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Climate effects on sulphate flux from forested catchments in south-central Ontario

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Abstract. Net export of sulphate from watersheds may delay the response of surface waters to changes in acid deposition. Long-term (18-yr) sulphate budgets were calculated for 8 headwater streams located in the acid-sensitive region of Muskoka-Haliburton, south central Ontario. Sulphate deposition in this region has decreased by almost 40% over the last 2 decades, and sulphate export from catchments has also generally declined over time, but most catchments are still a net source of sulphate to drainage streams. Net export of sulphate occurred in the majority of catchments in most years of record, but was particularly large following dry, warmer than average summers, when stream flow ceased for up to several weeks at a time. In years with warm dry summers, such as occurred in 1983/84 and between 1987/88 and 1990/91, inclusive, stream export from most catchments was between 1.5 and 2 times greater than was input via bulk deposition. Annual average sulphate concentrations in streams were strongly correlated with stream dryness, and were greater in years in which streams were dry for longer periods of time. Temporal patterns of annual sulphate concentrations and export were highly coherent among the 8 streams, and net sulphate export occurred in both wetland-draining and predominantly upland streams. Climate variables, specifically temperature and precipitation act on a regional scale and are likely responsible for similar temporal patterns of sulphate retention among these 8 physiographically different catchments. Net sulphate export from catchments may delay the recovery of acid impacted surface waters, despite reductions in industrial SO_2 emissions.

Introduction

Sulphur (S) loadings in eastern North America have decreased substantially over the past 2 decades in response to SO_2 emission reductions (Clair et al. 1995; Dillon et al. 1997; Stoddard et al. 1999). While sulphate levels in many lakes and streams have also declined, the magnitude and rate of decline were considerably less than anticipated from atmospheric deposition (Jeffries et al. 1995; Driscoll et al. 1995); and decreases in sulphate concentration have not consistently resulted in improvements in pH and alkalinity in surface waters (e.g., Clair et al. (1995); McNicol et al. (1998); Stoddard et al. (1999); Dillon and Evans (2000)).

Retention of deposited sulphate within the terrestrial catchment can modify the effect of acid deposition on surface waters, and may explain why some surface waters have shown a delayed, or only a modest response to changes in acid deposition. Sulphate retention in forested catchments may occur through vegetation uptake or microbial immobilization, or through adsorption to the soil matrix or precipitation as Al-sulfate minerals. These processes collectively regulate sulphate leaching or export *via* streamflow, which in turn regulates the flux of basic and acidic cations from forest ecosystems to surface waters. Loss of base cations, particularly Ca^{2+} and Mg^{2+} from upland soils (Fuller et al. 1985), also has important implications for soil fertility and long-term forest health (Likens et al. 1998).

Mass balance measurements from a number of long-term studies of whole catchments have indicated a net imbalance between sulphur inputs and exports (e.g., Mitchell et al. (1996a); Houle et al. (1997); Driscoll et al. (1998); Alewell et al. (1999)), such that many catchments are currently acting as a S source to drainage waters. A number of sources may account for this additional S output, including desorption from soils of sulphate that had been adsorbed when anthropogenic deposition was higher (Mitchell et al. 1996a; Driscoll et al. 1995), weathering of S-containing minerals (Baron et al. 1995), mineralization of S in soil organic matter (Driscoll et al. 1998), underestimation of dry deposition (Likens et al. 1990; Edwards et al. 1999), and drought-related oxidation and release of S stored in wetlands (Dillon and LaZerte 1992; Dillon et al. 1997). Identification of the sources of S contributing to export is necessary for the prediction of ecosystem response to changes in sulphate deposition. The wide variety of explanations suggested previously would suggest that sources of S export are catchment-specific; however, the potential for regional trends or patterns to exist in sulphate export and retention should also be considered (Driscoll et al. 1998).

One factor that acts on a regional scale, and has been shown to affect sulphur cycling in catchments, is climate. For example, drought effects on S-export from wetlands have been reported (Bayley et al. 1986; Van Dam 1988; Devito and Hill 1999), and increases in lake-sulphate concentrations have been found following drought-related exposure and mineralization of S-stored in the littoral sediment of contaminated lakes (Keller et al. 1992; Yan et al. 1996; Dillon and Evans 2000). Drought may also influence lake chemistry by disconnecting lakes from sources of solute inputs, such as groundwater (Webster and Brezonik 1995; Carvalho and Moss 1999).

Long-term measurements in small catchments are particularly useful for evaluating changes in the biogeochemical cycling of elements (e.g., Mitchell et al. (1996b)). A number of catchments located in the acid-sensitive region of Muskoka-Haliburton in south central Ontario have been studied since the mid-1970's. This region has been subject to high rates of S deposition for decades (Dillon et al. 1988), and has many lakes that have been acidified to the extent that biological damage is evident (Dillon et al. 1987). Sulphate concentration and alkalinity in many of the lakes in this region have not responded as expected to recent decreases in sulphate deposition (Jeffries et al. 1995; Dillon and Evans 2000) which suggests that S export from catchments may be retarding their recovery.

In this paper, we have compared sulphate export patterns among 8 physiographically distinct catchments located within a ~30-km radius of the Dorset Environmental Science Centre (DESC). Trends in sulphate export over time were compared among catchments in order to determine whether regional patterns in sulphate re-

Table 1. Description of the eight study catchments (From Jeffries and Snyder (1983); Dillon et al. (1997)). Shallow surficial deposits (glacial till + soil) are < 1 m in depth, deep surficial deposits are > 1 m depth.

