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The effect of seasonal drying on sulphate dynamics in streams across southeastern Canada and the northeastern USA

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Abstract Within the southeast Canada and northeast USA region, a peak in sulphate (SO_4^{2-}) concentration has been reported for some streams following periods of substantial catchment drying during the summer months (ON, Canada; VT, NH and NY, USA). However, it is currently unclear if a SO_4^{2-} response to seasonal drying is widespread across the broader region, or to what extent the level of response varies among catchments. In our study, SO_4^{2-} response to seasonal drying was compared in 20 catchments from 11 locations across southeastern Canada (ON, QC and NS) and northeastern USA (NH, NY, VT, WV and ME). Using long-term monitoring data of stream discharge and chemistry, the number of days for each month of the dry season (# d) when discharge (Q) was below a threshold level (25th percentile; Q_{25}) was calculated for each catchment to give a measure of 'seasonal dryness' (# d $Q < Q_{25}$). A SO_4^{2-} response

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score (*rs*) was then calculated for each catchment based on linear regression analysis of # d Q < Q_{25} versus either the annual SO_4^{2-} concentration, or the residual of annual SO_4^{2-} concentration as a function of time (year). The final *rs* values for each catchment provided an estimate of the proportion of variation in annual SO_4^{2-} concentration which could be explained by seasonal drying (possible *rs* range = 0–1). Of the 20 catchments, 13 exhibited some level of a SO_4^{2-} response to seasonal drying (*rs* = 0.04–0.72) with an additional two catchments exhibiting a SO_4^{2-} response for one or more seasons. SO_4^{2-} response scores were positively related to percent wetland area(*w*) ($rs = 1.000 - 0.978e^{-0.054*w}$, $r^2 = 0.44$) and percent saturated area (sat) ($rs = 0.481 - 0.488e^{-0.101*sat}$, $r^2 = 0.54$) indicating that wetlands/saturated areas were an important driver of regional variation in the SO_4^{2-} response to seasonal drying. Our results suggest that any shift towards drier summers as a result of climate change could impact SO_4^{2-} dynamics in a large number of catchments throughout the region.

Keywords Sulphate · Drought · Wetlands · Seasonal drying · Forested streams

Introduction

There have been substantial reductions in sulphur (S) deposition in northeastern USA and southeastern Canada since the 1970s (Stoddard et al. 1999; Driscoll et al. 2001; Environment Canada 2010; Mitchell et al. 2011). Across the region, SO_4^{2-} concentrations have also decreased in most streams and lakes (Driscoll et al. 2001; Likens et al. 2002; Jeffries et al. 2003a; Houle et al. 2004; Watmough et al. 2005). However, relative to declines in atmospheric S, declines in surface water SO_4^{2-} have been less than expected in some areas (Driscoll et al. 1995; Dillon et al. 1997). This discrepancy is likely to have contributed to the delay in the recovery of freshwater ecosystems from long-term acidification (Driscoll et al. 2001; Jeffries et al. 2003b; Laudon et al. 2004).

Mass balance studies have shown that catchments throughout southeastern Canada and northeastern USA are exporting S in excess of inputs from deposition (Houle and Carignan 1995; Likens et al. 2002; Eimers and Houle 2005; Watmough et al. 2005; Inamdar and Mitchell 2008; Mitchell et al. 2011). A number of factors operating alone or in combination may explain these imbalances. Potential explanations for a net loss of S are: (1) an underestimation of dry deposition (Driscoll et al. 1998), (2) mineral weathering of S rich bedrock (Bailey et al. 2004; Campbell et al. 2006; Inamdar and Mitchell 2008; Shanley et al. 2008), (3) net mineralization of organic S (Houle and Carignan 1995; Houle et al. 2001; Likens et al. 2002), (4) desorption of SO_4^{2-} from mineral soils (Nodvin et al. 1986; Rochelle et al. 1987) and (5) net losses of SO_4^{2-} from wetlands following periods of summer drought (Dillon and Lazerte 1992; Lazerte 1993; Devito et al. 1999; Eimers and Dillon 2002; Eimers et al. 2004a; Schiff et al. 2005). While there is a need to understand all of these processes better, the effect of seasonal drying on SO_4^{2-} dynamics is particularly important because of the potential for drier summers and an increased drought frequency as a result of climate change (Laudon et al. 2004; Aherne et al. 2006).

Climate models have predicted drier summers and an increase in the frequency of droughts across northeastern USA and southeastern Canada (Christensen et al. 2007; Colombo et al. 2007; Hayhoe et al. 2007). Therefore, in some catchments, there is potential for an increase in the frequency of drying induced peaks in SO_4^{2-} concentration in the future. What is not known however, is whether a SO_4^{2-} response to seasonal drying is widespread across the region, or how the degree of response varies among catchments. Therefore, our ability to predict if, and to what extent, changes in climate might impact the recovery of streams from long-term acidification at the regional scale is currently limited. In addition, there is the potential for climate change to increase the frequency of episodic acidification events. SO_4^{2-} pulses can contribute to the episodic acidification of surface waters (Kahl et al. 1992; Wigington et al.

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1992; Laudon et al. 2004), which can have a deleterious impact on aquatic ecosystems (Baker et al. 1996; Driscoll et al. 2003).

Much of our current understanding of the SO_4^{2-} response to seasonal drying in southeastern Canada and northeastern USA comes from studies conducted in southern Ontario (Dillon and LaZerte 1992; Lazerte 1993; Devito and Hill 1997; Warren et al. 2001; Eimers and Dillon 2002; Eimers et al. 2004a, b). Outside of this area, peaks in SO_4^{2-} concentration following periods of relatively high summer dryness have also been reported for streams in New York (Mitchell et al. 2006, 2008), Vermont (Mitchell et al. 2008; Mayer et al. 2010), New Hampshire (Wellington and Driscoll 2004; Mitchell et al. 2008), Quebec (Biron et al. 1999), and northwestern and central Ontario (Bayley et al. 1986; Jeffries et al. 2002; Schiff et al. 2005). While these results suggest that a SO_4^{2-} response to seasonal drying might be widespread, particularly where wetlands are present, a large number of catchments across the region have not been assessed. Furthermore, the influence of summer dryness has varied substantially from short-term pulses of SO_4^{2-} export during post-drought flows (Biron et al. 1999; Mitchell et al. 2006; Mayer et al. 2010), through to increases in the annual catchment S export (Eimers and Dillon 2002). Therefore, it is not just the occurrence of a drying response that needs to be considered, but also how seasonal drying influences SO_4^{2-} dynamics at different temporal scales (e.g. short-term, seasonal or annual) in different catchments. However, our ability to make these types of comparisons has been limited by the lack of a standardized approach to measure and categorize the response of SO_4^{2-} to seasonal drying.

