Solute sources in stream water during consecutive fall storms in a northern hardwood forest watershed: a combined hydrological, chemical and isotopic approach

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Abstract. Understanding the effects of climate change including precipitation patterns has important implications for evaluating the biogeochemical responses of watersheds. We focused on four storms in late summer and early fall that occurred after an exceptionally dry period in 2002. We analyzed not only the influence of these storms on episodic chemistry and the role of different water sources in affecting surface water chemistry, but also the relative contributions of these storms to annual biogeochemical mass balances. The study site was a well studied 135-ha watershed in the Adirondack Park of New York State (USA). Our analyses integrated measurements on hydrology, solute chemistry and the isotopic composition of NO_3^- ($\delta^{15}N$ and $\delta^{18}O$) and SO_4^{2-} ($\delta^{34}S$ and $\delta^{18}O$) to evaluate how these storms affected surface water chemistry. Precipitation amounts varied among the storms (Storm 1: Sept. 14–18, 18.5 mm; Storm 2: Sept. 21–24, 33 mm; Storm 3: Sept. 27–29, 42.9 mm; Storm 4: Oct. 16–21, 67.6 mm). Among the four storms, there was an increase in water yields from 2 to 14%. These water yields were much less than in studies of storms in previous years at this same watershed when antecedent moisture conditions were higher. In the current study, early storms resulted in relatively small changes in water chemistry. With progressive storms the changes in water chemistry became more marked with particularly major changes in C_b (sum of base cations), Si, NO_3^-, and SO_4^{2-}, DOC and pH. Analyses of the relationships between Si, DOC, discharge and water table height clearly indicated that there was a decrease in ground water contributions (i.e., lower Si concentrations and higher DOC concentrations) as the watershed wetness increased with storm succession. The marked changes in chemistry were also reflected in changes in the isotopic composition of SO_4^{2-} and NO_3^-. There was a strong inverse relationship between SO_4^{2-} concentrations and $\delta^{34}S$ values suggesting the importance of S biogeochemical redox processes in contributing to SO_4^{2-} export. The isotopic composition of NO_3^- in stream water indicated that this N had been microbially processed. Linkages between SO_4^{2-} and DOC concentrations suggest that wetlands were major sources of these solutes to drainage waters while the chemical and isotopic response of NO_3^- suggested that upland sources were more important. Although these late summer and fall storms did not play a major role in the overall annual mass balances of solutes for this watershed, these events had distinctive chemistry including depressed pH and therefore have important consequences to watershed processes such as episodic acidification, and the linkage of these processes to climate change.

Introduction

The evaluation of climate change including the linkages with storm responses has important implications in the biogeochemical and hydrological analyses of watersheds. The importance of events in affecting both hydrological and chemical response of drainage waters has been documented for a variety of catchment types ranging from snow dominated systems where snowmelt dynamics play a critical role (Sickman et al. 2003) to arid catchments where antecedent moisture conditions are especially important (Castillo et al. 2003). Hydrological events may contribute substantial amounts of hydrological, solute and sediment export in drainage waters. Moreover, the evaluation of the hydrographic and solute response of storms also provides important information on watershed attributes including evaluations of how different water sources affect surface water chemistry (Dewalle et al. 1997; Frank et al. 2000; Burns 2002). Hydrologic events have been shown to be particularly important for evaluating the sources of NO_3^-, dissolved organic carbon (DOC) and SO_4^{2-}. Storms may result in elevated NO_3^- concentrations in the surface waters of forested watersheds (Creed and Band 1998; Brooks and Williams 1999; Inamdar et al. 2004). Similarly studies of DOC have shown marked changes associated with discharge patterns during both storm and snowmelt events (Hornberger et al. 1994; Boyer et al. 2000; Inamdar et al. 2004; Wellington and Driscoll 2004). Storm events that increase SO_4^{2-} export have been implicated in episodic acidification (Wigington et al. 1996b; Mitchell 2005). The role of SO_4^{2-} in acidification, however, varies among watersheds and events with SO_4^{2-} in discharge generally decreasing during snowmelt (Wigington et al. 1992; Mitchell 2005), but often increasing after periods of extended drought (Eimers and Dillon 2002). The importance of storms and snowmelt in affecting surface water chemistry has also been emphasized with particular attention to the effects of these events on depressing acid neutralizing capacity (ANC) (Eshleman et al. 1992; Wigington et al. 1992, 1996a; Davies et al. 1999; Laudon et al. 2004).

   For the Arbutus Lake Watershed (ALW) in the central Adirondack Mountains of New York State, a number of studies have evaluated hydrological and biogeochemical relationships (e.g., Mitchell et al. 1996a, b, 2001a, 2003; McHale et al. 2000; Park et al. 2003). More specifically, two previous studies focused on the role of storm events in affecting NO_3^- (McHale et al. 2002) and DOC (Inamdar et al. 2004). These two studies suggested the importance of antecedent moisture conditions (e.g., McHale et al. 2002) in affecting solute transport and how the hydrological connectivity of the watershed varied during storms and hence influenced solute export (Inamdar et al. 2004). These earlier studies provided only limited evidence on the actual solute sources and did not provide results using stable isotopic analyses. The only previous study that utilized solute isotopes in this watershed was that of Piatek et al. (2005) who evaluated the role of different NO_3^- sources (direct atmospheric vs. internal sources) on surface water NO_3^- during snowmelt using $\delta^{15}N$ and $\delta^{18}O$ measurements.

The overall objective of the current study was to determine the effects of an extended dry period on surface water chemistry and to ascertain the changes in solute sources to surface water as the watershed wetness increased. Our study included a detailed evaluation of sources of SO_4^{2-} and NO_3^- using a combination of hydrologic, chemical and isotopic ($\delta^{34}S$, $\delta^{18}O$ of SO_4^{2-}; $\delta^{15}N$, $\delta^{18}O$ of NO_3^-) analyses of four storms in the later summer and early fall of 2002. We hypothesized that the extreme dry conditions would lower the water table resulting in the oxidation of previously reduced sulfide to SO_4^{2-}. With increasing catchment wetness the relative importance of groundwater solute sources was predicted to decrease with a concomitant increase in the contribution of upland soil and wetland solute sources including the mobilization of oxidized sulfur (SO_4^{2-}) and nitrogen (NO_3^-).

Methods

Site description

The study was conducted in a 135-ha Archer Creek Watershed of the ALW at the Huntington Wildlife Forest (HF) in Adirondack Park of New York State (43°59′ N, 74°14′ W) (Figure 1). Archer Creek is the main inlet to Arbutus
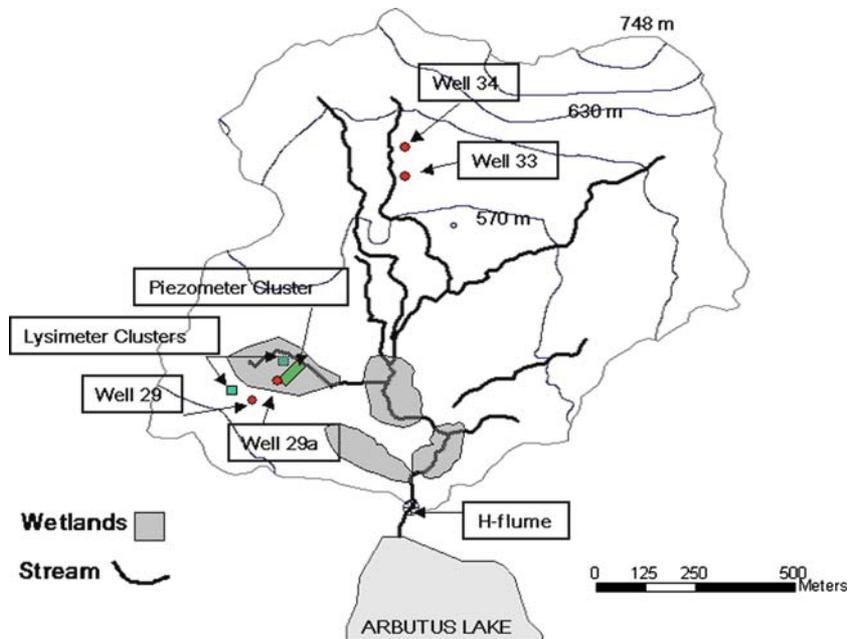
Figure 1. Archer Creek watershed at the Huntington forest in the Adirondack Mountains of New York State.

Lake. Granitic gneiss dominates the bedrock at HF (Fisher 1957). Glacial till deposits from the continental glaciation that retreated 10,000–15,000 years ago dominate the parent material. High sand (75%) and low clay (<10%) content of the soil result in well-drained soils. Upland soils are coarse loamy, mixed, frigid, Typic Haplorthods of the Beckett-Mundal association, less than 1-m thick. Wetlands consist of Greenwood mucky peats from 1 to 5 m thick (Somers 1986; McHale 1999).

The HF is under the influence of a cool and moist continental climate, with mean annual temperatures of 4.4 °C and mean annual precipitation of 1010 mm (Shepard et al. 1989). Vegetation consists of the northern hardwood forest. Mixed hardwood-conifer stands occupy lower elevations, with *Tsuga canadensis* (eastern hemlock) and *Picea rubens* (red spruce) dominating the overstory. *Fagus grandifolia* (American beech) and *Acer saccharum* (sugar maple) dominate the overstory at mid- and higher elevations. Individuals of *Abies balsamea* (balsam fir) are scattered throughout. A few small wetlands support a N-fixing species, *Alnus rubrum* (speckled alder) (Bischoff et al. 2001; Hurd et al. 2001).

Precipitation amount, stream discharge and water chemistry

Precipitation amounts and wet-only precipitation chemistry data were obtained from the nearby NADP/NTN site located 1.3 km from the watershed. Solute fluxes for precipitation were computed by multiplying precipitation inputs by concentrations. Stream discharge has been monitored in the Archer Creek Watershed continuously since 1994. An H-flume, located 10 m away from the lake inlet, has automated stage-height recording at 15-min intervals. For the current study, 15-min data were averaged per hour. Stream samples were collected with an ISCO sampler installed at the H-flume. The ISCO collected 500-ml samples for changes in stream stage of 1.2 cm over 15 min or 6.1 cm over 24 h. Discharge rates and % water yields were compared among storms in the current study as well as for storms evaluated in previous studies at this site.

Samples for chemical analyses were transported to the Biogeochemistry Laboratory at SUNY-ESF, and were analyzed as follows: DOC on a Tekmar–Dohrmann Phoenix 8000 TOC analyzer, and cations (Al, Ca, Mg, K, Si, Na) on a Perkin–Elmer ICP-AEC Div 3300 instrument. Total dissolved N (TDN) was determined using persulfate oxidation (Ameel et al. 1993) followed by colorimetric analysis on an autoanalyzer. Ammonia was also determined on an autoanalyzer using the Berthelot Reaction followed by colorimetric analysis. Anion concentrations (SO_4^{2-}, NO_3^-, Cl^-) were determined on a Dionex IC. Concentrations of DON were estimated by subtracting NH_4^+ and NO_3^- from TDN. All samples were filtered with 0.5 μm filter prior to analysis. The laboratory is a participant in the United States Geological Survey (USGS) 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. 2001a).

