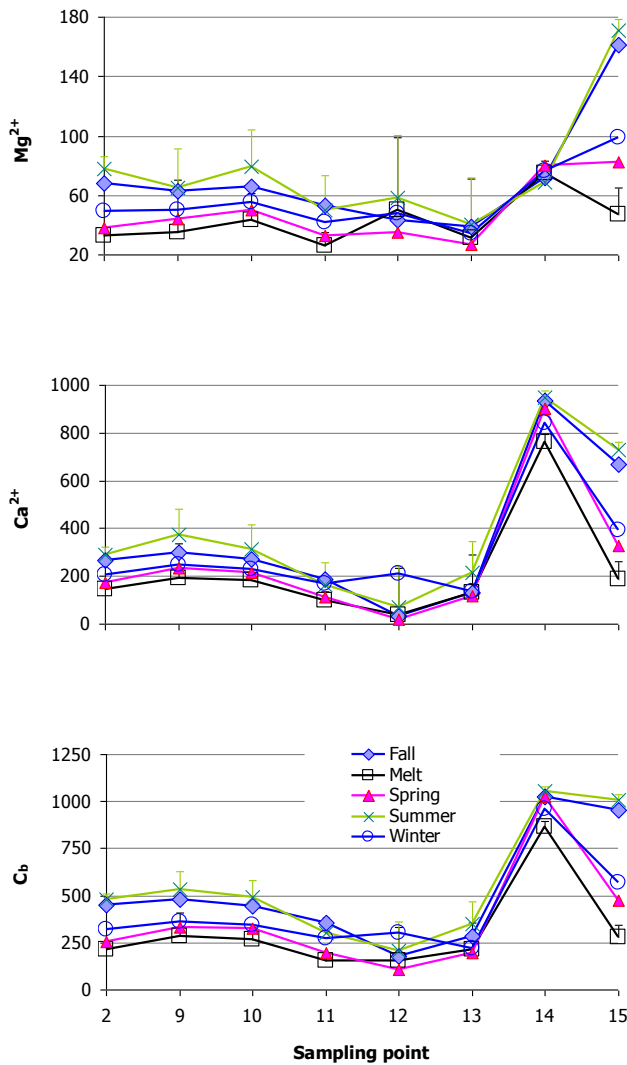
Fig. 3. Average concentrations (μmol L^{-1}) of Mg^{2+}, Ca^{2+}, and sum of base cations C$_b$ (C$_b$ includes K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}) for individual sampling locations during discharge periods within the Archer Creek watershed. Standard errors (+) shown for snowmelt and summer only.

Fig. 4. Average pH and concentrations (μmol L^{-1}) of Si[1], and total Al for individual sampling locations during five discharge periods within the Archer Creek watershed. Standard errors (+) shown for snowmelt and summer only. [1]Si concentration not available for several interactions.

snowmelt and spring, and S11 additionally during fall. Summer and fall also exhibited among the lowest Al at S9 and S12 at nearly 0. Both S14 and S15 exhibited consistently low Al throughout the year (Fig. 4).

3.3 Relationships among solutes across sampling locations

Increases in Si concentration coincided with increases in the concentration of Mg^{2+}, Ca^{2+}, C$_b$, and SO$_4^{2-}$. Decreases were observed for NO$_3^-$, DOC, DON, and total Al (Table 3, Fig. 5). Silica concentrations ranged from 50–250 μmol L^{-1} in most sampling locations but at S14, where it ranged from about 200 to 750 μmol L^{-1}, changing these relationships to some degree at S14. For example, the increase in C$_b$ con-
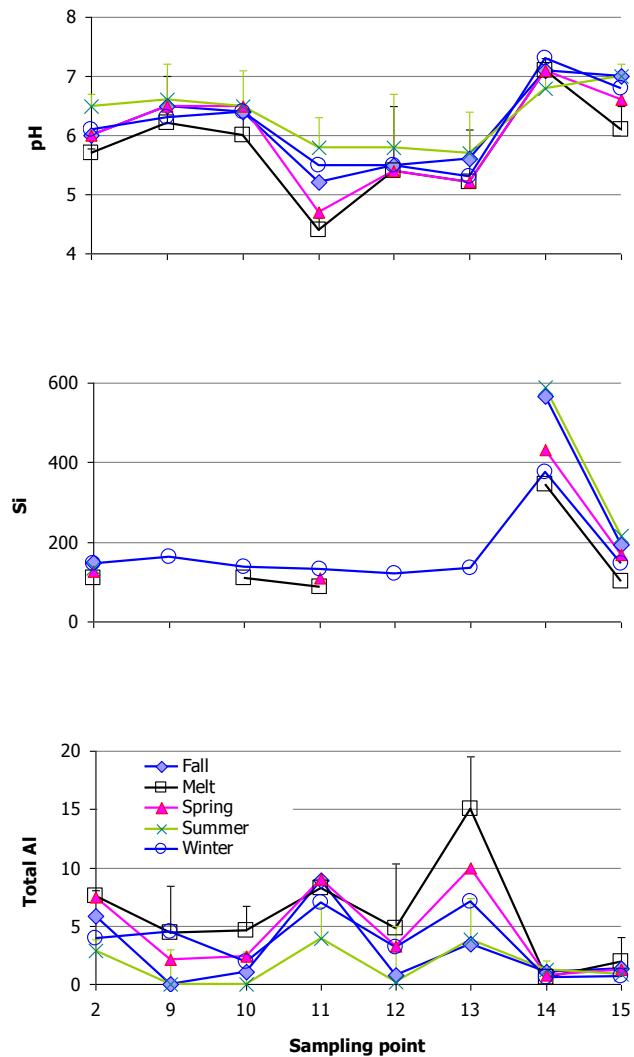
centration with Si was slower at S14 than elsewhere (Fig. 5), and the decrease in NO$_3^-$ with increasing Si was over much larger concentrations of both NO$_3^-$ and Si than elsewhere.

Concentrations of Mg^{2+}, Ca^{2+}, C$_b$, and SO$_4^{2-}$, and pH were negatively related to total Al (Table 3, Fig. 6). Ammonium was highly positively related to total Al at S2, weakly positively related at S11, negatively related at S14 and S15, and not related elsewhere (Table 3). Nitrate was positively related to total Al in most of the mid to upper locations, such as S10, S13, S14, and S15, but not related elsewhere (Table 3, Fig. 6). Dissolved OC was positively related to total Al, with some of the highest r^2 values (Table 3).

