SULPHATE MOBILIZATION AND PORE WATER CHEMISTRY IN RELATION TO GROUNDWATER HYDROLOGY AND SUMMER DROUGHT IN TWO CONIFER SWAMPS ON THE CANADIAN SHIELD

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Abstract. Variations in sulphate (SO_4^{2-}) concentration of porewater and net SO_4^{2-} mobilization were related to differences in water level fluctuations during wet and dry summers in two conifer swamps located in catchments which differed in till depth and seasonality of groundwater flow. Sulphate depletion at the surface and in 20 cm porewater coincided with anoxia and occurred mainly during the summer when water levels were near the peat surface and water flow rates were low in both catchments. There was an inverse relationship between net SO_4^{2-} mobilization and water level elevation relative to the peat surface, explaining variation in SO_4^{2-} dynamics between the swamps during summer drought periods. Aeration of peat to 40 cm and a large net SO_4^{2-} mobilization (10–70 mg SO_4^{2-} m^{-2} d^{-1}) occurred during a dry summer in which the water level dropped to 60 cm below the surface in the swamp receiving ephemeral groundwater inputs from shallow tills within the catchment. This resulted in high SO_4^{2-} concentrations in the surface water and porewater (30–50 mg L^{-1}), and elevated SO_4^{2-} concentrations remained through the fall and winter. In contrast, within the swamp located in the catchment with greater till depth (> 1 m), continuous groundwater inputs maintained surface saturation during the dry summer, and SO_4^{2-} mobilization and concentrations of SO_4^{2-} in the pore water during the following fall did not increase. Susceptibility to large water table drawdown and mobilization of accumulated SO_4^{2-} is influenced by the occurrence of ephemeral vs. continuous groundwater inputs to valley swamps during dry summer periods in the Canadian Shield landscape. This study reveals that extrapolation of results of SO_4^{2-} cycling from one wetland to another requires knowledge of the hydrogeology of the catchment in which the wetlands are located.

Keywords: catchment hydrology, conifer swamp, groundwater, peat, porewater, sulphate mobilization, summer drought, water levels

1. Introduction

Valley bottom wetlands in acidified landscapes have received considerable study as their location makes them a critical interface in the regulation of sulphur and other element fluxes between uplands and aquatic ecosystems (Wieder, 1985; Urban and Bayley, 1986; LaZerte, 1993). Recently, interest has focused on catchments where reductions in acidic deposition have resulted in decreased sulphate export from forested uplands, but acid and SO_4^{2-} loading downstream of some wetlands persists (Dillon and LaZerte 1992).

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Sulphur metabolism in anoxic wetland sediments and the frequency of aeration of surface and deeper sediments appear to be the most important conditions influencing long term S accumulation and SO_4^{2-} concentrations in runoff waters (Hemond, 1980; Brown and McQueen, 1985; Weider and Lang, 1988). Peat anoxia and peat chemistry are controlled largely by the amplitude and period of water table fluctuations and the rate and magnitude of water flow (Sparling, 1966; Devito and Dillon, 1993; Devito, 1995). Although previous research has revealed contrasting behaviour in wetland S cycling with seasons or in response to dry summer conditions (Urban and Bayley, 1986; Lundin and Bergquist, 1990; LaZerte, 1993), few studies have examined catchment hydrology and the amplitude and periodicity of wetland water table fluctuations concurrently with wetland S dynamics. Consequently there has been little focus on the variability of cyclic SO_4^{2-} oxidation and reduction in wetlands, or on which wetland sites within the landscape are likely to be influenced most by dry periods. Furtermore, mass balance studies (e.g. Urban and Bayley, 1986; LaZerte, 1993) have not examined the vertical extent of cyclic SO_4^{2-} oxidation and reduction within and between wetlands, or how these spatial patterns may influence the total S available for export following drought periods.

Hydrologic factors influencing water table fluctuations and water flow are controlled by catchment physiography and peat retention capacity (Dai *et al*., 1974; Devito *et al*., 1996). The extent and seasonality of groundwater connection to wetlands can be important in moderating water table fluctuations and maintaining surface saturation during summer dry periods (Roulet, 1990). Research relating peat anoxia and S cycling to the period and amplitude of water table fluctuations as controlled by catchment hydrogeology is needed to extrapolate existing data and explain the variability in wetland response at the landscape scale.

This study examines SO_4^{2-} cycling in two conifer swamps situated in catchments with till depths that lie at either end of the physiographic continuum characteristic of the shallow till-rock ridge physiographic region of the southern Canadian Shield. Devito *et al*. (1996) have shown that in these two headwater catchments differences in basin physiography produce a range in duration of upland-wetland groundwater connections and different seasonal patterns of swamp water levels and peat saturation. Mass balance studies have shown net export of SO_4^{2-} following summer droughts in the forested swamp located in the catchment with shallow till, but net SO_4^{2-} retention occurred during the same period in the forested swamp in a catchment with deeper till (Devito, 1995). Net SO_4^{2-} mobilization rates and detailed patterns of pore water redox potential and SO_4^{2-} concentration in the two swamps were measured over a two year period that included a dry and a wet summer. Our objectives were to: (1) determine if there is a relationship between water table elevation and rate of SO_4^{2-} mobilization or immobilization in surface peat to explain differences in SO_4^{2-} export from wetlands during drought periods; and (2) estimate the depth to which SO_4^{2-} mobilization occurs in order to make initial quantification of SO_4^{2-} stores available for future export pulses following water table drawdown.

2. Study Sites

The two swamps are in headwater catchments of Harp Lake (45° 23′ N, 79° 08′ W) and Plastic Lake (45° 11′ N, 78° 50′ W) which are situated near the southern limit of the Precambrian Shield in south central Ontario. Annual precipitation in the area is 900–1100 mm with 240–300 mm falling as snow between December an April. The mean January and July air temperatures are –10 and 17.7°C, respectively. Annual runoff is similar in both catchments, varying from 400 to 600 mm.

