**Hydrology and
Earth System
Sciences
Discussions**

Spatial and temporal dynamics of stream chemistry in a forested watershed impacted by atmospheric deposition

K. B. Piatek[1], **S. F. Christopher**[2], **and M. J. Mitchell**[3]

[1]West Virginia University, Division of Forestry and Natural Resources, P.O. Box 6125, Morgantown, WV 26506, USA
[2]State University of New York, College at Buffalo, The Great Lakes Center, Buffalo, NY 14222, USA
[3]State University of New York, College of Environmental Sciences and Forestry, 1 Forestry Drive, Syracuse, NY 13210, USA

Correspondence to: K. B. Piatek (kathryn.piatek@mail.wvu.edu)

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Abstract

We analyzed spatial and temporal dynamics of solute chemistry in a forest watershed impacted by atmospheric deposition in the Adirondack Mountains of New York State, USA. Spatial dynamics of solute chemistry and natural abundance isotopes of nitrate (^{15}N and ^{18}O) were examined in 6 locations and the watershed outlet in 2001 and 2002. Temporal dynamics were examined during 5 discharge periods: winter, snowmelt, spring, summer, and fall, which were based on discharge levels at the outlet. Solute concentrations were statistically significantly different ($p \leq 0.05$) among stream sampling locations and discharge periods, with no interaction effects. Groundwater sources located in upper watershed controlled stream chemistry at higher elevations with highest pH, Ca^{2+}, sum of base cations, Si, NO_3^-, total N, and SO_4^{2-} and lowest Al concentrations. Two low elevation wetlands had a substantial influence over stream chemistry at those locations contributing lowest NO_3^-, total N, and highest DOC and DON. Snowmelt exhibited among the lowest pH, sum of base cations, and SO_4^{2-}, and highest NO_3^-, total N, DON, 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 together with patterns of NH_4^+ versus NO_3^- dynamics indicated that NO_3^- was microbial, generated in fall and accumulated in winter in upper watershed soils, and flushed to stream during high discharge events. Highest discharge in snowmelt 2001, a summer drought in 2002, and fall storms following the drought were further evaluated for their specific effects on stream chemistry. Snowmelt 2001 had the lowest pH and highest NO_3^-, base flow during summer drought had the lowest total Al, and storms in fall 2002 had highest SO_4^{2-} of all periods, but all other solute concentrations were comparable to other discharge periods in this study. Depending on objectives, watershed outlet alone may sufficiently represent solute dynamics in the watershed, and high-discharge events may sufficiently describe solute fluxes for the watershed.

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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 in turn associated with the losses of Ca and Mg with possible increases in soil acidification 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, but it does not provide information on the spatial variation of surface water chemistry within the watershed (Ogawa et al., 2006; Ito et al., 2007).

Temporal dynamics of solute concentrations is a complex result of differing patterns of solute production and consumption integrated via hydrological 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, or relatively high rates of consumption.

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 is impacted by atmospheric N deposition at rates of 10.1 kg N ha^{-1} yr^{-1} (Park et al., 2003), and with stream NO_3^- exports of 4.2 kg N ha^{-1} yr^{-1} (Mitchell et al., 2001), it is considered at stage 1 of N saturation (Stoddard, 1994). 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 nitrate to groundwater, facilitated by steep slopes, probably serves to recharge groundwater nitrate (Inamdar et al., 2004). In this system, groundwater appears to become the primary source of nitrate to stream during periods of high N demand by biota (summer), low rates of nitrification (summer and winter), 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, snowmelt and other high-flow events result in increases in acidity in stream water, with potential consequences for aquatic habitat. This was especially acute during consecutive fall storms following 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 dynamics. 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 a year with a very high discharge at snowmelt, and a summer drought followed by several late summer/ early fall storms; we used those hydrologically distinct periods to test whether they produced marked differences in stream 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 spans 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 up to 90% calcium-rich feldspar. Upland soils are coarse loamy, isotic, frigid,

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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* (American beech) and *Acer saccharum* (sugar maple) dominate the overstory at mid- and higher elevations, while *Tsuga canadensis* (eastern hemlock) and *Picea rubens* (red spruce) dominate at lower elevations. *Abies balsamea* (balsam fir) and *Pinus strobus* (white pine) are scattered throughout the watershed. Some of the wetlands support *Alnus rubrum* (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 buy 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 100 feet 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 reading recorded 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:

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winter, snowmelt, spring, summer, and fall. Specific dates which correspond to these periods are listed in Table 1. For analysis, length of discharge period was adjusted to the same number of days in each year to allow comparisons of cumulative discharge per period (Table 1).

5   Stream water was sampled for chemistry at the H-flume weekly 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

10   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

15   and fast-flowing. Watershed outlet (S2) and 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.

20   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, 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 per-

25   sulphate 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. The 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 both years. Stream water in the tributaries and in mid-channel was tested once a month during the study period, except when snow hindered access. Reported 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, and analyzed on a Micromass IsoPrime stable isotope mass spectrometer. The reported values are defined as:

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

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

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^-. 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) discharge periods (winter, snowmelt, spring, summer, and fall), and stream sampling locations (S2 to S15) with analysis of variance in SAS (SAS Institute®). We used the

"weight" statement to adjust for unequal sample number across locations. First, we evaluated the following full statistical model:

$[S]_{ijk} = \mu + Y_i + P_j + (YP)_{ij} + L_k + (YL)_{ik} + (PL)_{jk} + (YPL)_{ijk} + e_{ijk}$, where

$[S]$ = solute concentration at any one instant

5   μ = overall mean observation

Y_i = fixed effect of year (i=1, 2)

P_j = fixed effect of discharge period (j=1–5)

YP_{ij} = fixed effect of interaction of year and discharge period

L_k = fixed effect of location of stream sampling points (k=2–15)

10   YL_{ik}= fixed effect of interaction of year and location of stream sampling point

PL_{jk} = fixed effect of interaction of discharge period and location of sampling point

YPL_{ijk} = fixed effect of a three-way interaction of year, period, and location, and

e = random error term.

    Second, if year and its higher level interactions were not significant ($p{\geq}0.05$), we

15 evaluated (in most instances) the following reduced model:

$[S]_{jk} = \mu + P_j + L_k + (PL)_{jk} + e_{jk}$.

2.5   Relationships among solutes across space and time

We graphed solute concentrations at their individual locations and at different discharge periods against key source indicators of groundwater (Si), mineral soil (Total Al), and

20 forest floor or wetland (DOC) to better understand how these relations change with space and time.

2.6   Relationships of solutes to discharge

We performed linear regression analyses of several discharge parameters with solute concentrations to better understand how these relations change across space depend-

25 ing on daily, current cumulative, and previous cumulative discharge. Daily discharge was discharge on a given day in mm per day, current cumulative discharge was total

discharge added for adjusted number of days per period (the same in both years) in mm per period, and previous discharge was cumulative discharge for the period immediately preceding the one tested, in mm per period.