Groundwater and soil water sampling

Groundwater samples for chemical analyses were obtained from a series of wells and piezometers located at various locations within the watershed. These ground water wells were installed in the summers of 2000 and 2001 using 5.08 cm diameter PVC piping coupled to sections from 30 to 38 cm long with screening. For the current study, water chemistry is presented for four wells: 29 (upland of Subcatchment 11), 29a (wetland of Subcatchment 11), 33 (upland of Subcatchment 14) and 34 (riparian zone in Subcatchment 14). Subcatchment 11 contains a relatively large conifer swamp (Figure 1) and Subcatchment 14 is notable for its high NO_3^- concentrations (Christopher et al. 2005). Well chemistry was monitored at approximately monthly intervals from April through November 2002. Additional chemistry measurements were also obtained from piezometers located within the wetlands in the Archer Creek in Subcatchment 11. Head height was monitored hourly using capacitance rods. Piezometers were arranged in two transects perpendicular to the stream and grouped in pairs at 70 and 100 cm depths. Piezometers were assembled using 3.81 cm outside diameter PVC pipe attached to 4 cm depth screening and capped on the end. Piezometers were monitored from April through November 2002 with chemistry samples taken at ~6 week intervals. Soil water was obtained by monthly sampling from April through August 2002 from porous tension cup lysimeters located in 6 clusters at 15 and 50 cm depths in the uplands and wetlands of Subcatchment 11. Details of the lysimeter design are provided in Mitchell et al. (2001b).

Sample collection for chemical and isotopic analyses

Throughfall and ambient precipitation were sampled from Sept. 27–28, 2002 (Storm 3). Two specially-made collectors were placed under a deciduous canopy, coniferous canopy, and outside of the tree canopies. Each collector consisted of three 1-m long sections of plastic gutter delivering precipitation through a screen (to filter particulates) into a common capped bucket. For Storm 3, samples were collected continuously beginning shortly after the start of the storm until its end (approximately a 12-h period). Stream samples were collected into pre-rinsed plastic 20-l carboys prior to, periodically during, and shortly after each storm.

Isotopic preparation for NO_3^- followed the methods of Chang et al. (1999) and Silva et al. (2000). Particulate organic matter was filtered through a 0.45 µm filter capsule (Gelman Co.). Pre-filtered samples were allowed to drip through two resin columns mounted in series. First, the sample passed through

a cation resin (H$^+$ form, Biorad Co.), which partially removed and decreased the adsorption of DOC on the anion resin. Second, the sample passed through an anion resin (Cl$^-$ form, Biorad Co.). Samples on anion resins in columns were stored at 2 °C until further processing. However, by the time all the samples were concentrated on resins, there was a new method with better analytical precision available for use: the microbial denitrifier method (Sigman et al. 2001). Hence, samples were shipped to the USGS laboratory in Menlo Park, CA, where silver nitrate was redissolved, and the silver extracted by passing the sample through a cation resin (H$^+$ form, Biorad Co.). The resulting NO$_3^-$ was microbially converted to N$_2$O (Casciotti et al. 2002) for isotopic ratio determination on a mass spectrometer. Tests using NO$_3^-$ of known isotopic compositions showed that silver nitrate could be converted back to NO$_3^-$ by the extraction of silver using cation resins, and subsequently analyzed with the denitrifier method (S. R. Silva, pers. commun. 2004). With no isotope fractionation δ^{15}N values were not corrected for non-mass dependent ^{17}O. Analytical precision for our samples was 0.6‰ for δ^{15}N and 0.7‰ for δ^{18}O.

For SO$_4^{2-}$ isotope analyses, water samples were passed through anion exchange resin columns (Bio-Rad Polyprep, AG 1X-8) to retain the SO$_4^{2-}$ (Mayer et al. 2002; Rock and Mayer 2002; Bailey et al. 2004). Sulfate was eluted from each column with 15 ml 3 M HCl; 0.5 M BaCl$_2$ solution was added to precipitate BaSO$_4$, which was recovered by filtration, washed with deionized water, air-dried, weighed, and stored for isotope analysis. Sulfur dioxide (SO$_2$) for mass spectrometric analyses was generated by thermal decomposition in an elemental analyzer. Sulfur isotope ratios were determined by continuous flow (CF-IRMS) (e.g., Giesemann et al. 1994). For oxygen isotope analyses on SO$_4^{2-}$, BaSO$_4$–oxygen was converted to CO at 1450 °C in a pyrolysis reactor (Finnigan TC/EA). The resultant gas was subsequently swept with a He stream into a mass spectrometer (Finnigan MAT delta plus XL) for isotope ratio determinations in continuous-flow mode (CF-IRMS) (Gehre and Strauch 2003; Shanley et al. 2005). Analytical precision was $\pm 0.5‰ \delta^{34}$S and $\pm 0.8‰ \delta^{18}$O for isotope measurements of SO$_4^{2-}$.

All isotope ratios are expressed in the usual "δ notation" in per mil (‰) with respect to the internationally accepted standards AIR for nitrogen isotope measurements, Vienna Standard Mean Ocean Water (V-SMOW) for oxygen isotope measurements, and Canon Diablo Troilite (V-CDT) for sulfur isotope measurements.

Results and discussion

Hydrological response the storms of late summer and early fall of 2002

Information on the storms analyzed for the current study is provided in Table 1 along with comparisons of storms from previous studies in this same watershed. The summer of 2002 was exceptionally dry resulting in

Table 1. Summer and fall storms at Archer Creek watershed.

Reference	Storm #	Dates	Precipitation (mm)	Discharge (mm)	% Water yield
Current Study	1	Sept. 14–18, 2002	18.5	0.32	2
Current Study	2	Sept. 21–24, 2002	33.0	1.23	4
Current Study	3	Sept. 27–29, 2002	42.9	3.9	9
Current Study	4	Oct. 16–21, 2002	67.6	9.4	14
Inamdar et al. (2004)	Floyd Storm	Sept. 16–25, 1999	138	21	15
McHale et al. (2002)[a]	*1*	Oct. 14, 1995	34.3	8.9	26
	2	Oct. 21, 1995	70.9	34.7	49
	5	June 10, 1996	13.5	14.0	104
	6	July 4, 1996	13.0	11.8	91

[a]Storms 3 and 4 were snow melt events and thus not included in this comparison.

lower annual discharge (548 mm yr^{-1}) than for other previous years (x = 718 mm yr^{-1} from 1995 to 2001). The marked dryness of the watershed was also shown in the low water yield compared to previous studies on storm response in this watershed (Table 1). Discharge in Archer Creek was so low that the water ceased to flow over the H-flume from the beginning of July (Figure 2), a condition not previously observed since the beginning of
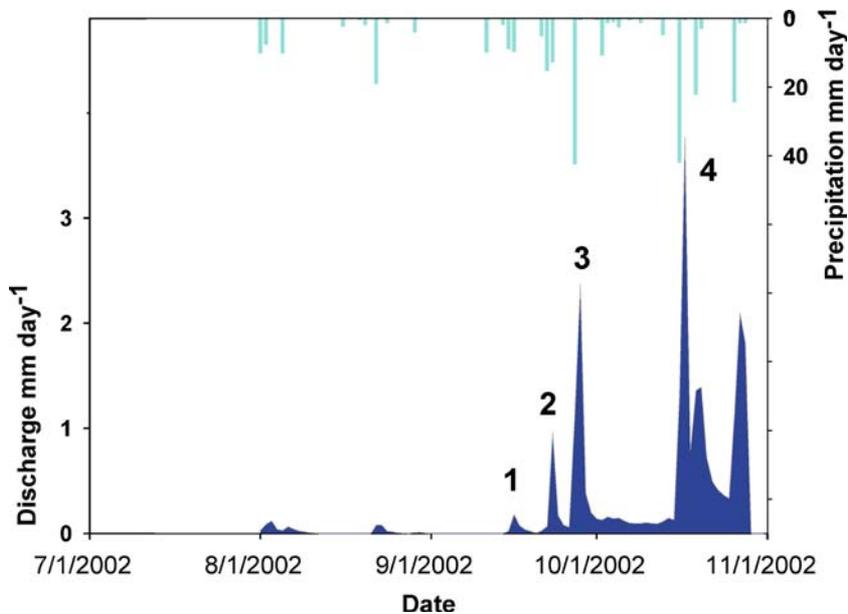
Figure 2. Precipitation and discharge in Archer Creek Watershed from July 1 to Nov. 1, 2002. Four storms analyzed are designated with numbers over peak discharge.

monitoring in 1994. Early August brought the first notable precipitation and discharge, followed by 10 dry days. The next significant precipitation of 19.0 mm occurred on August 22, and resulted in a discharge of 0.08 mm day^{-1} (Figure 2). A series of rainy days that started in early September culminated in a storm on September 27. Precipitation that day reached 42.4 mm. Discharge steadily rose from mid-September on, with a peak of 2.38 mm day^{-1} on September 28. This increase and the resultant continual discharge also coincided with the marked reduction of transpiration due to the onset of leaf loss from the deciduous trees that dominate this watershed. The next substantial storm occurred with 41.9 mm of rain on October 16 and discharge of 3.8 mm day^{-1} one day later. A second wave of rain, which passed through 3 days later, produced a smaller peak in discharge of 1.4 mm day^{-1} on October 20 (Figure 2). The overall hydrological response of the Archer Creek Watershed was also evident in the measurements from the piezometers in Subcatchment 11 (Figure 3). There was a marked decline in water table height through the summer with a minimum being found in early September. During the fall, there was a rise in the water table that coincided with the storm events and the reduction of transpiration.

Watershed chemistry during late summer and early fall 2002

Throughfall

Throughfall pH was lower (3.6) under conifers than (4.5) under deciduous trees and solute concentrations were higher respectively for all solutes (C_b [sum of base cations] = 177 vs. 11 μmol_c l^{-1}; SO_4^{2-} = 74 vs. 5 μmol_c l^{-1}; Cl$^-$ = 1 vs. 12 μmol_c l^{-1}; NH_4^+ = 10 vs. 2 ; DON = 46 vs. 4 μmol l^{-1}; DOC = 2992 vs. 94 μmol l^{-1}) except for NO_3^- for which concentrations were similar (2 and 4 μmol_c l^{-1}, respectively). Similar differences between hardwood and conifer throughfall have been reported previously for other stands in the Huntington Forest (Mollitor and Raynal 1982).

Ground water and soil water

The patterns varied among the wells across the watershed (Figure 4). Typically wells showed some decreases in SO_4^{2-} and NO_3^- concentrations during the summer. The two wells in the wetland (29a) and riparian (34) zones showed marked increases in SO_4^{2-} concentrations in late summer coinciding with the fall storms and increased SO_4^{2-} concentrations in surface waters as discussed below. The patterns in NO_3^- concentrations generally coincided with those of SO_4^{2-} with variation in these overall concentrations reflecting the contributions of reduction/oxidation processes to the water at each of these locations. It would be expected that NO_3^- would be depleted before SO_4^{2-} under low oxygen conditions associated with elevated water tables in wetlands due to the energetic preference of the former solute as an alternate electron acceptor for dissimilatory reduction (Stumm and Morgan 1970). For example, Well 29a had

no detectable NO_3^- and the lowest SO_4^{2-} concentrations of the three wells, but the SO_4^{2-} showed highest concentrations later in the year. The chemistry of piezometers in the Archer Creek Watershed clearly showed the role of reduction processes with almost no NO_3^- and lowered SO_4^{2-} concentrations in these wetland sites especially at the deeper depths (Table 2). Comparisons of lysimeters from upland and wetland sites from Subcatchment 11 showed similar results with lower NO_3^- and SO_4^{2-} concentrations in wetland sites especially at deeper depths (i.e., 50 vs. 15 cm) (Table 3).

