

Sulfate exports from multiple catchments in a glaciated forested watershed in western New York, USA

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Abstract Sulfate (SO_4^{2-}) concentrations and fluxes were studied for multiple storm events in the Point Peter Brook watershed, a glaciated, forested watershed located in Western New York, USA. Investigations were performed across one large (696 ha) and three small (1.6–3.4 ha) catchments with varying extent of riparian and wetland areas. Concentrations of SO_4^{2-} in groundwater sources (mean values: 238–910 $\mu\text{mol}_c \text{L}^{-1}$) were considerably greater than concentrations recorded for rainfall (60 $\mu\text{mol}_c \text{L}^{-1}$) and throughfall (72–129 $\mu\text{mol}_c \text{L}^{-1}$). Seasonality in SO_4^{2-} concentrations was most pronounced for valley-bottom riparian waters with maximum concentrations in late winter–spring (February–March) and a minimum in late summer (August). Concentrations of SO_4^{2-} in wetland water were considerably less than riparian water indicating the likelihood of SO_4^{2-} reduction in anoxic wetland conditions. Storm events displayed a dilution pattern in SO_4^{2-} concentrations with a minimum coinciding with the maximum in throughfall contributions. End member mixing analysis (EMMA) was able to predict the storm event

concentrations of SO_4^{2-} for four of the six comparisons. Concentrations of SO_4^{2-} at the outlet of the large (696 ha) catchment were much greater than values recorded for the smaller catchments. Exports of SO_4^{2-} in streamflow exceeded the inputs from atmospheric deposition suggesting that watersheds like Point Peter Brook may not show any immediate response to decreases in atmospheric SO_4^{2-} deposition.

Keywords Sulfur · Atmospheric deposition · Wetlands · EMMA · Storm events · Hydrochemistry

Introduction

Atmospheric deposition of sulfate (SO_4^{2-}) in the northeastern United States (US) has shown a decreasing trend over the last few decades (Likens et al. 2002). Although stream concentrations in most watersheds are also declining (Likens et al. 2002), the mass exports of SO_4^{2-} from others continue to exceed the inputs of SO_4^{2-} from atmospheric deposition (Hornbeck et al. 1997; Likens et al. 2002). The reasons for these mass balance discrepancies has not been completely ascertained, but possibilities include: (1) unaccounted inputs of dry deposition (Edwards et al. 1999; Likens et al. 2002); (2) net mineralization of sulfur (S) from soil organic matter (Eimers and Dillon 2002; Eimers et al. 2004; Shanley et al. 2005); (3) desorption of SO_4^{2-} from anion exchange sites in

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soils that previously adsorbed SO_4^{2-} during elevated periods of deposition (Alewell et al. 1999; Eimers and Dillon 2002; Eimers et al. 2004); (4) weathering of primary S minerals from geological substrate (Bailey et al. 2004; Baron et al. 1995; Mitchell et al. 2001a); and (5) release of SO_4^{2-} due to oxidation of reduced sulfide from wetlands (Bayley et al. 1986; Devito and Hill 1997, 1999; Lazerte 1993; Mitchell et al. 2006; Warren et al. 2001).

Mineral sources of SO_4^{2-} include oxidation products of iron sulfides (pyrite, FeS_2 ; pyrrhotite, FeS) which are common in bedrock formations of sedimentary and volcanic origin while other S-bearing minerals have been reported in the glacial till of northeastern US watersheds (Bailey et al. 2004; Shanley et al. 2005). Hornbeck et al. (1997) found that SO_4^{2-} exports from Sleepers River watershed in Vermont were more than two times the inputs from atmospheric deposition and attributed it to geologic release of S. Similarly, Mitchell et al. (1986) and Gibson et al. (1983) found substantial geological S sources for some catchments in the Rocky Mountains of North America.

Wetlands have been reported as sinks as well as sources of S depending on hydrologic conditions in the watershed (Bayley et al. 1986; Devito and Hill 1997; LaZerte 1993). Large releases of SO_4^{2-} have been reported from wetlands following dry summer periods which promote oxidation of reduced sulfides (Devito and Hill 1997; Eimers and Dillon 2002). In contrast, wetlands have been found to retain S in years with average or wet summers (LaZerte 1993). Sulfur dynamics in wetlands may also be influenced by hydrogeologic settings. Devito and Hill (1997) working in Precambrian Shield catchments of south central Ontario in Canada found that valley-bottom wetlands with thin glacial tills were susceptible to large water table drawdowns and therefore release of accumulated S due to oxidation. In comparison, wetlands with deeper till depths remained saturated year-round and thus efficiently retained S. Hydrologic connectivity of wetlands to streams has also been found to influence the export of SO_4^{2-} in streamflow (Warren et al. 2001). Although desorption of S from soils has been identified in a number of studies, Driscoll et al. (1998) and Bailey et al. (2004) assert that desorption may not be a significant source in geologically young soils of northeastern US.

These studies show that SO_4^{2-} exports from watersheds may be influenced by a variety of sources. Internal sources of SO_4^{2-} have important implications for how and when watersheds will respond to reduced atmospheric deposition and recover from deleterious impacts of SO_4^{2-} pollution. The exports of SO_4^{2-} may also vary with hydrologic flow paths in the watershed (Huntington et al. 1994; Lynch and Corbett 1989; Mitchell et al. 2006). Hence, to understand and quantify the processes affecting the exports of SO_4^{2-} it is critical we: (a) identify the internal sources; (b) determine the hydrologic flow paths that intersect these sources; and (c) determine how SO_4^{2-} exports vary across watersheds with wetlands and/or saturated areas. Investigations performed across multiple catchments with varying landscape characteristics and hydrologic conditions can especially provide important insights.

We explored the exports of SO_4^{2-} across one large (696 ha) and three small (1.6–3.4 ha) catchments with varying extent of saturated areas and wetlands. These catchments were located in the Point Peter Brook watershed, a glaciated, forested watershed in western New York, USA. Sulfate concentrations in streamflow at Point Peter Brook were much greater (as high as $1,000 \mu\text{mol}_e \text{L}^{-1}$) than values reported for many other watersheds in the Northeastern US and Canada suggesting that the Point Peter Brook watershed has a substantial internal SO_4^{2-} source. Sampling for SO_4^{2-} was performed during storm events and non-storm periods over three years. Special emphasis was placed on investigating the within-event patterns of SO_4^{2-} , the sources of SO_4^{2-} in the watershed, and the influence of valley-bottom wetlands and/or saturated areas on the export of SO_4^{2-} . Specific questions that were addressed in this study were:

- How do concentrations of SO_4^{2-} in the Point Peter Brook watershed compare with data from other watersheds? What are the sources of SO_4^{2-} in the watershed?
- How do SO_4^{2-} concentrations vary during and among storm events? Can storm-event patterns be explained by the relative contributions of watershed SO_4^{2-} sources?
- How do SO_4^{2-} concentrations and exports vary across catchments with varying extent of saturated and wetland areas?

Site description and monitoring

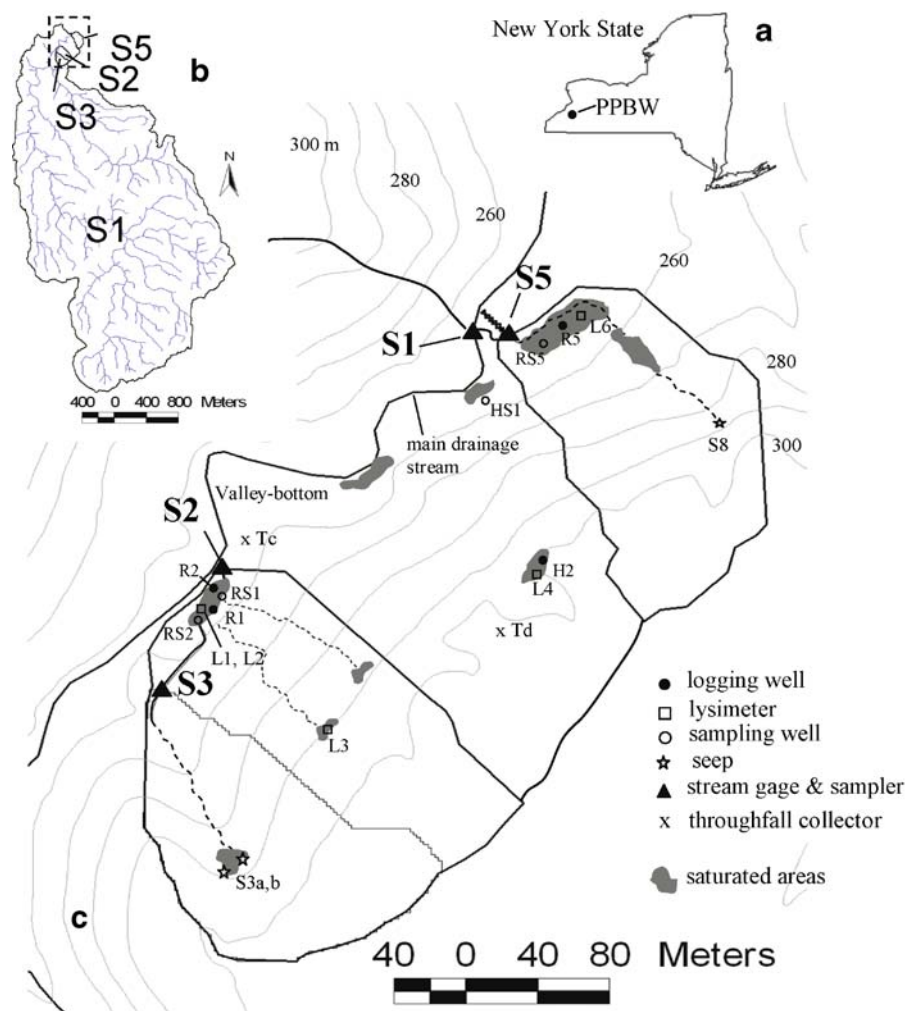
Site description

This study was conducted in the Point Peter Brook watershed (Fig. 1), located in Cattaraugus County and 55 km southeast of Buffalo in New York State, USA (42° 26' 30" N; -78° 55' 30" W). Mean annual winter temperature is -3°C and the mean summer temperature is 21°C. Annual precipitation averages 1,006 mm of which 200–250 mm occurs as snow (20 year average based on the National Atmospheric Deposition Program Weather Station at Chautauqua, NY; 35 km southwest of the Point Peter Brook watershed; NADP 2006). Atmospheric S deposition in the region is fairly high. The two-year (2003–2004) average

annual deposition of SO_4^{2-} recorded at the nearest NADP station in Chautauqua, NY amounted to 520 mol ha⁻¹ (NADP 2006).