2.7 Biogeochemical differences among hydrologically distinct discharge events

To evaluate differences in solute concentrations between specific discharge periods, we used data from the watershed outlet (S2) because these were most extensive. A still reduced ANOVA model was applied ($[S]_j = \mu + P_j + e_{jk}$, i.e. no location effect) and differences between periods were evaluated with a means separation procedure in SAS. To ensure overall protection level, we compared only specific periods of interest: snowmelt of 2001, which had the highest discharge of any other period in the two years of study, summer 2002, which experienced an unusual drought, and fall 2002, which had several storms following the prolonged summer drought.

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 patterns in water chemistry and isotopic composition

Statistically significant differences in chemistry values between sampling year 2001 and 2002 ($p \leq 0.05$) were found only for Total N and DOC. Therefore, all other solute comparisons were tested in a simplified model with the main effects of period and sampling location (Table 2). Stream sampling locations showed variable chemistry, with statistically significant differences for all solutes (Table 3).

The highest pH (7), sum of base cations (985 μmol L^{-1}), and Si concentrations (460 μmol L^{-1}) were observed at S14, which is fed by groundwater (McHale et al., 1999, 2002). Among base cation concentrations, Ca^{2+} dominated base cations at S14, while Mg^{2+} by far exceeded Ca^{2+} at S15. Among measured anions, NO$_3^-$ consis-
5   tently occurred at much higher concentrations at S14 than elsewhere, and SO$_4^{2-}$ was highest (>200 μmol L^{-1}) at both S14 and S15. S14 and S15 had lowest values of total Al (<2 μmol L^{-1}) (Table 3).

S13 and S11 had the highest concentrations of total Al. S11 additionally exhibited the lowest SO$_4^{2-}$, NO$_3^-$, and pH, and highest DOC and DON concentrations; in fact, wa-
10   ter color at S11 was strikingly brown due to high DOC contents. S11, S12 and S13 had relatively low pH, sum of base cations, and correspondingly low Ca^{2+} and Mg^{2+} (Table 3). S11 and the watershed outlet (S2) had among the highest DON concentrations, but the differences were not statistically significant (Table 3).

None of the values for natural abundance isotopes of NO$_3^-$ were statistically signifi-
15   cantly different among stream sampling locations. Values of δ^{15}N-nitrate tended to be lowest at S2 and S11, and highest at S10, but at average values of δ^{18}O-nitrate. Average δ^{18}O-nitrate appeared to be highest at the watershed deep groundwater source (S14) and in mid-elevation at S12, and lowest at S13, all at average values of δ^{15}N-nitrate (Fig. 2).

20   3.3   Spatial relationships among solutes

Across sampling locations, simultaneous increases in solute concentrations and Si were noted for base cations and SO$_4^{2-}$, and negative for NO$_3^-$, DOC, DON, and total Al (Fig. 3). All sampling locations had low Si concentrations between 50–250 μmol, but at S14, Si started at about 200 and ranged to 750 μmol. Invariably, the relationships
25   between solute concentrations were different at S14 than elsewhere in the watershed. Major cations and consequently C_b increased faster than Si concentration, but the increase was much slower at S14 than elsewhere, and Mg did not increase at all over

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a wide range of Si concentrations. Sulfate increased along the 1:1 ratio line between 50–250 μmol Si everywhere but at S14, where the rate of increase in SO_4^{2-} was much slower and at higher Si concentrations. pH increased sharply with increasing Si in most sampling locations, but was consistently high at S14. The decrease in NO_3^- at S14 was
5 over much larger concentrations of both NO_3^- and Si than elsewhere. Decreases in DOC, DON, and total Al concentrations at S14 occurred at lower solute concentrations but higher Si concentrations than elsewhere (Fig. 3).

Concentrations of DOC spanned a much wider range at S2 and S11 than elsewhere in the watershed (Fig. 3). Cation and SO_4^{2-} concentrations, and C_b, exhibited no rela-
10 tionship with DOC at S2 and S11, and they were negatively related to DOC elsewhere, with r^2 ranging from 0.1 to 0.7. Increases in NO_3^- were independent of DOC, while DON was negatively related to DOC at S13 and S12, not related at S9, and positively related elsewhere. pH decreased with increases in DOC concentrations.

Across the watershed, cations, C_b, SO_4^{2-} and pH were negatively related to total Al
15 (Fig. 3). Nitrate was positively related to total Al in most of the mid to upper locations, such as S10, S14, and S15, but nor related at S2, S9, S11, and S12. Dissolved OC was positively related to total Al, and exhibited some of the highest r^2. Dissolved ON was positively related to DOC except at S12, S13, and S14 were the two were independent.

Calcium concentration decreased in response to increases in NO_3^- in most locations,
20 but the rate of decrease was different at different locations (Fig. 3). At some of the low reaches of the watershed (S2, S9, S10), the decrease followed a linear function. At S11 and S12, the two were independent, and at S13 Ca slowly increased rather than decreased with NO_3^-. At S14 the relationship was a 2nd order polynomial decrease, and at S15 the decrease was a power function of NO_3^- concentration. Also, SO_4^{2-} was
25 negatively related to NO_3^- in all locations except at S11, where the two were not related.

3.4   Temporal variability in water chemistry and isotopic composition

Water pH ranged from a low of 5.7 during snowmelt to a high of 6.3 during summer, but these differences were not significant (Table 4). Magnesium and Ca^{2+} concentrations were low during snowmelt and high during summer, with significant differences between discharge periods (Table 4). Correspondingly, sum of base cation concentrations varied with sampling period ($p<0.0001$), and increased from a low of 305 at snowmelt to a high of 540 μmol L^{-1} during summer (Table 4).

Silica concentration was first measured in January 2002. During the study period, Si concentrations varied among periods ($p<0.0001$) with a low in winter (155 μmol L^{-1}) and a high in summer (376 μmol L^{-1}) (Table 4).

Average values of NO_3^- concentration peaked during snowmelt at ~55 μmol L^{-1}, with subsequent decreases from spring through fall (Table 4). Natural abundance ^{15}N-nitrate varied with sampling period ($p=0.0015$) with a low of +1.4‰ during snowmelt and a high +4.1‰ during fall, and a similar values of δ^{18}O-nitrate (Fig. 4). Isotopic values of ^{18}O-NO_3^- were lowest during low flow in summer at −0.82‰, and highest in winter at +7.71‰, both at the same value of δ^{15}N-nitrate (Fig. 4).

There were no significant differences in DOC, DON or SO_4^{2-} concentrations between sampling periods (Table 4), and each exhibited high variability. Total Al concentrations were significantly different ($p=0.0022$) among periods, with highest values (6.5 μmol L^{-1}) during snowmelt and lowest (2.4 μmol L^{-1}) in summer (Table 4).