Catchment	Area (ha)	Grade (%)	% organic	% shallow surficial deposits	% deep surficial deposits
Red Chalk 1	134	1	5	41	54
Blue Chalk 1	20	7	0	6	94
Plastic 1	23	6	13	76	11
Harp 6	10	8	0	55	45
Harp 6-A	15	10	9	85	6
Harp 4	119	5	5	39	56
Dickie 6	22	2	22	78	0
Dickie 5	30	1	25	75	0

tention exist and to identify some of the factors contributing to sulphate loss from catchments. Sulphate retention is defined here as the fraction of sulphate input to the catchment that was retained and not lost *via* stream discharge in a given year. In addition, we compared sulphate retention in individual catchments over time to determine whether sulphate export was greater than input in certain years and to identify potential relationships with climate.

Methods

Study site

Sulphate budgets were calculated using stream chemistry for 8 headwater catchments (Table 1) draining into 5 lakes, from 1980/81 (June 1 to May 31 hydrologic year) through 1993/1994 (Blue Chalk 1, BC1), or from 1980/81 through 1997/1998 (Dickie 5, DE5; Dickie 6, DE6; Harp 4, HP4; Harp 6, HP6; Harp 6A, HP6-A, Plastic 1, PC1; and Red Chalk 1, RC1). All 8 streams are located in the District of Muskoka or County of Haliburton, south central Ontario, Canada. This region is situated in the southern portion of the Boreal ecozone, and the climate is described as humid continental with long cool summers (Dfb), according to the Köppen Climatic Classification System (Ahrens 1991). Total annual precipitation over the 18-year study period ranged from 786 mm (1997/98) to 1213 mm (1982/83), with approximately 30% falling as snow. The average July and December temperatures are 18.4 and −11 °C, respectively, and the mean annual temperature over the 18-year period was 5.0 °C (range 3.5–6.4).

Catchments range in size from 10 ha (HP6) to 133.6 ha (RC1), and are either entirely upland (BC1, RC1, HP6), or have significant wetland coverage (e.g., DE5, DE6) as reflected by the proportion of organic soil in the catchment (Table 1). Average glacial till depths in the 8 catchments range from less than 1 m (DE5, DE6, PC1) to more than 1 m (HP4, BC1). Dominant soils types in the area are acidic brunisols and podzols that have formed on non-carbonate, generally coarse-grained glacial till, with moderate to well-drained slopes (Jeffries and Snyder 1983). Organic soils (including gleysols) are the dominant soil type in poorly drained regions, such as the stream riparian zone and bedrock depressions. All streams flow through forested (mainly coniferous or mixed hardwood) catchments, with no agricultural development, although some lakes (i.e. Dickie and Harp) have large cottage (seasonal and permanent) populations.

Chemical sampling and analysis

Stream samples were collected approximately weekly, or every other week between 1980 and 1998, although samples were collected more frequently during periods of high discharge. All samples were filtered (80-μm Nitex mesh) into pre-rinsed bottles, and transported to the laboratory in temperature-controlled containers. Water samples were analyzed for sulphate by ion chromatography (Ontario Ministry of Environment 1983). Although the majority of S in natural well-mixed (oxygenated) surface and soil waters is in the form of inorganic sulphate (SO_4^{2-}), organo-sulphur compounds may be important in some highly organic streams. In order to address this issue, water samples from all 8 streams were analyzed for both inorganic sulphate (ion chromatography) and total (i.e. inorganic + organic) sulphur (UV-irradiation) over an 11-month period beginning in March 1990. Following a method used for the determination of total dissolved nitrogen in water (Henriksen 1970), total sulphur in samples was photo-oxidized to inorganic sulphate using a Hg-vapour lamp and peroxide catalyst, and sulphate was then analyzed by ion-chromatography (IC). The precision of the IC for the sulphate ion was 1.0 μeq/l.

Hydrology

Stream stage was continuously monitored at a V-notched weir or flume located at the base of each catchment using Leopold Stevens A-71 water level recorders. Stage was converted to flow using established stage-discharge relationships derived for each stream (Scheider et al. 1983). Sulphate fluxes were calculated using integrated daily estimates of discharge and concentration values, and were summed for each hydrologic year (June 1–May 31). Export (flux per unit area) was calculated from the annual data.

Meteorological data

Temperature (°C) and precipitation (mm) were measured at 4 meteorological stations located within a 30 km radius of the Dorset Environmental Science Centre (DESC), and were used to obtain regional estimates of seasonal and annual precipitation and temperature. Average sulphate deposition (meq/m^2) to the region was calculated using sulphate concentrations measured at 4 (1980–1995) or 3 (1995–

1998) bulk deposition collectors located at the meteorological stations. Details on methods and instrumentation used for the collection of bulk deposition are given in Scheider et al. (1979). Although bulk collectors may underestimate total sulphate deposition in some regions (e.g., Likens et al. (1990); Edwards et al. (1999); Novak et al. (1996)), bulk deposition collectors are generally suitable in areas remote from point sources. Furthermore, comparisons of wet-only, and bulk sulphate deposition in the Muskoka-Haliburton area, indicated that wet sulphate deposition measurements were approximately 15–20% less than bulk estimates, a difference that was similar to dry deposition estimates from modelling calculations (Dillon et al. 1988). Therefore, for the purpose of this analysis we assume that sulphate deposition measured in collections of bulk deposition adequately represents total (i.e. wet + dry) sulphate deposition.