Magnesium, Ca^{2+}, C$_b$, and SO$_4^{2-}$ exhibited no relationship with DOC at S2, S11, and S15, and were negatively

Table 3. Significant ($p \leq 0.05$) r^2 values for regression analyses of individual solute concentrations with Si (groundwater indicator), total Al (mineral soil indicator), DOC (forest floor indicator), and NO_3^- at each sampling location at the Archer Creek watershed (Adirondack Mountains, New York, USA). +/− sign indicates the direction of the relationship. Blank cells indicate non-significant r^2 values. i.d.=insufficient data to evaluate.

	pH	NH_4^+	Mg	Ca	C_b^1	SO_4^{2-}	Si	NO_3^-	DON	Total N	DOC	Total Al
						– Si –						
2	+0.14		+0.22	+0.26	+0.24	+0.20	1	−0.11		−0.12		−0.24
9	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	1	i.d.	i.d.	i.d.	i.d.	i.d.
10	+0.46		+0.86	+0.86	+0.88	+0.96	1				−0.90	−0.85
11	+0.43		+0.71	+0.48	+0.63	+0.66	1				−0.11	
12	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	1	i.d.	i.d.	i.d.	i.d.	i.d.
13	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	1	i.d.	i.d.	i.d.	i.d.	i.d.
14	−0.25	+0.21		+0.59	+0.56	+0.83	1	−0.38	−0.14	−0.34	−0.39	−0.13
15	+0.30	+0.27	+0.83	+0.87	+0.86	+0.76	1	−0.66	−0.17	−0.52		−0.58
						– total Al –						
2	−0.32	+0.70	−0.25	−0.16	−0.26		−0.24		+0.29		+0.42	1
9							i.d.		+0.41	+0.24	+0.30	1
10	−0.55		−0.68	−0.69	−0.70	−0.61	−0.85	+0.31		+0.28	+0.84	1
11	−0.22	+0.20	−0.08			−0.21			+0.09		+0.62	1
12	−0.92		−0.37			−0.74	i.d.				+0.60	1
13	−0.80		−0.56		−0.58	−0.83	i.d.	+0.37		+0.35	+0.67	1
14	+0.08	−0.12		−0.12	−0.12		−0.13	+0.18		+0.15	+0.12	1
15	−0.26	−0.15	−0.55	−0.56	−0.57	−0.40	−0.58	+0.29	+0.29	+0.36	+0.43	1
						– DOC –						
2	−0.05	+0.07				+0.08		−0.13	+0.15		1	+0.42
9	−0.38		−0.59	−0.36	−0.45	−0.49	i.d.				1	+0.30
10	−0.42		−0.69	−0.70	−0.71	−0.57	−0.90				1	+0.84
11	−0.08	+0.24				−0.19	−0.11	−0.16	+0.12		1	+0.62
12	−0.49				−0.42		i.d.				1	+0.60
13	−0.43		−0.44	−0.46	−0.55	−0.55	i.d.				1	+0.67
14		−0.10	−0.07	−0.41	−0.40	−0.20	−0.39	+0.12		+0.14	1	+0.12
15									+0.17		1	+0.43
						– NO_3^- –						
2	−0.18		−0.15	−0.15	−0.14	−0.09	−0.11	1		+0.89	−0.13	
9	−0.64		−0.35		−0.25		i.d.	1		+0.86		
10	−0.22		−0.49	−0.50	−0.49	−0.25		1		+0.91		+0.31
11		−0.12						1		+0.52	−0.16	
12						−0.43	i.d.	1		+0.97		
13						−0.40	i.d.	1		+0.97		+0.37
14	+0.05			−0.34	−0.33	−0.22	−0.38	1		+0.76	+0.12	+0.18
15	−0.16						−0.66	1		+0.77		+0.29

$^1 C_b$ is the sum of basic cations: K^+, Na^+, Mg^{2+}, and Ca^{2+}.

related to DOC elsewhere, with r^2 ranging from 0.1 to 0.7 (Table 3, Fig. 7). Concentrations of DOC spanned a much wider range at S2 and S11 than elsewhere in the watershed. Increases in NO_3^- were independent of DOC, except at S2, S11, and S14 where the two were weakly negatively related (Fig. 7). Dissolved ON was weakly positively related to DOC at S14 only. pH decreased with increases in DOC concentration (Table 3).

Magnesium, Ca^{2+}, C_b, pH, SO_4^{2-}, and Si concentration decreased in response to increases in NO_3^- in many locations, or were not related (Table 3, Fig. 8). Ammonium was weakly related at S11 only, DON was not related, while total N was highly positively related to NO_3^- concentrations at each sampling location (Table 3).
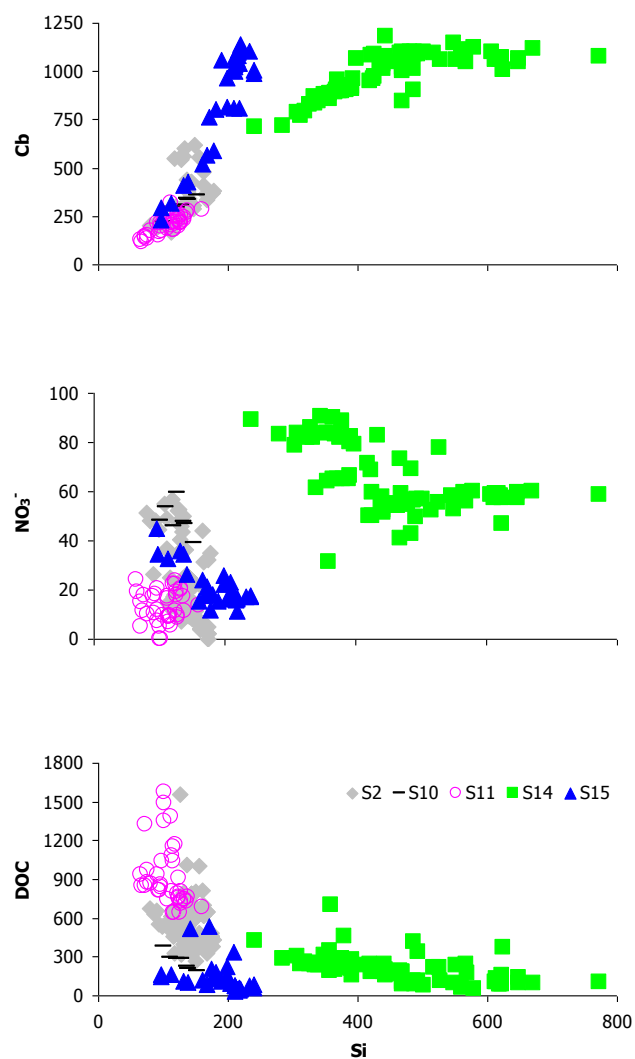
Fig. 5. Spatial relationships between concentrations (μmol L^{-1}) of sum of base cations (C$_b$), NO$_3^-$, DOC, and Si at several[2] sampling locations in the Archer Creek watershed. [2]Other locations had insufficient data to evaluate. C$_b$ includes K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}.
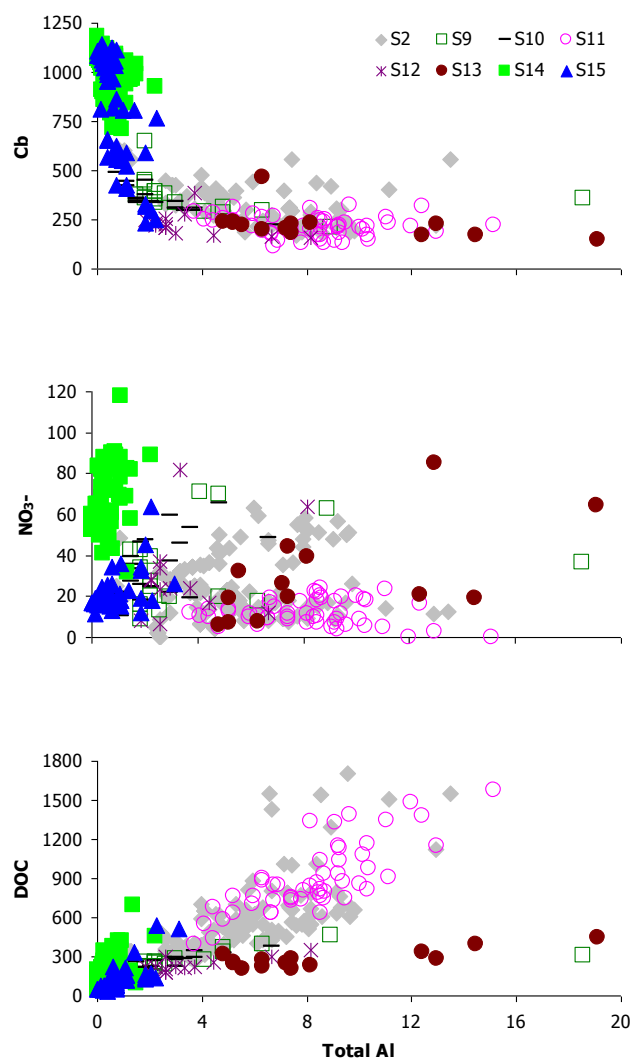
Fig. 6. Spatial relationships between concentrations (μmol L^{-1}) of sum of base cations (C$_b$), NO$_3^-$, DOC, and total Al at sampling locations in the Archer Creek watershed. C$_b$ includes K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}.