3.5   Temporal relationships among solutes

The relationships among solutes appeared to vary less across discharge periods than across space (Fig. 5). Thus cations including C_b increased with increasing Si at similar rates in each period (C_b shown in Fig. 5). Sulfate was positively related to Si, with the highest r^2 (0.73) in spring (Fig. 5). pH was positively related to Si in all periods. Nitrate increased with Si concentrations in all periods but snowmelt, and the increase in winter

was greatest (Fig. 5). Nitrate concentrations during snowmelt had no relationship to Si. Dissolved OC was negatively related to Si during spring, summer, and fall, but was not related during winter or melt. Dissolved ON was poorly related to Si across discharge periods, with highest r^2 of 0.18 in spring.

Cations, including C_b, SO_4^{2-}, and pH decreased with increasing total Al concentrations, with little variation in rates across discharge periods (Fig. 5). Nitrate varied in its response to total Al depending on period; during the spring, summer, and fall, NO_3^- decreased with increasing Al, but increased during winter and snowmelt. Dissolved OC increased with increasing Al. Dissolved ON was unrelated to DOC in fall, but positively related at all other times.

Concentration of DOC was not a good predictor of base cation concentration or C_b, except in spring (Fig. 5). Sulfate had a negative relationship to DOC during all periods but fall, when the two were variable and not related. Nitrate was negatively related to DOC in all discharge periods except in winter, when the two were weakly but positively related. Dissolved ON was positively related to DOC in all discharge periods, including snowmelt.

Calcium concentration increased in response to increases in NO_3^- in all discharge periods except snowmelt, when the two were not related. The strength of the positive relationship was high with r^2 from 0.29 (fall) to 0.89 (spring). Sulfate increased with NO_3^- in spring and summer, decreased in winter and snowmelt, and had no relationship in fall.

3.6   Relationships of solutes to discharge

Most solutes had significant regressions with daily discharge at S2, S10, S11, S14, and S15; NO_3^- was significant 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, while NO_3^- was significant only at S2 and S11 (Table 5).

3.7 Biogeochemical differences among hydrologically distinct discharge events

At the watershed outlet, S2, the year * period interaction was significant for total N, NO_3^-, total Al, DOC, C_b, SO_4^{2-}, and pH (Table 6). The means separation procedure revealed that snowmelt 2001 had the lowest pH and highest NO_3^-, while total Al, DOC,

5 C_b, and SO_4^{2-} were comparable to at least one other period in the two years of study. Summer of 2002 exhibited lowest Al, but pH, NO_3^-, DOC, C_b, and SO_4^{2-} were comparable to at least one other period. Fall 2002 had the highest SO_4^{2-} concentration of all periods, but all other tested solutes were comparable to at least one other period.

4 Discussion

10 ### 4.1 Spatial patterns in solute concentrations are driven by solute sources

The two wetlands draining to S11 and S2 exerted the primary influence on stream chemistry in those sampling locations through the high concentration of DOC and DON independent of discharge levels (Tables 3 and 4). Depleted values of δ^{15}N-nitrate, often observed at S2 and S11 (Fig. 2), have been associated with low rates of organic

15 matter turnover in water-logged conditions (Kendall, 1998). Moreover, increases in DOC with increases in total Al were distinct at S2 and S11 in that they covered a wide range of concentrations in both solutes (Fig. 3). Low NO_3^- concentrations at S11 may be due to either low rates of organic matter decomposition or denitrification, or both. High DOC and DON, low NO_3^-, and depleted δ^{15}N-nitrate are consistent with

20 incomplete and slow organic matter breakdown in conditions of low oxygen in wetlands.
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 further indicate that wetlands control DOC concentrations in the lower reaches of this watershed throughout the year. The positive relationships

25 between DOC and DON with total Al in all discharge periods, and strong relationship

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between DOC and Al in upper subwatersheds S10, S13, and S15 (Fig. 2) show that soil horizons in some of the mid and upper elevations also contribute these two solutes, especially DOC. In a synthesis approach, Michalzik et al. (2001) determined that forest floors were the largest sources of DOC and DON in temperate forests; their analyses most likely did not include areas with extensive wetlands. In our watershed, the relative contribution of wetlands appears to be far more important than that of the forest floor (Park et al., 2003; Inamdar et al., 2004; Piatek et al., 2005).

In the current analysis, SO_4^{2-} concentration was positively related to Si, but not 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 by isotopic analyses (Campbell et al., 2006). Wetland source of SO_4^{2-}, observed during fall storms following an unusually dry summer (Mitchell et al., 2006) now appears to be episodic. Because conditions facilitating oxidation in wetlands, i.e. prolonged dry spells (Mitchell et al., 2006), are not common, we do not expect wetlands to be a usual source of SO_4^{2-}. Climate change forecasts include extreme weather patterns, such as drought, so we may experience wetland-derived SO_4^{2-} more commonly under changing climatic conditions.

Groundwater at S14 and S15 exerted a major influence over stream chemistry at upper elevations, irrespective of discharge levels, supplying high base cation and Si concentrations (Table 3, Fig. 3). Nitrate was also consistently highest at S14. However, NO_3^- at S14 was negatively related to Si, the groundwater indicator, and positively related to Al in all locations except at S2 and S11; this indicates that the source of NO_3^- is soil, not groundwater. Further, all isotopic values of NO_3^- in stream water were well below atmospheric values for this site (Piatek et al., 2005), showing that nitrification was a source of this NO_3^- (Kendall 1998). This confirms earlier analyses in this watershed on the sources of NO_3^- (Ohrui et al., 1999; Piatek et al., 2005; Christopher et al., 2006).

S15 (located in close proximity to S14) was in stark contrast to S14 with respect to NO_3^- concentrations, on average 60% lower at S15 than at S14. High NO_3^- at S14 is related to vegetation type and it is also linked to Ca levels (Christopher et al., 2006;

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Page et al., 2008). For example, sugar maple (*Acer saccharum*), in high proportion in S14, is known for its association with high NO_3^- (Lovett et al., 2002; Lovett and Mitchell, 2004; Christopher et al., 2006). In the current analyses we detected another difference between S14 and S15, and that is the predominance of Ca in S14 and Mg in S15.

5 These differences are most likely due to the chemistry of parent material in these two subwatersheds.

S13 contributed the majority of Al to the Archer Creek system. Both S12 and S13 are much more acidic than other reaches of the watershed, except S11 with the dominating influence of the extensive wetland (Table 3). S13 has relatively high elevation

10 conducive to high rates of nitrification in this watershed, and with S14, and S15 may be "hotspots" for nitrification. Upper soil horizons were also hotspots for nitrification in the Catskill Mountains of New York, which have similar topography (Welsch et al., 2001). The extensive subwatershed area of 41.9 ha may allow soil-derived solutes, such as Al, to drain to Archer Creek in substantial amounts. By contrast, S12 has a much smaller

15 drainage area than other sampling locations, and in fact, during the particularly dry summer of 2002, surface water flow ceased in the entire channel of S12.