The occurrence of a SO_4^{2-} response to catchment drying has been identified using a number of different approaches. These include measuring the isotopic composition of SO_4^{2-} in post drought flows (Schiff et al. 2005; Mitchell et al. 2006, 2008; Mayer et al. 2010), comparisons of seasonal concentrations in dry versus wet years (Biron et al. 1999; Mitchell et al. 2006), correlation of summer dryness with SO_4^{2-}concentration (Eimers and Dillon 2002), and comparison of annual concentrations and/or fluxes in dry versus wet years (Lazerte 1993; Devito et al. 1999; Eimers and Dillon 2002). While these approaches have provided important insights into the importance of seasonal drying on SO_4^{2-} dynamics, a comparison of this effect across a large number of catchments requires a standardized approach to measure and categorize the effect of variation in seasonal drying on SO_4^{2-} dynamics.

The mechanism by which SO_4^{2-} increases as a result of catchment drying is thought to be associated with the transformation of S in areas subject to anoxic conditions, particularly wetlands. Wetlands are known to be an important sink for S via bacterial S reduction which converts SO_4^{2-} to S (Eimers et al. 2004a; Schiff et al. 2005; Inamdar and Mitchell 2008; Björkvald et al. 2009). However, during periods of drought, water tables recede, pools of reduced S are exposed to oxygen, and S is oxidized to form SO_4^{2-}, resulting in an increase in the SO_4^{2-} concentration of surface waters when the catchment is rewetted (Dillon and Lazerte 1992; Lazerte 1993; Devito et al. 1999; Eimers et al. 2004a; Schiff et al. 2005; Mitchell et al. 2006). While the importance of wetlands in the SO_4^{2-} response to drought is widely accepted, it is yet to be demonstrated that variation in the SO_4^{2-} response to drought across a regional scale can be attributed to differences in wetland coverage. Variation in historic S deposition across the region or differences in the extent to which catchments dry out during periods of abnormal dryness or drought may also be important drivers of variation in the SO_4^{2-} response to seasonal drying among catchments.

In our study, we developed and applied a standardized approach to quantify the SO_4^{2-} response to seasonal drying for a number of catchments throughout northeastern USA and southeastern Canada. The principal aim of this was to determine how widespread the SO_4^{2-} response to seasonal drying is across the region, and to compare the degree of the SO_4^{2-} response among a range of catchments. In addition, we aimed to determine the effect of seasonal drying on temporal streamwater trends in SO_4^{2-} concentrations and to determine the role of wetland coverage, S deposition and dry season hydrology as drivers of variation in the SO_4^{2-} response at the regional scale.

Methodology

Study sites

A total of 20 sites, from 11 locations, in three provinces in southeastern Canada and five states throughout northeastern USA were included in the study (Fig. 1). Additional information on the characteristics of these sites can be found in Mitchell et al. (2011) and Adams et al. (2007). Where there were data for multiple catchments from a single location, each catchment was analyzed individually. Locations with data sets for multiple catchments were Turkey Lakes Watershed (TLW c32, TLW c37, TLW c49 and TLW c50), Harp Lake (HP 3, HP 3A, HP 4, HP 6 and HP 6A), Moosepit/Mersey and the Hubbard Brook Experimental Forest (HBEF W6 and HBEF W9). These catchments were analyzed individually, rather than being pooled, to assess variability in the SO_4^{2-} response to seasonal drying among watersheds with similar geology and S deposition. It should be noted that the Bear Brook Watershed used in this study is the reference watershed (East Bear Brook) and not the experimentally acidified West Bear Brook Watershed. Similarly, the Fernow Experimental Forest site used in this study is the reference Watershed 4 and not the experimentally acidified Watershed 3.

The data used in this study were taken from long-term monitoring programs with a minimum of 10 years of record. When data sets longer than 10 years were available, the full data set was used rather than using a specific time period for all catchments (Table 1). This was done to maximize the likelihood that major drying events would be included in the analysis of each catchment. More detailed information on the sampling protocols for each catchment including the frequency of chemistry and discharge measurements can be found in Adams et al. (1993) (Fernow Experimental Forest), Fernandez et al. (2010) (Fernow Experimental Forest and Bear Brook) and Mitchell et al. (2011) (all locations except Fernow).

Methodology for measuring SO_4^{2-} response to seasonal drying

'Seasonal dryness' was quantified as the sum of days below the 25th percentile of long-term discharge for each month of the dry season (# d $Q < Q_{25}$). Discharge, rather than precipitation or temperature was used, because discharge is a more direct indicator of dry conditions in catchments (Eimers and Dillon 2002) and is more widely available than groundwater level data. Other percentile values were considered (5th and 10th) but the 25th percentile was chosen because it better described inter-annual variability in seasonal dryness relative to the 5th and 10th percentiles. In some catchments, there were a large number of 0 values when seasonal dryness was calculated based on the 5th and 10th percentiles. Therefore, the 25th percentile was chosen as the most appropriate metric for subsequent regression analysis. As such, the measure of seasonal dryness used in our study incorporates conditions ranging from abnormal dryness through to periods of extreme drought.

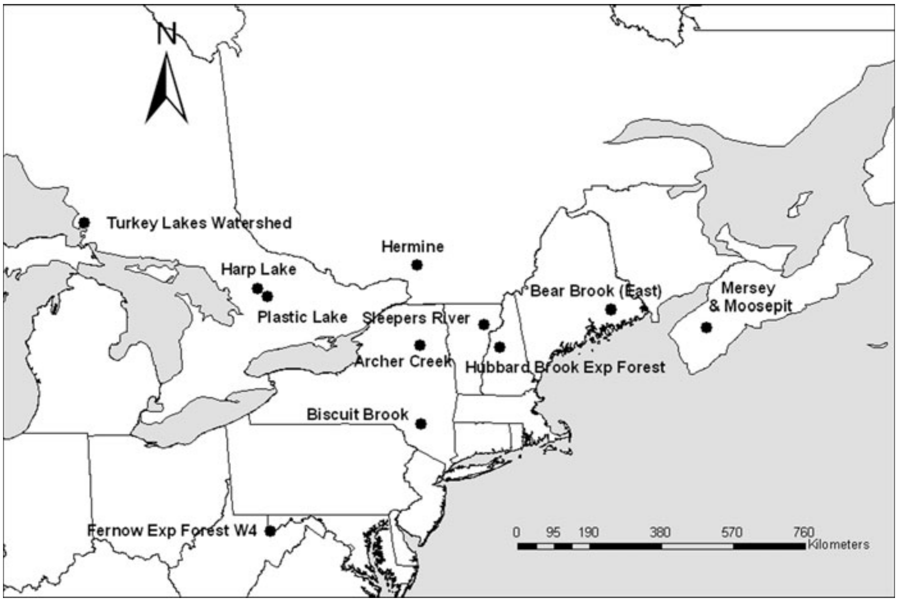


Fig. 1 *Map* showing the location of the study sites within southeastern Canada and the northeastern USA

Table 1 Length of data record and duration of dry season and rewetting periods for each of the study sites