Both catchments are underlain by impermeable Precambrian, metamorphic silicate bedrock covered with thin, basal till. Due to the shallow till only local groundwater aquifers develop, and the hydrology varies seasonally (Devito *et al.*, 1996). Peak runoff occurs during spring snowmelt, a period of about four weeks in late March and April that accounts for 40–50% of the annual runoff. Smaller peaks in runoff occur with rainstorms during late autumn. Overburden in Platic catchment is classified as thin till-rock ridges with depths generally less than 1 m. Due to the thin till both stream and groundwater flow within the catchment are ephemeral, running dry for up to several months during the summer and periodically during the winter low flow period (Devito *et al.*, 1996). For most of the catchment above Harp swamp the surficial geology is classified as minor till (> 1 m depth), with deposits of sand on the north side of the stream. Although the stream and groundwater flow are seasonal, some flow occurs throughout the summer dry periods and Harp swamp remains connected hydrologically to the surrounding uplands throughout the year (Devito *et al.*, 1996).

Plastic conifer swamp (2.2 ha) occupies a central bedrock depression which represents about 10% of the 21.1 ha catchment. The swamp is forested with white cedar (*Thuja occidentalis*) and black spruce (*Picea mariana*) with some birch (*Betula*) and maple (*Acer*). There is an understorey of *Alnus* spp, and *Ilex verticillata* and a well developed layer of *Sphagnum*. A hummock-hollow, micro-topography has developed throughout the swamp. The difference between hummock and hollow elevation is about 30 cm in the forested portion of the swamp and much less in areas where thickets are the predominant overstory. Peaty, humic mesisols up to 6 m depth (average 2–3 m) overlie regions of gyttja and deposits of silt, clay, sand and gravel up to 1 m thick in the bedrock basin (Devito, 1994, Devito *et al.*, 1996). Upland-swamp interactions are near the peat surface in Plastic swamp as groundwater from shallow soil and sandy basal till on adjacent hillslopes and stream inputs discharge along the swamp margin (Devito *et al.*, 1996).

Harp conifer swamp (1.2 ha) occupies the valley bottom and represents 5% of the 22.7 ha catchment. The swamp is dominated by white cedar with considerable beech (*Fagus*) and maple. It has a poorly developed shrub and bryophyte mat. Average swamp soil depth is 2–3 m of peaty, cumula humisols, with deposits in excess of 5 m occurring at two locations near H3 and H7 (Figure 1). The peat overlies significant layers of gyttja and pockets of silt, clay, sand and gravel (Devito, 1994; Devito *et al.*, 1996; Bunting *et al.*, 1996). In contrast to Plastic swamp, Harp swamp is situated in a groundwater discharge zone (Devito *et al*., 1996). Small amounts of groundwater discharge from beneath the peat throughout the year.

3. Methods

3.1. Hydrology

Hydrology and hydrologic measurements at both swamps are described in detail by Devito *et al*. (1996). Water tables in both swamps were measured at least twice a month during dry periods and several times a day during peak hydrographs at all well locations (Figure 1), At one location in the centre of each swamp (P15 and H16) the water table elevation was continuously monitored in a heated box throughout the year. At three other locations in each swamp the water table was continuously monitored during the ice free season (April 1–Nov 30).

3.2. Pore water chemistry

Surface water and pore water chemistry at 20, 40, and 60 cm depth was measured at several locations in each swamp (Figure 1). Five cm diameter piezometers permanently capped at the top and open at the bottom with a 5 cm perforated head covered with 500 μM Nitex mesh were installed to depth. Each piezometer was pre-pumped dry and allowed to refill prior to sampling. Water samples for oxidation-reduction potential (Eh_7), dissolved oxygen (DO) and sulphate (SO_4^{2-}) analyses were collected in gas-tight glass test-tubes. Redox and DO measurements were conducted, usually within 6 hr of sampling. Water for SO_4^{2-} analyses was refrigerated and analyzed usually within 24 hr of sampling.

Water samples were analyzed for SO_4^{2-} by a Wescan single-column ion chromatograph. Oxidation-reduction potential of the sampled pore water was determined using a platinum/calomel electrode standardized with Zobell solution (Devito and Dillon, 1993). The calomel electrode potential (EM) was converted to the standard hydrogen potential and corrected for temperature (T), where EH = EM + 223 + 0.76T (°C). The pH of the pore water often varied by more than 1 pH unit over 60 cm depth and more than 2 pH units between swamps. Oxidation-reduction potential was standardized to pH 7 (Eh_7) using a slope of –59 mV per pH unit. Dissolved oxygen concentration (mg L^{-1}) was determined using the Winkler method (OMEE 1984).

3.3. Sulphate mobilization

The buried polyethylene bag technique was used to measure changes in extractable SO_4^{2-} concentrations between August 1990–1992. This method measures the net result of all processes that influence extractable SO_4^{2-}. We use the terms mobilization and immobilization to denote an increase or decrease in SO_4^{2-} concentrations