Surface waters

The dominant base cation ($C_b = Ca^{2+} + Mg^{2+} + Na^+ + K^+$) was Ca^{2+} (67%), followed by Mg^{2+} (18%), Na^+ (13%) and K^+ (3%) (Table 4) within the drainage waters during these storm events. These proportions are very similar to those (69, 16, 12 and 2%, respectively) reported for an earlier period from 1995 to 1998 (Mitchell et al. 2001a) as well as for the entire 2002 year (68, 15, 15 and 2%, respectively) suggesting that storms had no marked effect on the relative compositions of these solutes in drainage waters on an annual basis. The total C_b values during these storms were, however, substantially higher (range 421–567 $\mu mol_c\ l^{-1}$) than the long term mean value both including (267 $\mu mol_c\ l^{-1}$) or excluding year 2002 (265 $\mu mol_c\ l^{-1}$, Table 5). These higher concentrations were likely due to role of the higher levels of
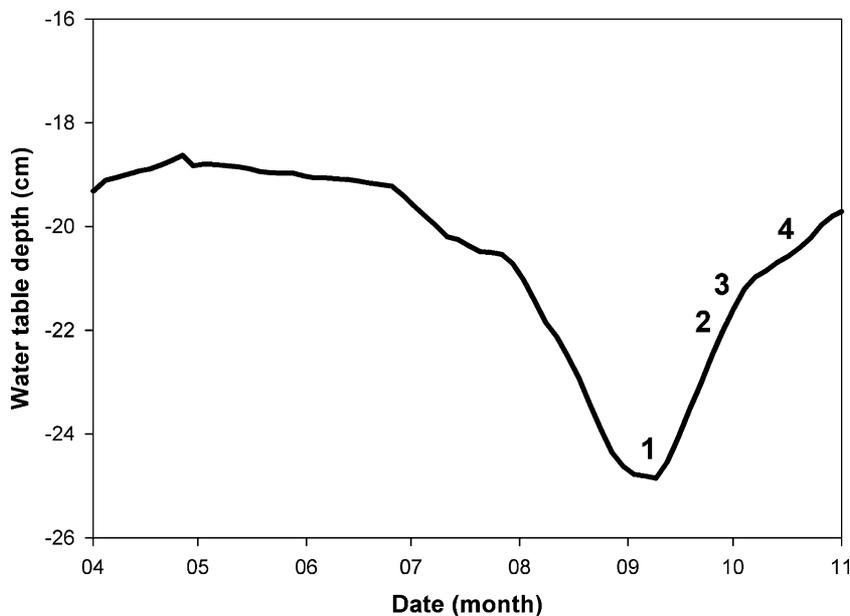
Figure 3. Peizometer (P29bs) water height from April 1 through Nov. 1, 2002. Numbers refer to storms described in Table 1.
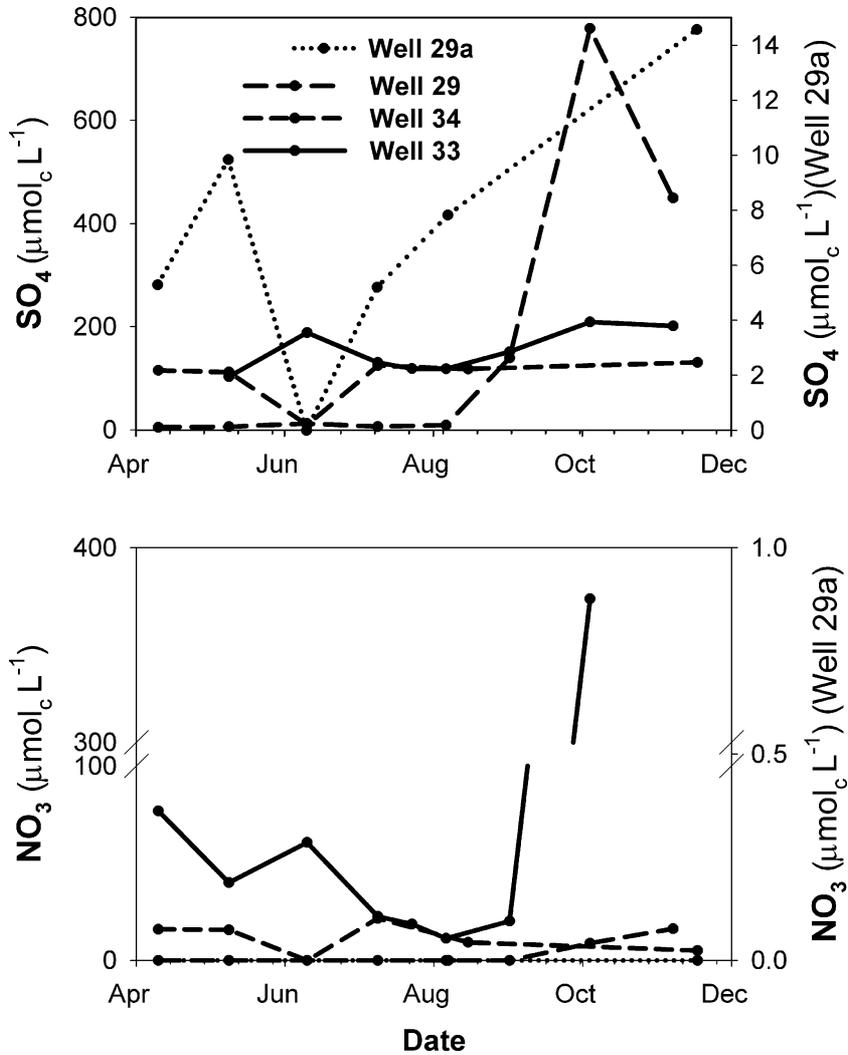
Figure 4. Concentrations of SO_4^{2-} and NO_3^- in wells 9, 29a 33 and 34 from April 1 through December 1, 2002.

Table 2. Piezometer chemistry for selected devices (100 cm depths) in wetlands from April through November 2002 sampled at ~6 week intervals ($N = 5$).

Device	pH	NH_4^+	C_b	Al	Si	Cl^-	NO_3^-	SO_4^{2-}	Total N	DON	DOC
P29Bs	4.6 (0.1)	19 (11)	166 (27)	8 (1)	134 (14)	14 (1)	0 (0)	9 (6)	87 (16)	68 (6)	1769 (506)
Pa	6.1 (0.2)	3 (1)	471 (48)	2 (1)	199 (9)	17 (2)	1 (1)	40 (10)	34 (6)	30 (6)	2868 (737)
Pi	5.5 (0.2)	17 (7)	257 (33)	8 (1)	208 (13)	11 (1)	0 (0)	13 (4)	60 (16)	44 (18)	1476 (172)

All concentrations in $\mu mol_c\ l^{-1}$ except for pH and Al, Total N, DON and DOC which are in $\mu mol\ l^{-1}$, means (SD).

Table 3. Lysimeter chemistry in subcatchment S11 within upland and wetland areas (April–August 2002). All concentrations in μmol_c l^{-1} except for pH and Al, Total N, DON and DOC which are in μmol l^{-1}, mean $\pm$ SD (N).

Location	Depth	Solute NH_4^+	Cb	Al	Si	Cl^-	NO_3^-	SO_4^{2-}	TDN	DON	DOC
Upland	15	27 ± 19 (11)	212 ± 75 (14)	74 ± 25 (14)	155 ± 91 (14)	13 ± 9 (12)	62 ± 60 (12)	75 ± 34 (12)	116 ± 55 (14)	48 ± 36 (10)	2270 ± 1142 (5)
	50	4 ± 3 (18)	177 ± 46 (17)	25 ± 14 (17)	152 ± 52 (17)	13 ± 8 (17)	35 ± 35 (17)	109 ± 26 (17)	58 ± 37 (18)	19 ± 5 (17)	60 ± 705 (14)
Wetland	15	6 ± 6 (21)	171 ± 25 (21)	27 ± 13 (21)	126 ± 34 (21)	9 ± 2 (21)	2 ± 6 (21)	53 ± 31 (21)	42 ± 16 (21)	33 ± 14 (21)	1498 ± 895 (21)
	50	28 ± 10 (24)	132 ± 34 (24)	23 ± 6 (24)	161 ± 25 (24)	10 ± 1 (24)	0 ± 1 (24)	24 ± 23 (24)	54 ± 13 (24)	26 ± 8 (24)	1166 ± 409 (24)

Table 4. Solutes in summer and fall storms at the Archer Creek watershed. Mean values are weighted by discharge for each event.

$\mu mol_c \, l^{-1} \mu mol \, l^{-1}$ (DOC) pH units	Storms Current study				Inamdar et al. (2004)	McHale et al. (2002)			
	1	2	3	4		*1*	*2*	*5*	*6*
SO_4^{2-} Mean	180	270	303	249	248	158	122	121	117
Max.	208	389	363	287	261	171	156	129	129
Min.	160	152	251	215	164	148	106	114	107
NO_3^- Mean	10	25	14	17	13	7	6	4	6
Max.	16	28	17	20	17	10	8	5	8
Min.	7	4	5	1	10	5	5	3	4
DOC Mean	442	915	1255	1343	1300	NA	NA	NA	NA
Max.	513	990	1510	1930	1579	NA	NA	NA	NA
Min.	326	322	443	520	535	NA	NA	NA	NA
C_b Mean	467	549	494	457	379	345	261	229	277
Max.	490	567	560	519	432	378	330	241	294
Min.	460	487	421	425	313	322	243	222	260
Si Mean	155	153	130	128	NA	NA	NA	NA	NA
Max.	164	165	173	175	NA	NA	NA	NA	NA
Min.	149	147	119	118	NA	NA	NA	NA	NA
pH Mean	5.6	5.8	5.1	5.3	5.8	6.1	5.4	6.3	NA
Max.	5.7	6.2	6.2	6.2	7.0	6.8	6.5	6.5	NA
Min.	5.4	5.2	4.8	5.0	5.4	5.8	5.0	6.2	NA

NA = not available.

mobile anions (e.g., SO_4^{2-} and Cl^-) contributing to the increased mobilization of these base cations (Reuss and Johnson 1986). During the 2002 storm events these mobile anions were markedly higher (Table 4) than the long term averages (Table 5). The concentrations for both cations and anions (Table 4) were much higher than those previously reported by McHale et al. (2002) and Inamdar et al. (2004) for storms at the same watershed again reflecting how the exceptionally dry conditions antecedent to the 2002 storms had a marked affect on watershed chemistry. The differences between these storms in 2002 and previously studied storms were shown in the much lower water yields (2–14% vs. 15–104%, Table 1). These extreme values associated with the storms of 2002 contributed to the differences in the mean surface water chemistry for year 2002 compared to mean values for years 1995 through 2001 (lower pH and higher C_b and SO_4^{2-} concentrations; Table 5). Combining all data from 1995 through 2002 (i.e., including year 2002 in the long-term average) resulted, however, in little change in the mean chemical composition of the surface water for the entire 7-year period (Table 5). These results suggest that although storm events, after periods of extensive drought, had substantial, short-term effects on surface water chemistry their influence on long-term mean chemistry is less due to the relatively low contribution of these events to total stream discharge.