Stream name	Duration of record	Dry season	Rewetting period
Archer Creek	1995/1996–2006/2007	Jun–Sep	Oct–Nov
Bear Brook	1990/1991–2000/2001	Jun–Aug	Sep–Nov
Biscuit Brook	1984/1985–2008/2009	Jun–Aug	Sep–Nov
Fernow[a]	1983/1984–2003/2004	Jun–Oct	Nov
Harp 3	1980/1981–2001/2002	Jun–Aug	Sep–Nov
Harp 3A	1980/1981–2001/2002	Jun–Aug	Sep–Nov
Harp 4	1980/1981–2001/2002	Jun–Aug	Sep–Nov
Harp 6	1980/1981–2001/2002	Jun–Aug	Sep–Nov
Harp 6A	1980/1981–2001/2002	Jun–Aug	Sep–Nov
Hermine[b]	1994/1995–2004/2005	Jun–Sep	Oct–Nov
HBEF W6	1963/1964–2004/2005	Jun–Sep	Oct–Nov
HBEF W9	1995/1996–2006/2007	Jun–Sep	Oct–Nov
Mersey	1980/1981–2007/2008	Jun–Sep	Oct–Nov
Moosepit	1983/1984–2006/2007	Jun–Sep	Oct–Nov
Plastic	1980/1981–2001/2002	Jun–Aug	Sep–Nov
Sleepers River W9	1992/1993–2003/2004	Jun–Sep	Oct–Nov
TLW c32[a]	1986/1987–2008/2009	Jun–Sep	Oct–Nov
TLW c37[a]	1981/1982–2008/2009	Jun–Aug	Sep–Nov
TLW c49[a]	1981/1982–2008/2009	Jun–Aug	Sep–Nov
TLW c50[a]	1983/1984–2006/2007	Jun–Aug	Sep–Nov

[a] Some years excluded due to missing monthly SO_4^{2-} concentration data—TLW c32 (1987–1988, 1991–1992, 1992–1993), TLW c50 (1994–1995, 2005–2006 and 2006–2007), Fernow(1985/1986, 1988/1989, 1992/1993, 1994/1995–1995/1996 and 1999/2000)

[b] Some years excluded due to missing discharge data—Hermine (1997/1998–1999/2000)

Our method of quantifying seasonal dryness included a number of steps. First, the dry season was determined for each catchment from long-term discharge data. Dry season was defined as a period of consecutive months when (a) the mean monthly discharge (mm) of each month was below the 12 month average (Jan–Dec) and (b) there was a continuous decline in mean total monthly discharge from the month when discharge first fell below the 12 month average (e.g. Biscuit Brook and Archer Creek, Fig. 2). For the majority of catchments, the dry season was the period from Jun-Aug or Jun-Sep (Table 1). Second, the 25th percentile of discharge was calculated for each individual month of the dry season using the full record of daily discharge for each stream. Third, the number of days with discharge below this value was then calculated for each month of the dry season for each year. Lastly, the number of days below the 25th percentile for each individual month of the dry season were summed to give the final measure of seasonal dryness for each catchment, for each year (# d $Q < Q_{25}$).

Using the # d $Q < Q_{25}$ values for each stream a SO_4^{2-} response score (*rs*) for each catchment was then calculated. The *rs* value represents the extent to which annual SO_4^{2-} concentration responds to variation in seasonal dryness (# d $Q < Q_{25}$) at each catchment. The *rs* was calculated based on regression analysis of: (A) mean annual SO_4^{2-} concentration as a function of time (year); (B) the residual of mean annual SO_4^{2-} concentration as a function of time versus # d $Q < Q_{25}$; or (C) mean annual SO_4^{2-} concentration as a function of # d $Q < Q_{25}$ (Fig. 3). For each stream, the mean monthly SO_4^{2-} concentration for each month (obtained from long-term monitoring data) was discharge weighted to calculate annual (Jun 1–May 31) mean SO_4^{2-} concentration (mg/L). Where there was a significant ($p < 0.05$) temporal trend in annual discharge weighted SO_4^{2-} concentration, the SO_4^{2-} response scores were calculated based on Eq. 1:

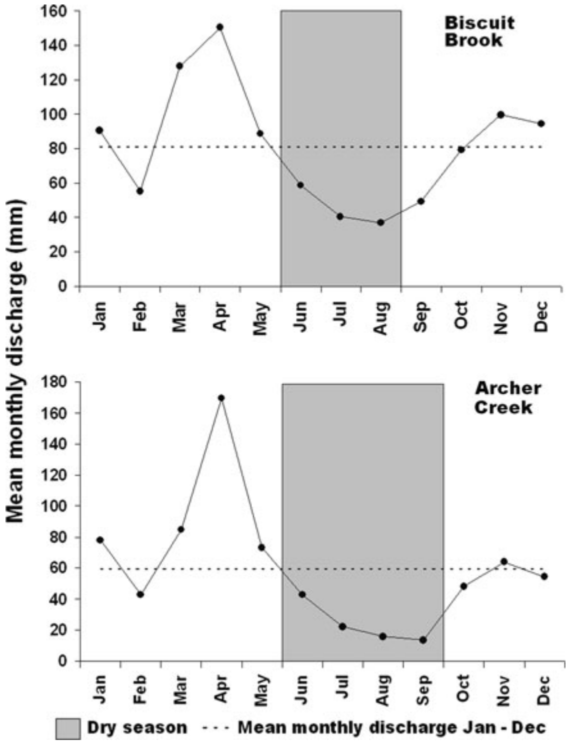


Fig. 2 Mean monthly discharge (mm) for the Biscuit Brook (1984–2009) and Archer Creek (1995–2007) streams. *Dotted line* is the mean monthly discharge from Jan–Dec (*solid line*) and the *shaded area* indicates the dry season for each stream as defined in this study

$$rs = \left(1 - r_A^2\right) * r_B^2 \quad (1)$$

where r_A^2 and r_B^2 are the r^2 values of regressions A and B.

Where there was not a significant temporal trend in annual SO_4^{2-} concentration ($P > 0.05$), the response score was calculated based on Eq. 2:

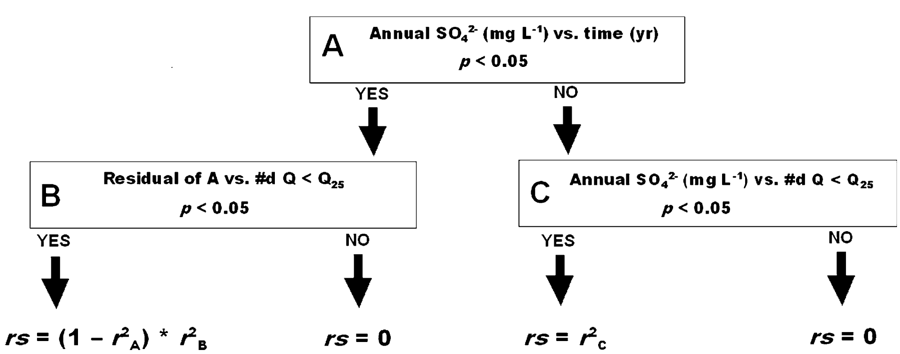
$$rs = r_C^2 \quad (2)$$

where r_C^2 is the r^2 value of regression C.

The *rs* values derived using Eqs. 1 and 2 provided an estimate of the proportion of variation in annual SO_4^{2-} concentration that could be attributed to # d Q < Q_{25}. These values allowed us to compare catchments which showed a significant temporal trend with catchments that did not. Catchments that did not show a significant relationship for regression B or C were given a score of 0 to give a potential range of *rs* values of 0 (no response) to 1 (100% of the variation in annual SO_4^{2-} concentration explained by # d Q < Q_{25}).