3.4 Temporal dynamics in solute concentration and isotopic composition

The main effect of period was significant for δ^{15}N$-$NO$_3^-$ only. All other solutes had significant interactions described below. Average δ^{15}N$-$NO$_3^-$ values ranged from a low of +1.4‰ during snowmelt to +4.1‰ during fall. Period interacted with year for pH, and for the concentrations of NH$_4^+$, NO$_3^-$, total N, DOC, and total Al (Table 2).

Snowmelt in 2001 exhibited the lowest pH among the studied period*year interactions. Summer during both years exhibited the highest pH, but it was not significantly different than pH in winter, spring, or fall (Fig. 9). Nitrate concentrations peaked during snowmelt of 2001 at ~69 μmol L^{-1}. Snowmelt 2002, and both winters exhibited next highest

NO$_3^-$ concentrations. Spring and fall had similar NO$_3^-$ concentrations in both years and periods (Fig. 9). Total N followed the NO$_3^-$ pattern closely. Dissolved OC peaked in spring and fall of 2001, and dipped in summer 2002, otherwise it stayed fairly consistent (Fig. 9). There was more total Al in spring, summer, and fall of 2001 than during those periods in 2002, with winter and snowmelt exhibiting similar values for both years (Fig. 9).

3.5 Relationships among solutes across periods

Magnesium, Ca^{2+}, and C$_b$ increased with Si; the highest regression coefficients (r^2 values) were observed during snowmelt and spring (Table 4, Fig. 10). Ammonium was not related to Si, but NO^{3-} was positively related, with highest
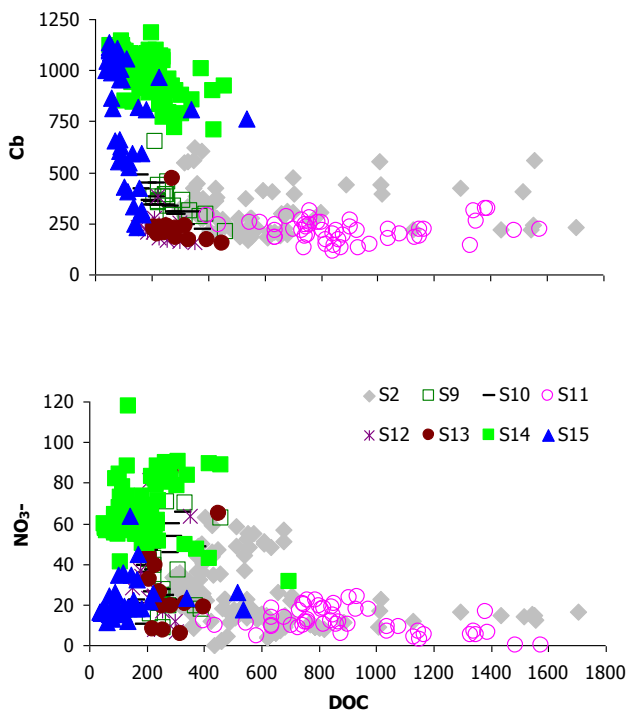
Fig. 7. Spatial relationships between concentrations (μmol L^{-1}) of sum of base cations (C$_b$), NO$_3^-$, and DOC at sampling locations in the Archer Creek watershed. C$_b$ includes K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}.

r^2 values during spring, summer, and fall (Table 4, Fig. 10). Sulfate was positively related to Si in all but fall period, with the highest r^2 in snowmelt (Table 4). pH was positively related to Si in all periods but summer. Dissolved OC and total Al were negatively related to Si with highest r^2 in spring (Table 4, Fig. 10). Dissolved ON was not related to Si except in spring, when the relationship was weak and negative (Table 4).

Total Al concentrations were negatively related to most solutes, except NH$_4^+$, DON, and DOC, which increased with increasing Al during most periods (Table 4, Fig. 11). Spring exhibited highest r^2 values for most solutes with Al, followed by fall (Table 4).

Concentration of DOC was not as strongly related to solute concentrations as Si or total Al (Table 4, Fig. 12). Except for NH$_4^+$, DON, and total Al, all other solutes were negatively related to DOC (Table 4).