Statistical comparisons among streams

The degree of similarity in year-to-year patterns among streams (synchrony or coherence) was quantified as the Pearson product-moment correlation coefficient (r), with observations paired by year (Webster et al. 2000). Sulphate retention, or the fraction of sulphate input to the catchment that was retained and not lost *via* stream discharge in a given year was calculated as input in bulk deposition (meq/m^2/yr) minus stream export (meq/m^2/yr), expressed as a fraction of input. Pearson correlation and linear regression analyses were used to compare annual sulphate export and mean concentrations (volume-weighted) among streams, and to investigate relationships with climate (temperature, precipitation) and hydrologic variables (zero-streamflow). In addition, annual sulphate export and stream sulphate concentration were standardized using Z-scores (annual observation minus the 18-year mean, all divided by the standard deviation) in order to facilitate comparisons among the 8 streams. In order to determine whether organo-sulphur compounds contributed to net sulphur export in streams, inorganic sulphate and total-S concentrations measured in each stream over an 11-month period were compared using a paired 2-sample t-test for means. Differences between means at $p < 0.05$ were considered significant.

Results

Atmospheric deposition

Bulk sulphate deposition in the Muskoka-Haliburton region decreased substantially between 1976/77 and 1997/98, although the greatest decrease in deposition occurred at the beginning of the monitoring period, between 1976/77 and 1983/84, and since then deposition has declined more gradually (Figure 1). For example, after 1993 sulphate deposition to the area has been relatively constant (between 40

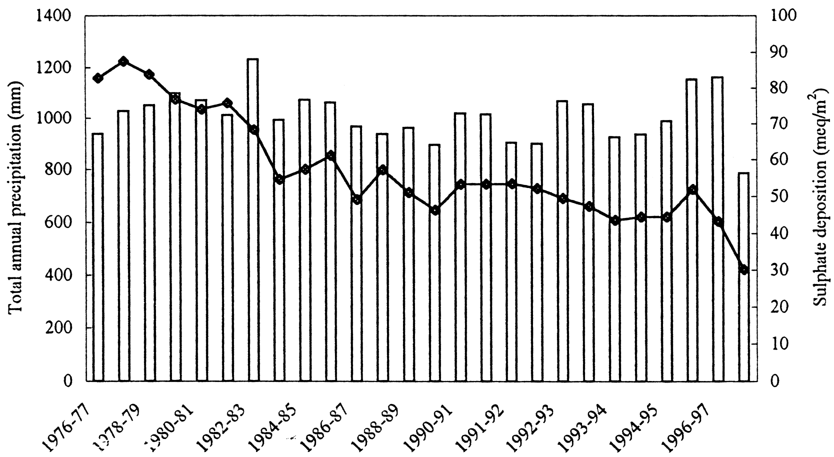

Figure 1. Total annual precipitation (bars) and sulphate deposition (line) in each hydrologic year (June 1– May 31) between 1976–77 and 1997–98.

and 50 meq/m^2/yr). Extremely low deposition measured in 1997/98 (~ 30 meq/m^2) is a result of unusually low precipitation (786 mm) in that year (Figure 1).

Sulphate concentration patterns in streams

Sulphate concentration in streams was extremely variable between years (Figure 2), and did not appear to follow changes in bulk deposition (Figure 1). Although sulphate deposition varied between years, the magnitude of difference in deposition between years was less than year-to-year differences in stream sulphate-concentrations. For example, between 1986/87 and 1987/88, the average sulphate concentration in HP6-A increased from 118 μeq/l to 266 μeq/l – a difference of 125%. Between the same two years, sulphate deposition to the region increased from 49 meq/m^2 to 57 meq/m^2 – a difference of 16%. Sulphate concentrations in streams (Figure 2) were always higher than in bulk deposition, which ranged between 75 μeq/l in 1981/82 and 37 μeq/l in 1996/97.

Although streams differed in their annual average sulphate concentrations, patterns in sulphate concentration among streams were remarkably synchronous over the 18-year study period (Table 2), considering their differences in catchment physiography (Table 1). For example, year-to-year changes in stream sulphate concentration were highly correlated (r = 0.91, $p < 0.05$) in BC1 and HP6-A, which drain an upland catchment with thick till deposits and a conifer wetland, respectively.

There was a tendency for sulphate concentrations in streams to decline over the study period, although large peaks in concentration were observed in certain years. For example, peaks in sulphate concentration in the majority of streams occurred in 1983/84 and 1987/88, whereas the lowest mean sulphate concentrations occurred in 1986/87 (Figure 2). The general decline in sulphate concentration, which occurred in all streams between 1983/84 and 1986/87 was reversed in 1987/88, when

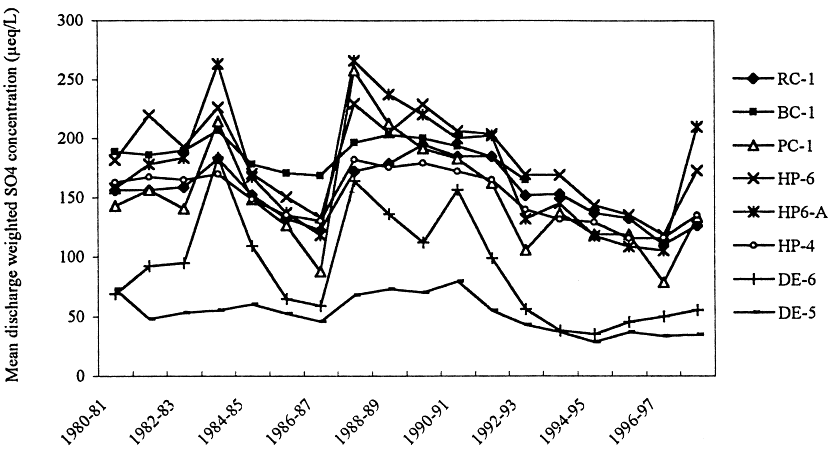

Figure 2. Mean annual discharge weighted sulphate concentration in each of the 8 study streams: 1980–81 through 1997–98.

Table 2. Correlation coefficients (r) for the relationship in annual mean volume weighted sulphate concentration in the 8 study streams. Correlations marked with an asterisk are significant at $p < 0.05$.