4.1.1 Is stream chemistry at the outlet representative of other locations?

Chemistry at S2, the watershed outlet was similar to chemistry at other sampling locations for many solutes tested. Comparison of means in Table 3 shows that solutes

20 originating in groundwater were not statistically different at sampling locations from S2 to S13. This similarity is probably due to the fact that no major other sources of these solutes were identified beyond S14 and S15, so their concentrations after entry to the system would not be expected to change at any given discharge level. Nitrate at S2 was not statistically different from that of S9, S12, S13, or S15; this does not correspond to

25 rates of nitrification as inferred from isotopic values (Fig. 2) and probably results from a complex interaction of hydrology with nitrate production. Total Al at S2 was similar to that at S9 and S12, and DOC levels were unique for S2 at mid-level between a high at S11 and lows elsewhere in the watershed. Therefore, it appears that whether the

chemistry at the outlet is representative of solute levels elsewhere in the watershed or not depends on the distribution of sources and their connectivity with stream channel.

4.2 Temporal patterns in solute concentrations are driven by discharge dynamics

In general, snowmelt stood out as the most biogeochemically different among all other periods. Snowmelt, spanning at most 30 days around mid-April carried the largest percentage of the annual discharge in the shortest amount of time. This pulse of water had among the lowest pH, Ca^{2+}, sum of base cations, and SO_4^{2-}, and highest NO_3^-, total N, and total Al (Table 4). Snowmelt apparently diluted solutes originating in groundwater, such as Ca^{2+}, C_b, and SO_4^{2-}, and transferred to the stream channel solutes originating in soil horizons, such as NO_3^- and total Al. The year * period interaction was significant only for NO_3^- and driven by the very high NO_3^- discharge during snowmelt in 2001. Discharge in snowmelt 2001 constituted 46% of total that year, and it was 61 mm more than in 2002 (Table 1). This effect of high discharge illustrates that large volumes of water have the capacity to explore and flush a large percentage of the upland contributing areas with correspondingly higher amounts of soil-derived solutes.

By contrast, summers were characterized by lowest discharge levels, and some of the highest pH, Mg, Ca, and C_b, and lowest Al, DON, and DOC concentrations of all periods (Table 4). Low-discharge periods reflect maximum contributions from groundwater in our creek system (McHale et al., 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 storms, most of the values averaged for two summers were statistically similar to the solute averages of fall periods. This reflects variability in solute concentrations, and an important proportion of groundwater in fall discharge.

Temporal patterns of SO_4^{2-} versus Si also indicate that groundwater was the source of this solute (Fig. 3). Highest increase in SO_4^{2-} occurred in fall, less in summer, and

least in spring (Fig. 3). This reflects the addition of wetland-derived SO_4^{2-} in fall 2002 to SO_4^{2-} normally present in this watershed from groundwater (Fig. 2), with a small overall contribution to total flux (Mitchell et al., 2006). Therefore, addition of wetland-derived SO_4^{2-} may impact aquatic habitat as a result of the temporary increase in SO_4^{2-}
5 concentration and lowering of pH.

Throughout the year, nitrate, was microbial in origin (Kendall 1998; Piatek et al., 2005). We detected no evidence of atmospheric NO_3^- in this watershed at any of the sampled periods, as stream $\delta^{18}O$ values were well below those of atmospheric NO_3^- of +72.0‰ at this site (Piatek et al., 2005). This extends the evidence for lack of presence
10 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).

15 However, isotopic values of NO_3^- followed a cyclical pattern indicative of changes in nitrification rates with time of the year (Fig. 4). The highest value of $\delta^{15}N$-nitrate occurred in fall. Since enrichment is associated with higher N cycling rates (Kendall, 1998), fall appears to be a "hot moment" for nitrification (Creed et al., 1996) in our system. This is consistent with soil temperatures continuing to be favorable for microbial
20 activity generating NH_4^+ from organic matter mineralization, and lack of N sink allowing nitrification as plant N uptake decreases when leaves drop in fall. This is clearly supported by the relationship between NO_3^- and NH_4^+ in fall, when both increase; there is a conspicuous lack of such a relationship at other times of the year (Fig. 5). The depletion in $\delta^{15}N$-nitrate between fall and snowmelt can be explained by the slowing
25 of N cycling rates through the winter associated with low winter temperatures inhibiting microbial activity. Enrichment in $\delta^{15}N$-nitrate values started again in spring, probably in response to increasing soil temperatures.

These results also support earlier analyses of NO_3^- sources at this watershed based

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on chemical and isotopic hydrograph separations (McHale et al., 2002), and NO_3^- dynamics during storm discharge (Inamdar et al., 2004).

4.2.1 Are high discharge events representative of chemistry at other discharge volumes?

Evaluating differences in solute dynamics among individual periods can help us understand whether observed biogeochemical patterns represent marked changes. Specifically, we compared solute concentrations for snowmelt of 2001 which had 46% of annual discharge – the highest of any period in the two years of study, summer 2002 with the least discharge during drought, and fall 2002, featuring several storms which followed the prolonged summer drought. Such unusual weather patterns may be representative of more extreme weather predicted for climate change scenarios (Meehl et al., 2000; Kharin and Zwiers, 2005).

Highest NO_3^- and lowest pH during high-discharge snowmelt, lowest total Al during drought, and highest SO_4^{2-} during storm activity following the drought 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, favorable outcome of droughts on the presence of Al in water, but subsequently high SO_4^{2-} derived from wetland organic matter oxidation (Mitchell et al., 2006) in addition to the prevailing SO_4^{2-} from groundwater contribution.

4.2.2 A conceptual model of solute generation in Archer Creek watershed

Figure 6 is a graphic representation of our current understanding of solute generation in Archer Creek. Wetlands at low elevations and groundwater at high elevations determine spatial dynamics of water chemistry, while precipitation combines with antecedent soil moisture to determine temporal dynamics based on discharge interpolating between solute sources.

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Cation solutes, SO_4^{2-} and Si were negatively related to daily, cumulative, and previous cumulative discharge (Table 5); this has been previously detected in this watershed (McHale et al., 2002; Piatek et al., 2005; Christopher et al., 2006), and suggests a dilution of groundwater by atmospheric solutions. Because Mg concentrations at S14 were weakly but positively correlated with current cumulative and with previous cumulative discharge (Table 5), we conclude that an additional source of Mg exists that allows Mg concentrations to increase when more water is present in the system. This is consistent with a soil source of Mg, which would be subject to soil-flushing with rising saturation in the catchment. Solutes which are linked to soil organic matter mineralization – total N, DOC and DON at S14 and S15 were often positively related to current discharge. This relationship is also consistent with the flushing mechanism, in which rising waters explore more of the soil horizons, flushing stored solutes. Total Al at S11 was not at all related to discharge, indicating that reduced conditions in the wetland and slow water movement change the way discharge affects Al and how the two are related. Linkage of NO_3^- with DOC has also been suggested (Park et al., 2003; Piatek et al., 2005), but it has not been confirmed in this study, as evidenced by weak or no relationships between NO_3^- and DOC across space and time (Figs. 4 and 5).