A SO_4^{2-} response score was also calculated on a seasonal basis. This was done to examine the timing and duration of the SO_4^{2-} response and also to determine if catchments that did not exhibit a response based on annual SO_4^{2-} dynamics showed any response in one or more seasons. The methods used to calculate *rs* for each season were the same as those already described (Fig. 3, Eqs. 1, 2). The value of # d Q < Q25 used in each regression analysis, for each season, was the same value used for the calculation of *rs* on an annual basis. Four 'seasons' were defined based on discharge characteristics, rather than by conventional season. The first was the 'dry season' (typically Jun–Aug or Jun–Sept; Fig. 2), followed by a 'rewetting season' which extended from the end of the dry season (August or September) through to the end of November (Table 1), followed by the winter (Dec–Feb), and then spring (Mar–May). Seasons were classified in this way to account for major shifts in hydrology that might be important in the timing of the SO_4^{2-} response.

Fig. 3 Schematic diagram of the methodology used to calculate the SO_4^{2-} response score using linear regression analyses of different variables (*A*–*C*)



Analysis of potential drivers of inter-catchment variation in the SO_4^{2-} response to seasonal drying

Regression analysis was used to examine the relationship between SO_4^{2-} response scores and percent wetland coverage, dry season hydrology and S deposition. The SO_4^{2-} response scores for each catchment were used as the dependent variable in each analysis. Because the SO_4^{2-} response scores have an upper limit (i.e. $rs = 1$), the data were fitted to an asymptotic regression model. All statistical analyses were performed using SPSS version 17. To measure variation in dry season hydrology among catchments, we used the 25th percentile of daily discharge for each month of the dry season at each site (Table 2). An average deposition rate (kg S ha^{-1} year^{-1}) was calculated for each site from long-term monitoring data of annual wet deposition and analyzed against *rs*. These estimates do not include dry deposition and therefore, we also used values of total deposition (kg S ha^{-1} year^{-1}) obtained from Mitchell et al. (2011) based on the period from 1985 to 2002.

Wetland data for each catchment were provided by principal investigators from each site. It should be noted that a number of methods were used to estimate wetland coverage and therefore the values obtained for each catchment were not obtained using a uniform approach. To account for the potential issue of using values estimated using different methods, we also calculated wetland area for each catchment using a standard approach. These estimates were defined as areas of saturation to include the presence of cryptic wetlands (Creed et al. 2003) in addition to more traditional wetlands (e.g. *Sphagnum* peats).

The percent saturated area for each catchment was estimated using a standard methodology. A detailed explanation of the methods used to calculate percent wetland can be found in Creed et al. (2008). Briefly, provincial digital topographic contour datasets at 1:10,000 scale and 10 m contour intervals were interpolated to create 10 m digital elevation models (DEMs) for Ontario (Ontario Ministry of Natural Resources 2006) sites. Nova Scotia Topographic Database contour datasets at 1:10,000 scale and 5 m

Table 2 Comparison of the 25th percentile values (mm day^{-1}) of daily discharge for each month (Jun–Sep) at the 20 study streams

	25th percentile of daily discharge (mm)			
	June	Jul	Aug	Sep
Archer Creek	0.323	0.152	0.077	0.098
Bear Brook	0.247	0.000	0.000	0.000
Biscuit Brook	0.791	0.444	0.247	0.304
Fernow	0.140	0.066	0.019	0.019
HP 3	0.163	0.006	0.000	0.018
HP 3A	0.093	0.024	0.014	0.012
HP 4	0.232	0.097	0.078	0.102
HP 6	0.052	0.000	0.000	0.000
HP 6A	0.035	0.000	0.000	0.000
Hermine	0.197	0.000	0.000	0.000
HBEF W6	0.266	0.047	0.026	0.059
HBEF W9	0.227	0.090	0.042	0.071
Mersey	0.680	0.307	0.149	0.089
Moosepit	0.400	0.122	0.061	0.079
Plastic	0.059	0.000	0.000	0.002
Sleepers River W9	0.710	0.212	0.134	0.120
TLW c32	0.041	0.000	0.000	0.000
TLW c37	0.153	0.049	0.036	0.064
TLW c49	0.093	0.000	0.000	0.037
TLW c50	0.052	0.000	0.000	0.015

contour interval (Service Nova Scotia 1998) were used to interpolate 10 m DEMs for Nova Scotia sites. Light Detection and Ranging (LiDAR) DEMs at 2 m spatial resolution were provided by investigators at the Quebec sites and were resampled to 10 m resolution. USGS National Elevation Dataset 1/3 arc-second DEMs (United States Geological Survey 2010) were resampled to 10 m resolution for U.S. sites. DEM grid cells where the probability of the occurrence of a depression or flat (P_{dep}) was greater than a critical depression threshold ($P_{dep} \geq 0.35$) were defined as depressions or flats. Single isolated depression cells were removed and "holes" within depressions were filled using GIS analysis. Remaining depressions and flats were subsequently classified as saturated areas. Catchment boundaries from weir point coordinates were derived from DEMs conditioned by depression removal (Planchon and Darboux 2001). The total saturated area was divided by the total catchment area, minus lake area where applicable, to give the percent saturated area for each catchment.

Results

Temporal trends in annual SO_4^{2-} concentration in the 20 study catchments

The majority of streams exhibited a significant decline in mean discharge-weighted SO_4^{2-} concentration over time (Table 3). Despite the fact that the catchments are distributed over a wide area (Fig. 1), and that the temporal trends were analyzed across a range of time scales (Table 1), the rate of decrease relative to the long-term mean was similar at most sites (mean % decline per year ≈2%, Table 3). The major difference among these streams was in the degree of variation in the r^2 values of the SO_4^{2-} versus time relationships (0.25–0.92). Five streams did not exhibit a significant temporal trend in annual SO_4^{2-} concentration (Table 3). Therefore, the majority of catchments were assessed for a SO_4^{2-} response score based on analysis of the residuals of temporal trends as a function of seasonal dryness (#d $Q < Q_{25}$). For the remaining five catchments, *rs* was calculated based on analysis of

Table 3 Summary statistics of regression analysis of temporal trends (year) in annual SO_4^{2-} concentrations (mg S-SO_4^{2-} l^{-1}) for the 20 study catchments

Site	*P*	r^2	Slope (mg S-SO_4^{2-} l^{-1} $year^{-1}$)	Mean percent decline (mg S-SO_4^{2-} l^{-1} $year^{-1}$)
Archer Creek	**0.0017**	0.65	−0.040	−1.96
Bear Brook	**0.0007**	0.74	−0.027	−1.96
Biscuit Brook	**<0.0001**	0.78	−0.037	−2.51
Fernow	**0.0008**	0.42	−0.012	−1.71
HBEF W6	**<0.0001**	0.92	−0.022	−1.79
HBEF W9	**0.0049**	0.56	−0.026	−1.94
Hermine	0.0696	0.45	−0.018	−1.15
HP 3	**0.0051**	0.33	−0.044	−2.08
HP 3A	**0.0001**	0.54	−0.046	−2.03
HP 4	**0.0129**	0.27	−0.027	−1.30
HP 6	**0.0191**	0.25	−0.045	−1.89
HP 6A	0.1769	0.09	−0.039	−1.58
Mersey	**0.0003**	0.42	−0.016	−2.06
Moosepit	**0.0018**	0.36	−0.011	−1.48
Plastic Lake	0.1713	0.09	−0.038	−1.85
Sleepers	0.6769	0.02	−0.006	−0.27
TLW c32	**<0.0001**	0.63	−0.024	−1.33
TLW c37	0.9482	0.00	0.001	0.04
TLW c49	**<0.0001**	0.82	−0.029	−2.07
TLW c50	**0.0001**	0.54	−0.030	−2.07

P values in bold indicate a significant temporal trend in annual SO_4^{2-} concentration direct relationships between annual SO_4^{2-} concentration and #d $Q < Q_{25}$.