Bedrock geology in the region consists of stratified limestone, dolomite with gypsum and shale of the Upper Devonian period (Olcott 1995). Some shales can have high S contents; for e.g., the Devonian Shale in Ohio (Kane et al. 1990) has been reported to contain 5.35% S by weight. The parent material was derived from glacial till (Kent Drift of Woodfordian formed 19,000 y B.P.) (Phillips 1988). Vegetation on ridgetops and hillslopes is dominated by deciduous trees including sugar maple (*Acer saccharum*), black maple (*Acer nigrum*), American beech (*Fagus grandiflora*), yellow birch (*Betula alleghaniensis*) with larger proportions of conifers including hemlock (*Tsuga canadensis*) and

Fig. 1 a Location of Point Peter Brook watershed (PPBW) in New York State, USA; b the study catchments; and c instrumentation and sampling locations within the study catchments



white pine (*Pinus strobus*) in valley-bottoms. Topography of the entire watershed is fairly distinct with wide ridgetops, steep hillslopes, and narrow valley bottoms. Slope gradients in the watershed range from 0 to 69%, with a mean gradient of 14%. Elevation ranges from 254 to 430 m above mean sea level. A low-permeability clay layer, that is a part of the till layer, generates perched water tables and forces water to move as shallow subsurface flow on the steep hillslopes underlies the soils. The depth to the clay/till measured using soil cores varies from 1.2 to 1.7 m in the valley-bottom locations, 0.3–0.5 m along the side slopes and 0.6 m at the ridgetops.

The catchments that were studied (S1, S2, S3, and S5) are shown in Fig. 1. Outlet for S1 (696 ha) was located on the main drainage of the Point Peter Brook watershed, S2 (3.4 ha) was nested within S1 and S3 (1.6 ha) was nested within S2. The width of the stream at S1 (third order drainage) was 3.4 m. Catchment S3 drained a hillslope hollow with streamflow originating from two perennial seeps S3a and S3b that discharged at the channel head (Fig. 1). The width of the stream at S3 (first order tributary) was 0.40 m. Outlet S2 was located in a valley-bottom riparian area downstream of S3 and the width of the stream at S2 (first order tributary) was 0.38 m. Catchment S5 (1.9 ha) located outside and downstream of S1 enclosed a valley-bottom riparian wetland. Runoff to S5 also originated from a seep (S8) located more than two-thirds of the distance along the contributing hillslopes along the northeastern edge (Fig. 1). The

width of the stream at S5 (first order tributary) was 0.45 m.

Watershed boundaries, slope gradients, aspect, and spatial extent of hillslope and valley-bottom saturated areas for the catchments were determined using a combination of field surveys and GIS-based analysis (Inamdar and Mitchell 2006). The spatial distribution of wetness was characterized by the downslope wetness index (DWI) of Hjerdt et al. (2004) and is presented graphically in Inamdar and Mitchell (2006). The dominant slope aspect for all three small subcatchments was northwest, whereas 17% of the hillslopes for S1 were oriented to the west (Table 1). Field-surveyed surface-saturated areas were highest for S5 at 5.9% of the catchment area followed by S2 (2.0%) and S3 (0.8%). The valley-bottom wetland in S5 constituted 4.7% with 1.2% of the saturated areas on hillslopes. Organic matter concentrations of the wetland soil were ~ 70%. Soil thickness in the S5 wetland was 1 m or less (above gravel/loose unconsolidated material) and lower than that observed for the riparian area at S2 (1.5–2 m). The valley-bottom riparian area in S2 accounted for only 0.7% of the saturated area with the remaining saturation (1.3%) in discrete pockets on hillslope benches. The organic matter content of surficial (0–20 cm) soils in the riparian area at S2 was between 3 and 11%. Saturated areas in S3 were limited to the channel head (0.8%).

The field-surveyed saturated area % values for the small catchments were compared against wet areas corresponding to various thresholds on the DWI map

Table 1 Watershed characteristics and topographic attributes for the four subcatchments

Attribute	Subcatchments			
	S1	S2	S3	S5
Area (ha)	696	3.4	1.6	1.9
Relief (m)	254–430	255–307	260–307	255–304
Mean catchment gradient	14.1	14.3	15.0	14.9
Stream order and width (m)	3rd, 3.4	1st, 0.38	1st, 0.4	1st, 0.45
Field surveyed saturated area in % and m ² in parenthesis				
Total	–	2.0 (675)	0.8 (129)	5.9 (1122)
Valley-bottom	–	0.7 (231)	0	4.7 (896)
Hillslope	–	1.3 (444)	0.8 (129)	1.2 (226)
Downslope wetness index (DWI) moments				
Mean	5.12	5.39	5.28	5.67
Variance	1.98	1.34	1.36	2.60
Skew	1.61	0.90	0.91	1.44
% catchment area with DWI > 10	2.1	0.9	0.7	4.3

(Inamdar and Mitchell 2006). A threshold value of 10 produced the best fits between field-surveyed and DWI-derived % saturated area. The threshold value of 10 indicated a DWI saturated area of 4.3% for S5 which was comparable to the valley-bottom wetland area of 4.7% (Table 1). For S2 the DWI saturated area value was 0.9%, which was again comparable to the field-measured value of 0.7%. Using a threshold of 10, the extent of surface-saturation for S1 was computed to be 2.1%. Although the value of 2.1% for S1 likely represents the valley-bottom saturated areas and does not include the more dynamic hillslope-bench saturated areas, this value provides a useful estimate for comparison against the other catchments.

Watershed instrumentation and sampling

Precipitation in the Point Peter Brook watershed was recorded using a tipping-bucket rain gage located 400 m downstream from S1. Streamflow discharge measurements at S1 were initiated in November 2002, at S2 and S3 in May 2003 and at S5 in April 2004. Stream flow stage was recorded every 15 min using a pressure transducer with a recorder (Global Water Inc.). At S1, a stage-discharge relationship was developed for the stream channel. Parshall flumes were installed on streams at S2 and S3 and a V-notch weir was installed at the stream channel at S5. Groundwater elevations were recorded using pressure transducers (Global Water Inc.) nested within logging wells that were constructed of 5 cm (ID) PVC tubing. The logging wells were constructed by coring to the depth at which an impeding clay or loose/unconsolidated gravel or till was intersected. Two logging wells R1 and R5 were located in the valley-bottom riparian and wetland areas of S2 and S5 respectively (Fig. 1). One hillslope well (H2) was positioned in a saturated area on the hillslope bench.

Water chemistry was monitored by grab sampling and automatic sampling using ISCO samplers. Grab sampling was performed twice a month typically under baseflow or non-storm conditions for: valley-bottom and hillslope groundwater wells, surface seeps, and lysimeters located in valley-bottom and hillslope-bench saturated areas. Groundwater sampling wells were constructed of 5 cm (ID) PVC tubing and were cored to the depth at which an impeding clay or gravel layer was intersected (between 1.5 and 3 m). The wells were screened from 30 cm below the

soil surface to the bottom. Three groundwater-sampling wells (RS1, RS2, and RS5) were established in riparian and wetland valley-bottom locations (Fig. 1). Seep samples were collected from surface seeps at S3a and S3b (Fig. 1) in the catchment S3. Starting in spring 2005, samples were also collected downstream of the seep S8 located in catchment S5. Zero-tension lysimeters were constructed of 5 cm (ID) slotted PVC tubing and were inserted at a 45-degree angle to a depth of 30 cm from the soil surface. The lysimeters were installed to collect gravitational soil water from the A horizon. Lysimeters were installed in valley-bottom riparian and wetland areas (L1, L2, and L6) and hillslope-bench saturated areas (L3 and L4) (Fig. 1). Sample water was obtained from the groundwater wells and lysimeters using a hand-operated suction pump. In summer 2005, litter layer (O horizon) samplers were installed at two separate sites to collect litter leachate associated with storm events. The litter sampler was a 1 m² plastic tray with raised edges (3 cm) with a hole and plastic tube that connected to a 500 mL plastic bottle. The tray was inserted at the junction of the O and A horizon and was positioned such that water drained into the receiving bottle. Although only five samples (three rainfall events) were collected from the driest period of the year (August–September, 2005), this data was included to provide some estimate of the SO_4^{2-} contributions from litter leachate. Both litter samplers were placed on hillslopes.

Storm event sampling for the four catchments was performed using a limited number of ISCO samplers over 2003–2005. The automated ISCO sampler was triggered for event sampling when the rainfall rate exceeded a threshold of 2.8 mm within a 2-h period. The sampler was programmed on the “variable time” mode so as to sample more frequently on the hydrograph rising limb than on the recession limb. Composite precipitation samples were collected in a collector placed in the open; throughfall samples were collected from two collectors, one placed under a coniferous canopy (Tc) and one placed under a deciduous canopy (Td) (Fig. 1). Precipitation and throughfall collectors were 3.8 L plastic containers connected to funnels, which had a plastic mesh on the mouth to prevent entry of debris. All samples were collected within 24 h of an event in 250 mL Nalgene bottles.