Interestingly, NO_3^- had a positive relationship to daily and cumulative discharge in all locations, but no relationship to previous cumulative discharge in all but S2 and S11, where it was positive and negative, respectively (Table 5). This can be interpreted to mean that nitrification rates in soil are so high that they "keep up" with flushing from one discharge period to the next. This appears not to be true for DOC and DON, as these two solutes had either no relationship to, or a negative one with previous cumulative discharge except DOC at S10 (Table 5). Nitrate was also positively associated with Si concentration during all discharge periods but snowmelt (Fig. 5). We concluded based on spatial analyses of NO_3^- that soil nitrification was the primary source of NO_3^-. Nitrate then, after main production in fall and accumulation in winter in the soils of the upper reaches of the watershed is displaced during snowmelt to lower soil horizons. Under conditions of hydrological connectivity in the catchment, NO_3^- is flushed to stream by

the rising groundwater. Subsequently when receding waters disconnect source areas from stream, NO_3^- may drain to groundwater, which can become the secondary NO_3^- source when NO_3^- production slows in the system in response to plant N uptake in summer.

5   Conclusions

We have refined our understanding of solute generation in the Archer Creek watershed to include a three dimensional mosaic of space (sampling locations in the watershed with their associated vegetation and topographic attributes), time (discharge periods related to time of the year), and depth (groundwater exploration of soil profile). In this mosaic, nitrification in fall in soils of the upper ridges resulted in accumulation of NO_3^- in winter, when water movement through the soil profile is limited and plant uptake ceases. Accumulated NO_3^- is flushed during snowmelt when large volumes of water move through the system and raise groundwater level. Subsequently NO_3^- drains to groundwater which discharges to creek when nitrification is likely to be limited in soil because of biotic N uptake (spring and summer). Our analyses suggest that, in the absence of unusual climatic events such as droughts, most of the base cations and SO_4^{2-} are contributed by groundwater, discharging to the stream at upper elevations. As groundwater travels down the stream channel, solutes are diluted by shallow water sources at about mid-elevation in the watershed, which also contribute high Al. The contribution of shallow water sources is variable and changes during the course the year; the magnitude of these changes seems to be highly dependent on preceding hydrologic events. Wetlands assume a controlling role over water chemistry in the downslope locations, contributing much of the DOC and DON. Because the dynamics for some solutes were closely related to the location in the watershed (DOC, DON, Al, NO_3^-, C_b) and/or on discharge levels (NO_3^-), observations at the watershed outlet alone only partially represent solute dynamics within the entire watershed. Similarly, observations at high-discharge events alone do not characterize all solute dynamics at

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other discharge levels. However, depending on research objectives, many solutes are adequately represented at the outlet. This is even more true for high-discharge events because high discharge events are responsible for large solute fluxes.

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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).

	Adjusted # of days	2001		2002	
		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)
Winter	120	142.3 (147; 25%)	1 Jan–3 Apr 1–31 Dec (124)	173.2 (170; 24%)	1 Jan–28 Mar 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)	2.96 (3; 0.4%)	1 Jul–21 Sep (83)
Fall	70	31.7 (33; 6%)	30 Sep–30 Nov (72)	64.8 (65; 31%)	22 Sep–30 Nov (70)
TOTAL		586		561	

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Table 2. Anova table for full model and all solute concentrations (Type III SS). All values are weighted on the frequency of observations. n.s. = not significant; n.a. = not available.

	pH	Mg	Ca	Cb	SO_4^{2-}	NO_3^-	DON	Total N	DOC	Total Al	δ^{15}N-NO_3^-	δ^{18}O-NO_3^-
Year (Y)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Period (P)	n.s.	<0.0001	<0.0001	<0.0001	0.0250	<0.0001	n.s.	<0.0001	n.s.	0.0023	0.0136	n.s.
Sampling point (S)	<0.0001	<0.0001	<0.0001	<0.0001	0.0002	<0.0001	n.s.	<0.0001	<0.0001	<0.0001	n.s.	n.s.
Y*period	n.s.	n.s.	n.s.	n.s.	n.s.	0.0116	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Y*sampling point	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Period*sampling point	n.s.	n.s.	n.s.	0.0003	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Y*P*S	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.a.

Table 3. Solute concentrations (μmol/L) for sampling points 2–15 in the Archer Creek watershed (Adirondack Mountains, New York, USA). Shown are *ls*-means adjusted for unequal sample size. *Ls*-means followed by the same letter are not statistically significantly different from each other; n.e. = *ls*-means non-estimable, means given in italics; n.s. = not significant; n.a. = data not available.

	2	9	10	11	12	13	14	15
pH	6.1a	6.4ab	6.4ab	5.1c	5.4c	5.2c	7.1d	6.7b
Mg^{2+}	53.7ab	49.4ab	58.0abc	39.8ab	46.6ab	32.5ab	73.5bc	111.3d
Ca^{2+}	217.5abc	260.3abc	241.0ac	144.9c	126.9ac	138.3abc	870.8d	458.0e
Cb	341.9a	360.8a	357.0a	243.5b	220.8b	224.3b	985.4c	662.0d
Si	133.2	n.e.	n.e.	n.e.	n.e.	n.e.	462.0	164.9
	147.0	*162.0*	*128.3*	*107.0*	*121.4*	*133.9*	*460.1*	*202.7*
NO_3^-	23.6a	30.7ab	33.6b	12.5c	28.3ab	26.8ab	68.8d	27.0b
DON	10.9	7.6	8.3	14.3	6.3	7.9	9.2	6.4
Total N	39.9a	41.4a	41.8a	29.4a	40.2a	40.3a	79.6b	34.0a
SO_4^{2-}	141.8abc	141.4abcd	133.7abc	113.4abc	128.6abc	145.6abcd	203.7bcd	210.4cd
DOC	563.1a	291.7b	245.0b	911.7c	233.7b	292.9b	212.8b	135.4b
Total Al	5.4abe	4.08abce	2.5bcef	7.8d	3.4abce	9.1d	0.5cf	1.04cef

Table 4. Solute concentrations during five discharge periods (μmol/L). Shown are *ls*-means adjusted for unequal sample size for five discharge periods, and associated *p*-values. *Ls*-means followed by the same letter are not statistically significantly different from each other; n.a. = data not available; n.e. = *ls*-means non-estimable, means given in italics; n.s. = not significant.