Comparison of SO_4^{2-} response scores for the 20 study catchments

65% (13/20) of catchments assessed in this study exhibited some level of SO_4^{2-} response to seasonal dryness (Fig. 4). Streams located in south-central Ontario exhibited a relatively high level of response to seasonal drying ($rs > 0.4$). Of these streams, response scores were particularly high at the Plastic Lake (0.73), HP 6A (0.67) and HP 6 (0.54) catchments. Another group of catchments (HBEF W9, Archer Ck, Moosepit, HP 3A and TLW c37), distributed more widely across the region (NH, NY, NS, ON), also exhibited a substantial SO_4^{2-} response to seasonal dryness ($rs = 0.20$–0.40; Fig. 4). Three catchments (Mersey, TLW c49 and TLW c50), located in central Ontario and Nova Scotia, had SO_4^{2-} response scores ranging from 0.03 to 0.15. Based on the criteria used in our study, seven streams (TLW c32, Fernow, HBEF W6, Biscuit Brook, Bear Brook, Hermine and Sleepers River), located in Ontario, Quebec, Vermont, New Hampshire, New York, Maine and West Virginia, did not exhibit a SO_4^{2-} response to seasonal dryness (response score = 0; Fig. 4).

The relative importance of seasonal drying and time as drivers of variation in the annual SO_4^{2-} concentration of streams

Multiple stepwise regression demonstrated that annual discharge-weighted SO_4^{2-} concentration was best explained by a combination of # days $Q < Q_{25}$ and time at 12 of the 20 catchments (Fig. 5). There was a general pattern across the SO_4^{2-} response spectrum whereby the relative importance of time increased from catchments that showed a high response to seasonal drying, to catchments showing low responses to seasonal drying (Fig. 5). At one extreme (Plastic Lake, HP 6A and HP 6) time has played a subordinate role to # days $Q < Q_{25}$ as a driver of annual stream SO_4^{2-} dynamics. At HP 3 and HP 4, time and # days $Q < Q_{25}$ were almost equal in terms of their influence on annual SO_4^{2-} dynamics. Moving further across the response spectrum (Fig. 5; Archer Ck–TLW c49, excluding TLW c37), time was the dominant factor in annual SO_4^{2-} dynamics and # days $Q < Q_{25}$ played an increasingly subordinate role. In the remaining catchments (TLW c32–Bear Brook; Fig. 5), time but not # days $Q < Q_{25}$ has influenced annual stream SO_4^{2-} dynamics.

Comparison of SO_4^{2-} response scores by season for the 20 study catchments

Analysis of SO_4^{2-} response scores by season, found that for most catchments, the effect of # d $Q < Q_{25}$ extended well beyond the initial dry season (Fig. 6). Importantly, discharge during the post dry-season periods was independent of # d $Q < Q_{25}$ in most instances (Fig. 6). Regression analysis of annual versus seasonal response scores across the study sites found no significant relationship between SO_4^{2-} response scores during the dry season, and SO_4^{2-} response scores based on annual SO_4^{2-} dynamics ($P = 0.229$, $r^2 = 0.06$). However, significant relationships were found between SO_4^{2-} response scores for the rewetting ($P = 0.000$, $r^2 = 0.57$), winter ($P = 0.000$, $r^2 = 0.53$) and spring ($P = 0.000$, $r^2 = 0.66$) seasons and the SO_4^{2-} response scores based on

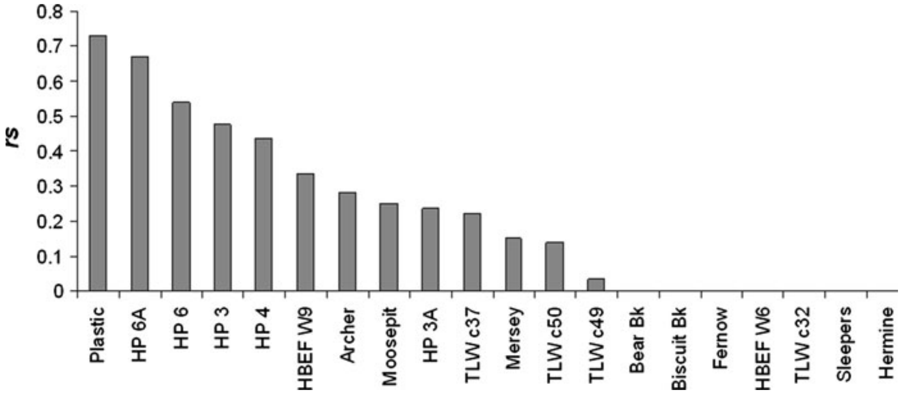


Fig. 4 Comparison of SO_4^{2-} response scores for 20 catchments in southeastern Canada and the northeastern USA

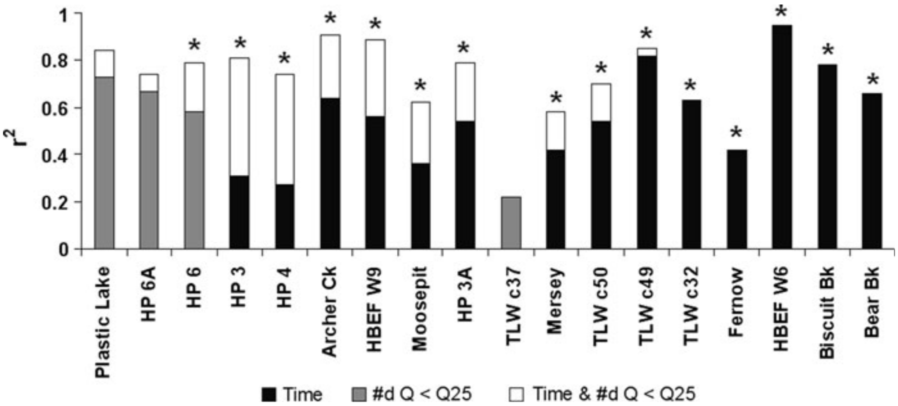


Fig. 5 Comparison of the proportion of variation (r^2) in annual SO_4^{2-} concentration explained by either time, seasonal dryness (# d $Q < Q_{25}$), or time and seasonal dryness in streams from highest (left of *x*-axis) to lowest (right of *x*-axis) SO_4^{2-} response score (* indicates streams where there was a significant temporal decline in annual SO_4^{2-} concentration at $P < 0.05$). Sleepers River and Hermine not included because there was not a significant relationship between annual SO_4^{2-} and either time or dryness ($P > 0.05$)