	RC1	BC1	PC1	HP6	HP6A	HP4	DE6
BC1	*0.81						
PC1	*0.75	*0.86					
HP6	*0.87	*0.85	*0.85				
HP6-A	*0.81	*0.91	*0.97	*0.88			
HP4	*0.87	*0.91	*0.87	*0.94	*0.88		
DE6	*0.71	*0.82	*0.89	*0.74	*0.91	*0.74	
DE5	*0.60	*0.66	*0.62	0.45	0.51	*0.66	0.54

concentrations rose to levels that were in some cases more than double the previous year (e.g., PC1, HP6-A, DE6). Sulphate concentrations in most streams declined steadily between 1987/88 and 1996/97, but in 1997/98 sulphate levels in many streams increased once more (Figure 2). For example, in HP6-A the mean volume-weighted sulphate concentration in 1997/98 was 210 μeq/l compared with 105 μeq/l in 1996/97. Sulphate concentrations in DE5 (range 30–80 μeq/l) were always lower than the other 7 streams (range 35–265 μeq/l), and year-to-year changes were less pronounced. However, when sulphate concentrations were standardized among streams (Z-scores), the temporal pattern in sulphate concentration in DE5 was similar to the other streams (Figure 3).

Total (UV-digested) and inorganic sulphate concentrations were measured concurrently in each stream between March 1990 and January 1991 in order to determine the importance of organic-S export. Average concentrations of total-S in DE5, DE6, RC1 and HP6-A were significantly greater than the level of inorganic sulphate (Table 3). While the difference between total-S and sulphate concentrations

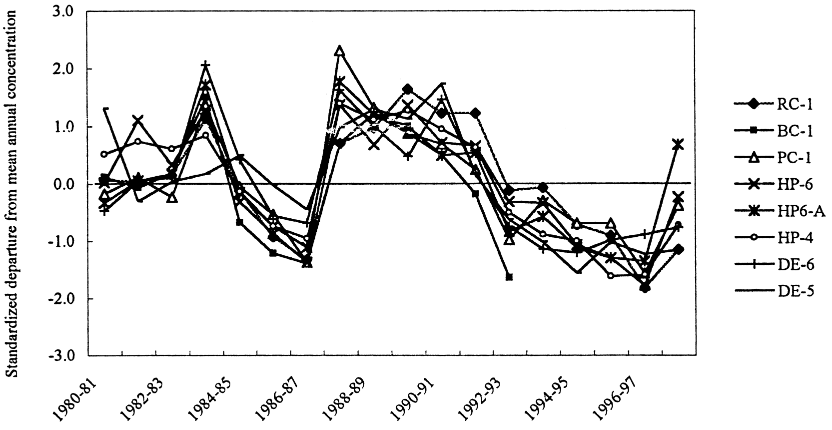

Figure 3. Annual sulphate concentration expressed as a Z-score (annual observation minus the 20-year mean, all divided by the standard deviation) in each of the 8 study streams.

Table 3. Comparison of total sulphur (UV-digestible) and inorganic sulphate concentrations in the 8 study streams. Values are mean ± SD. Values marked with asterisks are significantly different at $p < 0.05$.

Stream	n	t-statistic	Total (UV) sulphur (mmol/l)	Sulphate (mmol/l)
BC1	28	1.28	0.106 ± 0.018	0.104 ± 0.017
RC1*	32	3.43	0.098 ± 0.028*	0.094 ± 0.028*
PC1	74	-0.91	0.098 ± 0.051	0.099 ± 0.047
HP4	86	0.97	0.088 ± 0.002	0.088 ± 0.002
HP6	38	1.04	0.109 ± 0.035	0.116 ± 0.051
HP6-A*	32	-2.07	0.114 ± 0.058*	0.110 ± 0.054*
DE5*	36	4.84	0.033 ± 0.020*	0.027 ± 0.018*
DE6*	82	5.53	0.086 ± 0.084*	0.075 ± 0.081*

was minor (< 5%) in RC1 and HP6-A, organo-sulphur export may account for as much as 15% (DE6) to 23% (DE5) of total S export in the Dickie streams. Greater export of S in organic forms may also account for the generally poorer relationships observed between sulphate concentrations in DE5 and DE6 and the 6 remaining streams (Table 2).

Sulphate export

Changes in stream sulphate concentration were reflected in changes in catchment export. A high degree of synchrony was observed in year-to-year patterns of sulphate export in many of the streams (Table 4), although patterns were generally less clear (Figure 4) as export is also a function of streamflow, which varies considerably from year-to-year. Again, when sulphate export is standardized among streams the similarity in their patterns becomes clear (Figure 5). All 8 catchments

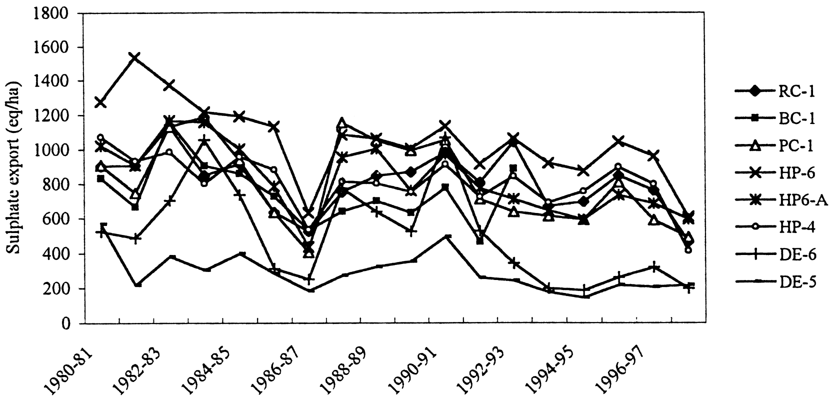

Figure 4. Mean annual sulphate export from each of the 8 study catchments: 1980–81 through 1997–98.