	Winter	Snowmelt	Spring	Summer	Fall
pH	6.2	5.7	5.9	6.3	6.1
Mg^{2+}	56.0_{acd}	41.7_{ac}	48.7_{ac}	74.0_{bd}	70.2_{abd}
Ca^{2+}	296.0_{ab}	224.0_{b}	270.2_{b}	389.4_{ac}	356.6_{ac}
Cb	407.0_{a}	305.0_{b}	365.2_{ab}	539.7_{c}	504.7_{c}
Si	169.1	n.e.	n.e.	n.e.	n.e.
	154.5	*173.3*	*331.6*	*376.1*	*163.5*
NO_3^-	37.9_{a}	54.7_{b}	22.8_{c}	21.1_{c}	20.5_{c}
DON	10.0	11.2	8.2	6.9	8.0
Total N	51.0_{a}	70.5_{b}	33.7_{c}	30.2_{c}	31.1_{c}
SO_4^{2-}	154.7	112.0	137.2	172.3	186.5
DOC	303.5	393.8	427.4	246.2	433.1
Total Al	3.81_{a}	6.47_{b}	5.26_{ab}	2.35_{a}	3.38_{a}

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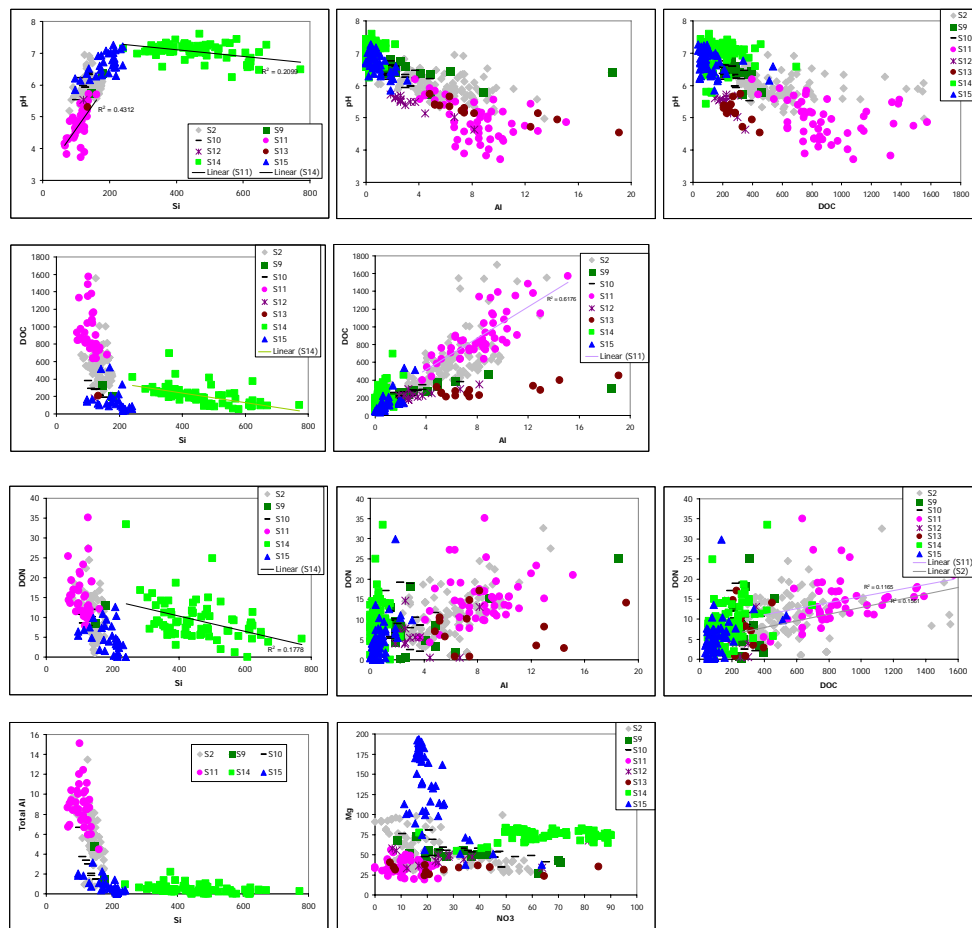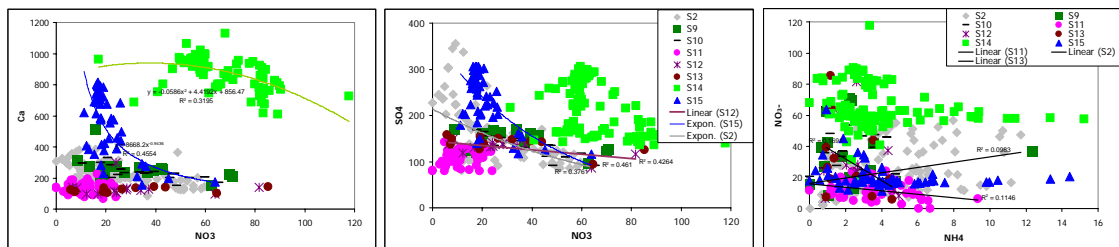
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Table 5. Significant p-values for regression analyses of daily, cumulative and previous cumulative discharge on solute concentrations across sampling locations at the Archer Creek watershed (Adirondack Mountains, New York, USA). +/- sign indicates the direction of the relationship. Non-significant *p*-values left blank. i.d. = insufficient data to evaluate.

	pH	Mg	Ca	Cb	SO_4^{2-}	Si	NO_3^-	DON	Total N	DOC	Total Al
				daily discharge (mm day^{-1})							
2	−0.010		−<0.000	−<0.000	−0.031	−<0.000	+<0.000			n.s.	+<0.000
9		−0.002					+0.020				
10		−0.001	−0.002	−0.002	−0.002	−0.002	+0.001			+0.002	+0.004
11	−0.008		−0.012	−0.002	−0.013	−0.000	+<0.000		+0.005		
12	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	+0.029	i.d.	i.d.	i.d.	i.d.
13		−0.033					+0.031				
14		−<0.000	−<0.000	−<0.000	−<0.000	−<0.000	+<0.000	+0.001	+<0.000	+<0.000	+0.033
15	−0.004		−<0.000	−<0.000	−<0.000	−<0.000	+<0.000		+0.000		+<0.000
				cumulative discharge (mm period^{-1})							
2	−0.004	−<0.000	−<0.000	−<0.000			+<0.000		+0.006		+0.000
9							+<0.000				
10		−0.022	−0.024	−0.022	−0.014	−0.016	+<0.000			+0.026	+0.029
11							+<0.000		+<0.000	−0.016	
12							+0.002				
13							+<0.000				
14	+0.000	+0.042	−<0.000	−<0.000	−<0.000	−<0.000	+<0.000	+0.010	+<0.000	+<0.000	+0.001
15	−0.056	−<0.000	−<0.000	−<0.000	−<0.000	−<0.000	+<0.000	+0.015	+0.000		+<0.000
				previous cumulative discharge (mm period^{-1})							
2	+0.032	−0.000	−<0.000	−0.000	−<0.000	−0.006	+0.000	−0.001	−0.000		
9											
10		−0.022	−0.024	−0.022	−0.014	−0.016				+0.026	
11	−<0.000	−0.000	−<0.000	−<0.000	−<0.000	−0.000	−0.022		−0.049		
12											
13											
14	+0.015	+<0.000			−<0.000	−0.000					−0.026
15								−0.008		−0.045	

