HYDROLOGICAL PROCESSES
Hydrol. Process. **22**, 4023–4034 (2008)
Published online 28 May 2008 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/hyp.7033

Evaluating sulfur dynamics during storm events for three watersheds in the northeastern USA: a combined hydrological, chemical and isotopic approach

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Abstract:

Concerns related to climate change have resulted in an increasing interest in the importance of hydrological events such as droughts in affecting biogeochemical responses of watersheds. The effects of an unusually dry summer in 2002 had a marked impact on the biogeochemistry of three watersheds in the north-eastern USA. Chemical, isotopic and hydrological responses with particular emphasis on S dynamics were evaluated for Archer Creek (New York), Sleepers River (Vermont) and Cone Pond (New Hampshire) watersheds. From 1 August to 14 September 2002, all three watersheds had very low precipitation (48 to 69 mm) resulting in either very low or no discharge (mean 0·015, 0·15 and 0·000 mm day^{-1} for Archer Creek, Sleepers River and Cone Pond, respectively). From 15 September to 31 October 2002, there was a substantial increase in precipitation totals (212, 246 and 198 mm, respectively) with increased discharge. Archer Creek was characterized by a large range of SO_4^{2-} concentrations (152 to 389 μeq L^{-1}, mean = 273 μeq L^{-1}) and also exhibited the greatest range in δ^{34}S values of SO_4^{2-} (−1·4 to 8·8 ‰). Sleepers River's SO_4^{2-} concentrations ranged from 136 to 243 μeq L^{-1} (mean = 167 μeq L^{-1}) and δ^{34}S values of SO_4^{2-} ranged from 4·0 to 9·0 ‰. Cone Pond's SO_4^{2-} concentrations (126–187 μeq L^{-1}, mean = 154 μeq L^{-1}) and δ^{34}S values (2·4 to 4·3 ‰) had the smallest ranges of the three watersheds. The range and mean of δ^{18}O-SO_4^{2-} values for Archer Creek and Cone Pond were similar (3·0 to 8·9 ‰, mean = 4·5 ‰; 3·9 to 6·3 ‰, mean = 4·9 ‰; respectively) while δ^{18}O-SO_4^{2-} values for Sleepers River covered a larger range with a lower mean (1·2 to 10·0 ‰, mean = 2·5). The difference in Sleepers River chemical and isotopic responses was attributed to weathering reactions contributing SO_4^{2-}. For Archer Creek wetland areas containing previously reduced S compounds that were reoxidized to SO_4^{2-} probably provided a substantial source of S. Cone Pond had limited internal S sources and less chemical or isotopic response to storms. Differences among the three watersheds in S biogeochemical responses during these storm events were attributed to differences in S mineral weathering contributions, hydrological pathways and landscape features. Further evaluations of differences and similarities in biogeochemical and hydrological responses among watersheds are needed to predict the impacts of climate change. Copyright © 2008 John Wiley & Sons, Ltd.

KEY WORDS climate change; drought; hydrology; stable isotopes; storms; sulfate; surface water; watersheds

Received 23 April 2007; Accepted 12 February 2008

INTRODUCTION

Climatic regimes in the north-east USA, as in other regions of the world, are currently showing major changes and recent reports have suggested that these changes are intensifying (Stager and Martin, 2002; Huntington *et al.*, 2004; NECIA, 2006). Recent studies have clearly shown that hydrological conditions in catchments can have a major influence on the export of various solutes including SO_4^{2-} (Eimers *et al.*, 2004ab; Mitchell *et al.*, 2006). A clear linkage has also shown that antecedent droughts can contribute to the oxidation of previously stored sulfide, especially in wetlands (Eimers *et al.*, 2006), resulting in increased SO_4^{2-} mobilization as watersheds are rewetted. The linkage of these sulfur biogeochemical processes with both short-term hydrological events as well as the potential influence of long-term climatic change needs further investigation. Previous studies have included analyses of multiple watersheds using chemical and hydrological information (Eimers and Dillon, 2002; Laudon *et al.*, 2004) as well as more detailed studies on individual watersheds that have used stable isotopic information to evaluate SO_4^{2-} sources (Eimers *et al.*, 2004a; Shanley *et al.*, 2005; Mitchell *et al.*, 2006). We are not aware of any previous study that has investigated the effects of droughts among watersheds on sulfur biogeochemical responses using a combination of hydrological, chemical and isotopic approaches.

The current study compares the hydrological, chemical and isotopic responses for three watersheds (Archer Creek, Sleepers River and Cone Pond) in the north-eastern USA that have had extensive biogeochemical research (Figure 1). The three watersheds have similar amounts of S deposition (Archer Creek, wet only

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† The contributions of Scott W. Bailey and James B. Shanley to this article were prepared as part of their official duties as United States Federal Government employees.

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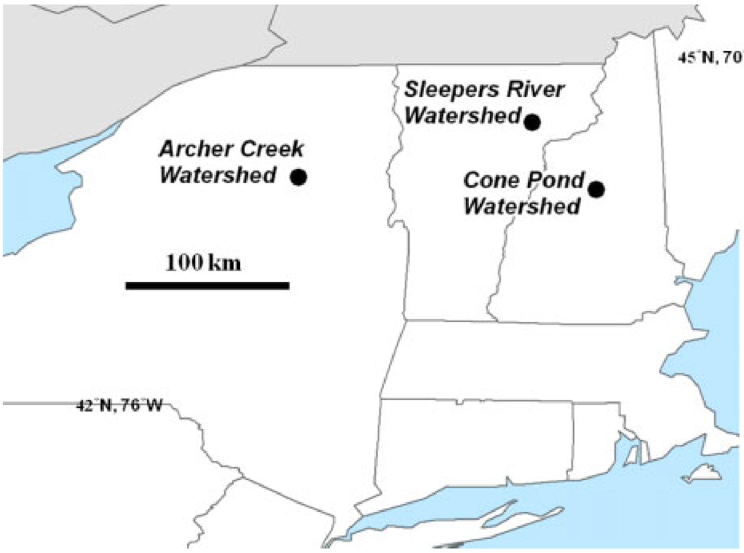

Figure 1. Location of study watersheds in the north-eastern USA

deposition: 5·7 kg S ha^{-1} yr^{-1}, 1985–1998, Mitchell *et al.*, 2001; Sleepers River, bulk deposition: 7·2 kg S ha^{-1} yr^{-1} 1992–1994, Hornbeck *et al.*, 1997; Cone Pond, bulk deposition: 7·7 kg S ha^{-1} yr^{-1} 1992–1994, Hornbeck *et al.*, 1997), but larger differences in discharge SO_4^{2-} drainage losses (Archer Creek: 15·9 kg S ha^{-1} yr^{-1}, 1985–1998, Mitchell *et al.*, 2001; Sleepers River: 17·1 kg S ha^{-1} yr^{-1} 1992–1994, Hornbeck *et al.*, 1997; Cone Pond: 13·4 kg S ha^{-1} yr^{-1} 1992–1994, Hornbeck *et al.*, 1997). These watersheds have substantial differences in geology and landscape features that may lead to marked differences in hydrological and biogeochemical responses especially during and after a period of unusual dryness. Information is provided on the major solutes of the surface waters of these three watersheds to demonstrate major differences in their biogeochemical relationships both over the long term as well as after an exceptionally dry period. The major objective of this study was to compare the overall differences in S biogeochemistry among three watersheds with particular emphasis on the responses of these watersheds to rewetting from a series of storms following this dry period.

STUDY WATERSHEDS

Archer Creek

The 135 ha Archer Creek Watershed is at the Huntington Wildlife Forest within the Adirondack Park, New York (43°59′N, 74°14′W) (Figure 2). Archer Creek is the main inlet to Arbutus Lake. Elevation ranges from 513–748 m. Vegetation consists of a 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 high-elevations. Individuals of *Abies balsamea* (balsam fir) are scattered throughout. Granitic gneiss dominates the bedrock at Huntington Forest with glacial till deposits dominating the surficial geology characterized mostly by well-drained soils with high sand (75%) and low clay (<10%) concentrations. Upland soils are coarse loamy, mixed, frigid, Typic Haplorthods of the Beckett–Mundal association, often less than 1 m thick. Wetlands consist of Greenwood mucky peats from 1 to 5 m thick and are generally located at the lower portions of the watershed (Figure 2). More details on this watershed are provided elsewhere (Mitchell *et al.*, 1996, 2001). Previous research at Archer Creek has evaluated the importance of both long-term changes (Mitchell *et al.*, 2001; Park *et al.*, 2003) and short-term events (McHale *et al.*, 2002; Inamdar *et al.*, 2004; Mitchell *et al.*, 2006) on hydrological and biogeochemical processes.