Calcium, C$_b$, SO$_4^{2-}$, and Si concentrations, and pH increased with increases in NO$_3^-$ in all discharge periods; r^2 ranged from 0.14 for SO$_4^{2-}$ in summer and fall, to 0.90 for Si in spring (Table 4, Fig. 13). Magnesium also increased with NO$_3^-$ from winter through spring, but these two solutes were not related in summer or fall. Total N increased in snowmelt through fall, but was not related in winter. Weakly negatively related to NO$_3^-$ were NH$_4^+$ and DON during snowmelt
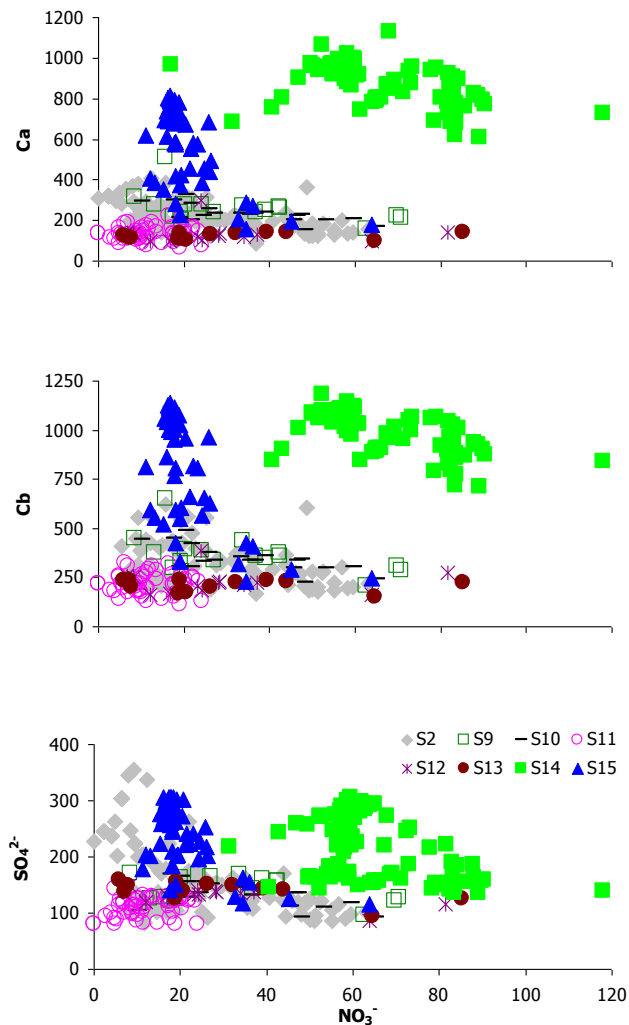

Fig. 8. Spatial relationships between concentrations (μmol L^{-1}) of Ca^{2+}, sum of base cations (C$_b$), SO$_4^{2-}$, and NO$_3^-$ at sampling locations in the Archer Creek watershed. C$_b$ includes K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}.

and spring only, and DON additionally in fall. Dissolved OC and total Al were negatively related to NO$_3^-$ all year around (Table 4).

3.6 Relationships of solutes to discharge

Most solutes exhibited significant regressions with daily discharge at S2, S10, S11, S14, and S15; NO$_3^-$ and daily discharge had significant r^2 in every sampling location (Table 5). Most solutes had significant regressions with adjusted cumulative discharge per period at S2, S10, S14, and S15, and NO$_3^-$ was significant in every sampling location. Most solutes had significant regressions with previous period's cumulative discharge at S2, S10, S11, and S14; NO$_3^-$ was highly positively related to previous cumulative discharge at S9, not related at S14 or S15, and could not be evaluated at S12 or S13 (Table 5).
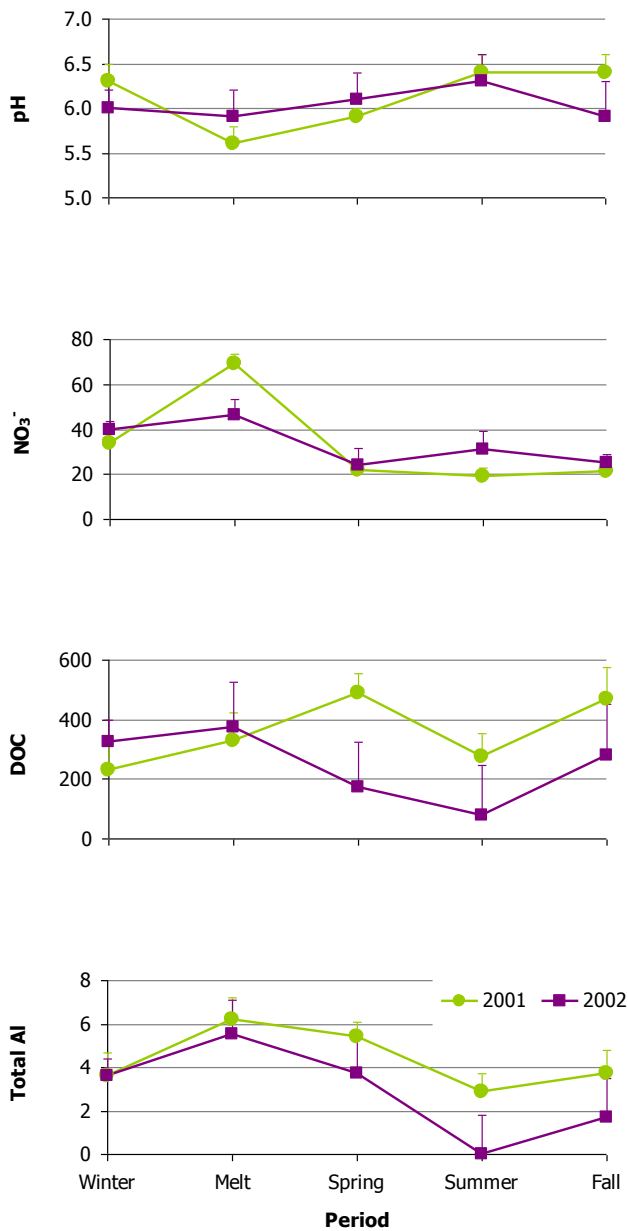
Fig. 9. Average pH, and concentrations (μmol L^{-1}) of NO$_3^-$, DOC, and total Al in two years at five discharge periods, with standard errors (+) shown.

Fig. 10. Temporal relationships between concentrations (μmol L^{-1}) of sum of base cations (C$_b$), NO$_3^-$, DOC, and Si across discharge periods. C$_b$ includes K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}.