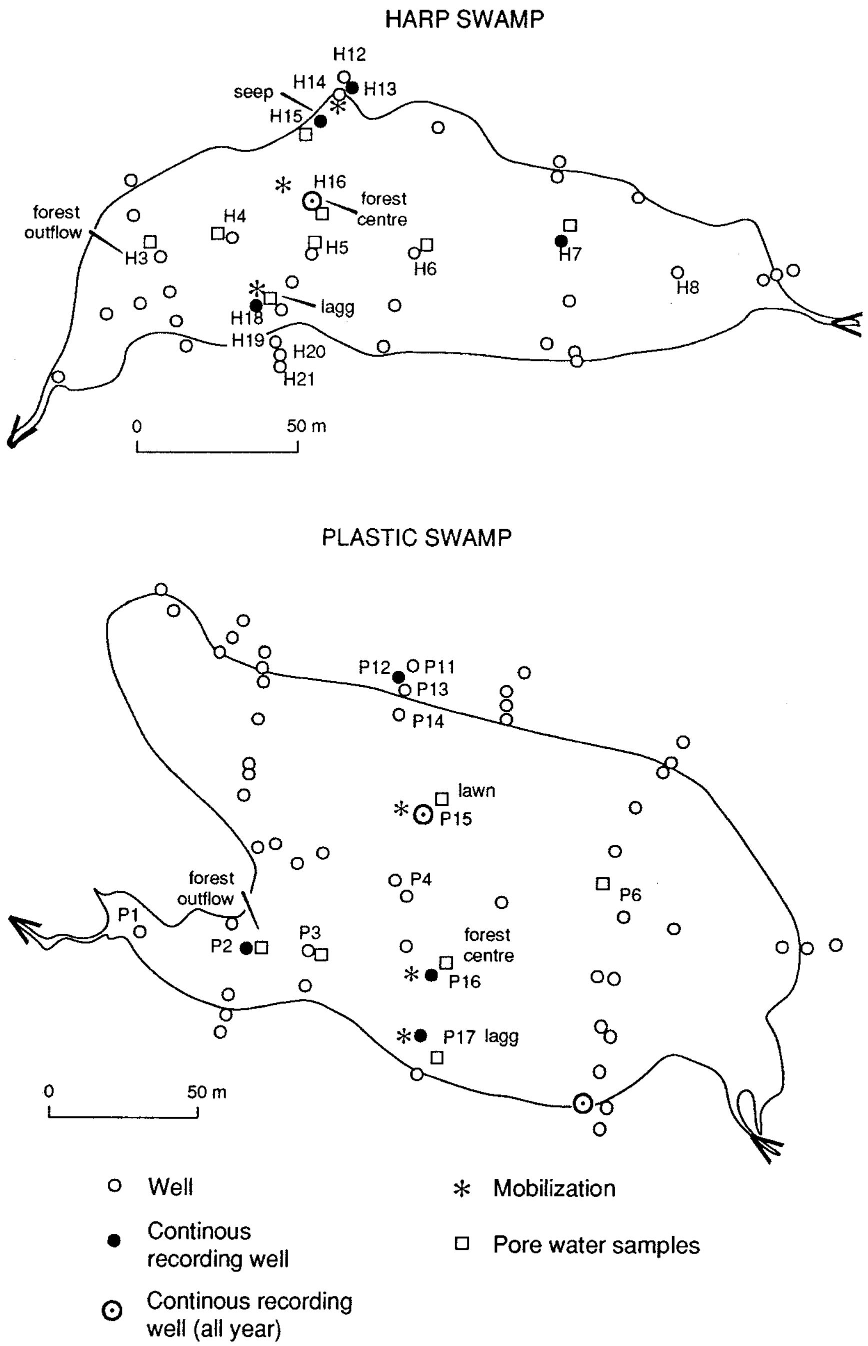

Figure 1. Plastic and Harp swamps showing the location of groundwater wells, piezometers for collecting pore water chemistry, and hollow sites for peat mobilization studies.

because mineralization, oxidation/reduction and adsorption processes cannot be separately identified.

Samples used in measuring SO_4^{2-} mobilzation and other soil properties were taken within a 5 m radius of the well at 3 hollow sites (Figure 1). At 2 to 4 locations at each site, 6 cm diameter by 10 cm deep peat cores were cut and placed undisturbed in 0.025 mm thick plastic bag and buried in the same hole. Non-incubated peat cores were collected within 20 cm of each incubation in order to determine initial SO_4^{2-} concentrations. Incubation intervals were approximately 4 or 8 weeks except for over winter incubation which occurred from 20 November 1990 to 7 May 1991 and 28 October 1991 to 2 March 1992.

The peat cores were taken from areas with ground elevations similar to the well locations. Depth to water table at each core location was assumed to be the same as that at the adjacent well. The temperature of surface water at each site and at the outlet stream of each swamp was recorded at regular intervals during the study. When the water table dropped more than 20 cm below the surface, peat temperature was assumed to be the same as the mean daily temperature recorded at a nearby meterological station.

Peat samples were returned to the lab and stored at 4°C until processed, usually within 24 hr. A 3–5 g wet mass sub-sample of each initial and incubated peat core was shaken for 1 hr with 30 mL of double-distilled water. Samples were centrifuged and filtered through 0.45 μm membrane filters and analyzed for SO_4^{2-} by ion chromatography. Another sub-sample was shaken with 30 ml NaH_2PO_4 containing 1000 mg/L P and analyzed for water-extractable SO_4^{2-} as described by Neary *et al*. (1987). The NaH_4PO_4-extractable SO_4^{2-} represents both water soluble and adsorbed SO_4^{2-} fraction. However, little difference was observed between the extraction methods (Regression slope 1.14 $\pm$ 0.04, intercept –0.02 $\pm$ 0.07, r^2=0.86, n=127), probably due to the high organic content (Neary *et al*., 1987), and only water extractable SO_4^{2-} was measured during the second year of the study.

The remainder of the core was dried at 60°C for 48 hr to estimate dry mass of extracted peat and % moisture. Net SO_4^{2-} mobilization estimates were obtained by subtracting initial values from final incubation values. Mobilization rates were converted from a per gram basis to an areal basis using peak bulk density and depth of incubation (10 cm). Bulk density was determined from the average of 30 to 50 cores collected from each site within the swamps during the study. Mobilization rates for each swamp and each date were determined from the mean and variance of all incubation cores at each of the hollow sites (2–4 cores for 3 hollow sites). For site comparisons, data for each site on each date are the mean and variance of 2–4 incubation cores.

Annual mobilization rates for each site were determined by time weighted summation of the mean rates of 2–4 cores for each incubation period in the year. The variances associated with the annual sum of SO_4^{2-} mobilization were calculated by first order error propagation of the variance of monthly means for each location in the swamp (Meyer, 1975).

3.4. Statistical analysis

Pearson correlation coefficients with Bonferroni – adjusted probabilities were used to determine the significance of linear relationships between peat pore water parameters and SO_4^{2-} mobilization, water table elevation and peat temperature. Differences between monthly mean extractable SO_4^{2-} and SO_4^{2-} mobilization were tested using pair-wised t-test using Bonferroni protection for multiple tests. Differences in annual SO_4^{2-} mobilization between swamps and years were tested using ANOVA. All tests were considered significant at probability α=0.05, and calculated using SYSTAT (version 6.0, 1996 SPSS Inc.) Statistical program.

Isolines for SO_4^{2-} and Eh_7 distribution were determined using the kriging algorithm with 100 ° 100 grid scale in SURFER version 4.15 computer software (Golden Software Inc., 1990).