Table 5. Average solute concentrations from Archer Creek Watershed from 1995 through 2002 weighted by daily discharge values.

PERIOD	pH	NH_4^+	C_b	Al	Cl^-	NO_3^-	SO_4^{2-}	Total N	DON	DOC
2002	5.8 (0.0)	1.9 (0.1)	280 (2.0)	5.9 (0.1)	11.9 (0.1)	26.4 (0.6)	133.7 (2)	38 (0.7)	9.0 (0.1)	457 (5)
1995–2001	6.4 (0.0)	1.2 (0.0)	265 (1.0)	5.2 (0.0)	10.6 (0.1)	26.4 (0.3)	130.3 (0.4)	31 (1)	11.0 (0.1)	NA
1995–2002	6.1 (0.0)	1.2 (0.0)	267 (1.0)	5.2 (0.1)	10.8 (0.1)	26.4 (0.3)	130.6 (0.4)	47 (3)	10.8 (0.1)	NA

All concentrations in $\mu mol_c\ L^{-1}$ except for pH and Al, Total N, DON and DOC which are in $\mu mol\ L^{-1}$ with SE's in "()".
NA = not available.

Differences in the contributions of water sources of DOC and Si among storms

The results from these storms provide information on the contributions of various sources to surface waters draining the Archer Creek Watershed and how these contributions changed as a function of watershed wetness. The overall changes in water sources as a function of watershed wetness and discharge are clearly shown by the strong inverse relationship between DOC and Si concentrations ($r = -0.857$, $p < 0.001$; Figure 5a). As storms progressed there was a general increase in DOC and decrease in Si (Table 4) as well as greater water yield (Table 1). Concentrations of Si had a strong negative relationship to discharge (Figure 5b) while DOC had a strong positive relationship (Figure 5c). High Si concentrations have often been used to indicate the contribution of deep soil and/or ground water sources to surface waters. High Si concentrations are often associated in post-glacial landscapes such as the Adirondacks with till groundwater (Hendershot et al. 1992; Hinton et al. 1994). High DOC concentrations in stream waters generally indicate water sources from the organic rich forest floor or wetlands (Hornberger et al. 1994; Boyer et al. 1997, 2000; Michalzik et al. 2001; Inamdar et al. 2004). For the current study, these patterns were clearly evident with high DOC and low Si concentrations in wetlands and upland soils, especially at shallow depths (Tables 2 and 3). Thus, with increasing watershed wetness there was decreasing
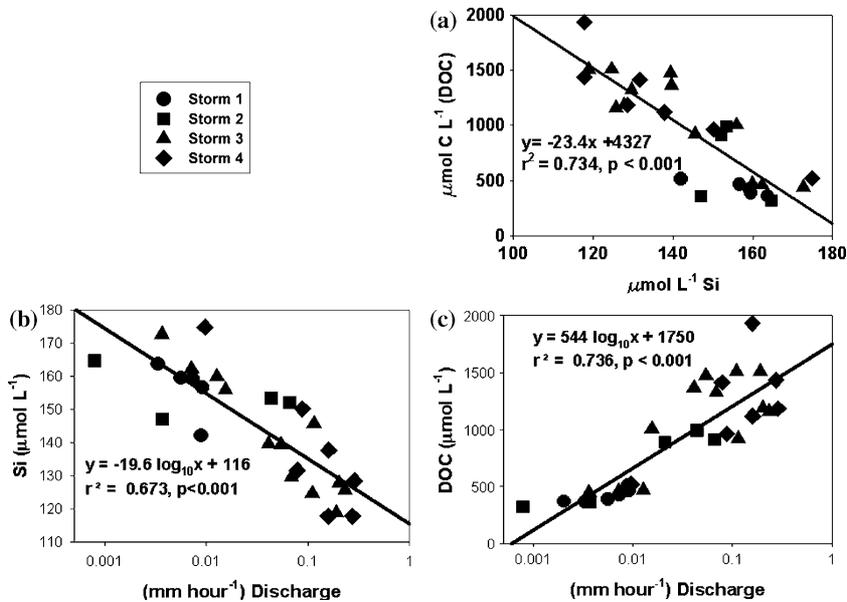
Figure 5. Relationships between DOC and Si concentrations and discharge ($\log_{10}$) for all four storms in 2002. Storm dates are given in Table 1.

contribution of ground water and an increasing contribution of water from wetland and upland sources.

Relationships between other solutes among storms

There were marked changes in other solutes during this study period (Figure 6). Both SO_4^{2-} (Figure 6a) and NO_3^- (Figure 6b) concentrations showed significant increases with discharge with highest discharge rates being associated with the later storms (e.g., 3 and 4) as storm size increased and the catchment became wetter. Highest mean and maximum SO_4^{2-} concentrations were found in storms 3 and 2, respectively while NO_3^- concentrations had highest maximum and mean concentrations in Storm 3 (Table 4). Concentrations of H^+ (Figure 6d) showed an overall significant increase with discharge. Storm 3 had the lowest minimum and average pH. Total Al showed the strongest relationship ($r^2 = 0.751$) of all major solutes to discharge (Figure 6c). The oxidation of both reduced S and N generates H^+ ions that combined with the mobilization of SO_4^{2-} and NO_3^- (Reuss and Johnson 1986) would contribute to the draining of total Al and H^+ into these surface waters. For other solutes (Cl^-, NH_4^+ and C_b)
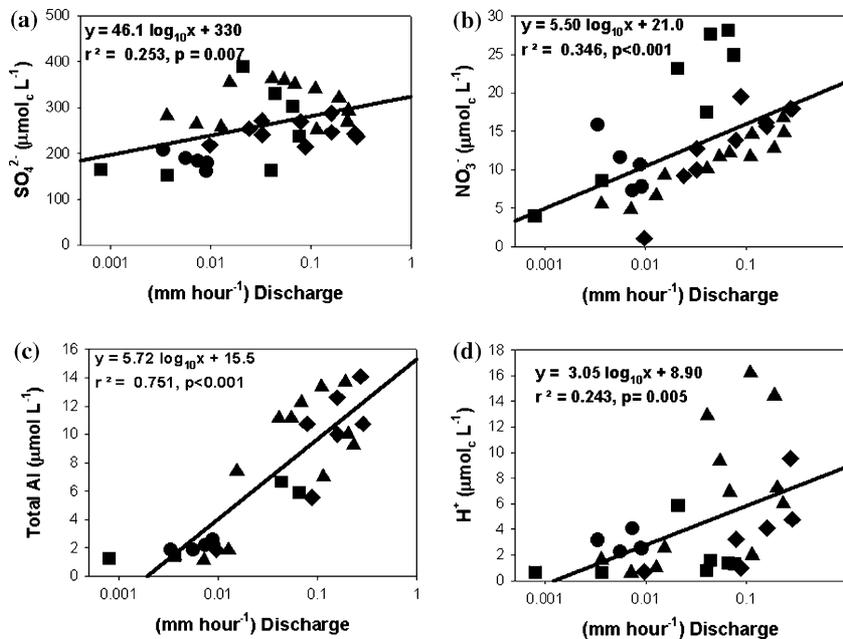
Figure 6. Relationship between SO_4^{2-} (a), NO_3^- (b), total Al (c) and H^+ (d) concentrations and discharge ($\log_{10}$) for all four storms in 2002. Storm dates are given in Table 1. Storm symbols are given in Figure 5.

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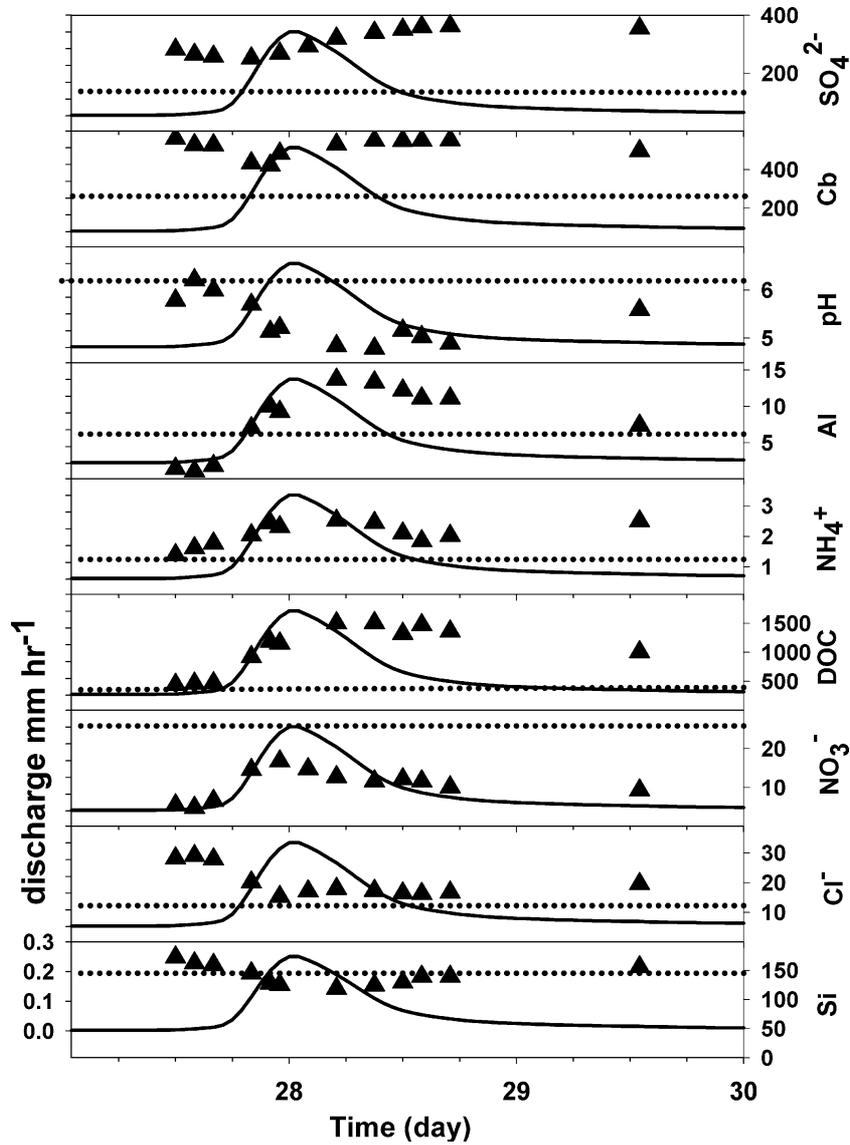
Figure 7. Changes in chemistry and discharge for Storm 3 from September 27–29, 2002. Dotted lines are the average concentrations for surface water solutes from 1995 through 2002 except for Si which is for 2002 only.

the overall relationships between concentrations and discharge were not significant ($p > 0.05$). Storm 3 had, however, the lowest minimum concentration of C_b (Table 4) that would have contributed to the lowest pH (4.8) ever recorded for the surface waters of Archer Creek.