Sleepers River

Sleepers River Research Watershed (Figure 2) in north-eastern Vermont (44°29′N, 72°9′W) is a 11 125 ha basin that includes several gauged watersheds of various size and land cover (Shanley *et al.*, 2002, 2005). This study was conducted within the 41 ha forested W-9 catchment. Elevation ranges from 519 to 686 m. The forest vegetation is northern hardwoods dominated by *A. saccharum, Betula alleghaniensis* (yellow birch), *Fraxinus americana* (white ash) with a small component of *F. grandifolia*. Spruce and fir compose <5% of the total basal area. The Sleepers River watershed is underlain primarily by the Waits River Formation, a sulfidic calcareous granulite interbedded with micaceous phyllites and biotite schists (Hall, 1959; Bailey *et al.*, 2004). The bedrock is mantled with one to several meters of silty basal till derived mostly from the Waits River Formation. This calcareous lithology generates base rich, high-pH, bicarbonate sulfate waters. Wetlands constitute ~4% of the watershed area and are mostly found in the upper reaches of the catchment (Figure 2) (Hornbeck *et al.*, 1997). Wetlands have been a focal point of mercury research in this watershed (Schuster *et al.*, 2008), and

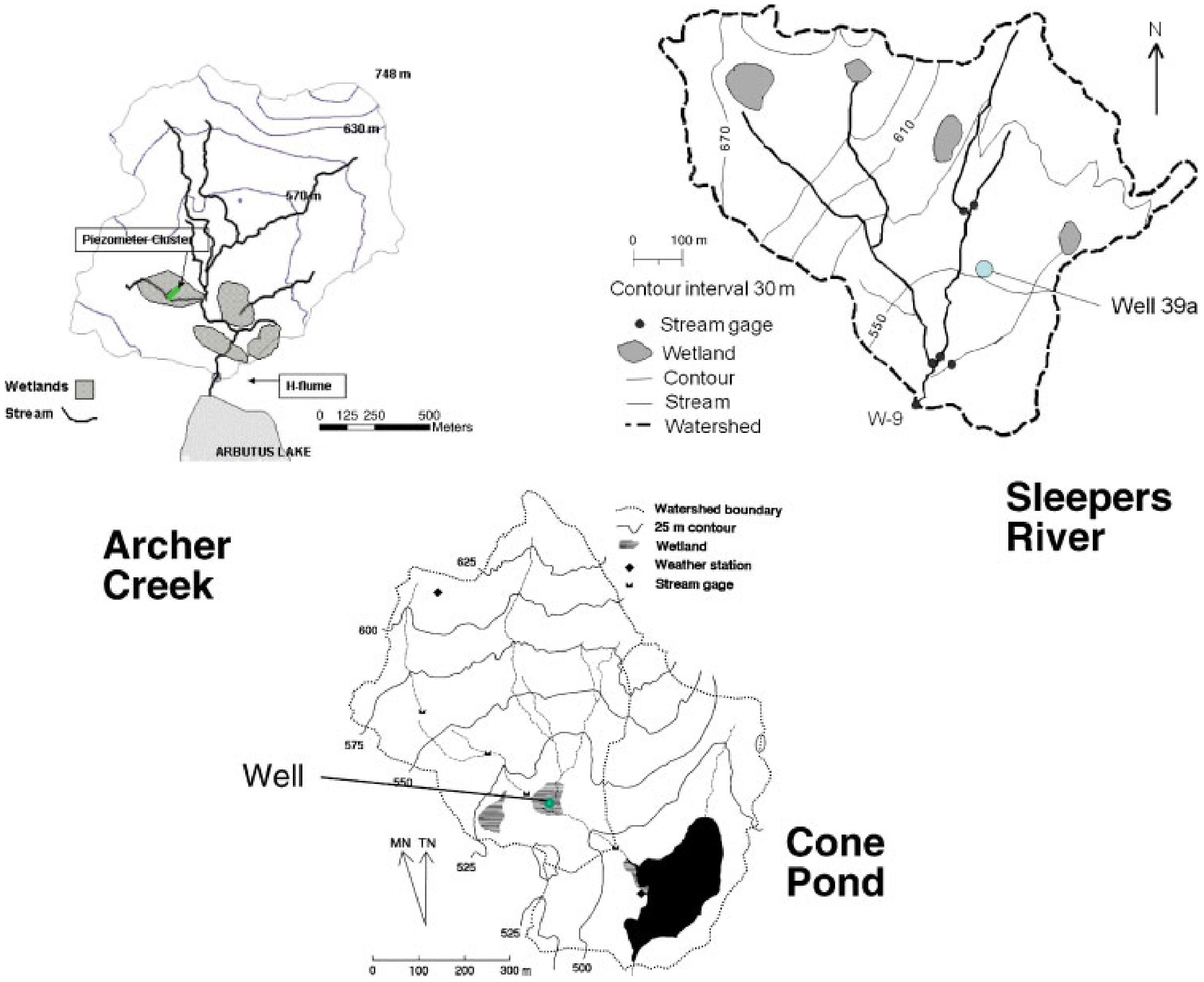

Figure 2. Watershed maps for Archer Creek, Sleepers River and Cone Pond

investigations are ongoing on the role of wetland S in the generation of methylmercury.

Cone Pond

The Cone Pond Watershed (45°54′N, 71°36′W) in New Hampshire has 33 ha of mixed age forest dominated (80%) by conifers (*Picea rubens, A. balsamea* and *Tsuga canadensis*) with 15% being hardwoods (*F. grandifolia, B. Alleghaniensis* and *A. saccharum*) and 5% being bedrock outcrop (Figure 2). Elevation ranges from 481–649 m. The watershed is the major inlet to Cone Pond and is underlain by sillimanite-grade metapelites of the Perry Mountain Formation of Silurian age. Surficial geology is loamy glacial till (<2·5 m thick) derived from local metapelitic and granitic rocks. Soils include Typic, Lithic and Aquic Haplorthods, with small areas of Typic and Terric Borohemists in the wetlands associated with the inlet. Wetlands compose ~5 to 10% of the inlet catchment area, with some of the wetlands being close to the stream and some having deep pockets (~2 m) of organic matter some of which is derived from peat (Figure 2). More details on the biogeochemistry have been previously provided including documentation of high Al and $SO_4{}^{2-}$ concentrations during a summer storm event (Bailey *et al.*, 1995). There has been no timber harvesting but 85% of the watershed was heavily burned in 1820. This fire history has been suggested to be a major factor in affecting the strong N retention for this watershed (Campbell *et al.*, 2004). The surface waters are characterized by relatively low base cation concentrations and low pH values that are coupled to high Al concentrations (Hornbeck *et al.*, 1997; Lawrence *et al.*, 1997).

METHODS

Hydrology and chemical monitoring

Archer Creek. Precipitation amounts were measured at the nearby (1·3 km away) National Atmospheric Deposition/National Trends Network (NADP/NTN) station. Stream discharge is monitored at 15 min intervals using an H-flume, located 10 m upstream from the lake. Stage height measurements (pressure transducer) were converted to discharge using formula from an empirical rating developed from flow measurements. A flow duration curve (Searcy, 1959) was calculated using discharge from 1 January 2001 to 31 December 2003. Groundwater dynamics were assessed from piezometers monitored electronically within the wetlands in the Archer Creek in Subcatchment 11 (Mitchell *et al.*, 2006). For the current study, the focus was mostly on measurements taken

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DOI: 10.1002/hyp

from 1 August to 31 October 2002. Stream water samples for chemical and isotopic analyses were collected weekly from 15 September to 31 October 2002 with additional samples collected for changes in stream stage of 1·2 cm over 15 min or 6·1 cm over 24 h. Chemical determinations included all major solutes. For more details on these measurements see Mitchell *et al.* (2006).

Sleepers River. Precipitation was sampled in a forest clearing adjacent to the W-9 weir and the chemical composition was determined. Solute and water inputs to the basin were adjusted for elevation using weighing bucket gauges at this site and a high-elevation site near the top of the watershed. Stream stage (potentiometer driven by float/counterweight) was recorded at 5 min intervals at a broad-crested weir. A flow duration curve was calculated using discharge from 1 January 2001 to 31 December 2003. Water table height was obtained from monitoring well 39A by manual readings. Stream samples for chemical and isotopic analyses were collected at least weekly by hand, and by automatic sampler during events throughout the observation period. Weekly samples were analysed for major solutes at U.S. Forest Service, Durham, NH. Event samples were analysed for major solutes at SUNY-ESF.

Cone Pond. Precipitation amounts were measured at the gauging station and at the top of the watershed. Stream discharge was monitored continuously at a V-notch weir with an FW-1 water level recorder at the mouth of the inlet to Cone Pond. A flow duration curve was calculated using discharge from 1 January, 2001 to 31 December 2003. Water table height was obtained by manual readings at monitoring Well G5 located in the major wetland of the watershed. Timing of stream samples and solutes measured was similar to Archer Creek. Major solutes were analysed at the US Forest Service, Durham, NH.