4. Results

4.1. Water table fluctuations

The period and amplitude of water level relative to the surface in both Plastic and Harp swamp showed marked seasonal trends as would be expected for systems connected only to local aquifers (Figure 2). Groundwater from shallow soils and stream inputs to Plastic swamp ceased for most of each summer and the water level varied considerably within and between summers in response to rain events (Figure 2). There was little rainfall in the summer of 1990 and the water table dropped to about 60 cm below the surface. In the summer of 1991 there was nearly twice the rainfall of 1990 and the water table dropped only to about 20 cm below the surface. The water table rose to the surface during July in response to two rain storms. Frequent rainfall maintained the water level within 10 cm of the peat throughout the summer of 1992. In contrast to Plastic swamp, groundwater and stream inputs to Harp swamp occurred continuously and the water table remained relatively stable, within 10 cm of the peat surface during the three summers of study (Figure 2).

The water table was above the peat surface during late fall to early winter and spring in both swamps. Saturated overland flow was the dominant pathway of water through the swamps during this period (Devito *et al.*, 1996).

4.2. Pore water chemistry

Mean monthly pore water SO_4^{2-}, DO and EH_7 for all sites sampled in Plastic and Harp swamp are shown in Figure 2. All three parameters were negatively correlated with depth in both swamps (Table I, Figure 2). Mean monthly pore water SO_4^{2-} were correlated with DO concentrations and Eh_7 over the four depths pore water was sampled. Analyses specific for each depth show similar coefficients but were generally not significant ($p > 0.05$), however, due to reduced sample sizes (data not

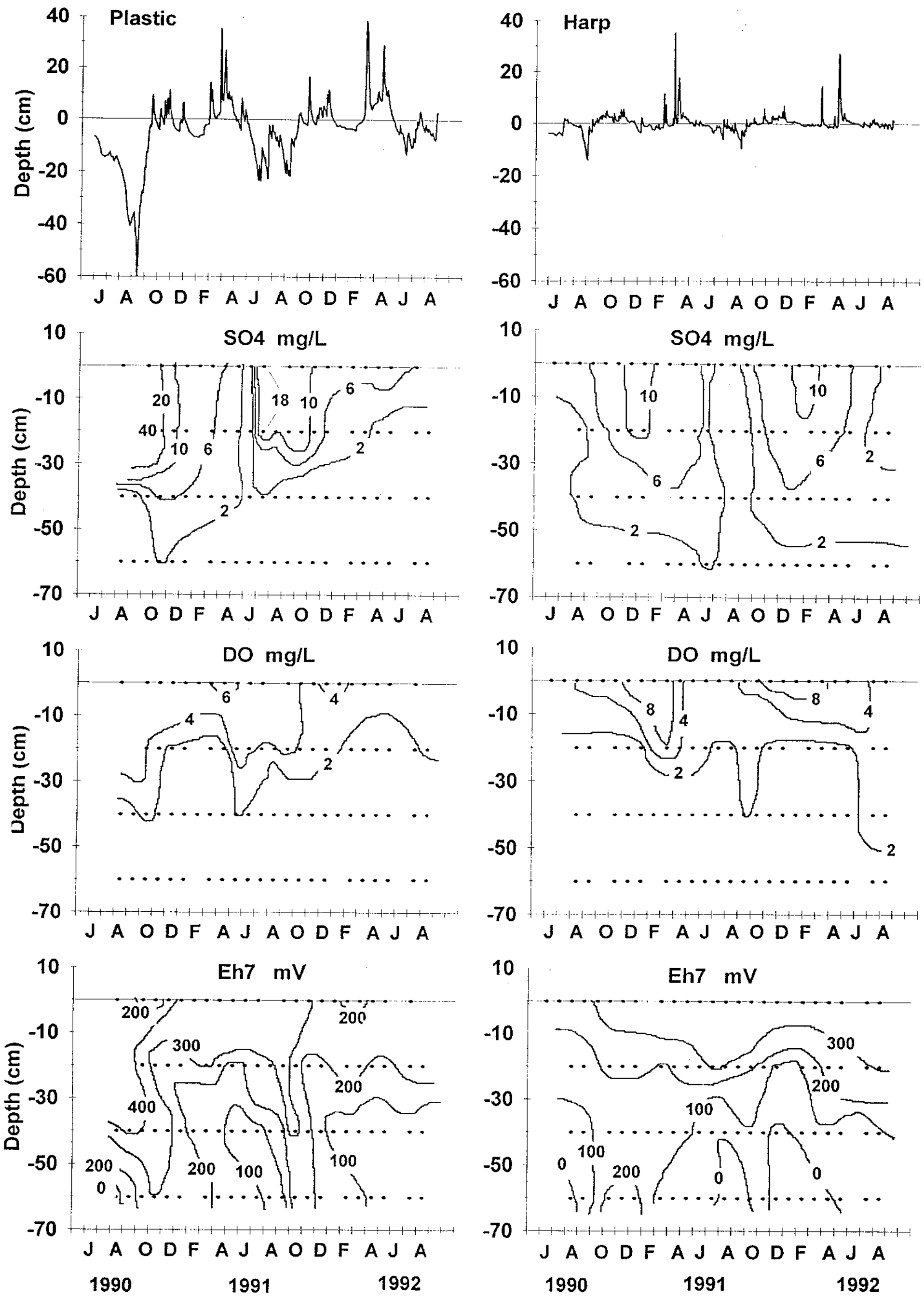

Figure 2. Continuous water table elevations for the central site and isolines of mean monthly pore-water calculated from all piezometers nests in Plastic and Harp swamp for August 1990 to August 1992 (see Figure 1 for location of sites). Dots represent depth and month with mean estimates.