4 Discussion

4.1 Spatial patterns in solute concentrations are driven by solute sources and may be moderated by discharge levels

Archer Creek watershed has a complex topography which includes two wetlands and two groundwater sources. The forested wetland at S11 and deep groundwater at S14 exerted dominant influence over stream water chemistry at thei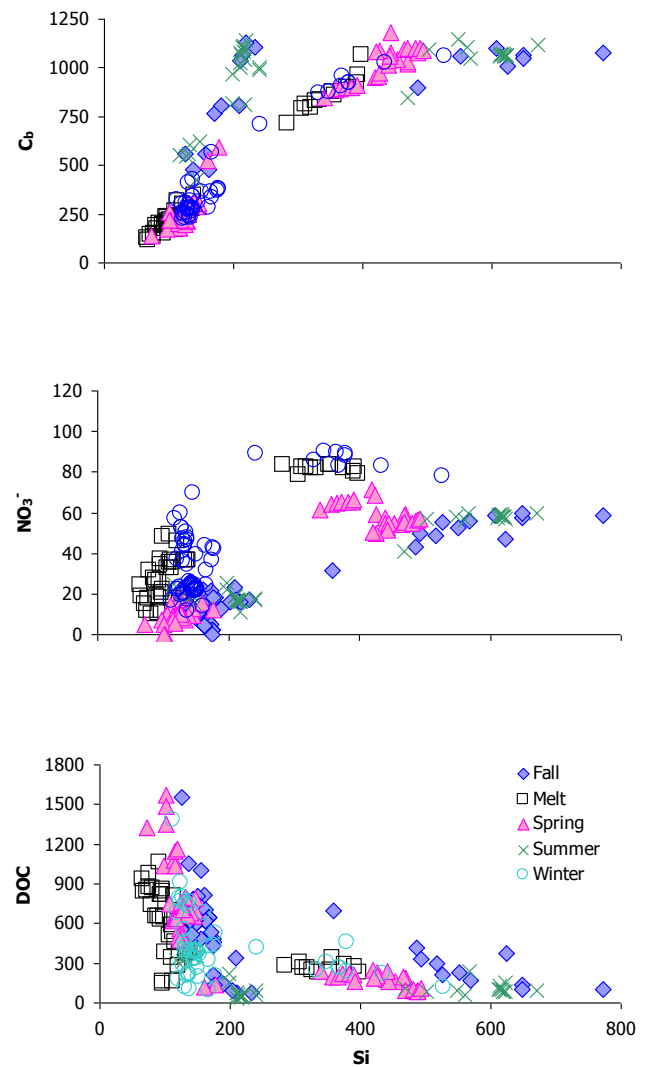r respective locations. That dominance was attenuated else-where. The importance of a smaller, alder-supporting wetland at S2 (watershed outlet), and shallow groundwater at S15 was moderated by discharge levels. We also identified discharge-dependent source areas for individual solutes, including total Al at S13 and NO$_3^-$ at S14 during snowmelt. We discuss these and other observations in detail below.

The wetland draining to S11 exerted its dominance over stream water chemistry through highest DOC, and some of the lowest NO$_3^-$ concentrations observed in Archer Creek. Further, S11 exhibited discharge-dependent peaks in total Al and troughs in pH (Table 2; Fig. 4). High DOC and low NO$_3^-$ are consistent with incomplete and slow organic matter breakdown in conditions of low oxygen in wetlands. Low NO$_3^-$ concentrations may be additionally due to denitrification. A trend toward depleted values of δ^{15}N$-$NO$_3^-$,

Table 4. Significant ($p \leq 0.05$) r^2 values for regression analyses of individual solute concentrations with five discharge periods at the Archer Creek watershed (Adirondack Mountains, New York, USA). +/− sign indicates the direction of the relationship. Blank cells indicate non-significant r^2 values. i.d.=insufficient data to evaluate.

	pH	NH$_4$	Mg	Ca	C$_b^1$	SO$_4^{2-}$	Si	NO$_3^-$	DON	Total N	DOC	Total Al
					– Si –							
Winter	+0.63		+0.54	+0.94	+0.93	+0.52	1	+0.59		+0.49	−0.14	−0.30
Snowmelt	+0.72		+0.90	+0.98	+0.98	+0.80	1	+0.76		+0.74	−0.41	−0.68
Spring	+0.66		+0.79	+0.98	+0.98	+0.68	1	+0.90	−0.22	+0.90	−0.65	−0.81
Summer			−0.37	+0.67	+0.33	+0.12	1	+0.85		+0.71	−0.14	−0.21
Fall	+0.21		−0.21	+0.72	+0.47		1	+0.93		+0.79	−0.27	−0.41
					– total Al –							
Winter	−0.54	+0.19	−0.43	−0.29	−0.33	−0.35	−0.30	−0.13	+0.21		+0.48	1
Snowmelt	−0.66		−0.67	−0.57	−0.59	−0.56	−0.68	−0.28	+0.15	−0.23	+0.46	1
Spring	−0.66	+0.19	−0.76	−0.66	−0.68	−0.72	−0.81	−0.62	+0.13	−0.49	+0.65	1
Summer	−0.29	−0.12	−0.24	−0.53	−0.60	−0.31	−0.21	−0.20		−0.13	+0.74	1
Fall	−0.63	+0.15		−0.38	−0.38			−0.41	−0.31	+0.66	+0.89	1
					– DOC –							
Winter	−0.40		−0.31	−0.17	−0.19	−0.38	−0.14	−0.13	+0.15	−0.05	1	+0.48
Snowmelt	−0.67	+0.12	−0.51	−0.32	−0.34	−0.44	−0.41	−0.62	+0.30	−0.49	1	+0.46
Spring	−0.45	+0.40	−0.50	−0.40	−0.42	−0.65	−0.65	−0.43	+0.22	−0.26	1	+0.65
Summer	−0.18		−0.18	−0.39	−0.43		−0.14	−0.10	+0.11		1	+0.74
Fall	−0.45	+0.20		−0.21	−0.22		−0.27	−0.22	+0.74		1	+0.89
					– NO$_3^-$ –							
Winter	+0.37		+0.06	+0.56	+0.51	+0.07	+0.59	1			−0.11	−0.13
Snowmelt	+0.62	−0.15	+0.58	+0.51	+0.52	+0.38	+0.76	1	−0.12	+0.95	−0.62	−0.28
Spring	+0.58	−0.10	+0.55	+0.86	+0.84	+0.50	+0.90	1	−0.12	+0.90	−0.43	−0.62
Summer	+0.11			+0.55	+0.36	+0.14	+0.85	1		+0.83	−0.09	−0.20
Fall	+0.24			+0.55	+0.36	+0.14	+0.93	1	−0.12	+0.87	−0.22	−0.31

[1]C$_b$ is the sum of basic cations: K$^+$, Na$^+$, Mg^{2+}, and Ca^{2+}.

observed at both wetland-influenced sampling locations, has been associated with low rates of organic matter turnover in water-logged conditions (Kendall, 1998).

Our observations support earlier work in this watershed by Inamdar et al. (2004), who noted that wetlands controlled DOC concentrations during a summer storm at the watershed outlet. Our data indicate that wetlands control DOC concentrations in the lower reaches of this watershed throughout the year, with S11 contributing more than S2. The positive relationships between DOC and total Al in all discharge periods, and strong relationship between DOC and Al at S10, S12, and S13 (Fig. 6; Tables 3 and 4) indicate that soil horizons in some of the mid elevations also contribute DOC. Forest floors constitute the largest sources of DOC across temperate forests (Michalzik et al., 2001), but it is not clear how that changes when wetlands are present. In our watershed, the relative contribution of wetlands to DOC appears to be far more important than that of the forest floor (Fig. 2 this study; Park et al., 2003; Inamdar et al., 2004; Piatek et al., 2005).

Groundwater at S14 clearly exerted a major influence over stream chemistry at upper elevations, providing high pH through high concentrations of Mg^{2+}, Ca^{2+} and Si, and low Al. Water at S14 originates from deep groundwater sources (McHale et al., 2002). Calcium, SO$_4^{2-}$ and Si were negatively related to daily, cumulative, and previous cumulative discharge (Table 5) suggesting dilution of groundwater by atmospheric solutions mostly during high discharge.