Isotopic analyses

For SO_4^{2-} isotope analyses, water samples were passed through anion exchange resin columns (Bio-Rad Polyprep, AG 1X-8 (Bio-Rad, Hercules, California)) to retain the SO_4^{2-} (Rock and Mayer, 2002; Bailey *et al.*, 2004). Sulfate was eluted from each column with 15 mL 3 molar HCl; 0·5 molar $BaCl_2$ 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 analyser. Sulfur isotope ratios were determined by continuous flow isotope ratio mass spectrometry (CF-IRMS) (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 (Thermo Electron Bremen, Barkhausenstrasse, Bremen, Germany)). 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). All isotope ratios are expressed in the conventional 'δ notation' in per mil (‰) with respect to the internationally accepted standards, Canon Diablo Troilite (V-CDT) for S isotope measurements and Vienna Standard Mean Ocean Water (V-SMOW) for oxygen isotope measurements. Analytical precision was ±0·5‰ for $\delta^{34}S$ and ±0·8‰ for $\delta^{18}O$ measurements on SO_4^{2-}.

RESULTS AND DISCUSSION

Precipitation and discharge response. All three watersheds had extremely dry conditions with very low precipitation (~one-third of long-term averages for this period) at Archer Creek, Sleepers River and Cone Pond (total 69, 48, 68 mm, respectively) resulting in either very low or no discharge during the late summer (1 August to 14 September) (Figure 3). At Archer Creek and Cone Pond the mean and maximum discharge amounts during this period were 0·015 and 0·119, 0·000 and 0·003 mm day^{-1}, respectively. Sleepers River was relatively wet during the preceding 7 week period (from mid-June to end of July) with 227 mm of precipitation compared to the Archer Creek (85 mm) and Cone Pond (95 mm) for the same period. The discharge from 1 August to 14 September at Sleepers River was thus greater (mean 0·15 mm day^{-1}, maximum 0·745 mm day^{-1}) due to its wetter antecedent condition, as it was still receding from the peak in discharge earlier in the summer (July). The relatively dry, late summer period was followed by a gradual rewetting of all three watersheds and increased discharge. From 15 September to 31 October 2002 there was a substantial increase in precipitation totals (212, 246 and 219 mm, for Archer Creek, Sleepers River and Cone Pond, respectively). The mean and maximum daily discharge values for this same period were 0·50 and 3·77, 0·78 and 2·57, 0·88 and 5·86 mm day^{-1} for Archer Creek, Sleepers River and Cone Pond, respectively (Table I). Even though the discharge showed a substantial increase, the percentage water yields [100× (mean discharge/precipitation)] from 15 September to 31 October were very low 11, 22 and 18% for Archer Creek, Sleepers River and Cone Pond, respectively, reflecting the very dry antecedent conditions.

Flow duration and groundwater response. Flow duration curves (Searcy, 1959) based on three years of flow were used for comparing the overall hydrological responses of the three watersheds (Figure 4). Archer Creek and Sleepers River had similar distributions except for the lowest 5% of flows, where Sleepers maintained base flow while Archer ceased to flow ~3% of the time. Archer Creek was somewhat flashier than Sleepers, showing higher discharges (up to 4 mm h^{-1} compared to 2 mm h^{-1} at Sleepers) at the upper ~0·2% of the flow range. Cone Pond was the flashiest (e.g. greater range of discharge) watershed of the three, with a high flow regime

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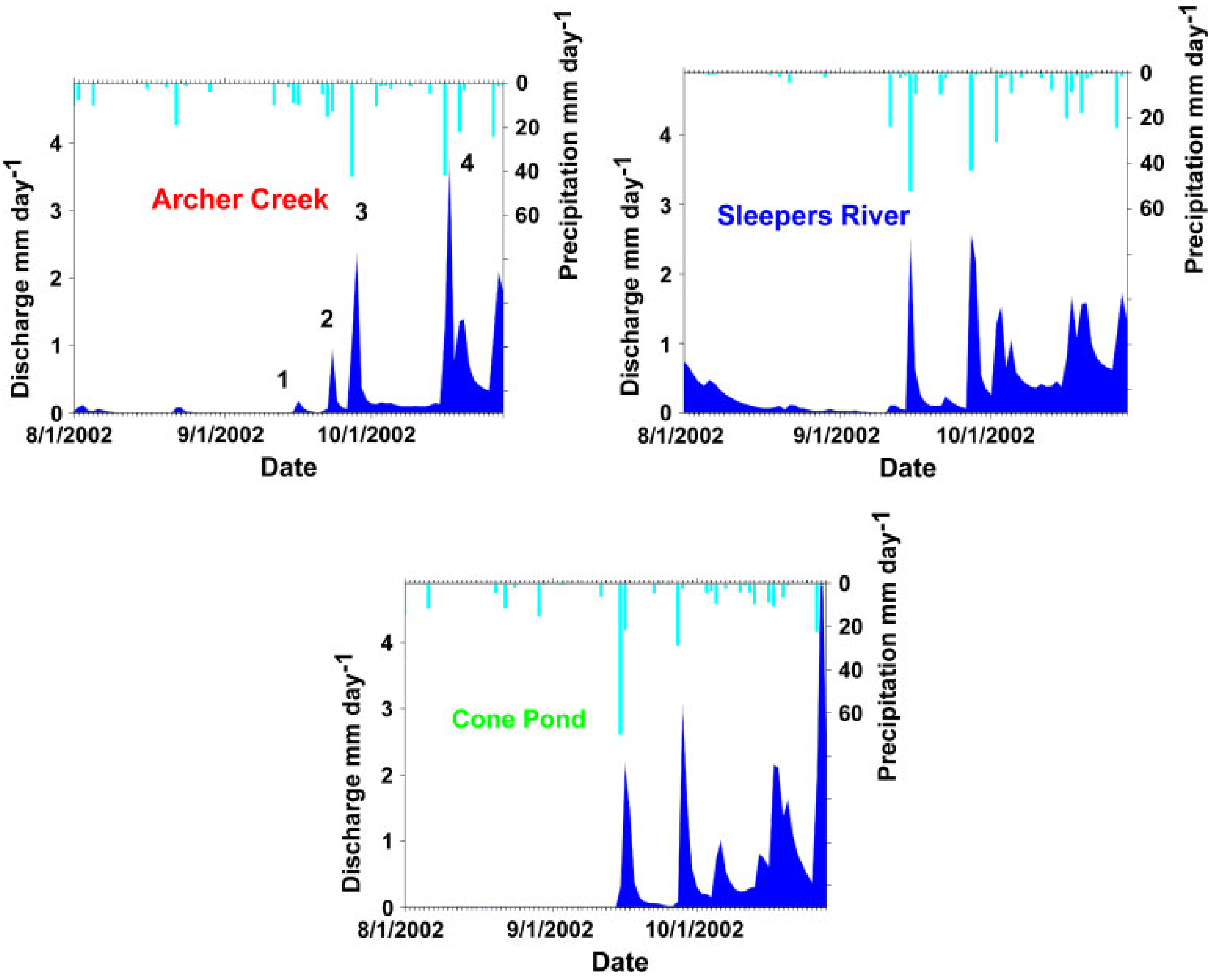

Figure 3. Precipitation and discharge for Archer Creek, Sleepers River and Cone Pond from 1 August to 31 October 2002

(peaking at 8 mm h^{-1}) elevated relative to the other sites for nearly 1% of the time, which equates to a considerably greater percentage of water leaving that basin at high flow. All three curves are nearly coincident in the 90–99% range, indicating that the moderately high flow regime is similar at all sites. The Cone curve then falls below the other two, compensating for the greater high-flow discharge at Cone and suggesting relatively rapid drainage and less groundwater storage in that basin. Cone flow ceased ~10% of the time.

Some limited results on groundwater fluctuations in each of the watersheds were available. Groundwater levels were lowest suggesting minimal watershed wetness through mid-September at Archer Creek and Cone Pond and late September for Sleepers River (Figure 5). The period of lowest groundwater coincided directly with the lowest discharge rates in each of the watersheds. Groundwater levels rose in response to precipitation in September and October. The well in Cone Pond showed a more rapid response in water table height than the piezometers in Archer Creek. Sleepers River had only monthly measurements at an upland well, but groundwater levels declined markedly through the summer and recovery lagged the onset of these late summer and fall storms.