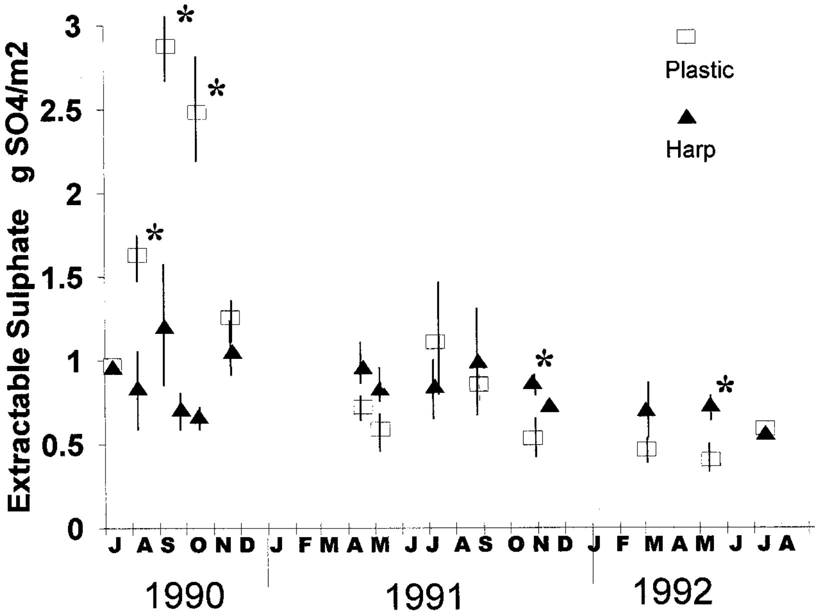

Figure 3. Mean water extractable sulphate of surface peat (0–10 cm) at Plastic and Harp swamps from 10 July 1990 to 15 July 1992. Values are mean ± standard error (SE) of all cores at 3 hollow sites (2–4 cores per site). * = significant difference between swamps for that sampling data, $p < 0.05$.

shown). Temporal variations in pore water chemistry were largely restricted to the top 40 cm of peat and in both swamps pore water Eh_7, DO and SO_4^{2-} concentrations were consistently below 200 mV, 1.0 and 1–2 mg L^{-1}, respectively at 60 cm in the peat.

Clear seasonal patterns in SO_4^{2-} and DO concentrations of 0–40 cm porewater were observed in Harp swamp (Figure 2). Porewater chemistry in 0–40 cm peat was strongly associated with seasonal changes in mean monthly temperature and somewhat with mean monthly water table fluctuations (Table I). Sulphate concentration < 2 mg L^{-1}, and low DO was observed throughout the peat column in Harp swamp during each of 3 summers when water tables were near the surface, water residence times were high, due to low runoff inputs, and peat temperatures were warmer (Figure 2). With increased water levels and water flow and decreased temperatures during fall-early winter to spring the DO and SO_4^{2-} concentrations of the surface water in the swamps were generally similar to the chemistry of shallow groundwater and stream water entering Harp swamp and the swamp outlet streams (Eh_7 > 350 mV, DO > 4 mg L^{-1}, SO_4^{2-}, 8–12 mg L^{-1}).

The differences in upland-wetland connection and greater seasonal water table variations resulted in marked differences in porewater chemistry between Harp and Plastic during and following dry summer periods. The seasonal patterns in SO_4^{2-} and DO concentrations of 0–40 cm porewater observed in Harp swamp appear to be disrupted by large water table drawdowns in the summer of 1990 and 1991

TABLE I

Pearson correlation coefficients for linear relationships between mean monthly pore water parameters for each depth (0, 20, 40 and 60 cm), water table elevation and surface water temperatures in Plastic and Harp swamp, from June 1990 to August 1992

	Peat depth	Water table	Surface temp °C	Eh_7	DO
Plastic Swamp					
Water Table (cm)	–0.096				
Surface Temp.	0.084	–0.634[c]			
Eh_7 (mV)	–0.416[b]	–0.041	0.253		
DO (mg L^{-1})	–0.633[c]	0.023	0.210	0.393[a]	
SO_4^{-2} (mg L^{-1})	–0.562[c]	0.028	0.086	0.446[b]	0.394[a]
Bartlett Chi-Square Statistic 90.39; DF = 15, p = < 0.001					
Harp Swamp					
Water Table (cm)	0.022				
Surface Temp.	0.004	–0.682[c]			
Eh_7 (mV)	–0.721[c]	0.088	–0.187		
DO (mg L^{-1})	–0.702[c]	0.235	–0.579[b]	0.646[c]	
SO_4^{-2} (mg L^{-1})	–0.622[c]	0.312[a]	–0.903[c]	0.409[b]	0.633[c]
Bartlett Chi-Square Statistic 218.3; DF = 15, p = < 0.001					

[a] $p < 0.05$, [b] $p < 0.01$, [c] $p < 0.001$.

in Plastic swamp (Figure 2). Porewater chemistry was not significantly correlated with water table elevation or peat temperature in Plastic swamp (Table I). However, porewater could only be sampled in the piezometers after the water table rose and no measures during the large water table drawdown were available for the correlation analyses. Clearly, peaks in porewater SO_4^{2-} and DO concentration were associated with summer water table drawdown. Following the water table drawdown to 60 cm at Plastic swamp in the summer of 1990, pore water DO > 2 mg L^{-1} and Eh_7 > 400 mV were observed at 20 to 40 cm depth. Peaks in mean SO_4^{2-} concentrations occurred to 20–40 cm depth at all sampling sites located in Plastic swamp (30–50 mg L^{-1}) and elevated concentration remained in the peat porewater after the peat was flooded until December of that year (Figure 2). SO_4^{2-} concentrations in surface and 20 cm peat decreased from winter values of 6–10 mg L^{-1} to less than 2 mg L^{-1} by mid-May, 1991, as the water table dropped to just below the peat surface. Aeration of peat and peaks in mean SO_4^{2-} concentrations near 20 mg L^{-1} occurred to a depth of 20 cm following two dry periods later in the summer of 1991 when the water table dropped to 20 cm below the surface. In contrast, during the wet summer of 1992 pore water chemistry in Plastic swamp was similar to Harp swamp. DO and Eh_7 indicated anoxic conditions and SO_4^{2-} concentrations remained < 2 mg L^{-1} at the surface and 20 cm depth.

The seasonal variation and peaks in water chemistry of shallow hillslope groundwater and stream inputs were much less than the peat porewater in both swamps. Groundwater and stream water entering Harp and Plastic swamps were aerobic (Eh_7 > 350 mV, DO > 4 mg L^{-1}) with SO_4^{2-} concentration generally remaining within 6 to 12 mg L^{-1} and 6 to 15 mg L^{-1}, respectively (Devito, 1994; Devito and Hill, 1997).