Table 4. Correlation coefficients (r) for the relationship in sulphate export among the 8 study catchments. Correlations marked with an asterisk are significant at $p < 0.05$.

	RC1	BC1	PC1	HP6	HP6-A	HP4	DE6
BC1	*0.83						
PC1	*0.68	0.60					
HP6	*0.79	0.55	0.46				
HP6-A	*0.85	*0.77	*0.91	*0.73			
HP4	*0.75	0.62	0.43	*0.84	*0.71		
DE6	0.54	0.52	*0.91	0.36	*0.80	0.24	
DE5	0.54	0.56	0.40	0.36	0.56	*0.76	0.23

exhibited minimum sulphate export values in 1986/87 and 1997/98, which were generally more than 1 standard deviation less than average (Figure 5). In contrast, sulphate export in 1987/88 was substantially greater, and was in some cases more than double the previous year. For example, sulphate export in PC1 increased from 40 meq/m^2 in 1986/87 to 120 meq/m^2 in 1987/88 (Figure 4).

Although stream export of sulphate was quite variable over time, in most years sulphate export from catchments exceeded input *via* bulk deposition. Sulphate retention (defined as input from the atmosphere minus stream export expressed as a proportion of input) in most catchments was therefore negative or near zero (Figure 6). For example, in 1983/84 and between 1987/88 and 1990/91, sulphate retention in most catchments was between −0.5 and −1.0 (Figure 6), indicating that catchments exported between 1.5 and 2 times more sulphate than was input *via* bulk deposition. Only in the DE5 catchment, and occasionally DE6, was sulphate export continually less than input, and there was net retention within the catchment. However, export of sulphur in organic forms was not included in budget calculations because total S concentrations in streams were only measured over an 11-month period. In the majority of the long-term monitored streams in this region,

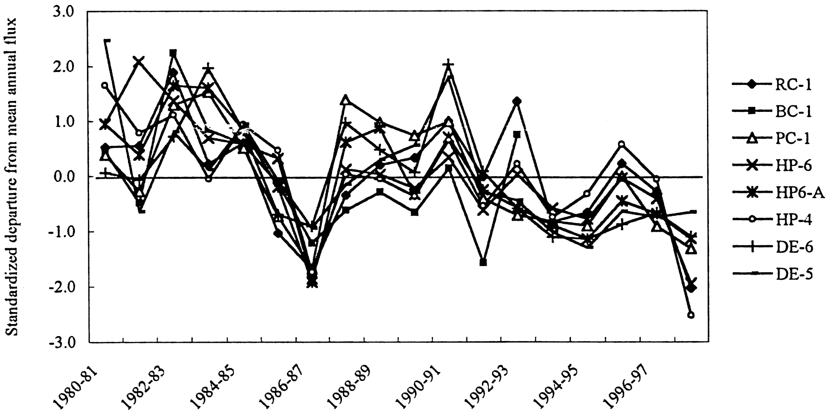

Figure 5. Annual sulphate export expressed as a Z-score (annual observation minus the 20-year mean, all divided by the standard deviation) in each of the 8 study catchments.

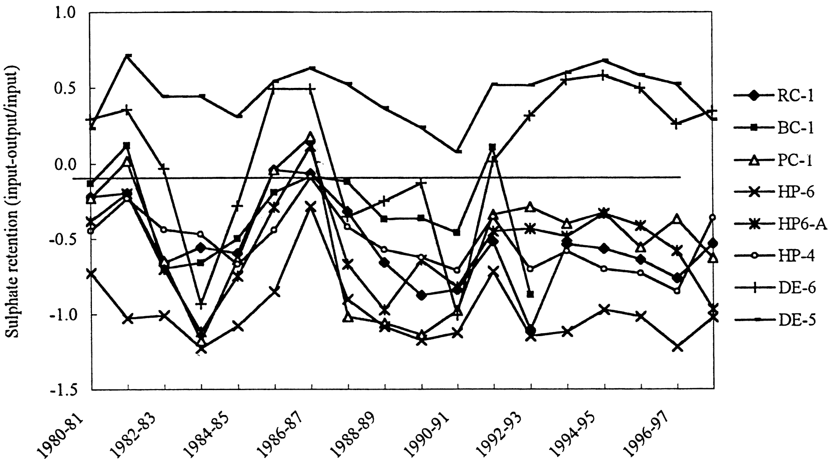

Figure 6. Annual sulphate retention in the 8 study catchments. Sulphate retention is defined as the proportion of sulphate input to the catchment in deposition that is not exported via streamflow.

inorganic sulphate is the dominant form of S export (Dillon, unpublished), and so measurement of sulphate concentrations in streams is adequate for determining S-export from most catchments. However, measurement of total-S concentrations may be necessary in order to approximate the magnitude of S flux in high DOC streams that drain wetland-dominated catchments such as DE5 and DE6.