All samples were filtered with 0.5 μ m filter prior to analysis. Analyses performed on the samples included:

DOC on a Tekmar-Dohrmann Phoenix 8000 TOC analyzer, cations on a Perkin-Elmer ICP-AEC Div 3300 instrument, and anions on a Dionex IC. The laboratory is a participant in the United States Geological Survey (USGS) performance evaluation program, that helps ensure data quality (Mitchell et al. 2001b).

Selection of storm events

Multiple storm events were monitored for S1, S2, S3, and S5 over the period May 2003 through August 2005. Because of budget, equipment and personnel restrictions not all catchments were sampled simultaneously for all events. Events that are evaluated in this study include: July 27 and August 9, 2003 (summer events); April 12, May 20 and May 27, 2004 (spring events); and August 30, 2005 (summer event). These six events were selected since: (a) they showed clear and distinct temporal patterns in the solutes; (b) were representative of the events for those seasons; and (c) had the most complete data set across the catchments. Of these, four events – July 27 and August 9, 2003; May 20, 2004; and August 30, 2005 were selected to display the detailed within event patterns of the SO_4^{2-} .

Event computations and statistics

The start of the event was defined when a perceptible rise in discharge was observed after precipitation or the occurrence of first ISCO sample, whichever occurred earlier. The end of the event was defined by the first occurrence of when discharge returned to pre-event values or when a subsequent event began. Discharge per unit area or specific discharge (mm) was the total volumetric flow for the event divided by the catchment area. Antecedent moisture conditions for each storm were computed by: (a) summation of the precipitation amounts for 7 days prior to the event (antecedent precipitation index-API₇); and (b) average of ground water elevations (antecedent groundwater index-AGI₇) for 7 days prior to the event. AGI₇ values were computed using the riparian wells R1 and R5 and the hillslope-bench well H2. Groundwater elevations at H2 varied over a larger range of values compared to wells R1 and R5 and thus provided a more dynamic picture of the changes in catchment wetness.

Runoff sources determined from EMMA and a model for runoff response

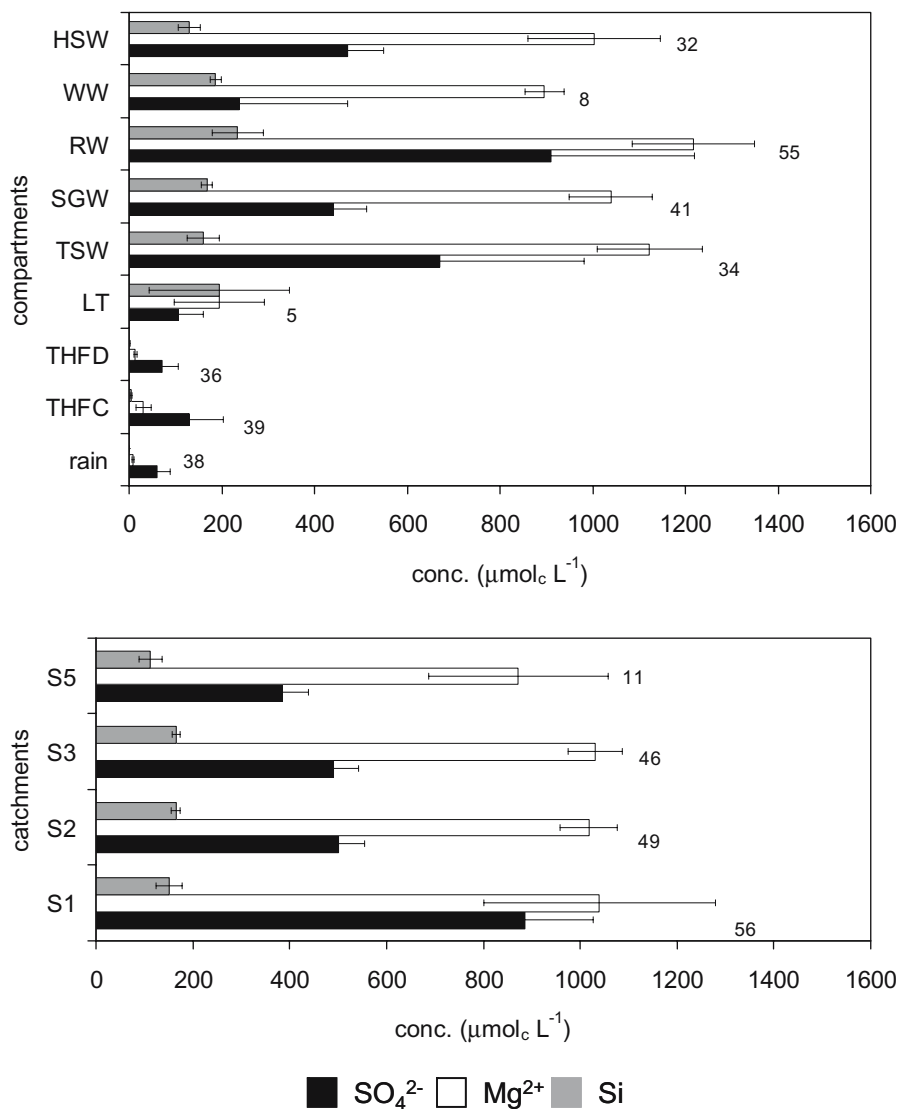
Spatial sources of runoff in the Point Peter Brook watershed were previously identified by Inamdar and Mitchell (2006) using silica (Si), magnesium (Mg^{2+}), and dissolved organic carbon (DOC) as tracers in an end member mixing analysis (EMMA) model (Burns et al. 2001; Christopherson and Hooper 1992). EMMA identified groundwater discharged at seeps (SGW), throughfall (THF), and riparian water (RW) as the end members for stream chemistry. A three-stage model explaining the role of topography in runoff generation and the temporal expression of the three end members has been developed for the Point Peter Brook watershed (Inamdar and Mitchell 2007a). The three stages of runoff generation were: (a) Prior to storm events and during baseflow conditions, streamflow was composed of seep and riparian groundwaters; (b) In the early part of the storm and on the rising limb of the hydrograph, throughfall was intercepted on saturated areas and contributed to streamflow as saturation overland flow; (c) During hydrograph recession, hydraulic gradients associated with subsurface hillslope runoff displaced riparian water into the stream.

Results

Concentrations of SO_4^{2-} in watershed compartments

The concentrations of SO_4^{2-} varied considerably across the watershed compartments (Fig. 2). In addition to SO_4^{2-} , concentrations of Mg^{2+} and Si were also included in Fig. 2. High concentrations of Mg^{2+} and Si typically indicate groundwater or water that have been in contact with bedrock, till, and/or saprolite. Sulfate concentrations in rainfall and snow were the lowest at 60 and 24 $\mu\text{mol}_c \text{L}^{-1}$, respectively. Concentrations of SO_4^{2-} increased slightly as precipitation percolated through the forest canopy and litter layer. Sulfate concentrations in conifer throughfall (129 $\mu\text{mol}_c \text{L}^{-1}$) were nearly twice the deciduous value (72 $\mu\text{mol}_c \text{L}^{-1}$). Concentrations in seep groundwater and hillslope groundwater (well HS1) were similar (442 and 472 $\mu\text{mol}_c \text{L}^{-1}$, respectively) but nearly eight times the precipitation value. While

Fig. 2 Concentrations of SO_4^{2-} , Mg^{2+} ($\mu\text{mol}_c \text{L}^{-1}$) and Si ($\mu\text{mol}_c \text{L}^{-1}$) in various watershed compartments and catchment baseflow. Number of samples for each category are listed next to the bars. Watershed compartments include – rainfall (*rain*), conifer throughfall (*THFC*), deciduous throughfall (*THFD*), litter layer (*LT*), topsoil water (*TSW*), seep groundwater (*SGW*), riparian water (*RW*), wetland water (*WW*) and hillslope groundwater (*HSW*)

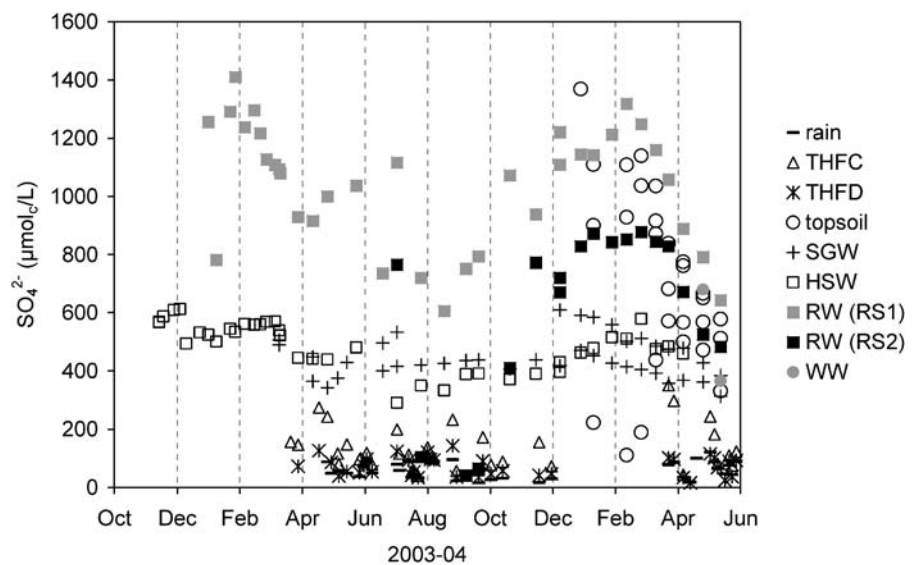


valley-bottom riparian water ($910 \mu\text{mol}_c \text{L}^{-1}$) recorded the highest SO_4^{2-} concentrations, the corresponding values for wetland water ($238 \mu\text{mol}_c \text{L}^{-1}$) were surprisingly low. This difference in SO_4^{2-} concentrations between in riparian and wetland waters was especially noteworthy since the corresponding difference in Mg^{2+} and Si concentrations was much smaller (Fig. 2). Although topsoil waters also recorded high ($671 \mu\text{mol}_c \text{L}^{-1}$) SO_4^{2-} concentrations we believe these were likely influenced by upwelling groundwater since all lysimeters were located in riparian and wetland groundwater discharge zones (see Fig. 1).