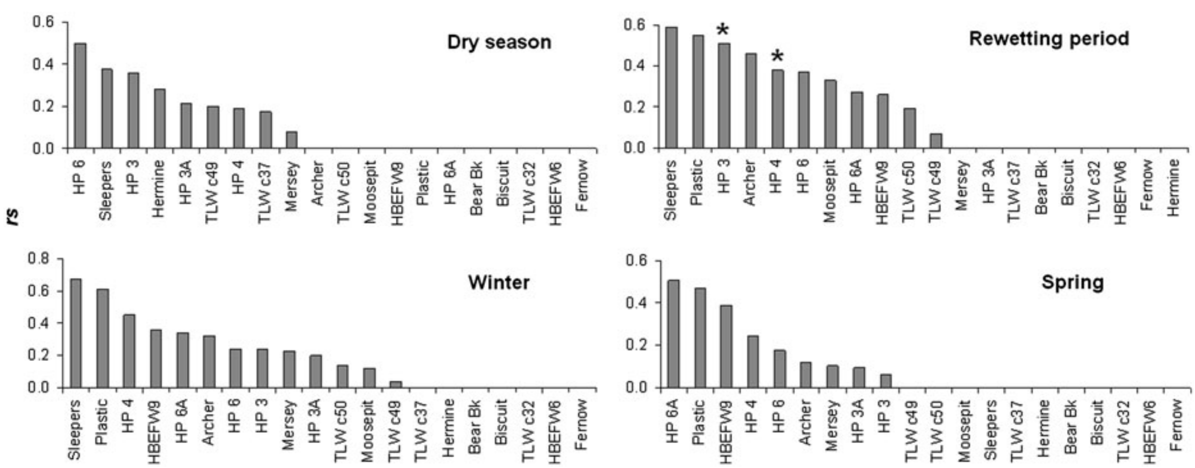


Fig. 6 Comparison of SO_4^{2-} response scores for the 20 study catchments during the dry season, rewetting, winter and spring periods (* indicates a significant relationship ($P < 0.05$) between # d $Q < Q_{25}$ and stream discharge during the rewetting, winter or spring period)

annual concentration. Two catchments (Hermine and Sleepers River) that did not exhibit a SO_4^{2-} response based on annual concentrations or residuals, had relatively large SO_4^{2-} response scores for one (Hermine; dry season) or more (Sleepers River; dry season, rewetting period and winter) seasons (Fig. 6). While there was no SO_4^{2-} response on an annual basis for Sleepers River, it should be noted that the relationship between annual SO_4^{2-} concentration as a function of # d $Q < Q_{25}$ was positive and produced a *P* value of 0.062 and an r^2 of 0.34.

Analysis of SO_4^{2-} response scores as a function of wetland coverage, deposition and dry season hydrology

Relationships between SO_4^{2-} response score and percent wetland coverage (*w*) and percent saturated area (sat) were fitted to asymptotic regression models (Figs. 7 and 8). Percent wetland coverage explained approximately 44% of the variation in *rs* across the region ($rs = 1.000 - 0.978e^{-0.054*w}$, $r^2 = 0.44$), while percent saturated area explained approximately

54% ($rs = 0.481 - 0.488e^{-0.101*sat}$, $r^2 = 0.54$). Catchments with relatively high wetland and/or saturated areas for the most part exhibited relatively high response scores. Conversely, catchments with little to no wetland or saturated area generally did not exhibit a SO_4^{2-} response to seasonal drying. Regression analysis of *rs* as a function of mean annual total S deposition (kg ha^{-1} year^{-1}) found no significant relationship ($P = 0.255$), indicating that regional variation in the SO_4^{2-} response to seasonal drying cannot be explained by differences in mean annual deposition (1985–2002) among catchments. In terms of the importance of dry season hydrology as a driver of regional variation in the SO_4^{2-} response to seasonal drying, we found no significant relationship between *rs* and the 25th percentile of daily discharge for each month of the dry season ($P > 0.05$).

Discussion

The prevalence and intra-regional variability of a SO_4^{2-} response to seasonal drying in southeastern Canada and northeastern USA

Our results indicate that SO_4^{2-} dynamics respond to seasonal drying across a number of sites throughout southeastern Canada and northeastern USA. When the seasonal response of Sleepers River and Hermine are included, 15 of the 20 study catchments exhibited an increase in SO_4^{2-} concentration as a result of increased seasonal dryness. Given that the *P* value of annual SO_4^{2-} versus dryness at Sleepers River was close to being significant, and that this site showed a response for 3 out of 4 seasons, the effect of drying on

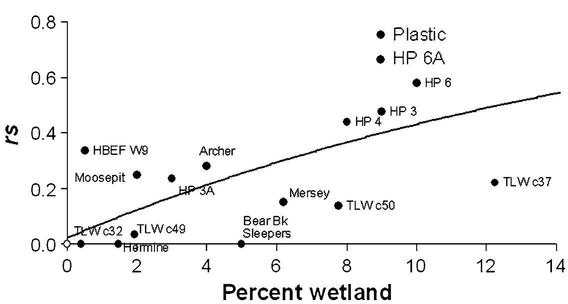


Fig. 7 The relationship between percent wetland coverage and SO_4^{2-} response score. *Open circle* symbol represents values ($rs = 0$ and wetlands $= 0$) for the Biscuit Brook, Fernow and HBEF W6 catchments

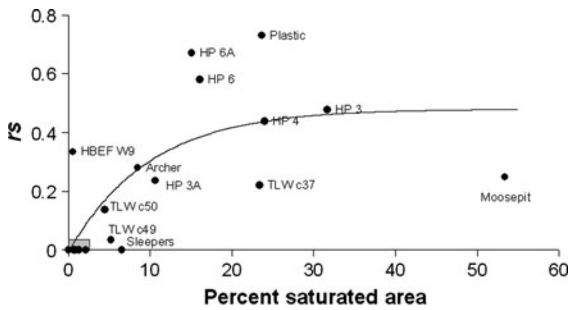


Fig. 8 The relationship between percent saturated area and SO_4^{2-} response score. *Shaded area rs* of 0 and percent saturated area of 0 (TLW c32 and HBEF W6), 0.65 (Bear Brook), 0.87 (Fernow), 1.28 (Biscuit Brook) and 2.15 (Hermine). *Note*: no % saturated area calculated for Mersey watershed due to corrupted DEM

SO_4^{2-} dynamics at this site is probably higher than the value given in Fig. 4 would suggest. It should be noted that if we assigned a response score to Sleepers River based on annual SO_4^{2-} concentrations, the *rs* value would have been 0.34, which is probably a more accurate estimate of the importance of drying at Sleepers River relative to the broader region. If we look at the proportion of sites showing a SO_4^{2-} response to seasonal drying based on the broad location of our study catchments (i.e. 11 geographical locations; Fig. 1), then 8 of the 11 areas included in our study had catchments which showed a SO_4^{2-} response. This suggests that processes associated with seasonal drying are important components of S biogeochemistry across a broad geographic region. Furthermore, by analyzing individual catchments within larger watersheds, we have also shown that the presence and degree of that response varies substantially among neighbouring watersheds. This was evident at the Turkey Lakes, Harp Lake and HBEF watersheds, where the range of *rs* values among sub-catchments indicates that streams in these regions exhibited highly variable SO_4^{2-} responses across relatively small spatial scales.