Climate effects

The potential relationship between climate (precipitation and temperature) and sulphate flux from catchments was explored using linear regression analysis. The best predictors of annual sulphate concentrations in streams were summer (Jun-Aug) precipitation and temperature (Table 5). Correlations were not very strong for some streams; however, this is likely partly a function of comparing annual average sulphate concentrations with precipitation and temperature averages for a 3-month period. Catchments generally exhibited greater net sulphate export, or more negative retention (Figure 6) in years having summers that were drier and warmer than average (18-year mean) (Figure 7). Streamflow, however, is a better indicator of dry conditions in catchments than either precipitation or temperature. Due to the predominantly thin till which dominates most of the catchments (Table 1), the majority of streams cease to flow for variable lengths of time during the summer months when conditions are generally warmer and drier than other months (Figure 8). Of the 8 catchments considered in this study, streamflow is only continuous year-round in HP4, which has significant glacial till deposits that maintain elevated groundwater levels adjacent to the stream (Hinton et al. 1993). The other 7 streams tended to be dry (zero discharge) for a greater number of days in years with warmer, and drier than average summers (Figures 7 and 8). Correlation coefficients between zero-streamflow and sulphate concentration in these 7 streams ranged from r = 0.69 (DE5) to r = 0.87 (PC1) (all at $p < 0.05$). For example in the PC1 and HP6-A catchments, standardized average sulphate concentrations and zero-streamflow followed very similar patterns over time (Figure 9). In contrast, there was no significant relationship between zero discharge and sulphate concentration in HP4 (r = 0.13, $p > 0.05$) because groundwater connections maintain continuous baseflow in this stream (Hinton et al. 1993). Nevertheless, it is likely that dry conditions similar to the other catchments existed in much of the HP4 catchment in 1983/84 and from 1987/88 through 1990/91, and temporal patterns of sulphate concentration were similar in HP4 compared to the other streams (Table 2).

Discussion

Patterns in stream chemistry

The fact that all 8 streams exhibited similar patterns in both sulphate concentration and export, despite their physiographic differences, suggests that large-scale, or basin-wide processes such as climate are involved. Although specific regions may be characterized as having a particular climate type (e.g., Köppen Climatic Classification System) based on their long-term patterns in average temperature and precipitation, climate over the short-term (year-to-year) may be very variable. For example, El Niño events occur with a frequency of approximately 4 to 7 years, and can significantly affect global precipitation and temperature (see Philander (1990)). Four of the strongest El Niño events since 1900 occurred during the monitoring period (1982/83, 1986/87, 1991/92 and 1997/98). In our study area, summers following El Niño events generally had lower than average precipitation, and temperatures that were higher than average, which often results in complete cessation of stream flow. The summer of 1992/93 did not follow this pattern, however, pos-

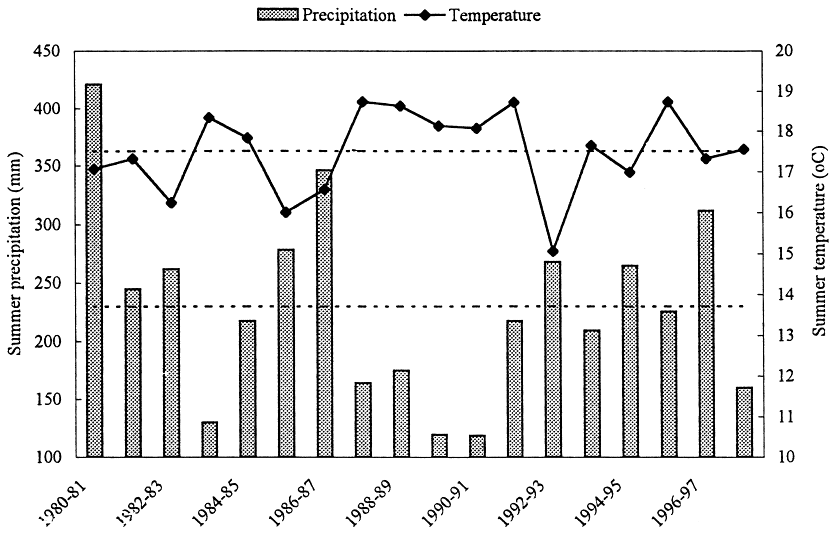

Figure 7. Total summer (June–August) precipitation and mean summer temperature in the Dorset region: 1980–81 through 1997–98. Dashed lines represent the 18-year average summer precipitation and temperature, respectively.

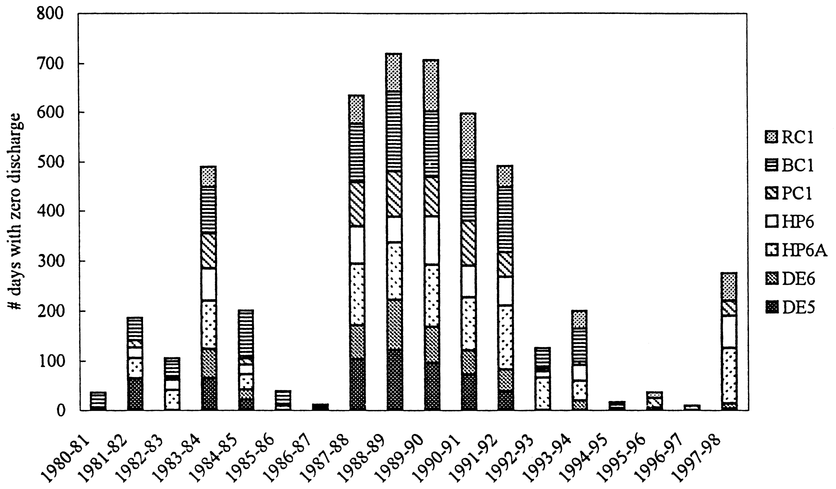

Figure 8. Total number of days with zero discharge for each of the 7 study streams that exhibit variable flow during warm, dry summers. HP4 flows continuously.

sibly due to the eruption of Mount Pinatubo in the Philippines in June 1991, which had globe-wide effects on climate (Hansen et al. 1996). Dry conditions persisted between 1987 and 1990, as both total annual and summer precipitation depths (892–949 mm, and 119–175 mm, respectively) in each of these 4 years were below the 18-year averages (1015 and 230 mm, respectively). Drought conditions during this period were also reported in England (Wilby 1994), Europe (Van Dam 1988)