Among watershed compartments, seasonality in

SO_4^{2-} concentrations was most pronounced for riparian and topsoil waters (Fig. 3). Sulfate concentrations for riparian sampling wells RS1 and RS2 were displayed separately in Fig. 3 since they were sampled over different periods and differed considerably in their concentrations. This suggests that SO_4^{2-} concentrations vary considerably even over small distances within the same riparian area. Riparian water concentrations were at their highest during winter (January–February); declined through the spring, with a minimum in late summer (august). Although the sampled period for topsoil concentrations was much less, they followed a seasonal pattern

Fig. 3 Seasonal pattern of SO_4^{2-} concentrations ($\mu\text{mol}_c \text{L}^{-1}$) in various watershed compartments. Watershed compartments include – rain, conifer throughfall (THFC), deciduous throughfall (THFD), topsoil, seep groundwater (SGW), hillslope groundwater (HSW), riparian water (RW – wells RS1 and RS2), and wetland water (WW)



similar to that for riparian water. However unlike riparian water, the other watershed compartments did not reveal any distinct seasonal patterns in SO_4^{2-} concentrations. Sufficient data on wetland water was not available to identify any seasonal trends.

Concentrations in stream baseflow

Baseflow concentrations of SO_4^{2-} for the largest (696 ha) catchment S1 (Mean=885 $\mu\text{mol}_c \text{L}^{-1}$) were significantly greater ($p < 0.01$) than the values for the

smaller catchments (Fig. 2). In contrast, the mean concentrations of Mg^{2+} and Si for catchment S1 were not very different from the small catchments (Fig. 2). The ratio of mean SO_4^{2-} concentrations for S1 and S2 was 1.77 while the corresponding values for Mg^{2+} and Si were 1.02 and 0.92, respectively. Among the smaller catchments, mean baseflow SO_4^{2-} concentrations were least for the wetland catchment S5 (385 $\mu\text{mol}_c \text{L}^{-1}$). Concentrations for catchment S5 were significantly different from S2 and S3 ($p < 0.01$), however there was no significant difference between

Table 2 Hydrologic parameters for the six selected storm events across the four catchments

Catchments	Parameter	Events					
		2003		2004			2005
		Jul 27	Aug 9	Apr 12	May 20	May 27	Aug 30
	Rain (mm)	24	11	16	11	11	66
	Peak 10-minute rain intensity (mm)	8.4	3.0	2.3	6.9	3.8	2.5
	API ₇ (mm)	47	31	0.2	23	83	1.8
	AGI ₇ -H2 (cm)	12	2	2	12	-4	134
	AGI ₇ -R1 (cm)	23	27	27	19	12	37
	AGI ₇ -R5 (cm)				4	4	12
S1	Discharge (mm)	6.6	1.8	3.1	1.2	2.8	8.6
	Runoff ratio	0.27	0.16	0.19	0.11	0.26	0.13
S2	Discharge (mm)	6.9	3.0	5.9	2.0	3.4	22
	Runoff ratio	0.29	0.27	0.37	0.18	0.32	0.35
S3	Discharge (mm)			7.8	3.2	3.5	
	Runoff ratio			0.49	0.28	0.33	
S5	Discharge (mm)				1.9	3.2	24
	Runoff ratio				0.17	0.30	0.36

Shaded areas indicate events that were not sampled or data was not available.

the concentrations for catchments S2 and S3 ($p=0.3$) (Table 2). Baseflow concentrations of SO_4^{2-} for catchments S2 and S3 displayed a pronounced seasonal trend (Fig. 4) with a minimum in late spring (May–June) and a maximum in winter (December–January). While concentrations of SO_4^{2-} from the large catchment S1 were also high in winter, the seasonal pattern in concentrations was not as pronounced as that observed for catchments S2 and S3. Sampled data for S5 was not sufficient to identify any seasonal patterns for SO_4^{2-} . Unlike SO_4^{2-} , concentrations for Mg^{2+} and Si did not reveal any seasonal patterns for any of the catchments.

Sulfate concentrations during storm events

A pronounced dilution of the SO_4^{2-} concentrations is seen for all the 2003–2004 events (Figs. 5, 6, 7). Concentrations of SO_4^{2-} are high at the start of the event, decrease through the hydrograph rising limb,

reach a minimum at or near the discharge peak, and then recover through hydrograph recession. The pattern in SO_4^{2-} concentrations was very similar to that observed for Mg^{2+} but contrasted with DOC. DOC concentrations increased through the rising limb of the hydrograph, peaked after the discharge peak, and then decreased thereafter. When compared with end member runoff contributions (Figs. 5, 6, 7 lower panels), SO_4^{2-} values were at a minimum at or around the time when throughfall contributions were at their maximum. Storm- event SO_4^{2-} concentrations consistently dropped below the mean baseflow concentrations (indicated by a horizontal dashed line). In comparison to the 2003–2004 events, the temporal patterns of SO_4^{2-} for the event of August 30, 2005 (Fig. 8) were not as pronounced. Sulfate concentrations during the event of August 30, 2005 did not show an immediate decline in values at the outset of the event, especially for catchment S1 (even though Mg^{2+} displayed a pronounced decline). Antecedent moisture conditions

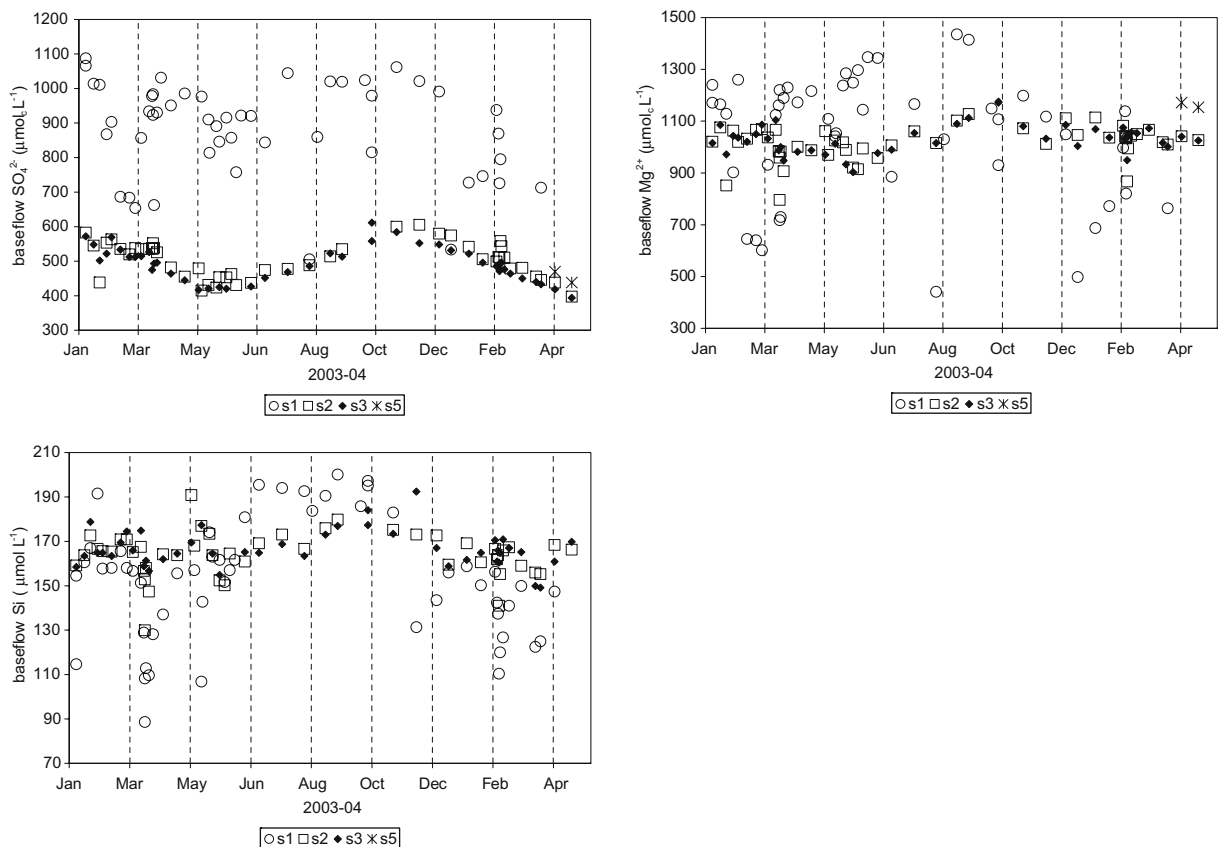


Fig. 4 Concentrations of SO_4^{2-} ($\mu\text{mol}_c \text{L}^{-1}$), Mg^{2+} ($\mu\text{mol}_c \text{L}^{-1}$) and Si ($\mu\text{mol}_c \text{L}^{-1}$) in stream baseflow over the period Jan 2003 to June 2004