Solute relationships within a storm

Further details on how solute sources can change during an event can be ascertained by looking at patterns within a storm. We examined such changes for Storm 3 which showed some of the most dramatic changes in solute chemistry (especially for NO_3^-, SO_4^{2-}, H^+, C_b and DOC) and discharge of the four storms examined in the current study (Figure 7). This storm had a 9% discharge water yield of the total storm precipitation. Storm 3 also resulted in notable changes in groundwater chemistry of some wells (Figure 4). Concentrations of NO_3^- in stream water increased from 5 to 17 μmol l^{-1} with maximum levels occurring just before peak discharge. Concentrations of SO_4^{2-} decreased slightly (251 μmol$_c$ l^{-1}) before peak discharge and continued to increase during and after the storm with maximum concentrations at 363 μmol$_c$ l^{-1} (Table 3). The temporal patterns of C_b were linked most closely to SO_4^{2-} ($r = 0.89$, $p < 0.01$) due to the dominant role of SO_4^{2-} as a mobile anion (Reuss and Johnson 1986). The inclusion of NO_3^- in this relationship resulted in no increase in the correlation to C_b ($r = 0.89$, $p < 0.01$). Concentrations of DOC increased from 443 μmol C L^{-1} reaching a maximum of 1510 μmol C L^{-1} after peak discharge and subsequently exhibiting a slow decline. The pH declined from 6.2 to 4.8 (an increase in 12 μmol H^+ l^{-1}) with lowest values being near the end of the storm. The highest H^+ (lowest pH) coincided with the highest Al (14 μmol l^{-1}) and lowest Si (119 μmol l^{-1}) concentrations. Groundwater domination prior to the storm was indicated by high Si and low DOC concentrations as discussed previously. The contribution of ground water decreased during the storm with highest NO_3^- and lowest Si concentrations occurring just before and after peak discharge, respectively. Thus, there were clear changes in relative contributions of various water sources within this storm. Further details on changes of water sources within storms are provided below in conjunction with the results on the stable isotopic analyses of SO_4^{2-} and NO_3^-.

Isotopic patterns of SO_4^{2-} and NO_3^- in Archer Creek watershed

$\delta^{34}S$ and $\delta^{18}O$ of SO_4^{2-}
For the throughfall samples, the $\delta^{34}S$ values were 4.1 and 3.1‰ under the hardwood and conifer canopies, respectively. The $\delta^{18}O$ value of SO_4^{2-} was 7.3‰ for the conifer throughfall (the $\delta^{18}O$ was not available for the hardwood throughfall due to sample size limitations). The SO_4^{2-} concentrations in both hardwood and conifer throughfall (5 and 74 μmol$_c$ l^{-1}) were much lower than that of the discharge water. The overall changes in SO_4^{2-} isotopic values when the results of all the storms are analyzed together indicate a strong relationship with lower $\delta^{34}S$ values with increasing discharge (Figure 8) and increasing SO_4^{2-} concentration (Figure 6a). At peak discharge, $\delta^{34}S$ values of stream water SO_4^{2-} were ~ -1‰ and hence more than 4‰ lower than throughfall
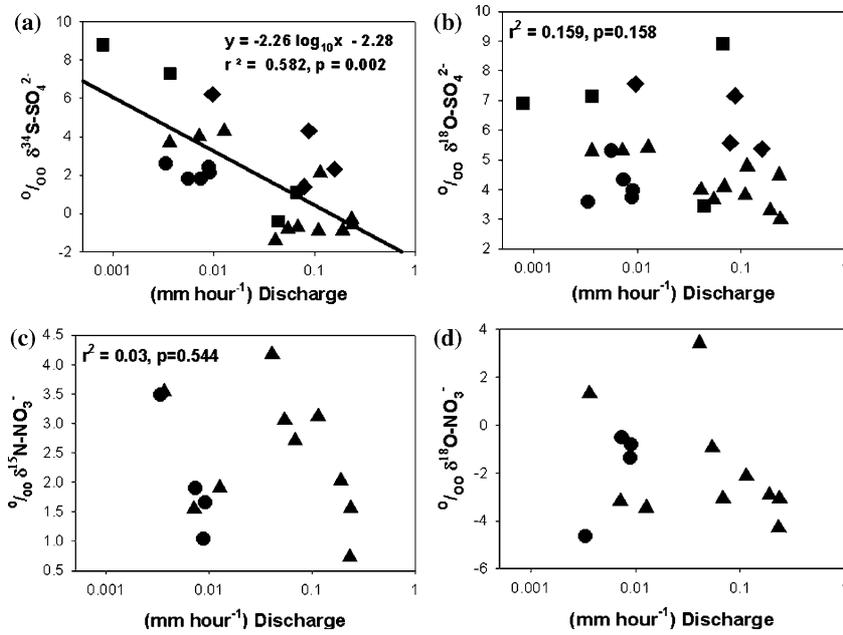
Figure 8. Relationships between $\delta^{34}S\text{-}SO_4^{2-}$ (a), $\delta^{18}O\text{-}SO_4^{2-}$ (b), $\delta^{15}N\text{-}NO_3^-$ (c) and $\delta^{18}O\text{-}NO_3^-$ (d) vs. discharge ($\log_{10}$) for all four storms in 2002. Storm dates are given in Table 1 and symbols in Figure 5.
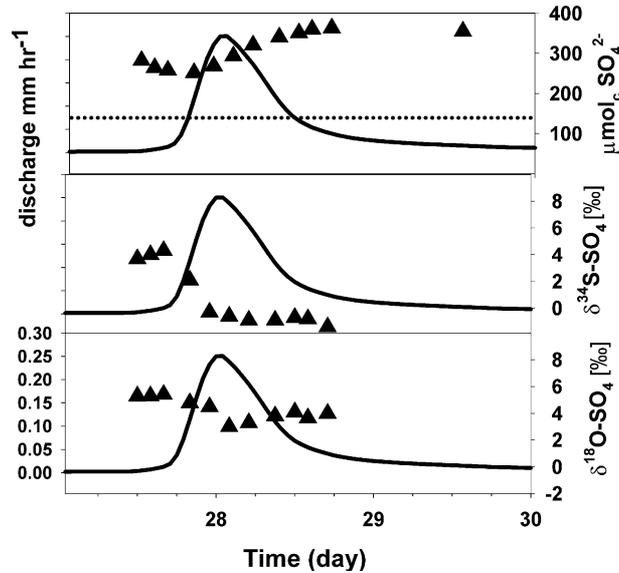
Figure 9. Changes in SO_4^{2-}, $\delta^{34}S\text{-}SO_4^{2-}$, $\delta^{18}O\text{-}SO_4^2$ and discharge for Storm 3 from September 27–29, 2002. Dotted line indicates discharge weighted mean SO_4^{2-} concentration from 1995–2002.

SO_4^{2-} values, suggesting an additional source of SO_4^{2-} with negative $\delta^{34}S$ values. Oxidation of reduced inorganic S species in wetlands is the likely source of this SO_4^{2-}.

There were differences, however, in the relationships between discharge, SO_4^{2-} concentrations and isotopic values. For example, at the beginning of Storm 3, SO_4^{2-} concentrations decreased and $\delta^{34}S$ values decreased, but as discharge increased the minimum SO_4^{2-} concentration coincided with an increase in $\delta^{34}S$ that was immediately followed by a decrease in $\delta^{34}S$ and monotonic increases in $\delta^{34}S$ and SO_4^{2-} concentration for the remainder of the storm including the descending limb (Figure 9). The beginning of the increase of $\delta^{34}S$ values coincided also with an increase in SO_4^{2-} concentration which declined during the initial portion of the storm with the concentration minimum coinciding with an increase in the $\delta^{34}S$ value. These results suggest that during the storm there was dilution of SO_4^{2-} from a source with elevated $\delta^{34}S$ values. With decreasing discharge, the lower SO_4^{2-} concentrations and the increase of $\delta^{34}S$ values are all consistent with an increasing contribution of S throughfall/soil sources. There was a significant relationship between the $\delta^{18}O$ and $\delta^{34}S$ values ($r = 0.665$, $p < 0.001$). Hence, values of $\delta^{18}O - SO_4^{2-}$ showed a similar temporal pattern to $\delta^{34}S$ values, with $\delta^{18}O - SO_4^{2-}$ values remaining $\sim 2\permil$ greater than prestorm values as the storm hydrograph receded (Figure 9).
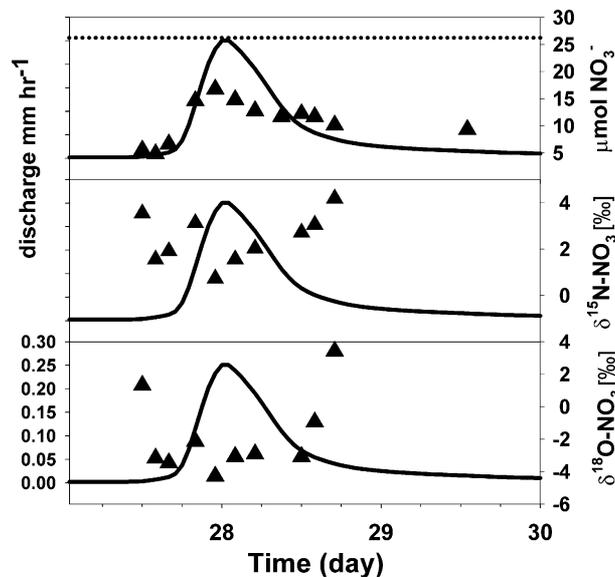
Figure 10. Changes in NO_3^-, $\delta^{15}N-NO_3^-$, $\delta^{18}O-NO_3^-$ and discharge for Storm 3 from September 27–29, 2002. Dotted line indicates discharge weighted mean NO_3^- concentration from 1995–2002.

$\delta^{15}N$ and $\delta^{18}O$ of NO_3^-

Throughfall and bulk precipitation isotopic values for $\delta^{15}N$–NO_3^- from September and October 2000 ranged from -6 to $+6‰$ (Piatek et al. 2005). Nitrate $\delta^{18}O$ values for atmospheric NO_3^- ranged from $+58‰$ in throughfall under a deciduous canopy to $+77‰$ in throughfall under a coniferous canopy (Piatek et al. 2005). Similar to SO_4^{2-}, there was a decrease followed by an increase in $\delta^{15}N$ values at the beginning of the storm (Figure 10). As discharge increased the minimum $\delta^{15}N$ and $\delta^{18}O$ values coincided with the highest NO_3^- concentration. However, unlike SO_4^{2-} in which concentrations increased, the concentrations of NO_3^- continued to decrease with increasing $\delta^{15}N$ values for the remainder of the storm (Figure 10; Table 3). Both the $\delta^{15}N$ and $\delta^{18}O$ values in stream discharge showed narrower ranges (0.5–4‰ and -5 to $+4‰$, respectively) than for values found previously in atmospheric inputs. There was a positive relationship ($r = 0.513$) between $\delta^{15}N$ and $\delta^{18}O$–NO_3^- values, but this relationship was only significant at $p = 0.06$. The highest $\delta^{15}N$ value was found ~ 15 h after the peak when discharge had returned to base flow (Figure 10). These isotopic values are within the range expected for microbially derived NO_3^- (i.e., N mineralization and nitrification) (Kendall 1998). However, the 6–8‰ changes in $\delta^{18}O$–NO_3^- values in the beginning and at the end of the storm indicate possible differences in NO_3^- sources during the storm.