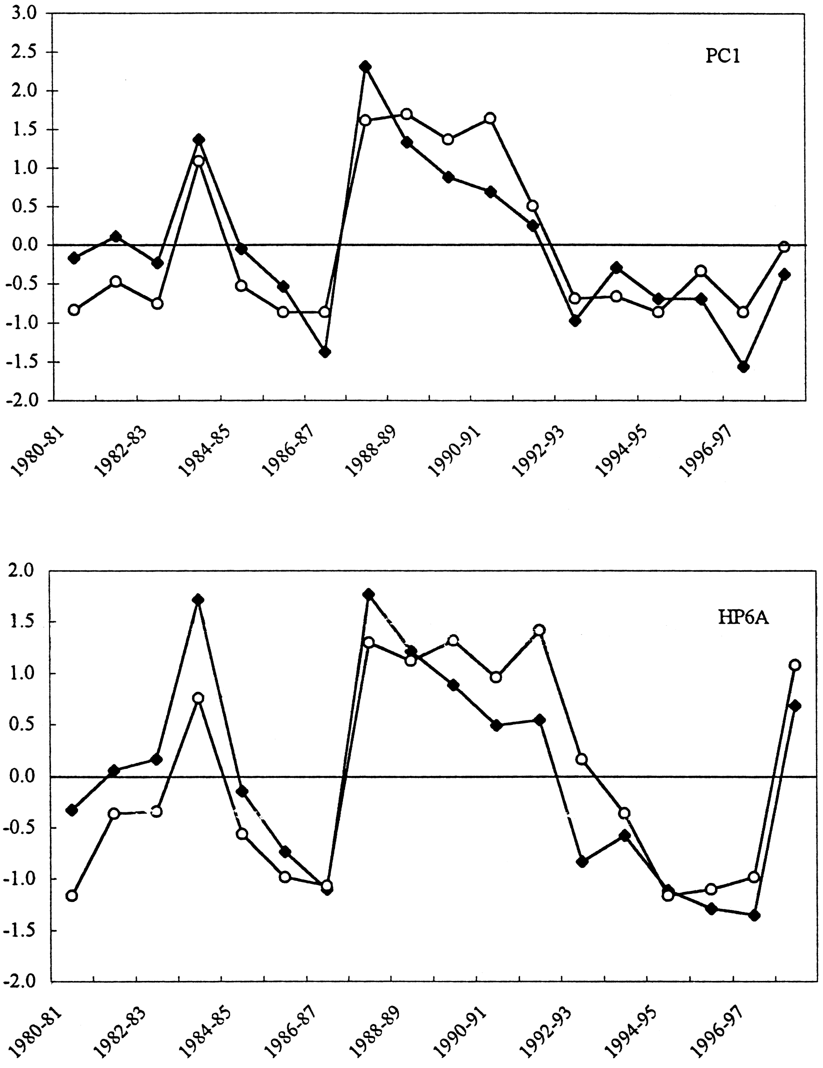

Figure 9. Z-scores of mean annual sulphate concentration (closed diamonds), and number of days with zero-discharge (open circles) for PC1 (r = 0.87, $p < 0.05$) and HP6-A (r = 0.85, $p < 0.05$).

and much of the northeastern United States (Webster et al. 2000), and were related to changes in surface water chemistry. For example, Wilby (1994) reported a substantial increase in surface water acidity between 1988 and 1990, a period which was ranked as having the 3rd most severe drought since records began in 1698. They further noted that a major effect of the extreme climate experienced during this period was an enhancement of the existing hydrologic regime, such that summer low- and zero-flow periods were extended (Wilby 1994).

Table 5. Correlation coefficients (r) for the relationship between mean annual volume weighted sulphate concentration in each of the 8 study streams and average summer (June–August) precipitation and temperature. Correlations marked with an asterisk are significant at $p < 0.05$.

	RC-1	BC-1	PC-1	HP-6	HP6-A	HP-4	DE-6	DE-5
Precipitation	-0.60^{*}	-0.62^{*}	-0.66^{*}	-0.60^{*}	-0.69^{*}	–0.45	-0.61^{*}	–0.26
Temperature	0.47^{*}	0.76^{*}	0.63^{*}	0.42	0.55^{*}	0.37	0.51^{*}	0.33

In the Muskoka Haliburton region, sulphate concentrations in all streams were higher than average in years with dry, warm summers (e.g., 1987/99 through 1990/91). Increases in sulphate concentration (Figure 3) were translated into substantial increases in sulphate export (Figure 5), and were therefore not simply a product of lower flow volumes during dry years. Average sulphate concentration in streams and catchment export of sulphate were as much as 2-times greater in years having warm, dry summers. Although most catchments exhibited net sulphate export throughout the monitoring period, net losses were particularly large following drought events, and represent a substantial increase in S-export to downstream lakes.

Wetlands (swamps, beaver ponds) are a common landscape feature in this region, and depending on their location within the catchment, may significantly affect the S-chemistry of drainage streams through redox-related processes (Devito et al. 1999). For example, large conifer-*Sphagnum* swamps located near the catchment outflows of PC1 and HP6-A funnel the majority of drainage water from upland soils, and the patterns of sulphate export in these 2 catchments are very similar (r = 0.91, $p < 0.05$). During dry periods, water table drawdown and aeration of previously submerged wetland soil causes re-oxidation of stored sulphides to sulphate, which is flushed into drainage streams when normal hydrologic conditions resume (e.g., Bayley et al. (1986); Van Dam (1988); Devito et al. (1999)). The Dickie catchments (DE5, DE6) have extensive wetland coverage, and DE6 exhibits a similar pattern of sulphate export compared to PC1 and HP6-A (Figure 4), although the magnitude of sulphate export in DE6 is generally less. In contrast, the DE5 catchment exports the least sulphate on an area basis, and appears to retain sulphate in many years. However, S-export from DE5 and DE6 may be underestimated, as total (inorganic + organic) S-concentrations in these streams were on average higher than inorganic sulphate concentrations by as much as 23% (Table 3). Dissolved organic carbon (DOC) concentrations in the Dickie streams are generally very high (annual average concentration range: DE5 13.6–23.1 mg/l; DE6 18.7–26.1 mg/l). Houle et al. (1997) found that the contribution of dissolved organic sulphur (DOS) to total S concentrations in Quebec lakes was greater in lakes having higher DOC concentrations, as DOS is part of dissolved organic matter. Export of S in organic forms may therefore be important in the DE streams.