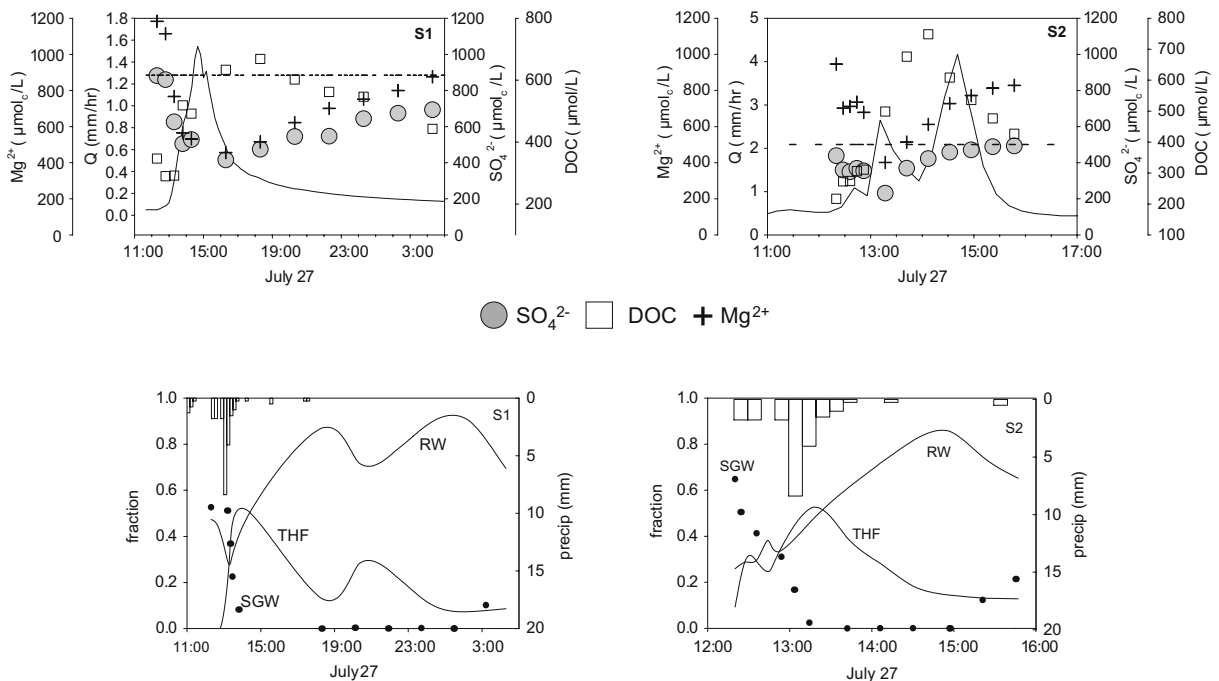


Fig. 5 Discharge (Q in mm h^{-1}) and concentrations of SO_4^{2-} , Mg^{2+} ($\mu\text{mol}_c \text{L}^{-1}$), and DOC ($\mu\text{mol L}^{-1}$) [top panel] and precipitation (mm) and fractional contributions of end members (throughfall [THF], seep groundwater [SGW], and riparian

water [RW]) [bottom panel] for the event of July 27, 2003. Catchment IDs are provided in corner of each plot. The horizontal dashed line on the plots in the top panel indicates the mean baseflow concentration of SO_4^{2-}

for the event of August 30, 2005 were considerably drier than the events of 2003–2004 (Table 2).

Among the catchments, storm-event SO_4^{2-} concentrations for catchment S1 were the highest while concentrations for the wetland catchment S5 were the lowest. Storm-event SO_4^{2-} concentrations for S1 also showed a sharper decline (on the hydrograph rising limb) compared to the smaller catchments. An inverse concentration–discharge relationship was observed for SO_4^{2-} across all catchments.

EMMA-predicted versus observed concentrations

To evaluate if EMMA-derived end members could explain the stream SO_4^{2-} concentrations we compared the EMMA-predicted SO_4^{2-} concentrations against the observed values for the events of July 27 and August 9, 2003 and May 20, 2004 (Fig. 9). Our previous work (Inamdar and Mitchell 2006) showed that EMMA was able to predict the concentrations of NO_3^- associated with storm events. The concentrations of SO_4^{2-} used for the end members for the comparisons in Fig. 9 are presented in Table 3 and the

fit between observed and predicted values was quantified using root mean square error (E). Across the seven plots (Fig. 9), best fits were observed for the event of May 20, 2004 while the largest discrepancies in the concentrations were recorded for catchment S2 for the event of May 27 and catchment S1 for the event of August 9. There were no systematic differences—for the event of July 27 the predicted S2 concentrations were greater than observed, especially during the latter part of the event. In contrast, for the event of August 9, the predicted concentrations for S1 were less than the corresponding observed values. Overall, considering the large variability in riparian and wetland water concentrations (Fig. 2), the EMMA predictions were fairly close.

Flow-weighted SO_4^{2-} concentrations and flux for the six selected storm events

The six selected events represented a range in precipitation amounts (11–66 mm) and antecedent soil moisture conditions (API_7 : 0.2–83 mm) (Table 2). The largest amount of rainfall (66 mm) was associated

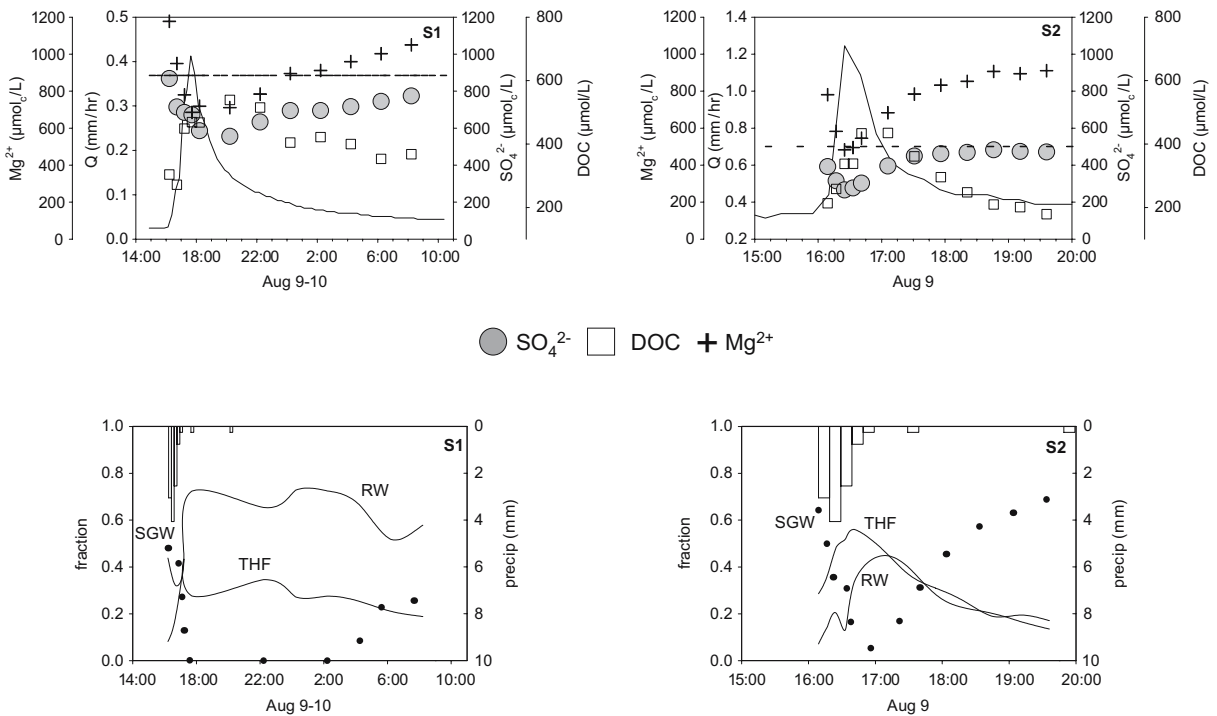


Fig. 6 Discharge (Q in mm h^{-1}) and concentrations of SO_4^{2-} , Mg^{2+} ($\mu\text{mol}_c \text{L}^{-1}$), and DOC ($\mu\text{mol L}^{-1}$) [top panel] and precipitation (mm) and fractional contributions of end members (throughfall [THF], seep groundwater [SGW], and riparian

water [RW]) [bottom panel] for the event of August 9, 2003. Catchment IDs are provided in corner of each plot. The horizontal dashed line on the plots in the top panel indicates the mean baseflow concentration of SO_4^{2-}

with the event of August 30, 2005 (remnants of Hurricane Katrina) which occurred when antecedent soil moisture conditions in the catchments were very dry ($\text{API}_7=1.8 \text{ mm}$; AGI_7 for $\text{H2}=134 \text{ mm}$). The

event of July 27, 2003 (24 mm) was the most intense and resulted in the peak discharges from S1 and S2 (1.5 and 4.2 mm h^{-1} , respectively) that were the highest for the year 2003. The summer event of