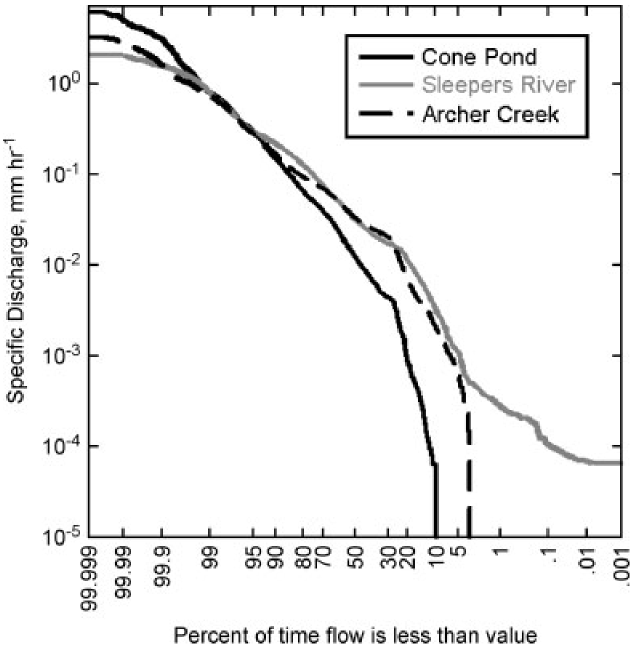

Figure 4. Flow duration curves for Archer Creek, Sleepers River and Cone Pond from 1 January 2001 to 31 December 2003

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Table I. Water Yield for Archer Creek, Sleepers River and Cone Pond (1 August to 31 October 2002)

Watershed	Period	Precipitation (mm) for period	Mean discharge (mm day^{-1}) [maximum]	Percentage water yield for period [100× (precip./disch).]
Archer Creek	1 August—14 September	69	0·015 [0·119]	1
	14 September—31 October	212	0·504 [3·772]	11
Sleepers River	1 August—14 September	48	0·15 [0·745]	20
	15 September—31 October	246	0·780 [2·570]	22
Cone Pond	1 August—14 September	68	0·000 [0·003]	0·02
	15 September—31 October	198	0·878 [5·864]	19

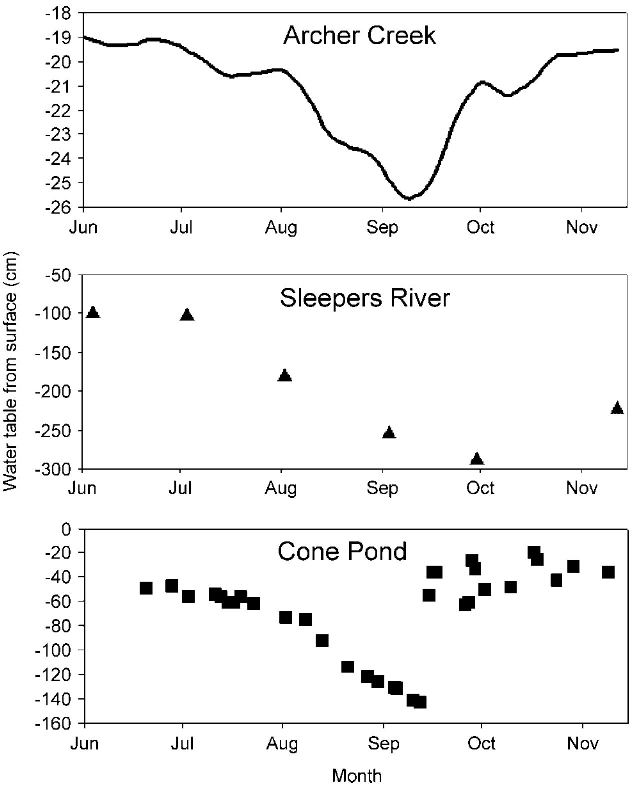

Figure 5. Groundwater response for individual locations at Archer Creek (Peizometer P29bs), Sleepers River (Well 39A) and Cone Pond (Well) from 1 August to 15 November 2002

Relationship to previous hydrological and biogeochemical studies at Archer Creek and Sleepers River. For Archer Creek, a detailed analysis of hydrological and chemical response was done at the same time as the current study in two small upland catchments (S14 and S15) with a focus on factors affecting the spatial and temporal patterns of NO_3^- concentration (Christopher *et al.*, 2008). Despite a similar hydrologic response, S14 and S15 exhibited markedly different surface water responses of NO_3^-. This difference was attributed to differences in the amount of NO_3^- generated by mineralization and nitrification. Other studies at Archer Creek have also shown that wetlands can affect stream water chemistry, but variation in wetland hydrological conditions, especially differences in hydrological conductivity and the proximity to surface waters, influence the relative contribution of individual wetlands (McHale *et al.*, 2004).

Sleepers River contains small wetlands and wetland-like areas (e.g., riparian zones with organic muck surface horizons) that exhibit anoxia (Schuster *et al.*, 2008). These areas are readily flushed during storms either by direct precipitation or by subsurface hillslope water draining through highly transmissive surface soils (Kendall *et al.*, 1999).

Chemical and isotopic responses

The precipitation chemistry among these three sites is quite similar. Using the results from nearby NADP (National Atmospheric Deposition Program) stations (Archer Creek: Huntington Wildlife Forest, NY20; Sleepers River: Underhill, VT99; Cone Pond: Hubbard Brook, NH02) for 2002 volume weighted SO_4^{2-} and C_b (sum of base cations) concentrations among these three sites ranged from 23·9 to 26·1 and 6·0 to 6·8 μeq L^{-1}, respectively. Previous studies have also established that the $\delta^{34}S$ and $\delta^{18}O$ values for SO_4^{2-} in precipitation either at the watersheds themselves (Archer Creek; 5·2 and 12‰, respectively, Campbell *et al.*, 2006) (Sleepers River; $\delta^{34}S$ and $\delta^{18}O$, 5·6 and 12 ‰, respectively; Shanley *et al.*, 2005) or a nearby site (~8 km) (Hubbard Brook; $\delta^{34}S$ 4·4 ‰; Alewell *et al.*, 1999) are remarkably similar.

The three watersheds have distinct differences in stream solute chemistry with Sleepers River having the most base rich surface waters that are reflected in high pH values and high concentrations of C_b (Table II). The Cone Pond Watershed is the most acidic with low C_b concentrations, low pH values and relatively high concentrations of total dissolved Al. The surface water conditions at Archer Creek showed an intermediate base status. The chemistry representative for the sampling period from 15 September to 31 October 2002 showed differences from the long-term averages and there was considerable variation among the three watersheds (Table III). For all three watersheds SO_4^{2-} concentrations were higher for the study period compared with the long-term means. For C_b the mean values during the study period were higher for Archer Creek and Cone Pond, but lower for Sleepers although maximum values were much higher than the long-term mean.

The differences among the three watersheds in chemical characteristics are clearly exhibited by the relationships between SO_4^{2-} and C_b concentrations during the study period (Figure 6). Sleepers River and Archer Creek showed strong positive, significant relationships between C_b and SO_4^{2-} concentrations ($r^2 =$

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Table II. Average solute concentrations in stream water weighted by discharge for Archer Creek, Sleepers River and Cone Pond watersheds. All concentrations in μeq L^{-1} except for total N, Al, DON and DOC which are in μmol L^{-1} and solute pH is in standard form. Standard errors in (); SE = square root (weighted sample variance/sum of weights); SAS (1994). The number of samples used in the analysis varied with solute and site (Archer Creek, 516–708; Sleepers, 645–928; Cone Pond, 404–806)

pH	NH_4^+	C_b	Al	Cl^-	NO_3^-	SO_4^{2-}	Total N	DON	DOC
Archer Creek Watershed (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
Sleepers River Watershed (1991–2002)									
7·5 (0·0)	1·4 (0·1)	979 (9·9)	1·8 (0·1)	8·8 (0·1)	20·1 (0·3)	133·6 (0·9)	25·6 (0·7)	9·3 (0·5)	238·4 (5·6)
Cone Pond Watershed (1989–2002)									
4·4 (0·0)	1·5 (0·1)	68·7 (0·5)	26·9 (0·1)	20·1 (0·3)	0·4 (0·1)	124·3 (0·5)	11·3 (0·2)	9·7 (0·2)	440 (4·4)

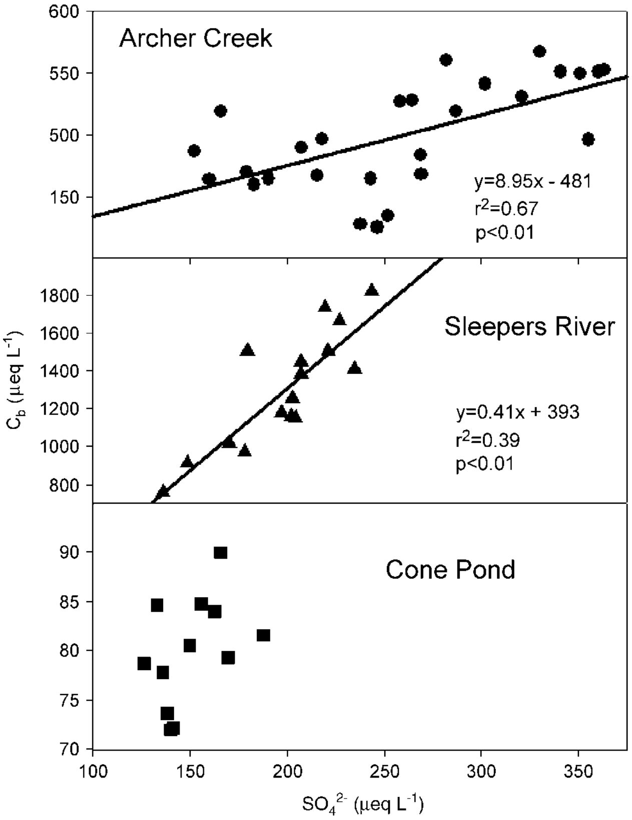

Figure 6. Relationships between SO_4^{2-} and C_b concentrations at Archer Creek, Sleepers River and Cone Pond from 1 August to 31 October 2002