4.3. Water soluble SO_4^{2-} and net SO_4^{2-} mobilization of surface peat

Temporal trends in SO_4^{2-} pools of the surface peat (0–10 cm) were different between Plastic and Harp swamp (Figure 3). In Plastic swamp, mean extractable SO_4^{2-} pools in surface peat ranged from 1500 to 3000 mg SO_4^{2-} m^{-2} during August to October, 1990, and were significantly greater than SO_4^{2-} pools in Harp swamp. The SO_4^{2-} pools remained within 500–1200 mg SO_4^{2-} m^{-2} from fall 1991 to summer 1992. The mean extractable SO_4^{2-} pools of Harp peat remained within 500–1200 mg SO_4^{2-} m^{-2} for each sampling period during the study (Figure 3).

High rates of net SO_4^{2-} mobilization were observed in the surface peat in Plastic swamp during August and September 1990 (> 30 mg SO_4^{2-} m^{-2} d^{-1}) and May-June 1991 (30 mg SO_4^{2-} m^{-2} d^{-1}) in association with water table drawdown and increases in porewater SO_4^{2-} concentration and extractable pools (Figure 4). Summer peaks in mobilization were followed immediately by significant immobilization during October-November, 1990 and September-October 1991. Net SO_4^{2-} immobilization was observed during the summer of 1992 in Plastic swamp. Although there was considerable variability during the summer of 1990, low mean SO_4^{2-} mobilization and net immobilization of SO_4^{2-} were measured throughout the study period in Harp swamp (Figure 4).

There was a significant inverse relationship between net SO_4^{2-} mobilization and minimum water table elevation during incubation at all hollow sites in Plastic swamp in 1990–91 (r = –0.771; $p < 0.001$) but no significant relationship in 1991–92 (r = 0.081; $p > 0.999$) (Figure 5). High net SO_4^{2-} mobilization occurred during incubations in which the minimum water table was more than 25 cm below the peat surface. Low rates of mobilization or net depletion occurred when the minimum water table was less than 20 cm below the peat surface during the incubation. Harp swamp experienced a small range in minimum water level and there was no significant relationship between net SO_4^{2-} mobilization and water table position in 1990–91 or 1991–92 (Figure 7; r = 0.065 and 0.457; $p < 0.999$). No significant linear relationship was observed between net SO_4^{2-} mobilization and mean surface peat temperature during incubation in Plastic swamp during 1990–91 (r = 0.395, p

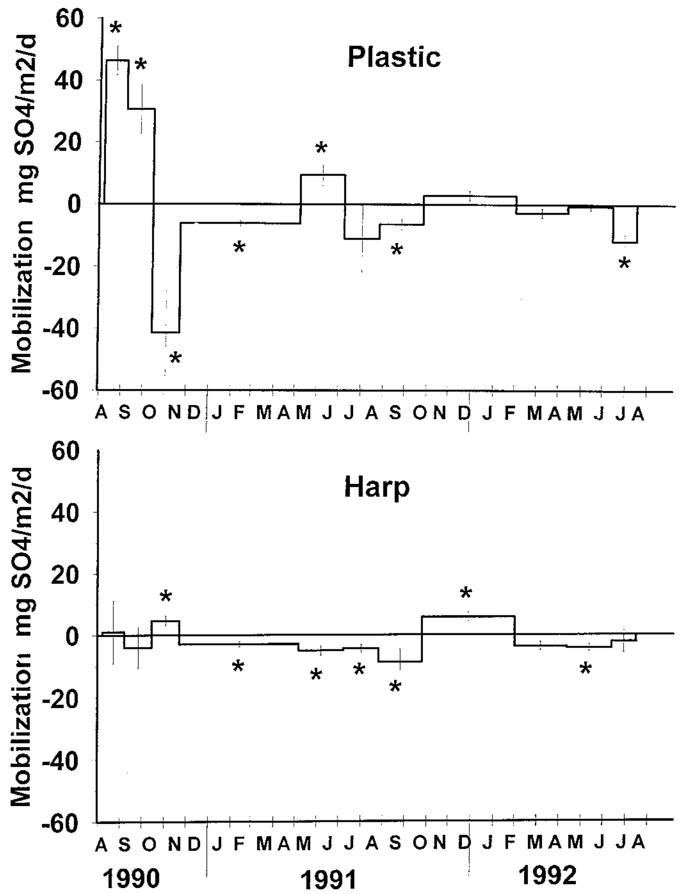

Figure 4. Mean net sulphate mobilization at Plastic and Harp swamp from 7 August 1990 to 15 August 1992. Shown are mean ± standard error (SE) of 6 to 12 cores (2–4 cores per site) from all hollow locations for each incubation period in each swamp. * = significantly difference from zero for that incubation, $p < 0.05$.

= 0.561) or 1991–92 (r = –0.555, p = 0.256) or in Harp swamp in both years (r = 0.011 and –0.295, p < 0.999). There was a poor but significant inverse relationship between minimum water elevation and mean peat temperature in Plastic swamp (r = –0.525, p = 0.002), but the relationship was not significant in Harp (r = –0.378, p = 0.063).

Although there is considerable variance associated with annual estimates for each hollow site, analyses of variance using estimates for the 3 hollow sites in each wetland indicates a significant interaction (F = 26.6; p = 0.001) and difference between swamps (F = 12.7; p = 0.007) and between years (F = 15.3; p = 0.004) in net annual SO_4^{2-} mobilization (Table II). In 1990–91 the net annual SO_4^{2-} mobilization in Plastic swamp was significantly greater than in Harp swamp (p = 0.011). The net annual SO_4^{2-} mobilization was observed at all hollow sites in Plastic swamp