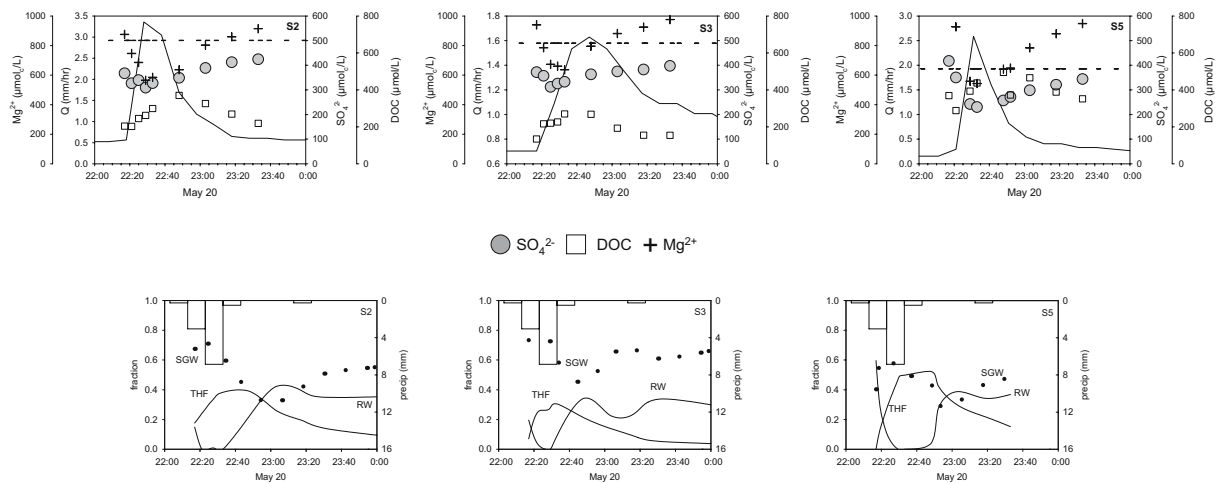
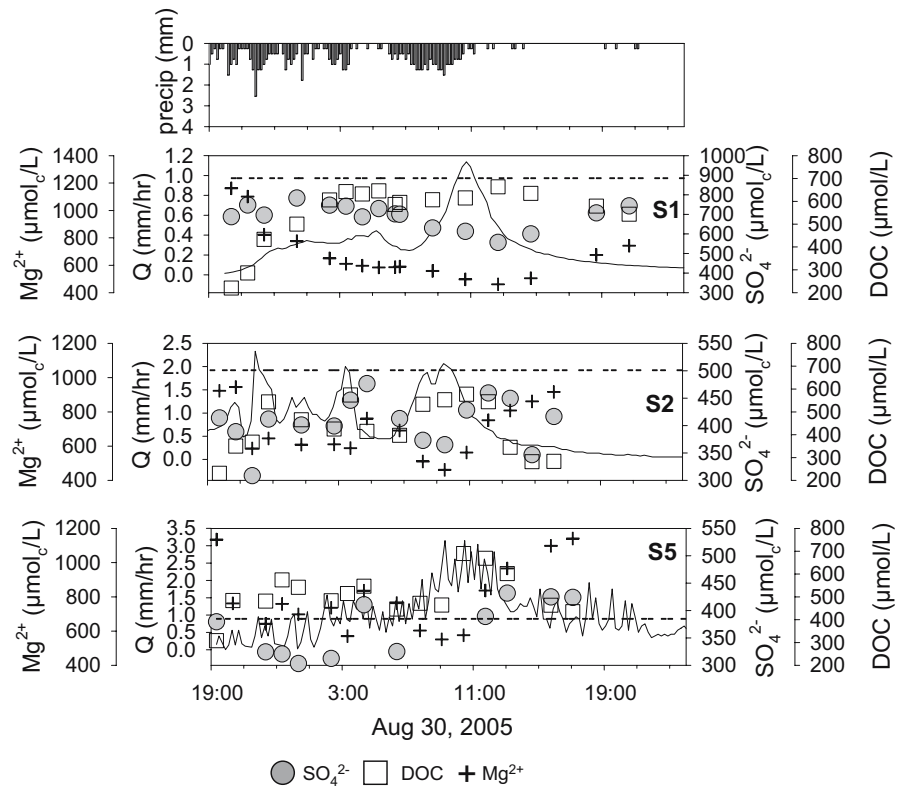


Fig. 7 Discharge (Q in mm h^{-1}) and concentrations of SO_4^{2-} , Mg^{2+} ($\mu\text{mol}_c \text{L}^{-1}$), and DOC ($\mu\text{mol L}^{-1}$) [top panel] and precipitation (mm) and fractional contributions of end members (throughfall [THF], seep groundwater [SGW], and riparian

water [RW]) [bottom panel] for the event of May 20, 2004. Catchment IDs are provided in corner of each plot. The horizontal dashed line on the plots in the top panel indicates the mean baseflow concentration of SO_4^{2-}

Fig. 8 Discharge (Q in mm h^{-1}) and concentrations of SO_4^{2-} , Mg^{2+} ($\mu\text{mol}_c \text{L}^{-1}$), and DOC ($\mu\text{mol}_c \text{L}^{-1}$) and precipitation (mm) for the event of August 30, 2005. Catchment IDs are provided in corner of each plot. The horizontal dashed line on the plots indicates the mean baseflow concentration of SO_4^{2-}



August 9, 2003 and the spring events of April 12 and May 20, 2004 were moderate in size and occurred under fairly wet antecedent soil moisture conditions. Antecedent moisture conditions ($\text{API}_7=83$) were wettest during the event of May 27, 2004 when water level at well H2 was 4 cm above the soil surface (Table 2). Discharge rate (mm) for individual storms was highest for the headwater catchment and decreased with increasing catchment area (Table 2).

Although SO_4^{2-} concentrations from S1 were much greater than those from the smaller catchments (Figs. 5, 6, 7, 8) the same was not true for fluxes (Fig. 10). On the contrary, SO_4^{2-} flux from the smaller catchments exceeded that from S1 for three (August 9, April 12 and August 30) out of the four events where data for S1 is presented (Fig. 10). Clearly the amount of runoff, which on a unit areas basis (Table 2) was greater for the smaller catchments, had a large influence on the SO_4^{2-} flux. While the export of SO_4^{2-} from the headwater S3 catchment was more than S2 for two (April 12 and May 20, 2004) out of the three events, the exports from the wetland catchment S5 was consistently the lowest among the small catchments.

When compared to the inputs of SO_4^{2-} in precipitation ($3\text{--}10 \text{ mol ha}^{-1}$), the range in catchment fluxes was fairly large ($6\text{--}91 \text{ mol ha}^{-1}$) (Fig. 10). Catchment SO_4^{2-} exports exceeded precipitation inputs for all events except the event of May 20, 2004. For the event of May 20, 2004 a net retention of 15 and 28% was recorded for catchments S2 and S5, respectively. In contrast, the net loss of SO_4^{2-} (negative retention in Fig. 10) from the catchments ranged from 19 to 1,203%.

Discussion

Comparison of concentrations of SO_4^{2-} from Point Peter Brook watershed against previous studies

A comparison of SO_4^{2-} concentrations from the Point Peter Brook watershed against other glaciated and non-glaciated sites from eastern North America reveals that SO_4^{2-} concentrations at Point Peter Brook were markedly high (Table 4). The only study in eastern North America that reported concentrations

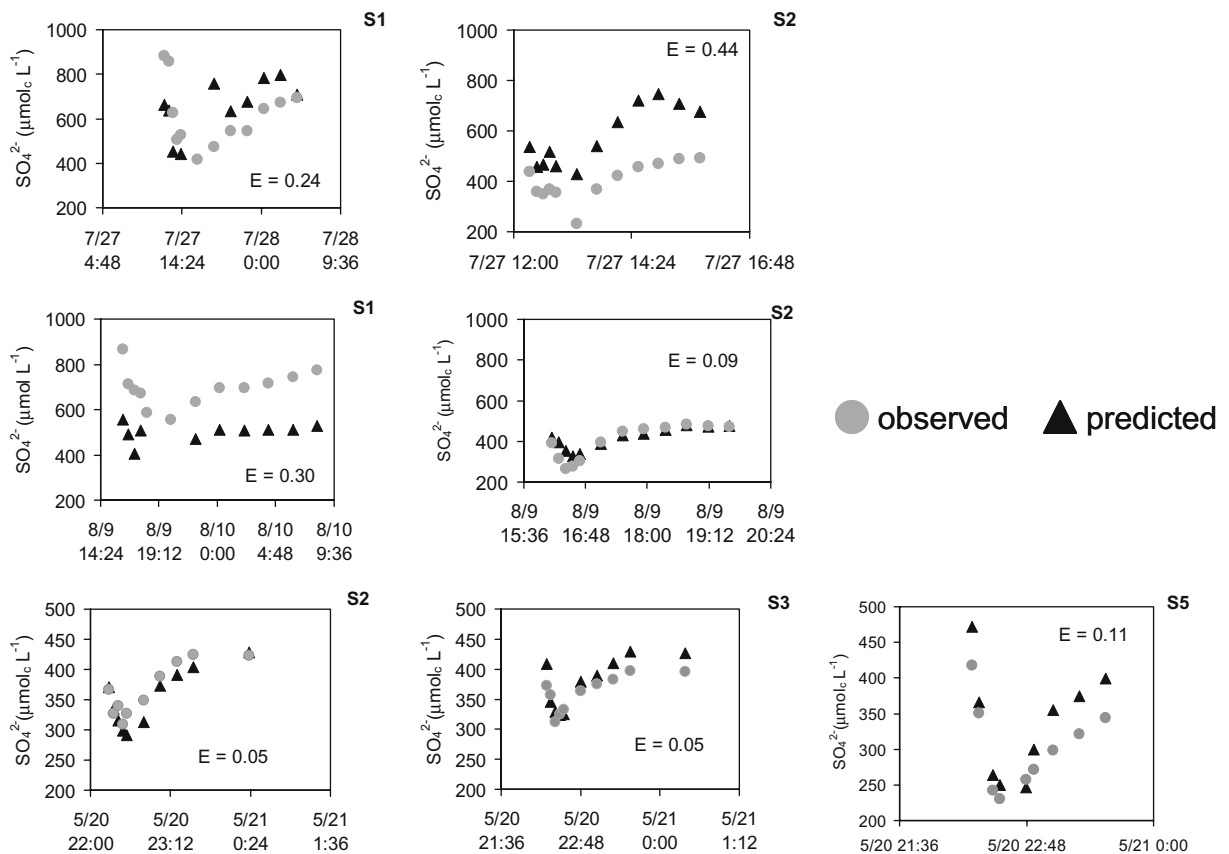


Fig. 9 Comparisons of observed and EMMA-predicted SO_4^{2-} concentrations ($\mu\text{mol}_c \text{L}^{-1}$) for the events of July 27 and August 9, 2003 and May 20, 2004. The fits between observed

and predicted values were quantified using root mean square error (E) and are included on the plots

higher than the Point Peter Brook watershed was located about 100 miles northwest in Hamilton, Ontario, Canada (Warren et al. 2001). In addition to high SO_4^{2-} concentrations in streamwater, Warren et al. (2001) also reported very high SO_4^{2-} concentrations in groundwater ($2,000 \mu\text{mol}_c \text{L}^{-1}$) and attributed them to S-rich substrates in the carbonate-rich bedrock and glacial till. High groundwater and stream SO_4^{2-} concentrations have also been observed for Precambrian Shield catchments in central Ontario, Canada (Devito and Hill 1997; Dillon and Lazerte 1992; Eimers et al. 2004; Steele and Buttle 1994) and have been attributed to the S-rich bedrock and/or glacial till. In the New England states of Vermont and New Hampshire, USA, Bailey et al. (2004) also reported the influence of S-rich geological substrates on stream water SO_4^{2-} concentrations (Table 4), but the magnitude of these values was considerably lower than concentrations observed at the Point Peter Brook