Table 6. Anova table for solute concentrations at S2 (Type III SS). n.s. = not significant; n.a. = not available.

	pH	Mg	Ca	Cb	SO_4^{2-}	NO_3^-	DON	Total N	DOC	Total Al	δ^{15}N-NO_3^-	δ^{18}O-NO_3^-
Year	n.s.	n.s.	0.0428	<0.0001	n.s.	0.0005	0.0108	0.0017	<0.0001	0.0362	n.s.	n.s.
Period	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0807	0.0290
Year*period	<0.0001	n.s.	n.s.	<0.0001	0.0138	<0.0001	n.s.	<0.0001	<0.0001	0.0001	n.s.	n.s.
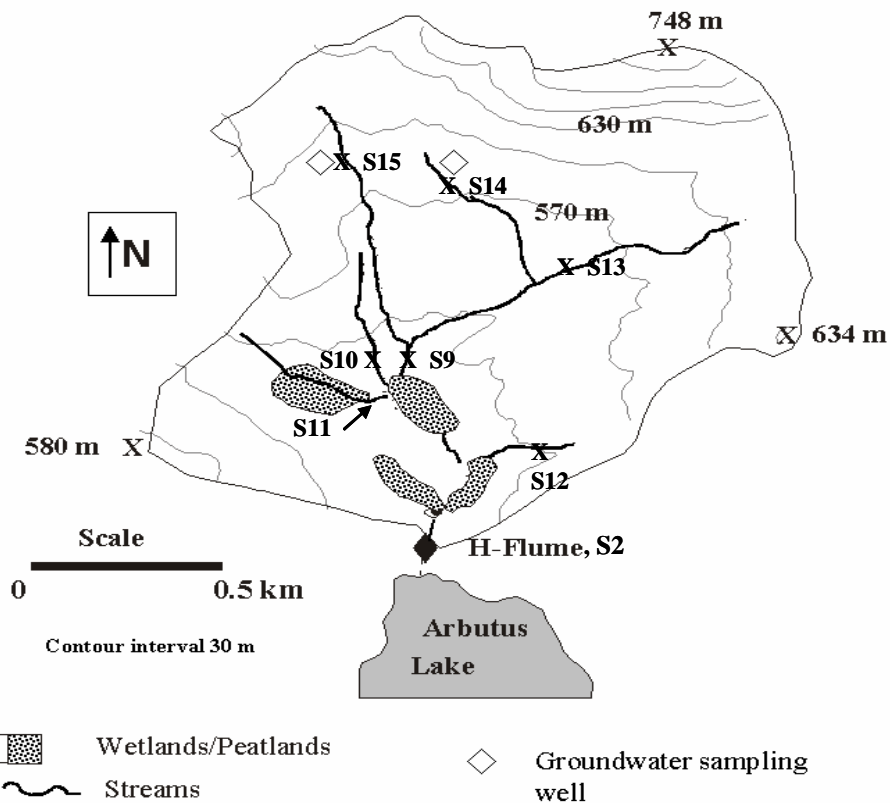
Fig. 1. Arbutus Lake Watershed in the Adirondack Mountains of New York, USA with locations of sampling points and topographic lines.
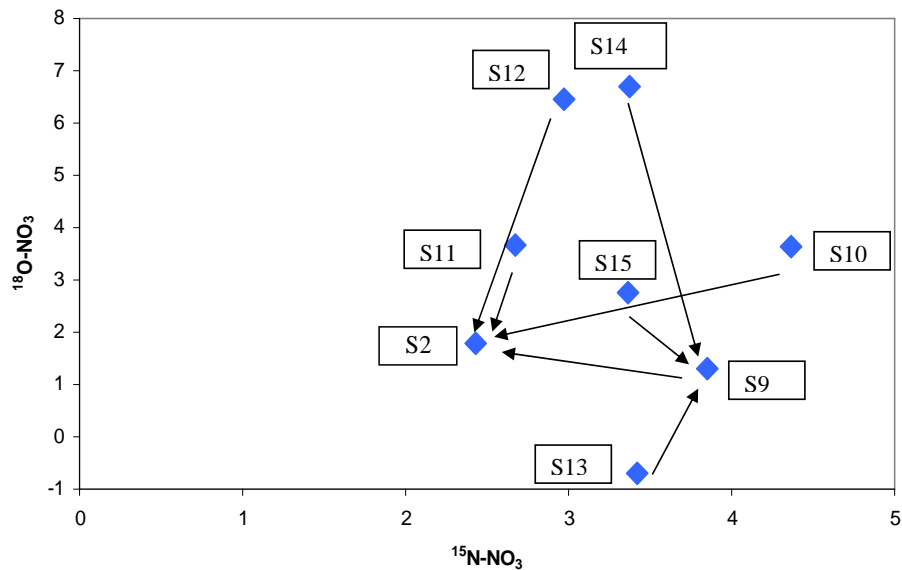
Fig. 2. Delta ^{15}N-nitrate versus ^{18}O-nitrate associated with stream sampling points. The direction of arrows indicates water flow between sampling locations.