Elevated SO_4^{2-} concentrations in streams following dry periods have previously been reported at Plastic Lake, HP 6, HP 6A, HP 4 and HP 3 (Dillon and LaZerte 1992; Devito and Hill 1997; Eimers et al. 2004b), HBEF W9 (Wellington and Driscoll 2004), Archer Ck (Mitchell et al. 2006; Mitchell et al. 2008), TLW c50 (Schiff et al. 2005), Sleepers River (Mayer et al. 2010) and Hermine (Biron et al. 1999). Of these catchments, our results showed a wide range of response levels (seasonal only at Hermine and Sleepers through to $rs > 0.60$ at Plastic Lake and HP 6A). Several catchments where a SO_4^{2-} response to seasonal drying has not previously been reported (Mersey, Moosepit, HP 3A, TLW c37 and TLW c49), also showed a response in our study. Again, there was a wide range of response levels in these catchments ($rs = 0.04$–0.25), further demonstrating that the extent to which seasonal drying influences stream SO_4^{2-} dynamics varies substantially across the region. Therefore, the potential effect of seasonal drying on the recovery of different streams from long-term acidification, or the potential impact of future climate change on SO_4^{2-} dynamics is not likely to be uniform across the region. Assuming that the Harp Lake and Plastic Lake catchments are representative of the broader region, our results suggest that streams in southern Ontario will be particularly susceptible to any future increases in drought frequency.

The potential impact of seasonal drying on the trajectory of temporal SO_4^{2-} trends in southeastern Canada and the northeastern USA

Most streams in our study showed a significant long-term decrease in annual SO_4^{2-} concentration. However, there was substantial variation among catchments in terms of the degree to which annual SO_4^{2-} concentrations deviated from the long-term trajectory of these temporal declines. If time is primarily a reflection of changes in atmospheric S deposition and the depletion of internal S pools, then these trends provide an indication of recovery from historical acid deposition. Our results suggest that variation in seasonal drying has imposed perturbations on these trends. For the majority of catchments, increased seasonal drying (i.e. high # d $Q < Q_{25}$) has resulted in the periodic elevation of SO_4^{2-} concentrations above long-term temporal trends. As the influence of seasonal drying on SO_4^{2-} dynamics increases (increasing *rs*), the proportion of variation in annual SO_4^{2-} concentration associated with the recovery of catchments from acid deposition (time) decreases. At the highest response level (Plastic Lake, HP 6A) mechanisms associated with summer dryness appear to have overridden the influence of declining deposition on stream SO_4^{2-} concentrations. This variability among catchments in terms of the relative importance of time versus seasonal drying has important implications for how models are used to project the recovery of streams from acidification across the region.

Aherne et al. (2006) modelled acidification recovery at Plastic Lake under average and variable climate scenarios. They found that the inclusion of inter-annual climate variability, which included six drought years over a 20 year cycle, substantially reduced the forecasted recovery potential (Aherne et al. 2006). Therefore, exclusion of summer drought from the model resulted in an overestimation of the potential benefit of reductions in atmospheric deposition in this catchment. Given that the response of SO_4^{2-} dynamics to seasonal drying varied substantially across the region, the incorporation of some measure of variation in seasonal drying into predictive models may be necessary to provide a more accurate, and catchment specific forecast of the likely benefits of various emission reduction scenarios. If seasonal drying impacts the trajectory of long-term declines in SO_4^{2-} concentrations as our results suggest, then the potential benefits of reductions in atmospheric deposition in heavily S-impacted areas may vary substantially among streams depending on the relative importance of summer dryness as a driver of annual SO_4^{2-} dynamics. At sites that exhibited little to no response to seasonal drying (e.g. Bear Brook, Biscuit Brook and Fernow), the incorporation of seasonal drying into acidification recovery models is unlikely to have an effect on the predicted outcomes. However, for a number of other sites (e.g. Archer Ck, Moosepit, Harp Lake and Plastic Lake), incorporation of seasonal drying into predictive models may be necessary to more accurately forecast the trajectory of recovery from acidification.

The potential impact of climate change on SO_4^{2-} dynamics

Climate models have predicted drier summers in the future throughout the region (Christensen et al. 2007; Colombo et al. 2007; Hayhoe et al. 2007). In catchments where SO_4^{2-} responds to seasonal drying, this scenario has the potential to further delay the recovery of surface waters from long-term acidification. Assuming that summers are drier in the future, the potential for further delays in stream recovery from acidification may ultimately depend on the size of the catchment S pool that is susceptible to release via drying (Dillon et al. 1997; Aherne et al. 2006). At Plastic Lake, studies have estimated that pools of S susceptible to drying are large enough to provide a source of SO_4^{2-} for the foreseeable future (Eimers et al. 2007). Therefore, shifts in climate towards drier summers are likely to further exacerbate the problem of surface water acidification in this region. However, in other catchments, S pools may not be large enough to sustain prolonged drying-induced SO_4^{2-} responses. In these systems, climate change has the potential to accelerate the recovery process by decreasing the time required to deplete S pools susceptible to drying. Across the broader region, the amount of S stored in pools that are susceptible to drying has not been widely quantified. In streams where a SO_4^{2-} response to seasonal drying was observed, this needs to be addressed if we are to understand the potential impact of climate change on the recovery of these streams from historic S deposition.

The importance of wetland coverage as a source of regional variation in the SO_4^{2-} response to seasonal drying

Given the weight of evidence linking elevated SO_4^{2-} concentrations following drought with wetlands (Dillon et al. 1997; Devito et al. 1999; Eimers et al. 2004a; Schiff et al. 2005; Mitchell et al. 2006), it is not surprising that wetlands would also be an important driver of variation in the SO_4^{2-} response to seasonal drying at the regional scale. The relationships between wetland/saturated area coverage and SO_4^{2-} response scores in our study are consistent with the oxidation of S being an important mechanism behind the observed SO_4^{2-} responses at our study sites. Based on analysis of δ^{34}S isotopes, this mechanism has been linked to post-drought pulses of SO_4^{2-} at Plastic Lake (Eimers et al. 2004a), Archer Creek (Mitchell et al. 2008), TLW c50 (Schiff et al. 2005) and at Sleepers River (Mayer et al. 2010). Therefore, it is reasonable to suggest that in many of our catchments the observed increase in SO_4^{2-} concentration with increasing summer dryness can also be attributed to the oxidation of S in wetlands.