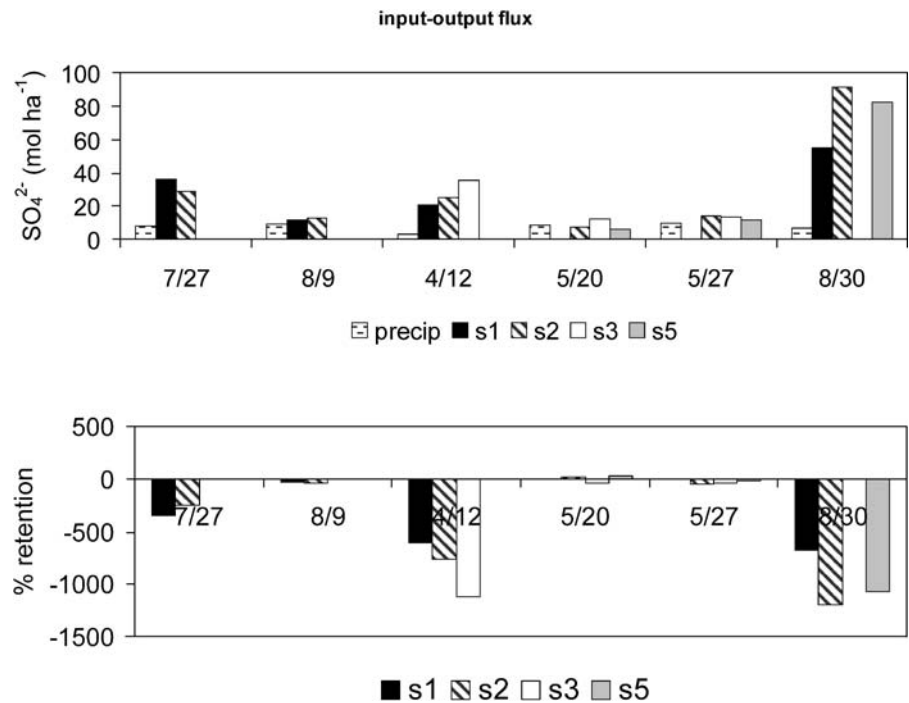
watershed. Bailey et al. (2004) found that watersheds with S-poor substrates typically had stream water SO_4^{2-} concentrations less than $100 \mu\text{mol}_c \text{L}^{-1}$, while those with S-rich substrates varied between 56 and $229 \mu\text{mol}_c \text{L}^{-1}$.

In contrast, studies performed in the non-glaciated southeastern US (Fitzhugh et al. 2001; Huntington

Table 3 Concentrations of SO_4^{2-} ($\mu\text{mol}_c \text{L}^{-1}$) for the end members used in EMMA predictions (Fig. 9) for the events of July 27 and August 9, 2003 and May 20, 2004

Events	End member SO_4^{2-} concentrations ($\mu\text{mol}_c \text{L}^{-1}$)		
	THF	SGW	RW
July 27, 2003	36	476	867
August 9, 2003	106	532	662
May 20, 2004	90	409	514

Fig. 10 Input–output fluxes (mol ha^{-1}) and % retention of SO_4^{2-} for the six selected storm events



et al. 1994; Nodvin et al. 1995; Shanley and Peters 1993) have reported lower concentrations (Table 4), both in stream water as well as groundwater. The low SO_4^{2-} concentrations in the southeastern US have

typically been attributed to atmospheric deposition with high retention of SO_4^{2-} via adsorption in the soil profile (Huntington et al. 1994; Shanley and Peters 1993) and little or no contributions from geologic or

Table 4 Comparison of concentrations of SO_4^{2-} ($\mu\text{mol}_c \text{L}^{-1}$) from Point Peter Brook watershed against other glaciated and non-glaciated sites from eastern North America

No.	Reference	Location	Mean streamflow concentrations ($\mu\text{mol}_c \text{L}^{-1}$)
Glaciated Sites			
1	This study	Point Peter Brook watershed, Western New York, USA	Storm events: 311 to 670 Baseflow: 385 to 885
2	Mitchell et al. (2006)	Archer Creek watershed, Adirondacks, New York, USA	Storms events: 180 to 249
3	McHale et al. (2002)	Archer Creek watershed, Adirondacks, New York, USA	Storms events: 117 to 158
4	Huntington et al. (1994)	Panola mountain, Georgia, USA	10 to 110
5	Bailey et al. (2004)	Cone Pond, Vermont, USA	135
		Hubbard Brook, New Hampshire, USA	100
		Sleepers River, Vermont, USA	160
6	Eimers and Dillon (2002)	Wetland catchment (DE5), south central Ontario, Canada	30 to 80
		Upland catchments, south central Ontario, Canada	75 to 265
7	Devito and Hill 1997	Harp swamp, Precambrian Shield south central Ontario, Canada	< 62 to 208 ^a
		Plastic swamp, Precambrian Shield south central Ontario, Canada	< 104 to 729 ^a
8	Warren et al. (2001)	Beverley Swamp, Hamilton, Ontario, Canada	104 to 5,229
Non-glaciated Sites			
9	Dow and Dewalle (1997)	Pennsylvania, USA	104 to 220
10	Fitzhugh et al. (2001)	Otter Creek Drainage, West Virginia, USA	100–150 ^b
11	Nodvin et al. (1995)	Nolan Divide watershed, North Carolina/Tennessee, USA	20–60

^a converted from mg/L; ^b derived from figure

groundwater sources. Rochelle et al. (1987) and Galloway et al. (1983) attributed the differences in sulfate retention among northern and southern regions of the North American continent to the extent of the last glaciation (Wisconsin) and the consequent impact on weathering and soil formation. Rochelle et al. (1987) found that sites north of the limit of the glaciation had zero net retention while sites south of the line were retaining 20 to 90% of the incoming S.

Sulfate concentrations in watershed compartments at the Point Peter Brook watershed (Table 2) clearly suggest that groundwaters were the largest source of SO_4^{2-} to the streams. We attribute the high concentrations of SO_4^{2-} in groundwater to the contributions of the weathering of S-containing minerals. The aquifers in the region are an example of carbonate-rock aquifers. Bedrock in the region consists of stratified limestone, dolomite with some gypsum, and abundant interbedded shale of marine origin. The high SO_4^{2-} concentrations observed in this study are likely partly derived from the dissolution of gypsum (Olcott 1995). It is also very likely that S-rich substrates in the shale and glacial till also contributed to groundwater SO_4^{2-} concentrations.

Sources of SO_4^{2-} in the Point Peter Brook watershed

The large difference in concentrations of SO_4^{2-} between atmospheric (precipitation, throughfall) and groundwater sources (Fig. 2) undoubtedly suggests that SO_4^{2-} fluxes in the Point Peter Brook watershed are regulated by groundwater sources. There were however, important differences in SO_4^{2-} concentrations among the groundwater compartments: (a) mean SO_4^{2-} concentrations for seep groundwater were not only lower but also had a narrower range than values measured for riparian water (Fig. 2); and (b) mean SO_4^{2-} concentrations for the wetland water were markedly lower than riparian water, but similar to riparian water displayed a wide range in concentrations.

We have previously (Inamdar and Mitchell 2006) proposed that two separate groundwater systems are likely responsible for the groundwater discharge at hillslope seeps and the recharge of valley-bottom riparian and wetland areas. The valley-bottom riparian areas are recharged by deeper groundwaters while the seeps are local groundwater systems (Inamdar and Mitchell 2006). This difference in flow paths could explain the higher SO_4^{2-} concentrations in riparian

water since deeper flow paths would have more contact time with the S-rich geologic substrate. In addition, it is also possible that riparian water concentrations in the valley-bottom positions are also influenced by the redox conditions in saturated and wetland areas at these locations. Reducing (or anoxic) conditions in saturated areas can lead to precipitation of SO_4^{2-} as sulfides and therefore a reduction in SO_4^{2-} concentrations (Mitsch and Gosselink 2000). Alternatively, oxidizing conditions can convert previously deposited sulfides to SO_4^{2-} and consequently result in an increase in SO_4^{2-} concentrations (Mitsch and Gosselink 2000). The role of redox conditions in influencing SO_4^{2-} concentrations has been highlighted in numerous studies in glaciated catchments in Northeastern America (Bayley et al. 1986; Devito and Hill 1999, 1997; Eimers and Dillon 2002; Warren et al. 2001). Furthermore, Devito and Hill (1997) showed that wetlands subject to groundwater variations yielded higher concentrations of SO_4^{2-} (associated with oxidation of sulfides) as opposed wetlands that were continuously moist year-round.

Redox influences would explain much lower SO_4^{2-} concentrations observed for wetland water (Fig. 2). Groundwater elevations in the wetland catchment S5 were close to the soil surface year-round (note the AGI values for wetland well R5 in Table 2) and thus likely provided a reducing environment for the reduction of SO_4^{2-} . Redox modification of SO_4^{2-} could also explain the seasonal pattern of SO_4^{2-} for riparian water (Fig. 2) and baseflow from catchments S2 and S3 (Fig. 3). Higher SO_4^{2-} concentrations during winter have been reported in numerous studies (e.g., Devito and Hill 1997) and can be attributed to oxidation of SO_4^{2-} during the preceding summer followed by flushing of SO_4^{2-} during wet winter months (Evans et al. 1997). However, the lack of a pronounced seasonal pattern for S1 is surprising, especially considering the strong seasonal expression at S2 and S3. It is possible that the combined influence of a variety of riparian and wetland areas at the large catchment scale (696 ha) may have contributed to muted response for S1.