Groundwater at S14 was also an apparent source of NO$_3^-$. However, the negative relationship across sampling points between NO$_3^-$ and Si – the groundwater indicator – and a positive one between NO$_3^-$ and Al – the mineral soil indicator – suggest that the source of NO$_3^-$ is soil rather than groundwater. Soil source of NO$_3^-$ is further supported by positive relationships of NO$_3^-$ with daily and cumulative discharge levels indicating that when more of the soil profile is flushed, stream responds with higher NO$_3^-$ levels. Formation of NO$_3^-$ in S14 was attributed in earlier studies in this
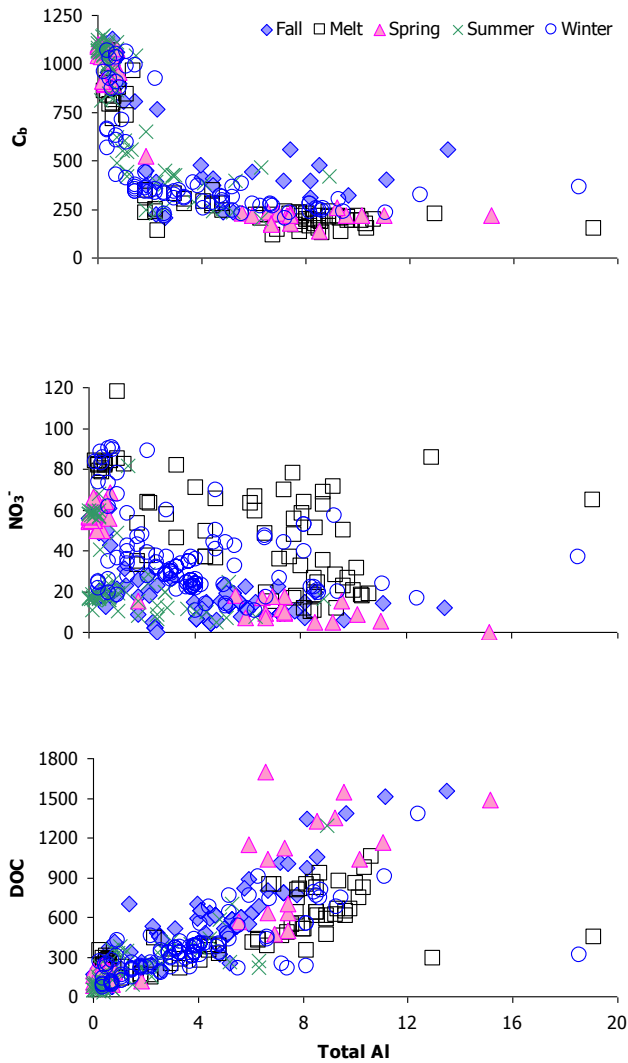
Fig. 11. Temporal relationships between concentrations (μmol L^{-1}) of sum of base cations (C$_b$), NO$_3^-$, DOC, and total Al across discharge periods. C$_b$ includes K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}.

Fig. 12. Temporal relationships between concentrations (μmol L^{-1}) of sum of base cations (C$_b$), NO$_3^-$, and DOC across discharge periods. C$_b$ includes K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}.

watershed to vegetation composition, and linked to Ca levels in soils (Christopher et al., 2006; Page et al., 2008). Sugar maple (*Acer saccharum*), in high proportion in the S14 sub-watershed, is known for its association with high soil NO$_3^-$ (Lovett et al., 2002; Lovett and Mitchell 2004; Christopher et al., 2006) probably due to fast decomposition of sugar maple foliar litter. Upper soil horizons were hotspots for nitrification in the Catskill Mountains of New York, which have similar topography to the Adirondack Mountains (Welsch et al., 2001).

Therefore, two sources of NO$_3^-$ are evident in the Archer Creek watershed. One source is discharge-independent and originates in groundwater (at S14), while the other is discharge-dependent and is flushed directly from the soil profile in upper watershed. The actual functioning of this most
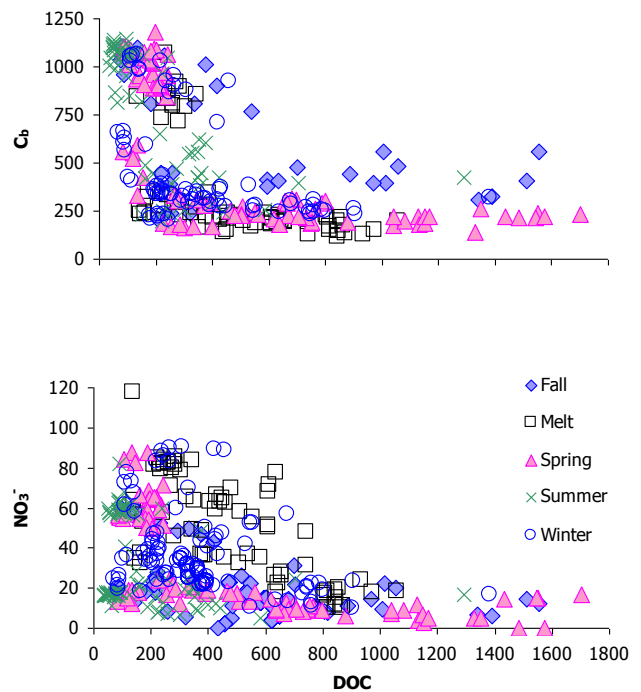
likely includes the flushing-draining mechanism described by Creed et al. (1996), in which once produced in soils, NO$_3^-$ movement may be to stream or to groundwater, depending on hydrologic connectivity at the sampling location. Thus, groundwater is probably recharged with NO$_3^-$ during periods when connectivity between soil and stream may be lost due to insufficient saturation in that location, which can still support draining. Groundwater serves as the secondary source of NO$_3^-$ when soil nitrate sources are likely to be disconnected from stream due to low soil saturation during the growing season.

Two sources of NO$_3^-$ are consistent with several earlier observations in this watershed. First, a combined isotopic and chemistry analysis showed that the main source of NO$_3^-$ during snowmelt was soil (Piatek et al., 2005). Second, the source of NO$_3^-$ during summer storms determined by hydrograph separations appeared to be groundwater (McHale et al., 2002). Further, isotopic values of δ^{18}O$-$NO$_3^-$ in stream water in this study were well below those for atmospheric NO$_3^-$ of +72.0‰ at this site (Piatek et al., 2005), showing that nitrification, not atmospheric deposition, was the source of NO$_3^-$ in stream water; both ground and soil water have similar isotopic values of NO$_3^-$ (Kendall, 1998; Piatek et al., 2005). This study extends the evidence for lack of presence of atmospherically-derived NO$_3^-$ in creek water from snowmelt and fall storms to other parts of the year in our watershed and elsewhere (Burns and Kendall, 2002; Pardo et

al., 2004; Piatek et al., 2005; Mitchell et al., 2006; Hales et al., 2007) and indicates high level of atmospheric NO_3^- retention by forests with long-term atmospheric N deposition and symptoms of N saturation (Aber et al., 1989, 1998; Stoddard, 1994).