Sulfate sources in the watershed

The increase in SO_4^{2-} concentrations across all storms as a function of discharge (Figure 6a) would be consistent with increasing contributions of wetlands or other zones of potential reduction and subsequent oxidation and mobilization with increasing watershed wetness. During the summer as conditions became drier there was a general decrease in the height of the water table (Figure 3). Freshwater wetlands retain S due to the reduction of SO_4^{2-} to sulfide and the incorporation of the sulfide into organic matter and iron compounds (Giblin and Wieder 1992). As the water table decreases, reduced sulfur compounds would be subject to reoxidation and potential mobilization of SO_4^{2-} when the watershed is rewetted. The contributions of these processes are indicated by the measurements of soil and sediment solutions within and outside of wetlands (Tables 2 and 3) and changes in ground water chemistry (Figure 4). The increase in SO_4^{2-} was also associated with higher DOC concentrations ($r = 0.64$, $p < 0.001$) for all storms except for Storm 1 during which both DOC and SO_4^{2-} concentrations remained low and there was a strong negative relationship between SO_4^{2-} and DOC ($r = -0.96$, $p < 0.001$). These results are consistent with this SO_4^{2-} being derived from sulfide oxidation in wetlands coinciding with high DOC concentrations during storms 2 through 4. The low concentrations of DOC and SO_4^{2-} and high concentrations of Si in Storm 1 are consistent with the stream water being dominated by ground water during the early phase of the rewetting of the watershed.

Wetland drying and wetting have been suggested to be important in affecting differences in the annual S budgets of forested catchments in southeastern Canada (Eimers and Dillon 2002). Laudon et al. (2004) also found in this same region that depression of ANC (Acid Neutralizing Capacity) in headwater streams was directly related to low antecedent moisture conditions and that the likely generation of SO_4^{2-} from wetlands. Dissimilatory reduction of SO_4^{2-} results in marked isotopic discrimination with the $\delta^{34}S$ values of the sulfide product being substantially lower than the $\delta^{34}S$ values of the remaining SO_4^{2-} (Thode 1991; Mitchell et al. 1998). The SO_4^{2-} isotopic results for all of the storms show a marked decrease in $\delta^{34}S$ values associated with increased discharge and SO_4^{2-} concentrations suggesting that sulfide that had been previously reduced was oxidized under dry conditions and then mobilized to surface waters with increased watershed wetness. The importance of the reoxidation of sulfide to SO_4^{2-} mobilization is clearly shown by the inverse relationship ($r = -0.73$, $p < 0.001$) (Figure 11) between $\delta^{34}S$ values and SO_4^{2-}. This relationship becomes even tighter if the results of Storm 1 are removed ($r = -0.91$, $p < 0.001$) again supporting the different response of this first storm which was dominated by ground water contributions. These patterns in $\delta^{18}O-SO_4^{2-}$ likely reflect the contribution of organic carbon S mineralization or sulfide oxidation. During both of these processes $\delta^{18}O-SO_4^{2-}$ values are re-set by incorporation of oxygen from water or the during the formation of the SO_4^{2-} molecule. During the conversion of C-bonded S to SO_4^{2-}, four new oxygen atoms predominantly derived from water are incorporated into the newly formed SO_4^{2-} molecule. Therefore, $\delta^{18}O-SO_4^{2-}$ values are typically several per mil lower than those of SO_4^{2-} in atmospheric deposition (Mayer et al. 1995ab; Shanley et al. 2005). Previous studies have established that only a limited atmospheric $SO_4^{2-}-\delta^{18}O-SO_4^{2-}$ signal is found after precipitation passes
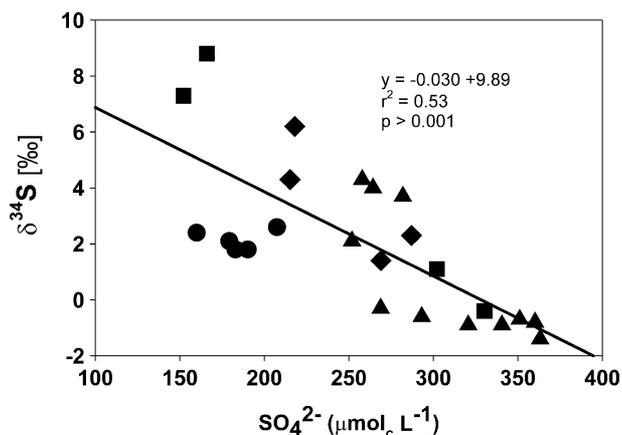
Figure 11. Relationship between $\delta^{34}S-SO_4^{2-}$ values and SO_4^{2-} concentrations for all four storms in 2002. Storm symbols are given in Figure 5.

through soil (Johnson et al. 2001; Kester et al. 2003; Shanley et al. 2005). Mayer et al. (1995a, b) showed a progressive decrease in the $\delta^{18}O$–SO_4^{2-} values in soil solution with depth, indicating that the immediate source of SO_4^{2-} was mineralization of C-bonded sulfur. Field experiments using amendments of ^{35}S–SO_4^{2-} have also confirmed that almost all of the S inputs to forest ecosystems pass through organic S soil pools (Schindler and Mitchell 1987; Dhamala and Mitchell 1995).

Nitrate sources in the watershed

Based on the NO_3^- isotopic values, we find no evidence of direct atmospheric NO_3^- contributions to surface waters during these storms, but rather the contribution of microbial nitrification. Although other evidence, including a dilution of Si concentrations, suggests decreasing contributions from ground waters during the storm progressions, we do not see any increase in the direct atmospheric NO_3^- addition, but rather additional contributions from upland soils. The highest NO_3^- concentrations that also coincided with the lowest SO_4^{2-} concentrations were found in Storm 2. The isotopic NO_3^- values clearly indicate that the N in the surface water had been microbially processed. Isotopic studies at Turkey Lake in Ontario, Canada Spoelstra et al. (2001), the Catskill Mountains of New York (Burns and Kendall 2002) and Hubbard Brook Experimental Forest in New Hampshire (Pardo et al. 2004) have also concluded that almost all of the surface water NO_3^- was microbially derived.

The results of the current study can be compared to results during snowmelt at Archer Creek Watershed when NO_3^- concentrations in surface waters are more elevated (e.g., > 40 μmol_c l^{-1}; Mitchell et al. 2001a; McHale et al. 2002; Park et al. 2003). Isotopic analyses of snowmelt events during 2001 and 2002 suggested that the NO_3^- in discharged water had passed through microbial pools and was derived from soil and ground water sources (Piatek et al. 2005). The importance of groundwater during snowmelt events for this same watershed has also been confirmed using EMMA (end member mixing analysis) in the 1996 during which snowmelt, soil water and till groundwater contributed 5, 15 and 75% of streamflow, respectively (McHale et al. 2002).

Nitrate flushing occurs when low soil moisture and water table levels allow NO_3^- to accumulate in the upper soil horizons followed by increasing soil moisture and a rise of the water table resulting in NO_3^- mobilization with highest concentrations occurring before peak discharge (Hornberger et al. 1994; Creed et al. 1996, Creed and Band 1998). The peak in NO_3^- concentrations before the peak discharge in Storm 3 is consistent with this flushing mechanism. It is notable that the peak in NO_3^- occurs prior to that of SO_4^{2-} and DOC suggesting different water sources among these two solutes. It is unlikely that the wetlands would be a substantial NO_3^- source since pore waters in the

wetlands generally have little if any NO_3^- (Tables 2 and 3). It is more likely that the NO_3^- is being derived from upland soil sources which can have relatively high NO_3^- concentrations (Table 3). The findings of the current study with respect to the role of watershed drying and rewetting are also consistent with other studies that have found that wetting and drying cycles can stimulate microbial N mineralization and nitrification (Kieft et al. 1987; Venterink et al. 2002). The role of these wetting and drying cycles in wetlands has also been implicated in the temporal and spatial patterns of NO_3^- concentrations in watersheds in Ontario, Canada (Watmough et al. 2004). Other studies have also suggested that even for upland soils that short periods of changing chemical oxidation/reduction conditions can influence NO_3^- loss and retention (Davidson et al. 2003; Sickman et al. 2003).

Overall watershed responses to storms

The topography of the Archer Creek Watershed is heterogeneous; it includes up-slope hollows and small up-slope wetlands both close to and away from the stream channel. Ridge areas appear to be primary sites for nitrification at our site (Ohrui and Mitchell 1998), as they are in other hardwood-conifer forests in the northeastern USA (Venterea et al. 2003). McHale et al. (2002) concluded that high NO_3^- soil water was present primarily at ridge tops at our site and was responsible for recharge of NO_3^- in groundwater. Inamdar et al. (2004) working in the same watershed, concluded that 'till water displacement' was responsible for NO_3^- and other solute discharge to stream waters during storm events. Due to the complexity of topography and the potential continuum in moisture conditions, the relative importance of various processes to surface water chemistry will be a function of storm intensity and antecedent moisture conditions. This current study and comparisons with previous analyses of storms at this watershed clearly shows that different antecedent moisture conditions and rainfall amounts resulted in distinct responses of hydrology and surface water chemistry. The analyses of Inamdar et al. (2004) developed a conceptual model showing how events alter the relative contributions of water sources to stream discharge. Our current study supports this conceptual model, but also demonstrates that during extreme drought conditions that the water chemistry of these different water sources (e.g., wetlands) can be dramatically altered.

Storms 1 and 2 resulted in only a small increase in discharge and relatively small changes in chemistry compared to storms 3 and 4 that had greater precipitation and also followed periods of increasing watershed wetness. The results from these latter storms suggest that after an extended dry period, followed by rewetting, a substantial amount of SO_4^{2-} was mobilized from organic rich locations in the watershed. Studies on the S constituents in areas adjacent to the Arbutus Watershed have not found that reduced inorganic sulfur species are major constituents in upland soils (David et al. 1987;

Schindler and Mitchell 1987). Thus, the major source of SO_4^{2-}, especially for Storms 3 and 4 were from wetlands or riparian zones. The importance of wetlands in the Archer Creek Watershed has been emphasized in other studies including that of Bischoff et al. (2001) who indicated that although wetlands compose a relatively small proportion ($\sim$4%) of the total watershed area that they play a disproportionate role in the storage ($\sim$15%) and cycling of nitrogen. There was no relationship ($r = 0.073$, $p = 0.80$) between the $\delta^{18}O$ values of NO_3^- and SO_4^{2-} suggesting the oxygen sources were not the same for those reduced N and S chemical species that were oxidized during these storms and hence the water sources of the reduced chemical species that were subsequently oxidized were likely different as well. Differences in the temporal patterns of solutes among storms and with discharge also suggest different sources for NO_3^- and SO_4^{2-}.