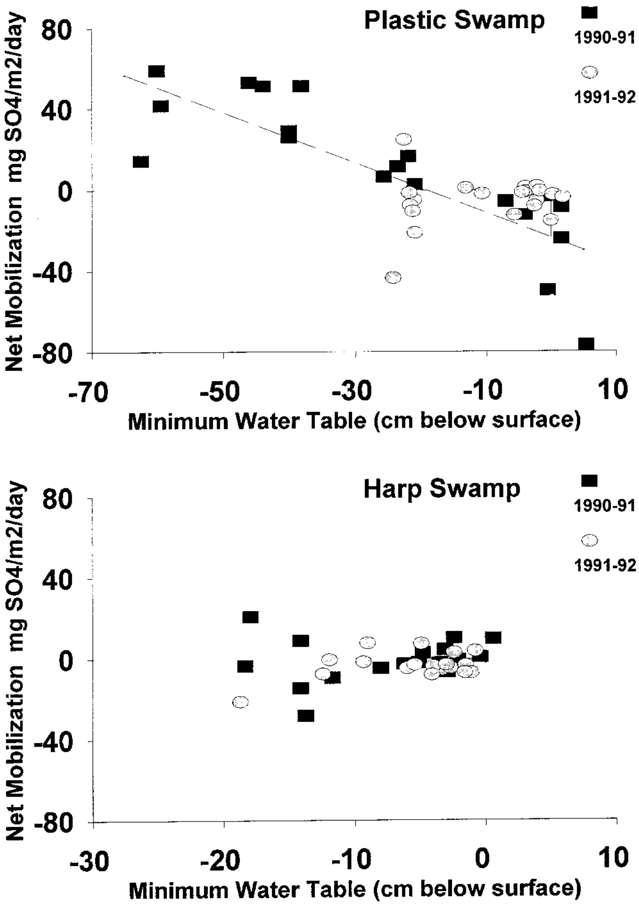

Figure 5. Mean net SO_4^{2-} mobilization in all hollow sites in relation to minimum water table depth (cm) for each incubation period in Plastic and Harp swamp. Values are means of 2–4 cores for each incubation period at each site from August 1990 to August 1992. Regression statistics for Plastic swamp hollow sites for August 1990 to August 1991: $Y = -23.6 \pm 6.6 - 1.24 \pm 0.21$ X, $r^2 = 0.593$, $p < 0.001$.

in 1990–91 and was significantly greater than in 1991–92 ($p = 0.004$) when net immobilization occurred at all sites (Table II). There was no significant difference between years in Harp swamp ($p = 0.398$) as net annual SO_4^{2-} immobilization was observed at all hollow sites in both 1990–91 and 1991–92.

5. Discussion

This study documents a direct relationship between net mobilization of SO_4^{2-} of surface peat and water level fluctuations which explains a large portion of the

TABLE II

Annual net SO_4^{2-} mobilization (mg SO_4^{2-} m^{-2} yr^{-1}) of 0–10 cm peat at 3 hollow sites in each swamp. Values are the sum of mean mobilization rates of 2–4 cores at each site for each incubation period in that year (Aug. 1 – July 31). Associated variances with annual sums of SO_4^{2-} mobilization were calculated by first order error propagation of the variance of monthly means for each location in the wetland (Meyer, 1975)

	site	1990–91 mean ± std	1991–92 mean ± std
Plastic swamp			
Lagg	(P17)	1052 ± 827	–1074 ± 377
Thicket	(P15)	2559 ± 1733	–934 ± 390
Forested	(P16)	1908 ± 2335	–664 ± 523
Mean and std of 3 sites		1840 ± 756[a,b]	–891 ± 208[a]
Harp swamp			
Seep	(H15)	–1542 ± 1789	–428 ± 844
Lagg-Channel	(H18)	–236 ± 958	–276 ± 414
Forested	(H16)	–584 ± 1439	–530 ± 389
Mean and std of 3 sites		–787 ± 676	–411 ± 127

[a] = significant difference between swamps
[b] = sign. diff between years, $p < 0.05$.

variability in peat and pore water SO_4^{2-} dynamics and stream export observed between the two forested swamps in this study (Devito, 1995; Devito and Hill, 1997; LaZerte, 1993). Although several previous studies have suggested that SO_4^{2-} release is linked to water table drawdown (eg., Bayley *et al*., 1986; LaZerte, 1993; Weider, 1985), this study is the first to document a statistical relationship between water table fluctuations and SO_4^{2-} mobilization in inland wetland systems. The period and amplitude of the water table fluctuations in the two study swamps, and thus peat anoxia, are strongly related to groundwater regime and summer rainfall patterns (Devito *et al*., 1996) emphasizing the need to place wetland SO_4^{2-} dynamics in the context of catchment hydrogeology (Devito, 1994; Steele and Buttle, 1994). Comparison of SO_4^{2-} pore water and mobilization rates in Harp and Plastic swamps sheds light on the variability of S-cycling in Shield regions impacted by high rates of SO_4^{2-} deposition. The study wetlands encompass the range of till depth, water table fluctuations and peaks in SO_4^{2-} export observed from a larger set of wetland catchments following drought periods in the southern Canadian Shield landscape (Devito *et al*., 1998).

There are limitations in using the buried bag technique to estimate net SO_4^{2-} mobilization, especially in water saturated soils. Micro-topography in the wetlands can result in variability in water table elevation and peat saturation adjacent to each recording well. Although attempts were made to select incubation sites at the same elevation of the adjacent well, small differences may have contributed to the spatial variability in SO_4^{2-} mobilization and an increase in the variances in the water table and net SO_4^{2-} mobilization relationship. During incubations peat moisture content and oxygen regimes may vary with conditions external to the bag. In addition, mobilization of SO_4^{2-} may not occur at a constant rate and thus variations in the length of incubation period may also introduce errors (Adams *et al*., 1989). However, concurrent increases in extractable pools and budget estimates showing a large export of SO_4^{2-} during 1990 (Devito, 1995) support the results from buried bag studies. Sulphate to Cl ratios of surface water in Plastic swamp increased following drought periods (unplished data), suggesting a net increase of SO_4^{2-} in the surface waters and not simply evaporative concentration.

The lack of relationship between net SO_4^{2-} mobilization and peat temperature observed would be expected because net SO_4^{2-} mobilization is the difference between gross mobilization (oxidation and mineralization) and gross immobilization (dissimilatory SO_4^{2-} reduction) rates and both rates increase with temperature (Feijtel *et al*., 1989; Spratt and Morgan, 1990). The dominance of anaerobic or aerobic processes at cool or warm temperatures is controlled largely by water table elevation which is related to peat saturation and water residence time. Thus fluctuations in water table elevation and measures of net SO_4^{2-} mobilization provide a useful measure of potential SO_4^{2-} retention or release from a wetland, particularly when extreme fluctuations in water table occur.