S15, located in close proximity to S14, exhibited contrasting stream chemistry to S14. Nitrate concentrations were on average 60% lower at S15 than at S14, and Mg^{2+} was almost twice as much at S15 in summer and fall than at S14. Chemistry at S15 varied with discharge levels clearly indicating a potential influence of soil water when discharge levels were high. This supports earlier studies on the sources of water in these two sampling locations; S15, discharging shallow groundwater, most likely has a more immediate connectivity with soil water than S14, the source of deep groundwater (McHale et al., 2002).

In the current analysis, SO_4^{2-} concentration, highest at S14 and S15, was highly positively related to Si, and negatively related to Al or DOC, suggesting that groundwater in upper elevation is an important contributor of this solute. An internal source of SO_4^{2-} in this watershed was also clearly shown using isotopic analyses (Campbell et al., 2006). Temporal patterns of SO_4^{2-} versus Si also indicate that groundwater was the source of this solute (Table 4). The high concentrations of SO_4^{2-} in fall and low during snowmelt (Table 5) reflect the addition of wetland-derived SO_4^{2-} in fall 2002 to SO_4^{2-} normally present in this watershed from groundwater (Mitchell et al., 2006), and dilution of groundwater and groundwater-related solutes during snowmelt.

Wetland source of SO_4^{2-}, observed during fall storms following an unusually dry summer (Mitchell et al., 2006) now appears to be episodic. In fact, both wetland-draining sampling locations, S2 and S11, had significantly lower average SO_4^{2-} concentrations than the groundwater sources. Models of climate change predict an increase in extremes in weather patterns such as droughts (Meehl et al., 2000; Kharin and Zwiers, 2005), therefore, wetland-derived SO_4^{2-} may be found more commonly under changing climatic conditions. Drought-induced oxidation of previously-reduced and wetland-stored sulfur was also described in catchments in Eastern Canada (Schiff et al., 2005).

S13 contributed the majority of Al to the Archer Creek system, with smaller amounts added by wetlands. Contributions were highly dependent on discharge, except at S11, where specific conditions may change the way discharge affects Al and how the two are related. At S13, the extensive subwatershed area of 41.9 ha (31% of total watershed) would be expected to contribute a large proportion of soil-derived solutes under conditions of hydrologic connectivity with the stream. A substantial decrease in Al between S13 and S9 may be indicative of dilution or a presence of an Al sink. S9, as a mixing area for S13, S14, and S15 (Fig. 1), receives high levels of Si, Ca^{2+}, Mg^{2+}, and SO_4^{2-}, making Al complexation and precipitation possible.
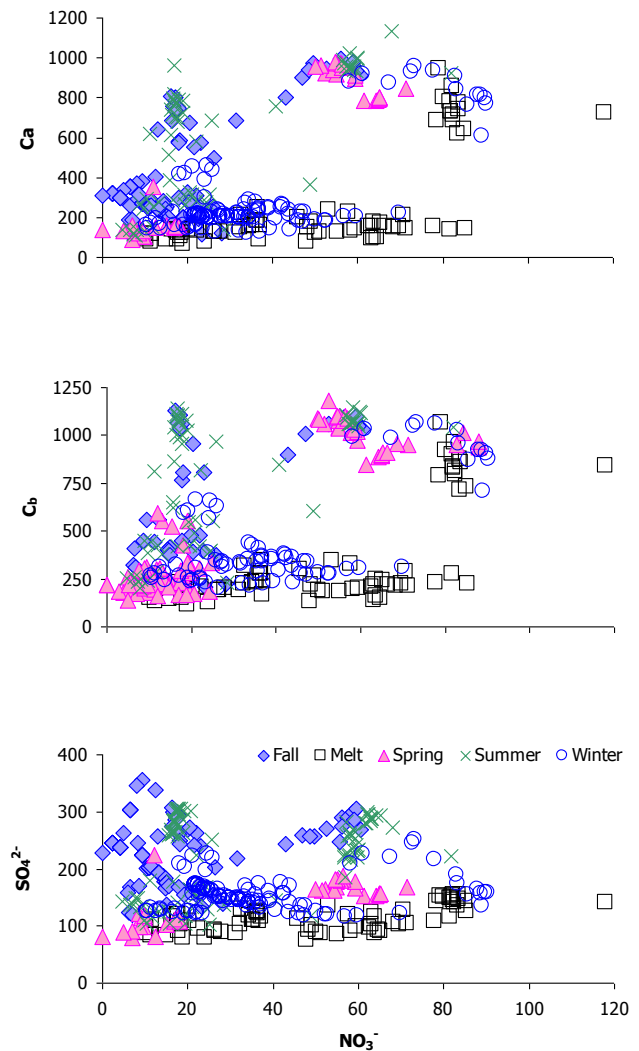

Fig. 13. Temporal relationships between concentrations ($\mu mol\,L^{-1}$) of Ca^{2+}, sum of base cations (C_b), SO_4^{2-}, and NO_3^- across discharge periods. C_b includes K^+, Na^+, Mg^{2+}, Ca^{2+}.

4.2 Does chemistry at the outlet adequately represent chemistry in the watershed?

Previous studies in this and in many other watersheds focused on chemistry at the watershed outlet only. As the mixing area, it is assumed that the outlet reflects the variety of sources and processes within the watershed. Our study sheds some light on the validity of this assumption. In this study, we have detected much spatial variation in surface water chemistry. The main effect of sampling location was significant for DOC, SO_4^{2-}, NO_3^-, and total N, while for many other solutes, the effect of sampling location was dependent on discharge period.

Pair-wise comparisons (each sampling location with every other one) indicated that most consistent differences in DOC,

Table 5. Significant ($p \leq 0.05$) r^2 values for regression analyses of daily, cumulative, and previous cumulative discharge on solute concentrations at sampling locations 2–15 in the Archer Creek watershed (Adirondack Mountains, New York, USA). +/− sign indicates the direction of the relationship. Blank cells indicate non-significant r^2 values. i.d.=insufficient data to evaluate.