Comparisons with previous studies of storms at Archer Creek watershed

Inamdar et al. (2004) attributed the rise in NO_3^- concentration in stream water during the remnant of the 1999 tropical storm *Floyd* to till water, and rising DOC concentrations to near-surface soil water. McHale et al. (2002) used end-member mixing analysis to determine that till groundwater and soil water dominated stormflow during the first of two consecutive fall storms in 1996. McHale et al. (2002) estimated that for the second of two summer storms of 1996 that till groundwater, soil water, and throughfall comprised 14, 48 and 38%, respectively of stream discharge. We did not observe in the current study intermediate NO_3^- isotopic values that would indicate mixing of nitrification-derived (ground and soil water sources) with atmospheric (throughfall) NO_3^-. The differences could be a function of the much greater watershed wetness for the 1996 storms compared to the 2002 storms as indicated by water yield (91 vs. 2–14%) (Table 1). In addition, analyses from end-member mixing analyses may provide different results than those from more direct measurements using isotopic evaluations. Regardless, these comparisons among storms show that sources of NO_3^- and SO_4^{2-} in stream waters are likely to be highly dependent on pre-event moisture and hence water yield (Table 1) in the watershed, and because those vary, different sources of these solutes have different relative contributions depending upon hydrological conditions. In the current study, mean and maximum SO_4^{2-}, NO_3^- and C_b concentrations were higher and pH lower than found in previous storms where moisture conditions were higher (Tables 1 and 4).

Effect of climatic change on hydrology and storm effects

The results of this study clearly show that changes in summer precipitation patterns and hence hydrology can have a major influence on watershed

biogeochemistry. Previous studies on biogeochemical budgets in Canadian watersheds have also shown that differences in hydrology and climate can have a major influence on S (Eimers and Dillon 2002) and N (Watmough et al. 2004) processes. Shanley et al. (2002) have also shown that antecedent soil moisture conditions at Sleepers River in Vermont were affected by hydraulic properties of the till and together controlled percent contributions of new and old water. Our current study shows that antecedent hydrological conditions can also have a major influence on event chemistry. The role of snowmelt including the role of the snowpack and interactions with climate in affecting soil freezing and NO_3^- loss has been emphasized in a number of studies (Mitchell et al. 1996a; Fitzhugh et al. 2001; Groffman et al. 2001; Campbell et al. 2005). The effect of winter temperature in affecting NO_3^- release in the Archer Creek Watershed has also been shown (Park et al. 2003). Other studies have also suggested that inter-annual climatic variation contributes to differences in annual NO_3^- losses (Aber and Driscoll 1997; Goodale et al. 2003). Recent studies have linked temperature variability in the northeastern USA to decadal trends in North Atlantic-Arctic Oscillation (NAO-AO), showing a positive relationship between NAO-AO indexes and temperature averages or maxima (Hurrell 1995; Wettstein and Mearns 2002). These variations in temperature and possibly precipitation patterns will have a major influence on watershed biogeochemistry especially if these conditions result in long-term major changes in hydrologic regimes. There has been concern related to the effects of episodic acidification to surface waters in acid sensitive areas such as the northeast USA (Wigington et al. 1996a, b). The current study suggests that dry conditions followed by storm events can result in markedly depressed surface pH values (e.g., 4.8, Table 4) even for a site with an average surface water pH of 6.4 (Table 5). Moreover, our study suggests that changes in the hydrological regimes result in different responses to the cycling of S and N. Understanding the linkages between watershed hydrology and biogeochemistry will be critical for understanding biogeochemical responses of watersheds over temporal scales ranging from storm events to long-term climatic change.

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References

Aber J.D. and Driscoll C.T. 1997. Effects of land use, climate variation and N deposition on N cycling and C storage in northern hardwood forests. Global Biogeochem. Cycles 11: 639–648.

Ameel J.J., Axler R.P. and Owen C.J. 1993. Persulfate digestion for determination of total nitrogen and phosphorous in low-nutrient waters. Am. Environ. Lab. 10: 1–111.

Bailey S.W., Mayer B. and Mitchell M.J. 2004. Evidence for the influence of mineral weathering on stream water sulphate in Vermont and New Hampshire. Hydrol. Proc. 18: 1639–1653.

Bischoff J.M., Bukaveckas P., Mitchell M.J. and Hurd T. 2001. Nitrogen storage and cycling of a forested wetland: implications for watershed N processing. Water Air Soil Pollut. 128: 97–114.

Boyer E.W., Hornberger G.M., Bencala K.E. and McKnight D.M. 2000. Effects of asynchronous snowmelt on flushing of dissolved organic carbon: a mixing model approach. Hydrol. Proc. 14: 3291–3308.

Boyer E.W., Hornberger G.M., Bencala K.E. and McKnight D.M. 1997. Response characteristics of DOC flushing in an alpine catchment. Hydrol. Proc. 11: 1635–1647.

Brooks P.D. and Williams M.W. 1999. Snowpack controls on nitrogen cycling and export seasonally snow-covered catchments. Hydrol. Proc. 13: 2177–2190.

Burns D.A. 2002. Stormflow-hydrograph separation based on isotopes: the thrill is gone-what is next? Hydrol. Proc. 16: 1515–1517.

Burns D.A. and Kendall C. 2002. Analysis of $\delta^{15}N$ and $\delta^{18}O$ to differentiate NO_3^- sources in runoff at two watersheds in the Catskill Mountains of New York. Water Res. Res. 38: 9/1–9/11.

Campbell J.L., Mitchell M.J., Groffman P.M. and Christenson L.M. 2005. Winter in northeastern North America: An often overlooked but critical period for ecological processes. Frontiers Ecol. 3: 314–322.

Casciotti K.L., Sigman D.M., Galanter Hastings M., Böhlke J.K. and Hilkert A. 2002. Measurement of the oxygen isotopic composition of nitrate in marine and fresh waters using the denitrifier method. Anal. Chem. 74: 4905–4912.

Castillo V.M., Gómez-Plaza A. and Martínez-Mena M. 2003. The role of antecedent soil water content in the runoff response of semiarid catchments: a simulation approach. J. Hydrol. 284: 114–130.

Chang C.C.Y., Langston J., Riggs M., Campbell D.H., Silva S.R. and Kendall C. 1999. A method for nitrate collection for $\delta^{15}N$ and $\delta^{18}O$ analysis from waters with low nitrate concentrations. Can. J. Fish. Aquat. Sci. 56: 1–9.

Creed I.F., Band L.E., Foster N.W., Morrison I.K., Nickolson J.A., Semkin R.S. and Jeffries D.S. 1996. Regulation of nitrate-N release from temperate forests: a test of the N flushing hypothesis. Water Res. Res. 32: 3337–3354.

Creed I.F. and Band L.E. 1998. Export of nitrogen from catchments within a temperate forest. Evidence for a unifying mechanism regulated by variable source area dynamics. Water Res. Res. 34: 3105–3120.

Christopher S.F., Page B.D., Campbell J.L. and Mitchell M.J. 2005. Contrasting stream water NO_3^- in two nearly adjacent catchments: The role of soil Ca and forest vegetation. Global Change Biol. In press.

David M.B., Mitchell M.J. and Scott T.J. 1987. Importance of organic sulfur constituents to sulfur cycling in a northern hardwood forest ecosystem. Biology Fert. Soils 5: 258–264.

Davidson E.A., Chorover J. and Dail D.B. 2003. A mechanism of abiotic immobilization of nitrate in forest ecosystems: the ferrous wheel hypothesis. Global Change Biol. 9: 228–236.

Davies T.D., Tranter M., Wigington P.J.Jr, Eshleman K.N., Peters N.E., Van Sickle J., DeWalle D.R. and Murdoch P.S. 1999. Prediction of episodic acidification in the North-eastern USA: an empirical/mechanistic approach. Hydrol. Proc. 13: 1181–1195.

Dewalle D.R., Edwards P.J., Swistock B.R., Aravena R. and Drimmie R.J. 1997. Seasonal isotope hydrology of three Appalachian forest Catchments. Hydrol. Proc. 11: 1895–1906.

Dhamala B.R. and Mitchell M.J. 1995. Sulfur speciation, vertical distribution, and seasonal variation in a northern hardwood soil: A ^{35}S tracer study. Can. J. For. Res. 25: 234–243.

Eimers M.C. and Dillon P.J. 2002. Climate effects on sulphate flux from forested catchments in south-central Ontario. Biogeochem. 61: 337–355.

Eshleman K.N., Wigington P.J.Jr, Davies T.D. and Tranter M. 1992. Modelling episodic acidification of surface waters: the state of the science. Environ. Pollut. 77: 287–295.

Fisher D. 1957. Bedrock Geology Map of New York State. NYS Museum Bulletin 221–4 Albany, New York.

Fitzhugh R.D., Driscoll C.T., Groffman P.M., Tierney G.L., Fahey T.J. and Hardy J.P. 2001. Effects of soil freezing disturbance on soil solution nitrogen, phosphorus and carbon chemistry in a northern hardwood ecosystem. Biogeochemistry 56: 215–238.

Frank H., Schleppi P., Peter W. and Hannes F. 2000. Export of dissolved organic carbon and nitrogen from Gleysol dominated catchments-the significance of water flow paths. Biogeochemistry 50: 137–161.

Gehre M. and Strauch G. 2003. High-temperature elemental analysis and pyrolysis techniques for stable isotope analysis. Rapid Commun. Mass Spectrom. 17: 1497–1503.

Giblin A.E. and Wieder R.K. 1992. Sulphur cycling in marine and freshwater wetlands. In Sulfur Cycling on the Continents. SCOPE 48. John Wiley and Sons, Inc. Publishers, Chichester, pp. 85–124.

Giesemann A., Jäger H.J., Norman A.-L., Krouse H.R. and Brand W.A. 1994. On-line sulfur-isotope determination using an elemental analyzer coupled to a mass spectrometer. Anal. Chem. 66: 2816–2819.

Goodale C.L., Aber J.D. and Vitousek P.M. 2003. An unexpected nitrate decline in New Hampshire streams. Ecosystems 6: 75–86.

Groffman P.M., Driscoll C.T., Fahey T.J., Hardy J.P., Fitzhugh R.D. and Tierney G.L. 2001. Effects of mild winter freezing on soil nitrogen and carbon dynamics in a northern hardwood forest. Biogeochemistry 56: 191–213.

Hendershot W.J., Courchesne F. and Schemenaue R.S. 1992. Soil acidification along a topographic gradient on Roundtop mountain, Quebec, Canada. Water Air Soil Pollut. 61: 235–242.

Hinton M.J., Schiff S.L. and English M.C. 1994. Examining the contributions of glacial till water to storm runoff using two- and three-component hydrograph separations. Water Res. Res. 30: 983–993.

Hornberger G.M., Bencala K.E. and McKnight D.M. 1994. Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. Biogeochemistry 25: 147–165.