0·67; $P = 0·0002$ and $r^2 = 0·39$; $P = 0·005$, respectively). In contrast, Cone Pond with its low base status showed no significant relationship ($r^2 = 0·20$; $P = 0·15$) between C_b and SO_4^{2-} concentrations. Other studies at Cone Pond watershed have shown a strong relationship between total Al and SO_4^{2-} concentrations indicating that release of the mobile SO_4^{2-} anion contributes to the mobility of Al at this site in which both soils (Lawrence *et al.*, 1997) and surface waters are highly acidic (Hornbeck *et al.*, 1997). The response of SO_4^{2-} to storms varied among the three watersheds. Archer Creek showed marked increases in SO_4^{2-} concentration versus flow, with highest concentrations occurring during the storm of 23/24 September (Figure 7). In subsequent storms (28–30 September and 16–21 October), highest concentrations were also found at peak discharge, but the maximum concentrations decreased with each successive storm suggesting that the additional source of the SO_4^{2-} was being depleted. At Cone Pond SO_4^{2-} concentrations were substantially lower than for the other two catchments and varied less in response to storms, but as at Archer Creek there was also a general decline in SO_4^{2-} concentrations with consecutive storms (16–18 September, 28–30 September, 18–22 October). Sulfate concentrations at Sleepers River were often higher than in the other two watersheds and SO_4^{2-} concentrations were at minima during peak discharge during storms (15/16 September, 28/29 September) (Figure 8). At Cone Pond, maximum SO_4^{2-} concentrations within a storm generally occurred just before peak discharge (Figure 9). These results suggest that internal SO_4^{2-} sources were especially large at Archer Creek during these storms as evidenced by the very high SO_4^{2-} concentrations (Table III). However, Sleepers River also tended to have higher SO_4^{2-} concentrations than Cone Pond, but other evidence (Shanley *et al.*, 2005) suggests that this SO_4^{2-} was derived from sulfide minerals (Table III). These patterns differ from the long-term chemical averages for these watersheds in which Sleepers River has the highest mean SO_4^{2-} (Table II).

The SO_4^{2-} isotopic responses also varied among the three catchments. Archer Creek with its large range of SO_4^{2-} concentrations in stream discharge (152 to 389 μeq L^{-1}, discharge weighted mean = 273 μeq L^{-1}) also exhibited the greatest range in $\delta^{34}S$ values (−1·4 to 8·8 ‰). Sleepers River's SO_4^{2-} concentrations ranged from 136 to 243 μeq L^{-1} (discharge weighted mean = 167 μeq L^{-1}) and had a discharge weighted mean $\delta^{34}S$ value of 5·9 ‰(range from 4·0 to 9·0 ‰) which was higher than the mean of either Archer Creek (1·6 ‰) or Cone Pond (3·3 ‰). Cone Pond's stream water showed the smallest range in $\delta^{34}S$ values (2·4 to 4·3 ‰) and SO_4^{2-} concentrations (126–187 μeq L^{-1}, discharge weighted mean = 154 μeq L^{-1}). The range and mean of $\delta^{18}O$-SO_4^{2-} values for Archer Creek and Cone Pond were similar (3·0 to 8·9 ‰, mean = 4·5‰; 3·9 to 6·3 ‰, mean = 4·9‰; respectively) while $\delta^{18}O$-SO_4^{2-} values for Sleepers River covered a larger range with the mean value being substantially lower (1·2 to 10·0 ‰, mean = 2·5‰). For all three watersheds, but

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Table III. Average solute concentrations weighted by daily discharge values with overall ranges in parentheses for Archer Creek, Sleepers River and Cone Pond watersheds for the period from 15 September to 31 October 2002. All concentrations in μeq L^{-1} except for total N, Al, DON and DOC which are in μmol L^{-1}; pH is in standard units

pH	NH_4^+	C_b	Al	Cl^-	NO_3^-	SO_4^{2-}	Total N	DON	DOC
Archer Creek Watershed ($n = 35$)									
5·3 (4·8–6·2)	4·2 (0·8–27)	479 (421–567)	10·5 (1·1–14·1)	26 (15–48)	16 (1–28)	274 (152–389)	47 (4–78)	43 (0–35)	1263 (322–1930)
Sleepers River Watershed ($n = 16$)									
7·6 (7·6–7·8)	0·1 (0·0–0·6)	951 (762–1818)	0·5 (0–1)	10 (7–15)	29 (4–36)	168 (135–243)	15 (10–20)	7 (6–10)	811 (120–1036)
Cone Pond Watershed ($n = 12$)									
4·3 (4·3–4·4)	0·1 (0–0·5)	80 (72–90)	33·7 (27·7–38·3)	28 (26–31)	0·8 (0–2·9)	153 (126–187)	18 (9–28)	17 (7–28)	652 (376–1053)

particularly for Sleepers River the $\delta^{18}O-SO_4^{2-}$ values in stream waters were lower than $\delta^{18}O-SO_4^{2-}$ values in precipitation, indicating that either inorganic sulfide oxidation and/or mineralization of organic S had occurred within the watershed (Bailey *et al.*, 2004; Shanley *et al.*, 2005). Such isotopic shifts would not be attributed to sulfate desorption, a process that does not show any marked isotopic discrimination (Mitchell *et al.*, 1998). Previous analyses of $\delta^{18}O-SO_4^{2-}$ values for surface waters throughout the north-east USA (Bailey *et al.*, 2004) and central Europe (Novak *et al.*, 2007) have also been used to evaluate the importance of internal S sources to SO_4^{2-} generation in watersheds.

For Archer Creek (slope = −0·030‰ $\delta^{34}S$/μeq SO_4^{2-} L^{-1}, $r^2 = 0{\cdot}54$, $P < 0{\cdot}0001$) and Cone Pond (slope = −0·026‰ $\delta^{34}S$/μeq L^{-1}, $r^2 = 0{\cdot}56$, $P = 0{\cdot}005$) there was a strong inverse relationship between SO_4^{2-} concentration and $\delta^{34}S$ values (Figure 10). In contrast at Sleepers River there was a weaker, but significant positive relationship between SO_4^{2-} concentration and $\delta^{34}S$ values in stream water (slope = 0·033‰ $\delta^{34}S$/μeq SO_4^{2-} L^{-1}, $r^2 = 0{\cdot}27$, $P = 0{\cdot}05$). There were no significant relationships between the $\delta^{18}O-SO_4^{2-}$ values and SO_4^{2-} concentrations in stream water at any of the three watersheds.

Causes of differences in chemical and isotopic sulfate responses among watersheds

Combinations of hydrological, chemical and isotopic information have been successfully used previously to look at sulfur sources within individual watersheds (Hubbard Brook, Alewell *et al.*, 1999; Sleepers River, Shanley *et al.*, 2005; Archer Creek, Mitchell *et al.*, 2006; Plastic Lake, Eimers *et al.*, 2004a). Such studies on specific watersheds have been most successful for determining sulfur sources if there are distinct differences in the isotopic ratios of these sources (minerals at Sleepers River, Shanley *et al.*, 2005) or when biogeochemical processes, especially bacterial dissimilatory sulfate reduction, have played a major role (Archer Creek, Mitchell *et al.*, 2006; Plastic Lake, Eimers *et al.*, 2004a). Bacterial dissimilatory sulfate reduction has been shown to often result in major changes in the isotopic values between reactants and products (e.g. sulfides with substantially lower $\delta^{34}S$ values than sulfate) (Mitchell *et al.*, 1998).