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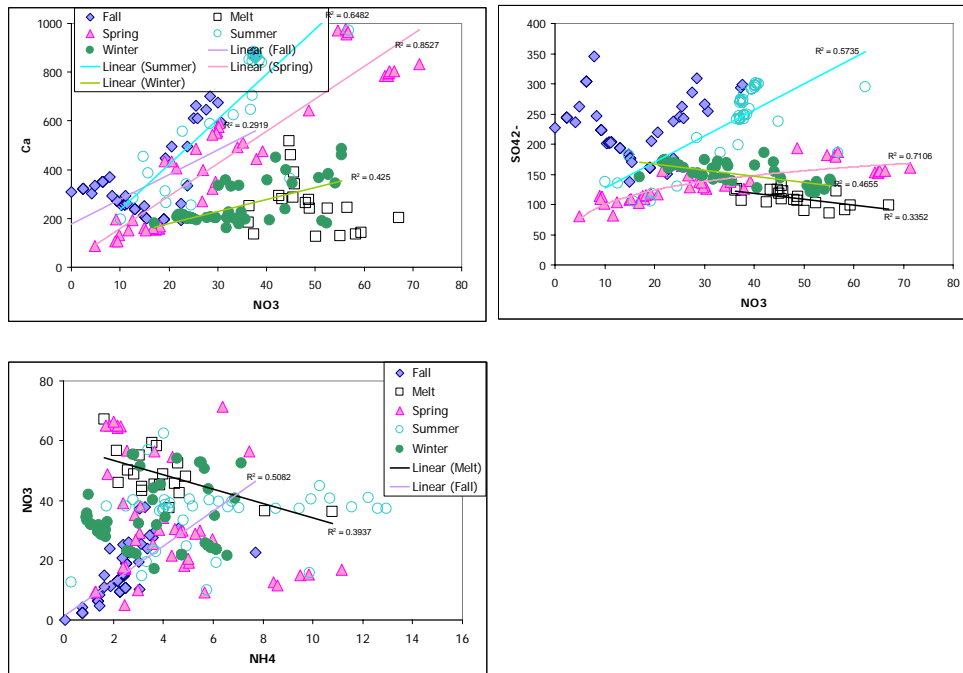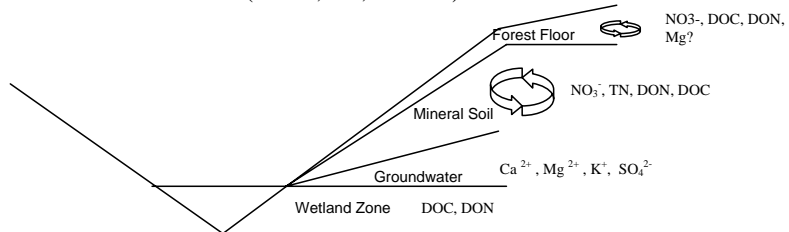Full Screen / Esc

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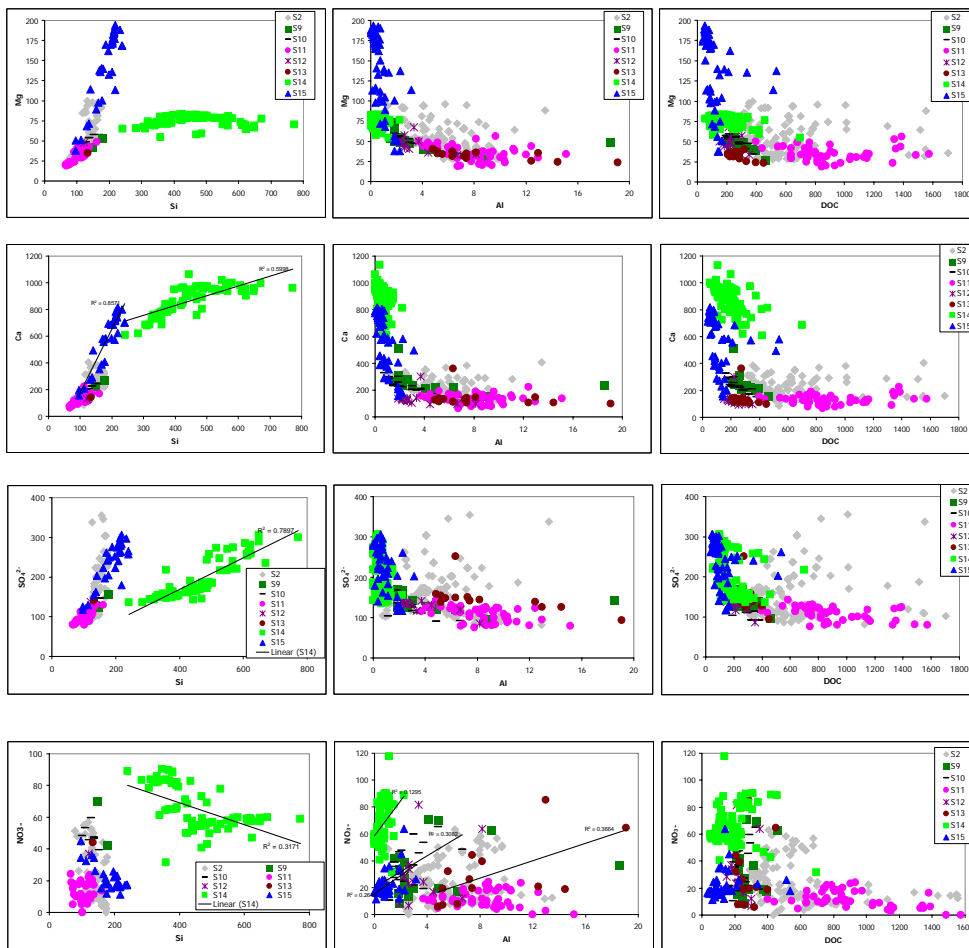
Fig. 3. Relationships among solute concentrations across the watershed.

Fig. 3. Continued.

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Fig. 3. Continued.
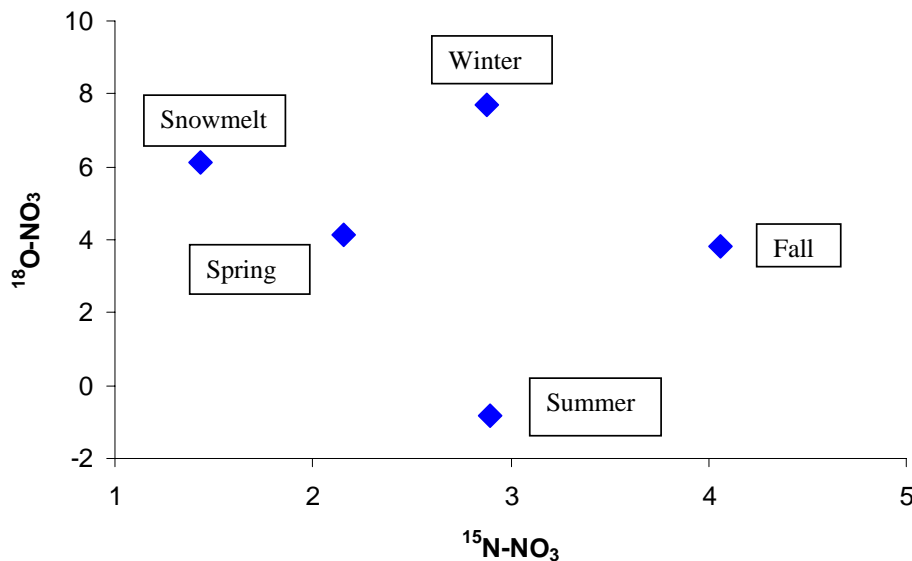
Fig. 4. Changes in the values of ^{15}N-nitrate and ^{18}O-nitrate associated with discharge periods.

Fig. 5. Temporal relationships among solute concentrations.

Fig. 5. Continued.

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Stream chemistry in a forested watershed

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Fig. 6. A conceptual diagram of the 3-dimensional view of solute generation in the Archer Creek watershed relating space, time, and the level of groundwater.