In other catchments, however, wetlands are either not present (BC1), or occupy a small proportion of the total catchment area (HP4, RC1). Furthermore, any wetlands in the HP4 and RC1 catchments are located more than 500m upstream of the water sampling stations, and their effect on stream chemistry is therefore less pronounced. In catchments without wetlands, other processes must be responsible for the net export of sulphate observed in certain years (Figure 6). The BC1, RC1 and HP4 catchments have substantial deposits of thick (> 1 m) till and soil profiles are consequently deeper, and more well developed (Jeffries and Snyder 1983). The sulphate adsorption capacity of soils in these catchments may therefore be greater than in catchments with predominantly thin till and soil, such as PC1 (e.g., Rochelle et al. (1987)). Desorption of sulphate that was previously adsorbed when deposition was higher, and a shift toward what Reuss and Johnson (1986) refer to as a new 'equilibrium state' in response to reduced atmospheric S-loading, may explain the net export of sulphate from upland soils observed in BC1, HP4 and RC1 (e.g., Driscoll et al. (1995)). While historically high atmospheric deposition is likely the ultimate source of stored S in these catchments, the fact that temporal patterns in sulphate concentrations in BC1, RC1 and HP4 are similar to patterns in zero-discharge over time suggest that climate variations are also important determinants of sulphate retention in these predominantly upland catchments. For example, variations in temperature and precipitation may affect the biological mineralization of organic-S compounds in upland soils, and therefore cause changes in sulphate retention in catchments (Driscoll et al. 1998). Sulphur cycling in a representative upland catchment (PC1-08) is currently being investigated, and preliminary results indicate that drying and re-wetting events increase the release of sulphate from organic surface horizons in upland soils. Indeed, drying of soils followed by re-wetting has been shown to cause a flush in carbon and nitrogen mineralization (e.g., Cabrera (1993); Leiros et al. (1999)) and can also stimulate the release of sulphate from organic forms (Williams 1967). Temperature can also exhibit a stimulatory effect on organic matter breakdown (Kirschbaum 1995) and mineralization (Leiros et al. 1999).

Other possible sources of net S-export

Although weathering may be an important source of S in some catchments (e.g., Turk et al. (1993)), and temperature-related increases in mineral weathering have been reported (Sommaruga-Wögrath et al. 1997), weathering is unlikely to be a significant source of S to catchments in the Muskoka-Haliburton region due to very low S concentrations in bedrock and soils (Jeffries and Snyder 1983; Neary et al. 1987). The other possible source of additional S is dry deposition, however the contribution of dry deposition to total S-input in Muskoka Haliburton is likely very low given its remote location. Furthermore, sulphur dioxide (0.75–2 μg/m^3) and particulate sulphate concentrations (1–2 μg/m^3) measured in this region are low relative to areas in the eastern United States, where many of the previous studies on dry deposition were conducted (Environment Canada 1997; USEPA 1999). Dry deposition is a notoriously difficult parameter to measure, and rather than increase our bulk deposition estimates by some arbitrary enrichment factor, we justified the use of bulk deposition as a surrogate of total sulphate deposition based on previous measurements and modelling calculations which took into account the low SO_2 and particulate SO_4 levels measured in this region (Dillon et al. 1988). Furthermore, the amount of additional dry deposition that would be required to balance the magnitude of net sulphate export would be unrealistically high (i.e. bulk deposition would have to be doubled in some years; see Figure 6). At most, Sirois and Barrie (1988) estimated that dry deposition could constitute 22% of the total sulphur deposition in southeastern Ontario, and their estimates were made using data collected between 1979 and 1982–a time period when deposition was notably higher. Furthermore, the magnitude of dry deposition would have to vary greatly between years in order to account for the large differences measured in net retention between contiguous years. These reasons combined suggest that dry deposition alone cannot explain either the magnitude of net export, or the variations in net export over time.

Conclusions

The possible linkage between sulphate export and climate conditions has a number of important implications. Firstly, the net export of sulphate following summer droughts is substantial, and represents a major increase in sulphate input to downstream lakes. As many of the lakes in the Muskoka-Haliburton region are currently acid-stressed (Dillon et al. 1987; McNicol et al. 1998), large changes in sulphate input to these lakes could have serious consequences for both their chemical and biological recovery. Secondly, changes in industrial emissions and subsequent acid deposition under conditions of varying climate may not be directly translated into changes in stream and lake chemistry. Sulphate concentrations in a number of long-term monitored surface waters have not decreased as much as predicted given recent reductions in industrial emissions, nor have measurable improvements in pH and alkalinity been achieved (Driscoll et al. 1998; McNicol et al. 1998; Stoddard et al. 1999). While many catchments may currently be exhibiting some form of 'delayed response' to reductions in acid deposition due to the time required for soils to achieve a new equilibrium with lowered inputs (Reuss and Johnson 1986; Driscoll et al. 1998), in this region climate conditions appear to have an important influence on S-retention and export. Thus, predicted future changes in climate including a greater frequency of extreme events such as drought (e.g., IPCC 1995) may have important implications for S biogeochemistry, and for the recovery of acid-impacted terrestrial and aquatic systems.

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