Weathering Contributions. In this current study that focused on comparisons among three watersheds, the difference in Sleepers River response was clearly due to the greater importance of weathering reactions in contributing SO_4^{2-} to stream water versus Archer Creek or Cone Pond. It has been estimated, using a modelling approach, that weathering reactions may contribute ∼11 kg S ha^{-1} yr^{-1} to SO_4^{2-} export at Sleepers River (P. Selvendiran, personal communication). Moreover, some of the S minerals in the bedrock of Sleepers River have $\delta^{34}S$ values up to 13 ‰ resulting in a trend of increasing $\delta^{34}S$ values in stream water sulfate

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DOI: 10.1002/hyp

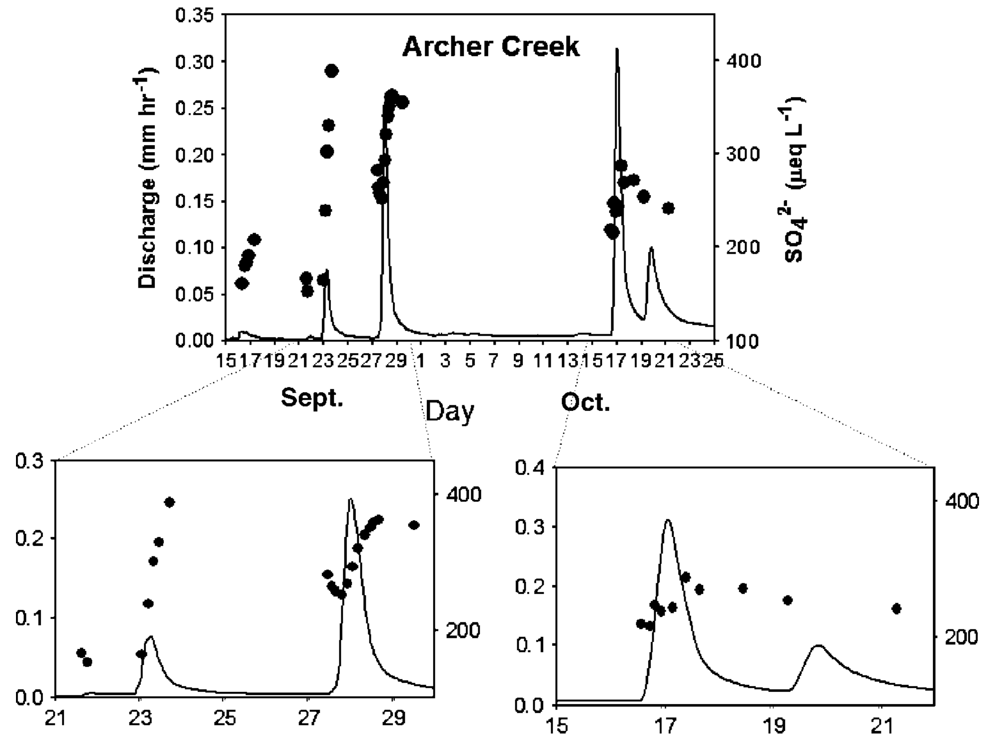

Figure 7. Temporal patterns of stream discharge and SO_4^{2-} concentrations for Archer Creek

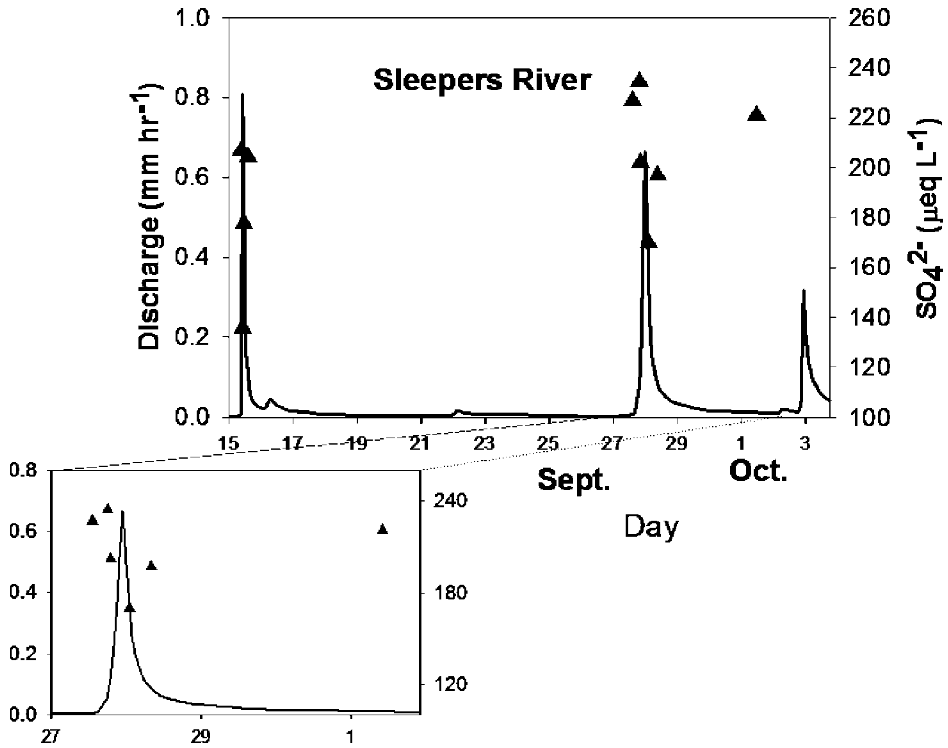

Figure 8. Temporal patterns of stream discharge and SO_4^{2-} concentrations for Sleepers River

with increasing concentrations. The strong relationship between C_b and SO_4^{2-} concentrations at Sleepers especially during base flow periods, demonstrates the dominance of deeper flowpaths within the bedrock containing calcite and sulfide minerals. In contrast, the soil at Sleepers has little sulfide or calcite except in deeper horizons in a few poorly drained pockets; chemical and isotopic patterns in stream water typical for calcite and sulfide mineral weathering must therefore imply inputs from deeper till or bedrock flow paths. For Archer Creek it has been established that there is a strong internal source of S within the watershed that may be contributing up to 10 kg S ha^{-1} yr^{-1} to stream SO_4^{2-} discharge, but how much of this source is due to weathering versus net organic S

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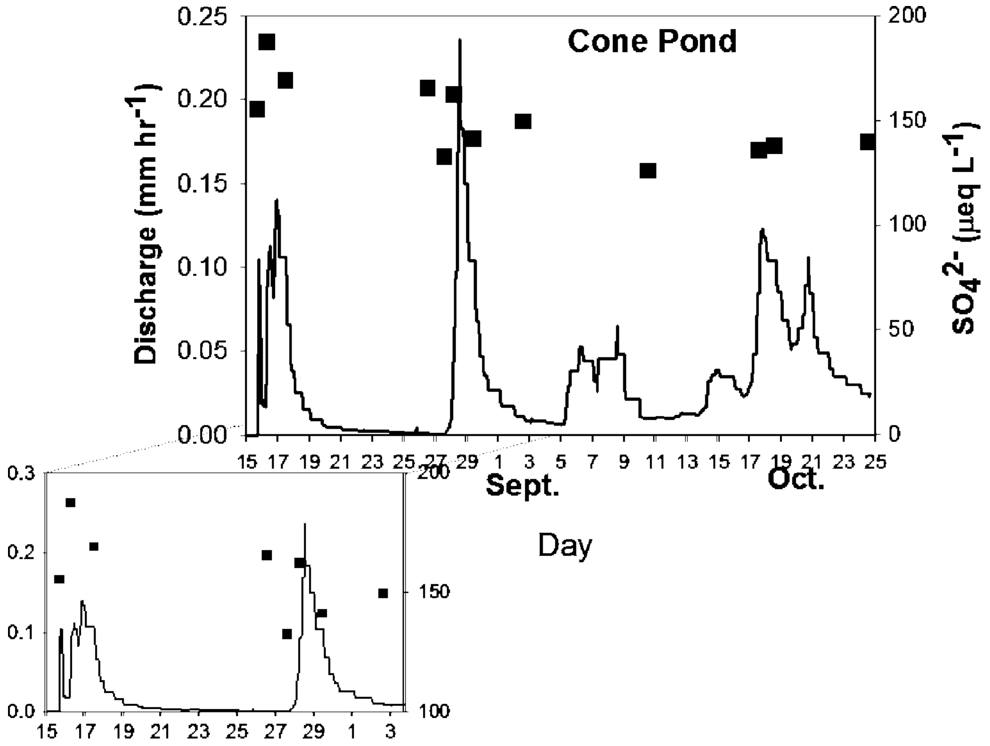

Figure 9. Temporal patterns of stream discharge and SO$_4^{2-}$ concentrations for Cone Pond

mineralization is not known (Park *et al.*, 2003; Campbell *et al.*, 2006). This long-term internal S contribution was augmented by an additional S source associated with watershed rewetting as described below. Although the weathering rate of S minerals at Cone Pond is also not known, it can be compared with estimates at the nearby Hubbard Brook watersheds where weathering has been estimated at 2 kg S ha^{-1} yr^{-1} (Likens *et al.*, 2002). However, Cone Pond has thinner soils and a greater extent of bedrock (e.g. Perry Mt. Formation schist and Kinsman Grandiorite versus Rangeley Formation at HBEF) with very low S concentrations (Bailey *et al.*, 2004) that would probably result in weathering rates being even lower ($<$2 kg S ha^{-1} yr^{-1}) than those suggested for Hubbard Brook (Likens *et al.*, 2002). The smaller contributions of internal S sources at Cone Pond versus either Sleepers River or Archer Creek would suggest a relatively greater importance of atmospheric sulfur deposition at Cone Pond. There were distinct differences in the relationships between discharge and the SO$_4^{2-}$ concentrations among the three watersheds during the study period. For Sleepers River there was a decrease in SO$_4^{2-}$ concentrations during storm events (15/16 September, 28/29 September) (Figure 8) reflecting a dilution of base flow enriched in SO$_4^{2-}$ from the weathering of sulfide minerals contained within the calcareous granulite interbedded with sulfidic micaceous phyllites and biotite schists (Bailey *et al.*, 2004). In contrast Archer Creek and Cone Pond both showed peaks in SO$_4^{2-}$ concentrations during storm events (Figures 7 and 9). At Sleepers River there was also a positive relationship between δ^{34}S-SO$_4^{2-}$ values and SO$_4^{2-}$ concentrations (Figure 10) indicating that during storms SO$_4^{2-}$ with lower δ^{34}S-SO$_4^{2-}$ values mixed with baseflow SO$_4^{2-}$ was highly positive δ^{34}S-SO$_4^{2-}$ values (up to 13 ‰) derived from S mineral weathering products (Shanley *et al.*, 2005).