While wetland coverage appears to be an important predictor of SO_4^{2-} response across the region, there was a considerable proportion of variation in *rs* (>50%) that could not be explained by either percent wetland or percent saturated area. This result raises questions over: a) the potential of other mechanisms or processes to increase mean annual SO_4^{2-} concentration in years with higher seasonal drying, and b) the ability of a simple measure of wetland/saturated area coverage to reflect the link between S oxidation in wetlands and SO_4^{2-} concentrations at the catchment outlet. In terms of the first point (a), these mechanisms would need to persist beyond the initial drying period. Our results clearly showed that the influence of seasonal drying extended into the rewetting, winter and in some cases spring periods. Therefore, a simple evapo-concentration effect can not explain the observed response because discharge during these periods was independent of # d Q < Q_{25}. Mechanisms that could potentially elevate SO_4^{2-} concentrations in dry years include a net imbalance between catchment inputs (e.g. dry deposition, mineralization) and outputs (discharge) during the summer (Biron et al. 1999; Edwards et al. 1999; Wellington and Driscoll 2004; Böhlke and Michel 2009); an increase in the proportion of discharge as groundwater flow in catchments with S-rich bedrock (Piatek et al. 2008; Mayer et al. 2010); net desorption of SO_4^{2-} from soils; and a peak in mineralization rates following rewetting of dried soils (Birch 1958; White et al. 2004; Jarvis et al. 2007; Borken and Matzner 2009; Unger et al. 2010).

Although desorption from soils can be an important source of SO_4^{2-} in the short-term (Houle and Carignan 1995), studies examining the effect of drying on adsorption have reported either no effect (Watwood et al. 1988; Eimers et al. 2003), or an increase in SO_4^{2-} adsorption (Singh 1984; Comfort et al. 1991; Courchesne et al. 2001) with drying. This is inconsistent with the increased SO_4^{2-} concentration as a function of increased seasonal drying observed in our study. Peaks in SO_4^{2-} concentration via a net imbalance between inputs and outputs during the dry season or an increase in mineralization rates following rewetting of dry soils are likely to be short-lived (Biron et al. 1999; Courchesne et al. 2001; Courchesne et al. 2005; Borken and Matzner 2009; Muhr et al. 2010), or small relative to releases from wetlands (Eimers et al. 2003). Therefore, while these processes may contribute to elevated SO_4^{2-} concentrations following periods of high seasonal drying, their effect on post dry season and annual SO_4^{2-} dynamics is probably relatively small in catchments with substantial wetland coverage. Having said this, further investigation into the effect of drying and rewetting on S mineralization over extended periods of time is warranted.

The measure of seasonal drying used in our study (# d Q < Q_{25}) likely included periods where a large proportion of streamflow was derived from baseflow and this could explain why some catchments with low wetland or saturated area coverage exhibited relatively high SO_4^{2-} response scores (e.g. HBEF W9). Assuming the concentration of SO_4^{2-} from baseflow is enriched relative to surface flows, baseflow could produce higher SO_4^{2-} concentrations during dry versus wet years. Again, for this source to be a major contributor to the SO_4^{2-} response to seasonal drying, the increased proportion of total flow as baseflow would need to persist well beyond the initial dry season (i.e. rewetting and winter). Based on analysis with δ^{34}S isotopes, an increased contribution from baseflow has been shown to elevate SO_4^{2-} concentrations in dry years at Sleepers River (Mayer et al. 2010). This increase occurred during the initial drying period, after which further increases in SO_4^{2-} concentration during the rewetting period were attributed to oxidation of secondary sulfides (Mayer et al. 2010). A detailed analysis of the relative contribution of S oxidation versus baseflow as a source of SO_4^{2-} in other catchments is beyond the scope of this study. However, given that many sites exhibited a SO_4^{2-} response to seasonal drying, this type of analysis is needed because each mechanism may have a substantially different impact on the acidity of stream waters.

Another potential explanation for the proportion of variation in *rs* not explained by wetland or saturated area coverage is that differences among catchments in the hydrological connectivity of wetlands, streams, and the catchment outlet, exert a substantial influence on the SO_4^{2-} response to seasonal drying across the region. The degree of hydrological connectivity between wetlands, surface water and groundwater flows is determined by the specific physiographic characteristics of the catchment (Winter 1999). The degree of hydrological connectivity between wetlands and streams can have a substantial effect on the flux of pollutants at the catchment outlet (Mitchell 2001; Warren et al. 2001; Branfireun and Roulet 2002; Piatek et al. 2008; Selvendiran et al. 2008; Creed and Beal 2009; Creed and Sass 2011). Therefore, in poorly connected wetlands, SO_4^{2-} produced via oxidation of S may be held within the wetland long enough to be transformed back to S or retained along transport pathways between the wetland and the stream. This could result in streams more directly connected to wetlands exhibiting a higher response to seasonal drying than streams with similar wetland area, but lower hydrological connectivity. In addition, the degree of connectivity between the wetland and the catchment outlet may also be an important determinant of the SO_4^{2-} response to seasonal drying. A lower than expected response in some catchments (based on wetland/saturated area coverage) may reflect a cascading effect whereby the influence of upstream wetlands may be buffered by intervening sites of retention/adsorption (e.g. mineral soils and stream biomass) (Branfireun and Roulet 2002).

Conclusions

This study provides the first comparison of the SO_4^{2-} response to seasonal drying across a broad range of catchments in northeastern USA and southeastern Canada. 75% of catchments assessed in this study showed some level of annual or seasonal SO_4^{2-} response, demonstrating the regional importance of seasonal drying in affecting S biogeochemistry. The extent to which seasonal drying influenced stream SO_4^{2-} dynamics varied substantially from explaining over 70% of the variation in annual SO_4^{2-} concentration, to having no effect at all on annual or seasonal means or residuals. Our results provide a regional context for catchments already known to exhibit a SO_4^{2-} response to seasonal drying and provide new information on SO_4^{2-} and climate interactions for a number of other catchments. Inclusion of some measure of the SO_4^{2-} response to seasonal drying, similar to the one used in this study, could substantially improve predictive models of SO_4^{2-} concentrations under changing deposition and climate change scenarios. Furthermore, the approach used in this study can be applied to other streams where long-term data are available, and the results contrasted against the 20 catchments assessed in this study.

While our results are consistent with earlier research identifying wetlands as important sites of SO_4^{2-} production during dry periods, more research is needed into: (a) the extent to which the hydrological connectivity between wetlands and streams accentuates or suppresses the SO_4^{2-} response at the catchment outlet and (b) the potential for mechanisms such as increased baseflow or increased mineralization rates to contribute to the SO_4^{2-} response of catchments to seasonal drying. Finally, while acidification and climate change present significant ecological challenges in their own right, the potential interaction between these two processes may be critical to the recovery of freshwaters from long-term acidification. Importantly, a shift towards drier summers will not have a uniform effect across the region because some streams are particularly vulnerable to drier summers. The long-term effect of drier summers on the recovery of streams from acidification may ultimately depend on the magnitude of S pools stored in wetlands which are susceptible to release via drying. Therefore a greater understanding of the size and sensitivity of these pools to drying is needed.

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