	pH	Mg	Ca	C_b^1	SO_4^{2-}	Si	NO_3^-	DON	Total N	DOC	Total Al
				– daily discharge (mm day^{-1}) –							
2	−0.13	−0.31	−0.32	−0.32	−0.10	−0.57	+0.29				+0.32
9	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.
10		−0.88	−0.88	−0.88	−0.87	−0.89	+0.46			+0.88	+0.84
11	−0.17	−0.28	−0.16	−0.24	−0.15	−0.47	+0.30		+0.19		
12	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	+0.36	i.d.	i.d.	i.d.	i.d.
13		−0.33					+0.36				
14		−0.07	−0.60	−0.58	−0.23	−0.41	+0.28	+0.16	+0.36	+0.26	+0.07
15	−0.27	−0.58	−0.59	−0.59	−0.60	−0.70	+0.65		+0.39		+0.49
				– cumulative discharge (mm period^{-1}) –							
2	−0.17	−0.68	−0.56	−0.66			+0.54		+0.15		+0.27
9	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	+0.66	i.d.	i.d.	i.d.	i.d.
10		−0.68	−0.67	−0.68	−0.73	−0.72	+0.73			+0.66	+0.65
11							+0.39		+0.41	−0.15	
12	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	+0.59	i.d.	i.d.	i.d.	i.d.
13	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	+0.80	i.d.	i.d.	i.d.	i.d.
14	+0.19	+0.06	−0.36	−0.34	−0.57	−0.69	+0.39	+0.10	+0.39	+0.37	+0.16
15	−0.26	−0.81	−0.87	−0.86	−0.69	−0.82	+0.49	+0.21	+0.44		+0.52
				– previous cumulative discharge (mm period^{-1}) –							
2	+0.10	−0.28	−0.31	−0.27	−0.49	−0.15	+0.10	−0.21	−0.26		
9	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	+0.80	i.d.	i.d.	i.d.	i.d.
10		−0.68	−0.67	−0.68	−0.73	−0.72				+0.66	+0.65
11	−0.34	−0.33	−0.40	−0.38	−0.46	−0.30	−0.10		−0.10		
12	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.
13	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.
14	+0.9	+0.25			−0.37	−0.18					−0.7
15								−0.24		−0.15	

$^1 C_b$ is the sum of basic cations: K^+, Na^+, Mg^{2+}, and Ca^{2+}.

SO_4^{2-}, NO_3^-, and total N were between watershed outlet and S14, the deep groundwater source, S15, the shallow groundwater source, and S11, the extensive wetland, and related to specific solute levels. However, discharge-related changes in concentrations at the source areas were well reproduced at the watershed outlet. Chemistry at the outlet was comparable to stream chemistry elsewhere in the watershed outside of the source areas, both in terms of specific concentrations and discharge-related dynamics. Interestingly, linkage of NO_3^- with DOC that has been suggested in earlier studies (Park et al., 2003; Piatek et al., 2005), has not been confirmed here, as evidenced by weak or no relationships between NO_3^- and DOC across both space and time (Tables 3 and 4). Lack of consistent relationships between NO_3^- and DOC across studies in this watershed is not surprising given that previous studies focused on watershed outlet, which has significantly

lower levels of solutes than their source areas, and individual source areas may be differently affected by discharge levels.

4.3 Temporal patterns in solute concentrations are driven by discharge dynamics

The main effect of period was limited to $\delta^{15}N-NO_3^-$, probably reflecting insufficient data in some of the observed periods. Otherwise, period interacted with sampling point for Mg^{2+}, Ca^{2+}, C_b, Si, pH, and Al, and with year for NO_3^-, total N, DOC, and Al (Table 2).

Snowmelt diluted solutes originating in groundwater at S14 and S15 and flushed to stream those solutes which originated in soil horizons. This effect of snowmelt was strongest at the respective solute sources. Snowmelt, spanning at most 30 days around mid-April, carries the largest percentage of the annual discharge in the shortest amount of time (Table 1).

This effect of high discharge is related to the steep topography of this watershed and illustrates that large volumes of water have the capacity to explore and flush a large percentage of the upland contributing areas which results in flushing of higher amounts of soil-derived solutes.

By contrast, periods with low discharge such as summer and fall were generally characterized by higher pH, Mg^{2+}, Ca^{2+}, C_b, and among the lowest Al and DOC concentrations (Figs. 3 and 4). Low-discharge periods reflect maximum contributions from groundwater in our creek system (McHale et al., 2002) and decreasing contributions of soil water as watershed saturation decreases and hydrologic connectivity is gradually lost. In extreme cases, water ceases to flow between sampling locations, as we observed at S12 during the drought of summer 2002. As mainly groundwater, characteristics of summer discharge may reflect the dominant type of parent materials in the watershed, one high in Ca (subwatershed S14), and one high in Mg (subwatershed S15). Despite a dry spell in one of the two observed summers (2002), and a series of storms in one of the two observed autumns (2002), these two periods did not result in stream water chemistry that stood out as statistically different (at $p \le 0.05$) from others. Most likely, this reflects variability in solute concentrations in this topographically-diverse catchment.

4.4 Are high or unusual discharge periods representative of average solute levels?

Unusual weather patterns may be representative of more extreme weather predicted for climate change scenarios (Meehl et al., 2000; Kharin and Zwiers, 2005). We had a unique opportunity to evaluate whether differences in biogeochemical patterns among periods with unusually low and unusually high discharges are still representative of patterns observed during average discharge. Specifically, we compared solute concentrations for snowmelt 2001, summer 2002, and fall 2002 with all other discharge periods. Snowmelt 2001 had the highest discharge of any period in the two years of study. Summer 2002 brought an unusually long drought, while fall 2002 featured several storms which followed the prolonged summer drought.

In general, snowmelt 2001 stood out as the most biogeochemically different among all other periods, with among the lowest pH and Mg^{2+}, highest NO_3^- and total N, and among the highest total Al (Fig. 9). Discharge in snowmelt 2001 constituted 46% of total that year, and it was 61 mm more than in 2002 (Table 1). Highest NO_3^- and lowest pH during snowmelt 2001, and among the lowest total Al and DOC during drought in summer 2002 suggest that, with an increase in extreme weather patterns, we could expect issues with stream acidity and the presence of high levels of NO_3^- during high-discharge snowmelts, and low DOC and AL inputs, during droughts.

Fall 2002, despite several storms and an additional source of SO_4^{2-} from wetland oxidation (Mitchell et al., 2006), was surprisingly similar to other periods. Therefore, whether high-discharge events adequately represent stream chemistry at average discharge levels depends on solute and discharge level. It appears that an understanding of watershed-specific temporal context of solute expression will be important in this regard.

5 Conclusions

We have refined our understanding of solute generation in the Archer Creek watershed to include a multi-dimensional mosaic of space and discharge periods. In this mosaic, base cations are derived from groundwater discharging in upper watershed, and DOC primarily from wetlands. In the absence of unusual climatic events such as droughts, SO_4^{2-} is also contributed by groundwater. Nitrate produced in soils is flushed to stream when catchment saturation allows hydrologic connectivity between source-areas and stream, otherwise NO_3^- apparently drains to groundwater at S14 which discharges it to stream when nitrification is likely to be limited or when soil source-areas are hydrologically disconnected from stream. Individual source-areas (S13) contribute most of the Al at high discharge. Watershed outlet does not appear to reproduce high concentrations typical of source-areas in the watershed. Similarly, observations at high-discharge events alone do not characterize solute dynamics at all other discharge levels. However, watershed outlet represents relative solute dynamics quite well, and high discharge events are responsible for the largest solute fluxes. Therefore, whether the spatial or temporal resolution obtained at watershed outlet or at high discharge events respectively is sufficient or not must be dictated by research objectives.

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