Contributions from previously reduced sulfide. For Archer Creek and Cone Pond there were strong negative relationships between δ^{34}S-SO$_4^{2-}$ values and SO$_4^{2-}$ concentrations (Figure 10). The δ^{34}S values associated with high SO$_4^{2-}$ concentrations at Archer Creek and Cone Pond were substantially different and lower than those of soil organic matter or SO$_4^{2-}$ in precipitation. These and other solute chemistry relationships strongly support the notion that the elevated SO$_4^{2-}$ concentrations were derived from previously reduced sulfide, which was oxidized to SO$_4^{2-}$ during antecedent dry conditions (Shanley *et al.*, 2008). Detailed analyses of the importance of this SO$_4^{2-}$ source at times preceded by an unusually dry period at Archer Creek, including other ancillary hydrologic and chemical data, were provided by Mitchell *et al.* (2006) who suggested that these high SO$_4^{2-}$ concentrations were caused by the oxidation of previously formed sulfides (with low δ^{34}S values) in wetlands. Studies in Canadian watersheds have also suggested the importance of oxidation of sulfides in wetlands during droughts in contributing to elevated SO$_4^{2-}$ fluxes after watersheds become rewetted (Eimers and Dillon, 2002; Eimers *et al.*, 2004a 2006; Laudon *et al.*, 2004). It is notable despite the similarities in the overall relationship between δ^{34}S-SO$_4^{2-}$ values and SO$_4^{2-}$ concentrations between Archer Creek and Cone Pond, that the ranges of both attributes were much smaller at Cone Pond. Other studies at Cone Pond have suggested the importance of fire history at

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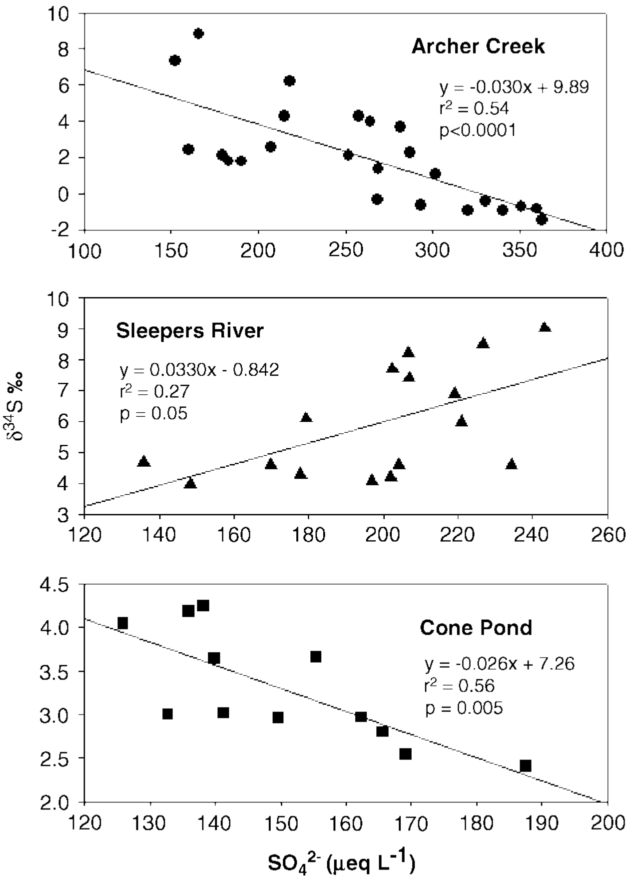

Figure 10. Relationship between stream water $SO_4{}^{2-}$ concentrations and $\delta^{34}S$ values for Archer Creek, Sleepers River and Cone Pond

this watershed to the dynamics of other elements including N and organic matter content (Campbell *et al*., 2004). Whether this fire history has also influenced the watershed response of S is not known, but it is possible if the fire removed substantial pools of organic matter and concomitantly decreased the amount of total organic S stored in the soil. For most forested ecosystems most of the S is stored as organic S in soil pools (Mitchell *et al*., 1992; Johnson and Mitchell, 1998). For the current study, the trend towards lower $\delta^{34}S$-$SO_4{}^{2-}$ values with $SO_4{}^{2-}$ increasing concentrations suggests some contribution of wetland derived S sources and that organic S mineralization is not the dominant source for the $SO_4{}^{2-}$ associated with storms at this site. The differences in chemical and isotopic responses for these three watersheds suggest that there is a complex set of interactions associated with watershed features (e.g. mineralogy, wetlands, land use history) that influence the biogeochemical responses both during and after drought events.

Future directions

These results and those of other studies (Eimers and Dillon, 2002; Eimers *et al*., 2004a, b) have clearly demonstrated that concomitant analyses of hydrological, chemical and isotopic parameters provide important information on $SO_4{}^{2-}$ sources both within and among watersheds. Studies that have combined these three approaches have often been conducted over relatively short periods. Evaluating long-term climatic changes on S dynamics will require detailed analysis over extended periods. For the north-east USA (NECIA, 2006) including the Adirondack Mountains of NY State (Stager and Martin, 2002), climatic changes are becoming increasingly evident. In the north-east USA by the end of this century, winters could warm by 4 to 7 °C and summers by 3 to 8 °C (NECIA, 2006.). The frequency and intensity of late summer and early fall droughts are expected to increase as well. Thus, it is expected that this marked change in the climate of the north-east USA will dramatically affect the hydrology and biogeochemistry of forest ecosystems. Furthermore, such changes in hydrology are expected to intensify throughout the world owing to climate change (Trenberth *et al*., 2007). Climatic conditions can alter hydrological pathways that control drainage water solute concentrations and fluxes (Schiff *et al*., 2002; Christopher *et al*., 2008). Any climatic change that alters the hydrological regime of a watershed both with respect to events as well as long-term changes may have a marked influence on $SO_4{}^{2-}$ dynamics of soils, groundwaters and surface waters. Understanding spatial patterns of $SO_4{}^{2-}$ response will require further analyses of how the response of these climate factors is influenced by watershed attributes.

ACKNOWLEDGEMENTS

This research was sponsored in part by the National Science Foundation (Ecosystem Studies), the Northeastern States Research Cooperative (NSRC), administered by the USDA Forest Service, and NYSERDA. Special thanks are also given to Sheila Christopher and Pat McHale for field and laboratory work at Archer Creek, to Ralph Perron for field work at Cone Pond, to Ann Chalmers, Jon Denner and Stew Clark for field work and Steve Sebestyen for laboratory work at Sleepers River, and Jane Hislop for laboratory work at Cone Pond and Sleepers River. Support from the Natural Sciences and Engineering Research Council of Canada (NSERC) to Bernhard Mayer is also gratefully acknowledged.

REFERENCES

Alewell C, Mitchell M, Likens G, Krouse R. 1999. Sources of stream sulfate at the Hubbard Brook Experimental Forest: long-term analysis using stable isotopes. *Biogeochemistry* **44**: 281–299. DOI: 10·1023/A:1006058913822.

Bailey SW, Driscoll CT, Hornbeck JW. 1995. Acid-base chemistry and aluminum transport in an acidic watershed and pond in New Hampshire. *Biogeochemistry* **28**: 69–91.

Bailey SW, Mayer B, Mitchell MJ. 2004. Evidence for the influence of mineral weathering on stream water sulphate in Vermont and New Hampshire. *Hydrological Processes* **18**: 1639–1653. DOI: 10·1002/hyp.1410.

Campbell JL, Hornbeck JW, Mitchell MJ, Adams MB, Castro MS, Driscoll CT, Kahl JS, Kochenderfer JN, Likens GE, Lynch JA, Murdoch PS, Nelson SJ, Shanley JB. 2004. Input-output budgets of inorganic nitrogen for 24 forest watersheds in the Northeastern United States: A review. *Water, Air and Soil Pollution* **151**: 373–396. DOI: 10·1023/B : WATE.0000009908·94219·04.

Campbell JL, Mitchell MJ, Mayer B. 2006. Isotopic assessment of NO_3^- and SO_4^{2-} mobility during winter in two adjacent watersheds in the Adirondack Mountains, New York. *Journal of Geophysical Research* **111**: 15 pp. DOI:10·1029/2006JG000208.