Pattern of SO_4^{2-} concentrations during and among storm events and the responsible mechanisms

Storm event SO_4^{2-} concentrations were consistently lower than baseflow values across all events. During

storms, the decline in SO_4^{2-} concentrations started on the rising limb of the hydrograph and reached a minimum at or near peak streamflow discharge (Figs. 5, 6, 7). The decline in SO_4^{2-} concentrations coincided with the rise in throughfall contributions and the minimum in SO_4^{2-} concentrations occurred when throughfall contributions were at their peak. This temporal pattern and the low concentrations of SO_4^{2-} in throughfall clearly indicate that groundwater SO_4^{2-} concentrations were diluted by atmospheric water (throughfall and precipitation) during storm events. The temporal match between SO_4^{2-} and Mg^{2+} concentrations and the simultaneous contrast with DOC values further confirm this assessment. Magnesium concentrations in streamflow at Point Peter Brook were primarily derived from groundwater sources while DOC concentrations were regulated by contributions from throughfall, litter leachate, and riparian water (Inamdar and Mitchell 2006, 2007b).

An inverse relationship between SO_4^{2-} and streamflow discharge was observed for all catchments. These inverse relationships contrast with strong positive C–Q relationships reported elsewhere (Huntington et al. 1994; Shanley and Peters 1993; Wigington et al. 1990). Huntington et al. (1994) and Shanley and Peters (1993) found high SO_4^{2-} in surface soil waters and low concentrations in groundwater for a watershed in Georgia, USA, and attributed the positive C–Q relationship to the flushing of SO_4^{2-} from surface soil horizons during periods of elevated wetness and discharge. Furthermore, they also found that increasing SO_4^{2-} concentrations were accompanied with decreasing concentrations of base cations (alkalinity) – a direct contrast with our observations for Point Peter Brook. The inverse relationships and the strong correspondence of SO_4^{2-} with Mg^{2+} clearly suggest SO_4^{2-} dynamics in Point Peter Brook was controlled by subsurface and not near-surface sources of SO_4^{2-} .

Although the dilution of SO_4^{2-} was observed across all events, the decline in SO_4^{2-} concentrations was not very pronounced during the initial portion of the event of August 30, 2005 (especially for catchment S1, Fig. 8). Antecedent moisture conditions for the event of August 30, 2005 were the lowest during the entire three-year (2003–2005) monitoring period (note API and AGI values in Table 2). Sulfate exports and concentrations in streamflow have been observed to increase following extended dry periods or summer droughts (Devito and Hill 1997; Eimers and Dillon

2002; Mitchell et al. 2006). The increase in SO_4^{2-} concentrations has been attributed to the flushing excess SO_4^{2-} generated by oxidation of previously-reduced SO_4^{2-} from wetlands and/or the release of SO_4^{2-} from organic matter due to mineralization. Mitchell et al. (2006) found that SO_4^{2-} concentrations increased continuously for a series of four storms as the catchment wetted-up following an extremely dry summer period. It is possible that the initial response for the event of August 30, 2005 at Point Peter Brook could have been associated with oxidation of SO_4^{2-} over the antecedent dry period and subsequent export of this excess SO_4^{2-} at the start of the event.

Influence of watershed SO_4^{2-} sources on stream concentrations

EMMA identified throughfall, seep, and riparian groundwaters as the potential end members for stream chemistry at Point Peter Brook (Inamdar and Mitchell 2006). Sulfate concentrations for riparian and seep groundwaters were high while those in throughfall were low. A comparison of EMMA-predicted and observed SO_4^{2-} concentrations indicated that four of the six events produced good fits. Previous comparisons of EMMA have provided mixed results. Devito and Hill (1997) were unsuccessful in predicting SO_4^{2-} concentrations for wetland catchments due to the large variation in concentrations resulting from the reactive behavior of SO_4^{2-} within the wetlands. In contrast, Steele and Buttle (1994), were successful in explaining the exports of SO_4^{2-} from a 2.4 ha wetland catchment during a snowmelt event. We hypothesize that the fits for Point Peter Brook were good because the influence of the reactive processes on SO_4^{2-} concentrations was small for the storm events or the strong groundwater SO_4^{2-} signal at Point Peter Brook overwhelmed any likely variations introduced by the reactive processes.

Sulfate concentrations and exports from catchments with varying extent of wetlands and riparian areas

Concentrations of SO_4^{2-} in wetland water (well located within catchment S5) were considerably lower (Fig. 2) than riparian water values (wells located in catchment S2) even though the corresponding values of Mg^{2+} and Si for these locations were not that different. Considering the large difference in wetland

and riparian water SO_4^{2-} concentrations, the stream-flow SO_4^{2-} concentrations for catchment S5 were only slightly lower than S2 and S3 (Fig. 2). We attribute this to the transport of seep groundwaters (which had high SO_4^{2-} concentrations) over the wetland substrate in S5 with limited mixing with the wetland waters (Inamdar and Mitchell 2006, 2007a). A number of previous studies have shown that wetlands reduce the concentrations of SO_4^{2-} through the reduction of SO_4^{2-} to sulfides under anaerobic conditions (Lazerte 1993; Devito and Hill 1997; Eimers and Dillon 2002; Warren et al. 2001). The work of Devito and Hill (1997) however, showed that groundwater elevations and hydrologic connectedness of wetlands was as a critical factor. Wetlands with large variation in ground water elevations alternated between sinks and sources of SO_4^{2-} while wetlands which were saturated year-round retained most of the SO_4^{2-} input (Devito and Hill 1997). Groundwater elevations in the S5 catchment in Point Peter Brook were close to the surface all year round (Table 2) and thus likely provided a continuous, stable, reducing environment for removal of SO_4^{2-} from wetland groundwater.

Sulfate concentrations for the largest (696 ha) catchment S1 were much greater and more variable than the smaller catchments (especially S2 and S3). Higher concentrations of SO_4^{2-} at S1 can be attributed to three possibilities – (a) a greater proportion of deeper groundwater contributions; (b) release of SO_4^{2-} via oxidation of previously reduced sulfides from valley-bottom riparian areas contained within S1; and/or (c) an unidentified source. We believe it is some combination of all of these three possibilities. The difference in concentrations of Mg^{2+} and Si among the catchments (Fig. 4) does suggest a slightly greater proportion of deeper groundwaters at S1; however, it is unlikely that deep groundwaters alone can explain the large difference in SO_4^{2-} concentrations. It is likely some contributions of SO_4^{2-} occurred from valley-bottom riparian areas which were subject to greater water level fluctuations than the wetlands. We also recognize that the intensive sampling performed in this study was limited to small portion of the large S1 catchment and it is possible that the sampling scheme did not capture the full range of SO_4^{2-} concentrations that influenced the outflow at S1. The differences in riparian well concentrations over a small distance (e.g., Fig. 3, wells RS1 versus RS2) highlight the variability in SO_4^{2-} values for this watershed.

Atmospheric deposition and watershed exports of SO_4^{2-}

The Point Peter Brook watershed is subject to one of the highest rates of atmospheric deposition of SO_4^{2-} in the continental US (NADP 2006). The two-year (2003–2004) average annual wet (SO_4^{2-}) deposition recorded at the nearest NADP station in Chautauqua, NY amounted to 520 mol ha⁻¹ (NADP 2006). Since no dry deposition was recorded at the NADP site, an estimate of potential dry deposition was determined from the nearest USEPA Clean Air Status and Trends Network (CASTNET) site – M.K. Goddard in Mercer County Pennsylvania, 170 km southwest of Point Peter Brook watershed (USEPA 2007). Data (2003–2004) from the CASTNET site indicated that annual dry S deposition (SO_4^{2-} plus SO_2) was on average 76% of the wet SO_4^{2-} input. Inamdar et al. (2006) estimated the annual export of SO_4^{2-} from catchment S1 at about 5130 mol ha⁻¹, of which 20% occurred during storm events and the remainder 80% during non-storm periods. A comparison of annual wet SO_4^{2-} input (520 mol ha⁻¹) and the corresponding export from S1 (5,130 mol ha⁻¹) indicates an annual net loss of SO_4^{2-} of 886% from the Point Peter Brook watershed. Even if all of the dry S deposition is assumed to be immediately available as SO_4^{2-} ($1.76 \times 520 = 915$ mol ha⁻¹), the net loss of SO_4^{2-} still amounts to 460%. This comparison highlights the importance of internal (geologic) sources in the exports of SO_4^{2-} from the Point Peter Brook watershed. Hornbeck et al. (1997) reported net annual losses of 47%, 72% and 138% for Hubbard Brook (NH), Cone Pond (NH), and Sleepers River (VT) watersheds, respectively. Warren et al. (2001) reported monthly exports of SO_4^{2-} as high as 614% for a swamp in a glaciated catchment in Hamilton, ON, Canada. In contrast, watersheds in the southeast US (Huntington et al. 1994) indicate a net SO_4^{2-} retention of 6 to 35%. Clearly, the impacts of decreasing atmospheric deposition will have very different implications for these watersheds with differing geology and climate conditions.

Conclusions

Concentrations and fluxes measured in this study indicate that SO_4^{2-} exports from the Point Peter Brook

watershed were regulated primarily by geologic (groundwater) sources and atmospheric inputs had little influence on the watershed SO_4^{2-} budgets. These results highlight the importance of internal geological sources and suggest that watersheds like Point Peter Brook may respond very slowly to decreases in atmospheric SO_4^{2-} deposition.

This study also indicated that while geologic sources had a dominant influence on SO_4^{2-} concentrations in Point Peter Brook, the valley-bottom riparian areas and wetlands likely played a role in modifying these concentrations through redox processes. This study suggests that wetlands that are saturated year-round may depress the SO_4^{2-} concentrations while riparian areas subject to greater fluctuations in water level may yield a wider range in SO_4^{2-} concentrations.

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