Hurd T.M., Raynal D.J. and Schwintzer C.R. 2001. Symbiotic N_2 fixation of Alnus incana sprugosa in shrub wetlands of the Adirondack Mountains, New York, USA. Oecologia 126: 94–103.

Hurrell J.W. 1995. Decadal trends in the North Atlantic Oscillation: regional temperatures and precipitation. Science 269: 676–679.

Inamdar S.P., Christopher S.F. and Mitchell M.J. 2004. Export mechanisms for dissolved organic carbon and nitrate during summer storm events in a glaciated forested catchment in New York, USA. Hydrol. Proc. 18: 2651–2661.

Johnson C.A., Mast M.A. and Kester C.L. 2001. Use of 17O/16O to trace atmospherically-deposited sulfate in surface waters: a case study in alpine watersheds in the Rocky Mountains. Geophys. Res. Lett. 28: 4483–4486.

Kendall C. 1998. Tracing Nitrogen Sources and Cycling in Catchments. Isotope Tracers in catchment hydrology, Elsevier Science, BV.

Kester C.L., Baron J.S. and Turk J.T. 2003. Isotopic study of sulfate sources and residence times in a subalpine watershed. Enviro. Geology 43: 606–613.

Kieft T., Soroker E. and Firestone M.K. 1987. Microbial biomass response to a rapid increase in water potential when dry soil is wetted. Soil Biol. Biochem. 19: 119–126.

Laudon H., Dillon P.J., Eimers M.C., Semkin R.G. and Jeffries D.S. 2004. Climate-induced episodic acidification of streams in central Ontario. Environ. Sci. Technol 38: 6009–6015.

Mayer B., Feger K.H., Giesemann A. and Jäger H.J. 1995a. Interpretation of sulfur cycling in two catchments in the Black Forest (Germany) using stable sulfur and oxygen isotope data. Biogeochemistry 30: 51–58.

Mayer B., Fritz P., Prietzel J. and Krouse H.R. 1995b. The use of stable sulfur and oxygen isotope ratios for interpreting the mobility of sulfate in aerobic forest soils. Appl. Geochem. 10: 161–173.

Mayer B., Boyer E.W., Goodale C., Jaworski N.A., van Breemen N., Howarth R.W., Seitzinger S., Billen G., Lajtha K., Nadelhoffer K., Van Dam D., Hetling L.J., Nosal M. and Paustian K. 2002. Sources of nitrate in rivers draining sixteen watersheds in the Northeastern U.S.: isotopic constraints. Biogeochemistry 57(58): 171–197.

McHale M.R. 1999. Hydrologic controls of nitrogen cycling in an Adirondack Watershed Ph.D dissertation. State University of New York, College of Environmental Science and Forestry, Syracuse, New York, p.230

McHale M.R., Mitchell M.J., McDonnell J.J. and Cirmo C. 2000. Nitrogen solutes in an Adirondack forested watershed: importance of dissolved organic nitrogen. Biogeochemistry 48: 165–184.

McHale M.R., McDonnell J.J., Mitchell M.J. and Cirmo C.P. 2002. A field based study of soil- and groundwater nitrate release in an Adirondack forested watershed. Water Res. Res. 38(4): 1029/2000WR000102 (17 pages).

Michalzik B., Kalbitz K., Park J.H., Solinger S. and Matzner E. 2001. Fluxes and concentrations of dissolved organic carbon and nitrogen – a synthesis for temperate forests. Biogeochemistry 52: 173–205.

Mitchell M.J. 2005. Episodic acidification. In: Lehr J.H. (ed.), Encyclopedia of Water. John Wiley and Sons Publishing, (In press).

Mitchell M.J., Driscoll C.T., Kahl J.S., Likens G.E., Murdoch P.S. and Pardo L.H. 1996a. Climatic control of nitrate loss from forested watersheds in the northeast United States. Environ. Sci. Technol. 30: 2609–2612.

Mitchell M.J., Raynal D.J. and Driscoll C.T. 1996b. Biogeochemistry of a forested watershed in the central Adirondack Mountains: temporal changes and mass balances. Water Air Soil Pollut. 88: 355–369.

Mitchell M.J., Krouse C.R., Mayer B., Stam A.C. and Zhang Y. 1998. Use of stable isotopes in evaluating sulfur biogeochemistry of forest ecosystems. In: Isotope Tracers in Catchment Hydrology. Elsevier, Amsterdam, pp. 489–518

Mitchell M.J., McHale P.J., Inamdar S. and Raynal D.R. 2001a. Role of within lake processes and hydrobiogeochemical changes over 16 years in a watershed in the Adirondack Mountains of New York State, USA. Hydrol. Proc. 15: 1951–1965.

Mitchell M.J., McGee G., McHale P. and Weathers K.C. 2001b. Experimental design and instrumentation for analyzing solute concentrations and fluxes for quantifying biogeochemical processes in watersheds. Methodology paper series of the 4th International Conference on ILTER in East Asia and Pacific Region, Ulaanbaatar-Hatgal, Mongolia 2001, 2001 ILTER Network. pp. 15–21

Mitchell M.J., Driscoll C.T., Inamdar S., McGee G., Mbila M. and Raynal D.J. 2003. Nitrogen biogeochemistry in the Adirondack Mountains of New York: hardwood ecosystems and associated surface waters. Environ. Pollut. 123: 355–364.

Mollitor A.V. and Raynal D.J. 1982. Atmospheric deposition and ionic movements in Adirondack forest soils. Soil Sci. Soc. Amer. J. 46: 1032–1036.

Ohrui K. and Mitchell M.J. 1998. Spatial patterns of soil nitrate in Japanese forested watersheds: importance of the near-stream zone as a source of nitrate in stream water. Hydrol. Proc. 12: 1433–1445.

Pardo L.H., Kendall C., Pett-Ridge J. and Chang C.C.Y. 2004. Evaluating the source of stream-water nitrate using $\delta^{15}N$ and $\delta^{18}O$ in nitrate in two watersheds in New Hampshire, USA. Hydrol. Proc. 18: 2699–2712.

Park J., Mitchell M.J., McHale P.J., Christopher S.F. and Myers T.P. 2003. Interactive effects of changing climate and atmospheric deposition on N and S biogeochemistry in a forested watershed of the Adirondack Mountains, New York State. Global Change Biol. 9: 1602–1619.

Piatek K.B., Mitchell M.J., Silva S.R. and Kendall C. 2005. Sources of nitrate in snowmelt discharge: evidence from water chemistry and stable isotopes of nitrate. Water Air Soil Pollut. 165: 13–35.

Reuss J.O. and Johnson D.W. 1986. Acid Deposition and the Acidification of Soil and Water. Springer-Verlag, New York.

Rock L. and Mayer B. 2002. Isotopic assessment of sources and processes affecting sulfate and nitrate in surface water and groundwater of Luxembourg. Isot. Environ. Health Stud. 38(4): 191–206.

Schindler S.C. and Mitchell M.J. 1987. Dynamics of 35S in horizons and leachates from a hardwood forest spodosol. Soil Biol. Biochem. 19: 531–538.

Shanley J.B., Kendall C., Smith T.E., Wolock D.M. and McDonell J.J. 2002. Controls on old and new water contributions to stream flow at some nested catchments in Vermont, USA. Hydrol. Process. 16: 589–609.

Shanley J.B., Mayer M., Mitchell M.J., Michel R.L., Bailey S. and Kendall C. 2005. Differentiating atmospheric and mineral sources of sulfur during snowmelt using $\delta^{34}S$, ^{35}S activity, and $\delta^{18}O$ of sulfate and water as tracers. Biogeochemistry 76: 161–185.

Shepard J.P., Mitchell M.J., Scott T.J., Zhang Y.M. and Raynal D.J. 1989. Measurements of wet and dry deposition in a northern hardwood forest. Water Air Soil Pollut. 48: 225–238.

Sickman J.O., Leydecker A., Chang, CCY, Kendall C., Melack J.M., Lucero D.M. and Schimel J. 2003. Mechanisms underlying export of N from high-elevation catchments during seasonal transitions. Biogeochemistry 64: 1–24.

Sigman D.M., Casciotti K.L., Andreani M., Barford C., Galanter M. and Böhlke J.K. 2001. A bacterial method for the nitrogen isotopic analysis of nitrate in marine and fresh waters. Anal. Chem. 73: 4145–4153.

Silva S.R., Kendall C., Wilkinson D.H., Ziegler A.C., Chang C.C.Y. and Avanzino R.J. 2000. A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. J. Hydrol. 228: 22–36.

Somers R.C. 1986. Soil classification, genesis, morphology, and variability with the Central Adirondack Region of New York PhD dissertation. State University of New York, College of Environmental Science and Forestry, Syracuse, NY, 746.

Spoelstra J., Schiff S.L., Elgood R.J., Semkin R.G. and Jeffries D.S. 2001. Tracing the sources of exported nitrate in the Turkey Lakes Watershed using $^{15}N/^{14}N$ and $^{18}O/^{16}O$ isotopic ratios. Ecosystems 4: 536–544.

Stumm W. and Morgan J.J. 1970. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters. Wiley-Interscience, New York.

Thode H.G. 1991. Sulphur isotopes in nature and the environment: an overview. In: Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment. SCOPE 43. Publisher John Wiley and Sons, Chichester, pp. 1–26.

Venterea R.T., Lovett G.M., Groffman P.M. and Schwarz P.A. 2003. Landscape patterns of net nitrification in a northern hardwood-conifer forest. Soil Sci. Soc. Am. J. 67: 527–539.

Venterink H.O., Davidsson T.E., Kiehl K. and Leonardson L. 2002. Impact of drying and re-wetting on N, P and K dynamics in a wetland soil. Plant Soil 243: 119–130.

Wellington B.L. and Driscoll C.T. 2004. The episodic acidification of a stream with elevated concentrations of dissolved organic carbon. Hydrol. Proc. 18: 2663–2680.

Watmough S.A., Eimers M.C., Aherne J. and Dillon P.J. 2004. Climate effects on nitrate export from forested catchments in south-central Ontario. Environ. Sci. Technol. 38(33): 2383–2388.

Wettstein J.J. and Mearns L.O. 2002. The influence of the North Atlantic-Arctic Oscillation on mean variance and extremes of temperature in the northeastern United States and Canada. J. Climate 15: 3586–3600.

Wigington P.J. Jr, Davies T.D., Tranter M. and Eshleman K.N. 1992. Comparison of episodic acidification in Canada, Europe and the United States. Environ. Pollut. 78: 29–35.

Wigington P.J. Jr, Baker J.P., DeWalle D.R., Kretser W.A., Murdoch P.S., Simonin H.A., Van Sickle J., McDowell M.K., Peck D.V. and Barchet W.R. 1996a. Episodic acidification of small streams in the northeastern United States: episodic response project. Ecol. Appl. 62: 374–388.

Wigington P.J. Jr, DeWalle D.R., Murdoch P.S., Kretser W.A., Simonin H.A., Van Sickle J. and Baker J.P. 1996b. Episodic acidification of small streams in the northeastern United Sates: ionic controls of episodes. Ecol. Appl. 62: 389–407.