Christopher SF, Mitchell MJ, McHale MR, Boyer EW, Burns DA, Kendall C. 2008. Factors controlling nitrogen release from two forested catchments with contrasting hydrochemical responses. *Hydrological Processes* **22**(1): 46–62. DOI: 10.1002/hyp.6632.

Eimers MC, Dillon PJ. 2002. Climate effects on sulphate flux from forested catchments in south-central Ontario. *Biogeochemistry* **61**: 337–355. DOI: 10·1023/A:1020261913618.

Eimers MC, Dillon PJ, Schiff SL. 2004a. A S-isotope approach to determine the relative contribution of redox processes to net SO_4 export from upland, and wetland-dominated catchments. *Geochimica et Cosmochimica Acta* **68**: 3665–3674.

Eimers MC, Dillon PJ, Watmough SA. 2004b. Long-term (18-year) changes in sulphate concentrations in two Ontario headwater lakes and their inflows in response to decreasing deposition and climate variations. *Hydrological Processes* **18**: 2617–2630. DOI: 10·1002/hyp.5570.

Eimers MC, Watmough SA, Buttle JM, Dillon PJ. 2006. Drought-induced sulphate release from a wetland in south-central Ontario. *Environmental Monitoring and Assessment* **127**: 399–407.

Gehre M, Strauch G. 2003. High-temperature elemental analysis and pyrolysis techniques for stable isotope analysis. *Rapid Communication in Mass Spectrometry* **17**: 1497–1503. DOI: 10·1002/rem.1076.

Giesemann A, Jäger HJ, Norman A-L, Krouse HR, Brand WA. 1994. On-line sulfur-isotope determination using an elemental analyzer coupled to a mass spectrometer. *Analytical Chemistry* **66**: 2816–2819. DOI: 10·1021/ac00090a005.

Hall LM. 1959. The geology of the St. Johnsbury Quadrangle, Vermont and New Hampshire, Bulletin No. 13, Vermont Development Commission, Montpelier.

Hornbeck JW, Bailey SW, Buso DC, Shanley JB. 1997. Streamwater chemistry and nutrient budgets for forested watersheds in New England: variability and management implications. *Forest Ecology and Management* **93**: 73–89. DOI: 10·1016/s0378-1127(96)03937-0.

Huntington TG, Hodgkins GA, Keim BD, Dudley RW. 2004. Changes in the proportion of precipitation occurring as snow in New England (1949 to 2000). *Journal of Climate* **17**: 2626–2636.

Inamdar S, Christopher SF, Mitchell MJ. 2004. Export mechanisms for dissolved organic carbon and nitrate during summer storm events in a glaciated forested catchment in New York, USA. *Hydrological Processes* **18**: 2651–2661. DOI: 10·1002/hyp.5572.

Johnson DW, Mitchell MJ. 1998. Responses of forest ecosystems to changing sulfur inputs. In *Sulfur in the Environment*, Maynard D (ed). Marcel Dekker, Inc.: New York; 219–262.

Kendall KA, Shanley JB, McDonnell JJ. 1999. A hydrometric and geochemical approach to testing the transmissivity feedback hypothesis during snowmelt. *Journal of Hydrology* **219**: 188–205.

Laudon H, Dillon PJ, Eimers MC, Semkin RG, Jeffries DS. 2004. Climate-induced episodic acidification of streams in central Ontario. *Environ Science Technology* **38**: 6009–6015.

Lawrence GB, David MB, Bailey SW, Shortle WC. 1997. Assessment of soil calcium status in red spruce forests of the northeastern U.S. *Biogeochemistry* **38**: 19–39.

Likens GE, Driscoll CT, Buso DC, Mitchell MJ, Lovett GM, Bailey SW, Siccama TG, Reiners WA, Alewell C. 2002. The biogeochemistry of sulfur at Hubbard Brook. *Biogeochemistry* **60**: 235–316. DOI: 10·1023/A:1020972100496.

McHale MR, McDonnell JJ, Mitchell MJ, Cirmo CP. 2002. A field based study of soil- and groundwater nitrate release in an Adirondack forested watershed. *Water Resources Research* **38**(4): 16 pp. 1029/2000WR000102.

McHale MR, Cirmo CP, Mitchell MJ, McDonnell JJ. 2004. Wetland nitrogen dynamics in an Adirondack forested watershed. *Hydrological Processes* **18**: 1853–1870.

Mitchell MJ, David MB, Harrison RB. 1992. Chapter 9 Sulfur dynamics of forest ecosystems. In *Sulfur Cycling on the Continents*, Howarth RW, Stewart JWB, Ivanov MV (eds). SCOPE Vol. 48. John Wiley and Sons: New York; 215–254.

Mitchell MJ, Driscoll CT, Raynal DJ. 1996. Temporal changes and solute mass balances in an Adirondack forested watershed. *Water, Air and Soil Pollution* **88**: 355–369. DOI: 10·1007/BF00294111.

Mitchell MJ, Krouse HR, Mayer B, Stam AC, Zhang Y. 1998. Use of stable isotopes in evaluating S biogeochemistry of forest ecosystems. In *Isotopic Tracers in Catchment Hydrology*, Kendall C, McConnell JJ (eds). Elsevier: New York; 489–518.

Mitchell MJ, McHale PJ, Inamdar S, Raynal DR. 2001. Role of within lake processes and hydrobiogeochemical changes over 16 years in a watershed in the Adirondack Mountains of New York State, U.S.A. *Hydrological Processes* **15**: 1951–1965. DOI: 10·1002/hyp.249.

Mitchell MJ, Piatek KB, Christopher S, Mayer B, Kendall C, McHale P. 2006. Solute sources in stream water during consecutive fall storms in a northern hardwood forest watershed: a combined hydrological, chemical and isotopic approach. *Biogeochemistry* **78**: 217–246. DOI: 10·1007/s10533-005-4277-1.

NECIA. 2006. Climate Change in the U.S. Northeast. UCS Publications, 2 Brattle Square, Cambridge, MA 2238–9105.

Novák M, Mitchell MJ, Jaková I, Buzek F, Schweigstillová J, Erbanová L, Pikryl R, Fottová D. 2007. Processes affecting oxygen isotope rations of atmospheric and ecosystem sulfate in two contrasting forest catchments in Central Europe. *Environmental Science and Technology* **41**: 703–709.

Park J, Mitchell MJ, McHale PJ, Christopher SF, Myers TP. 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 Biology* **9**: 1602–1619.

Rock L, Mayer B. 2002. Isotopic assessment of sources and processes affecting sulfate and nitrate in surface water and groundwater of Luxembourg. *Isotopes in Environmental & Health Studies* **38**: 191–206.

SAS Institute Inc. 1994. *Statistical Analysis Software for Microcomputers*. SAS Institute Inc.: Cary, NC.

Schiff SL, Devito KJ, Elgood RJ, McCrindle PM, Spoelstra J, Dillon P. 2002. Two adjacent forested catchments: Dramatically different NO_3^- export. *Water Resources Research* **38**: 1292–1304.

Schuster PF, Shanley JB, Marvin-Dipasquale M, Reddy MM, Aiken GR, Roth DA, Taylor HE, Krabbenhoft DP, DeWild JF. 2008. Mercury and organic carbon dynamics during runoff episodes from a northeastern USA Watershed. *Water Air & Soil Pollution* **187**: 89–108. DOI 10·1007/s11270-007-9500-3.

Searcy JK. 1959. Flow-duration curves. Water Supply Paper 1542-A, U.S. Geological Survey, Reston, Virginia.

Shanley JB, Kendall C, Smith TE, Wolock DM, McDonnell JJ. 2002. Controls on old and new water contributions to streamflow in some nested catchments in Vermont, USA. *Hydrological Processes* **16**: 589–609. DOI: 10·1002/hyp.312.

Shanley JB, Mayer B, Mitchell MJ, Michel RL, Bailey S, Kendall C. 2005. Tracing sources of streamwater sulfate during snowmelt using S and O isotope ratios of sulfate and 35S activity. *Biogeochemistry* **76**: 161–185. DOI: 10·1007/s10533-005-2856-9.

Shanley JB, Mayer B, Mitchell MJ, Bailey S. 2008. Annual and event variations in ^{34}S values of stream sulfate in a forested catchment implications for S sources and cycling. *Science of the Total Environment* (In Press).

Stager JC, Martin MR. 2002. Global Climate Change and the Adirondacks. *Adirondack Journal of Environmental Studies* Spring: 6–13.

Trenberth KE, Jones PD, Ambenje P, Bojariu R, Easterling D, Klein Tank A, Parker D, Rahimzadeh F, Renwick JA, Rusticucci M, Soden B, Zhai P. 2007. Observations: surface and atmospheric climate change. In: *Climate Change 2007: The Physical Science Basis*. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL (eds). Cambridge University Press: Cambridge and New York.

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