The relationship between water table fluctuation and SO_4^{2-} mobilization rates in wetlands may be complex due to interactions with temperature, runoff rates, and peat hydraulic properties. The capillary fringe and anoxic conditions in peat can extend to 20 cm above the water table (Williams, 1974; Ingram, 1983). The water table drawdowns during all summers in Harp swamp and non-drought periods in Plastic swamp were not great enough to bring the capillary fringe much below the peat surface and allow for complete aeration of the peat. Furthermore, water table elevations within 0–20 cm of the surface were associated with low flow rates and increased probability of anoxia as the water stagnates, which have been observed in previous studies (Devito and Dillon, 1993) and other wetlands (Sparling, 1966). Dissimilatory SO_4^{2-} reduction has been shown to be important in removing SO_4^{2-} during similar conditions in wetlands (Brown and MacQueen, 1985; Bayley *et al*., 1987; Westermann and Ahring, 1987). Proportional increases in dissimilatory SO_4^{2-} reduction may explain the low net SO_4^{2-} mobilization or net immobilization of SO_4^{2-} within the peat during non-drought periods in Plastic swamp, and during all summers in Harp swamp. Although seasonal reductions in pore water SO_4^{2-} concentrations observed in this study are probably influenced by temporal patterns of plant uptake (Bayley *et al*., 1987; Urban *et al*., 1989), net SO_4^{2-} depletion observed in buried bags, which excluded plant uptake, suggest that dissimilatory sulphate reduction is an important process in surface peat during periods of plant growth.

During dry conditions a theshold response of increased SO_4^{2-} mobilization occurs once the water table drops to a depth where the capillary fringe no longer extends to the surface and the peat finally drains and is aerated. Observations of peat soil moisture (unpublished data) and mobilization rates indicate that for peat with the physical properties characteristic of Plastic and Harp swamp a drop in water table of 25 cm or more below the surface is required for consistent drainage and aeration resulting in large net SO_4^{2-} mobilization. Net SO_4^{2-} immobilization will likely occur if the water table is within 25 cm of the surface and the peat remains saturated. This non-linear relationship has been observed in other systems. Results of incubation studies in wetland plots in Scotland showed that lowering the water level to about 20 cm below the surface significantly decreased the net N mineralization but further lowering of the water level resulted in mineralizations increasing significantly (Williams, 1974).

Quantification of S pools, which may contribute to SO_4^{2-} release in peat, is necessary to determine the recovery period required for reduction of long term export of SO_4^{2-} and acidification of systems downstream of valley wetlands following recent reductions in SO_4^{2-} deposition to the landscape (see Dillon and LaZerte, 1992). Although mobilization rates do not distinguish between inorganic S oxidation or organic S mineralization, they can provide an estimate of the total amount of S available for export. Net SO_4^{2-} mobilization rates of 0.04 g SO_4^{2-} m^{-2} day^{-1} over the 3 summer months during 1990 in Plastic swamp represent about 3–4 g SO_4^{2-} m^{-2}. These are close to the independent estimate of 1–2 g SO_4^{2-} m^{-2} increase in available water soluble SO_4^{2-} and a net export of 3–5 g SO_4^{2-} m^{-2} determined from a mass balance for fall 1990 in Plastic swamp (Devito, 1995).

The total availability of S for export depends on the depth of the water table drawdown as well as the pool of S in the previously saturated peat which is exposed. The time of peat aeration is probably also important, particularly if organic S is the primary source of SO_4^{2-} (Weider and Lang, 1988). The depth to which elevated SO_4^{2-} concentrations occurred following the dry summer of 1990, depths of peak Cr^{+2}-reducible S, and stable C:S ratios (Devito, 1994) indicate that S mobilization probably occurs to a depth of 30–40 cm in the peat of Plastic swamp. Devito (1994) determined the total available inorganic and total S pool in the top 0–40 cm of peat in Plastic swamp to be 30 ± 2 g S m^{-2} (about 90 g SO_4^{2-} m^{-2}) and 160 ± 7 g S m^{-2} (480 g SO_4^{2-} m^{-2}), respectively (Devito, 1994). Turnover of both inorganic and organic S would contribute to the available SO_4^{2-} over the length of time the peat was aerated (1–2 months) in Plastic swamp (Weider and Lang, 1988). Assuming the available pool for export is derived from 0–40 cm of peat and the average export during dry simmers is similar to that in 1990 the standing stock of total S in the peat of Plastic swamp represents many decades of SO_4^{2-} export and acidification of downstream systems.

A major implication of intermittent release of accumulated SO_4^{2-} in wetland peat is that the recovery resulting from current reductions in S deposition in north eastern North America by streams draining valley wetlands located in catchments which have previously received increased acidic S deposition will be much longer than recovery periods observed or predicted for upland forests soils (Dillon and LaZerte, 1992; Houle and Carignan, 1995). Furthermore, the rate of recovery of a particular aquatic system may be influenced by the physiography and groundwater regime of the catchments containing wetlands that drain into these water bodies (Devito and Hill, 1998).

In light of predictions of warmer temperature and increased frequency of drought for eastern North America (e.g. Manabe and Wetherald, 1986) the influence of climate change on spring and summer recharge to local aquifers in the Shield landscape is an important consideration. Not only would such changes in climate result in larger water table drawdown and increase the S export from peat in wetlands with historically ephemeral groundwater inputs, but may influence wetlands which at present are not susceptible to drought. The upland storage to sustain continuous groundwater inputs in Harp catchment, for example, is small and slight changes in recharge depths within the catchment could result in the development of an ephemeral groundwater flow pattern and increased amplitude of water level fluctuations. The total S pools in the top 0–40 cm of peat in Harp swamp are 243 ± 20 g S m^{-2} (730 g SO_4^{2-} m^{-2}) which is about 1.5 times the total S pool in Plastic swamp (Devito, 1994). Wetlands which have historically received continuous groundwater inputs may have larger pools of S from both natural and anthropogenic sources. Water table drawdown in these systems would be expected to result in large rates of SO_4^{2-} mobilization and export and potential acidification of downstream systems.

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