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Sulphate dynamics in a northern wetland catchment during snowmelt

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Abstract. Fluxes and stores of SO_4^{2-} were measured in a small Canadian Shield basin during the 1989 snowmelt. Sulphate flux from the unsaturated zone (14.1 ± 7.3 kg ha^{-1}) was four times the amount supplied in meltwater and precipitation (3.5 ± 0.4 kg ha^{-1}). This reflects flushing of soluble SO_4^{2-} from organic and upper mineral soil horizons during melt, which counteracted potential dilution of groundwater SO_4^{2-} levels by large water inputs to the basin. 35.6 ± 12.4 kg SO_4^{2-} entered the saturated zone during melt, supplied equally by leaching from overlying soils and conversion of the capillary fringe to phreatic water due to rising water table levels. Streamflow conveyed 70% of the total SO_4^{2-} export of 10.1 ± 2.3 kg ha^{-1}, and was largely supplied by groundwater discharge from a wetland in the lower portion of the basin. The remaining 30% of total export was via shallow subsurface flow. Results highlight the importance of unsaturated and saturated zone processes for SO_4^{2-} dynamics and export during snowmelt.

Introduction

Considerable research has focussed on SO_4^{2-} dynamics in forested ecosystems, largely due to the association of SO_4^{2-} with acidic precipitation and its subsequent influence on soil, groundwater and surface waters. Mitchell & Fuller's (1988) review of ecosystem models concluded that an appreciation of S dynamics in terrestrial ecosystems depends on assessing such processes as organic and inorganic S transformations, basin hydrology, SO_4^{2-} adsorption and solubility, and uptake by vegetation. Hydrological controls on SO_4^{2-} mobility have received particular attention in recent studies (Lynch & Corbett 1989; Schnabel et al. 1993; Huntington et al. 1994). These controls have often been examined using SO_4^{2-} mass balances conducted at the basin scale (e.g. Likens et al. 1977; Cadle et al. 1984; Stottlemyer 1987; Galloway et al. 1987; Probst et al. 1992).

Mass balance studies have provided valuable information on long term trends in basin response to surface inputs by developing annual SO_4^{2-} budgets (e.g. Johnson 1984; Probst et al. 1992). In addition, they have often detected enhanced short-term SO_4^{2-} fluxes through various stores in the basin as a result of rapid surface inputs. Spring snowmelt represents the major period of hydrological activity in many northern basins, and is associated with pH depressions in surface and subsurface waters in acid-sensitive terrain. There is increasing evidence of over-winter SO_4^{2-} accumulation in soils as a result of anthropogenic inputs and natural processes, and rapid flushing of SO_4^{2-} from the soil during spring melt (Barry et al. 1984; Ferrier et al. 1989; Hazlett et al. 1992). Thus, research into SO_4^{2-} dynamics during this period may enhance our overall appreciation of the influence of acidic precipitation upon aquatic ecosystems. Nevertheless, mass balance studies have often concentrated on precipitation inputs and stream outputs to the exclusion of SO_4^{2-} behavior in the unsaturated and saturated zones (cf. Hazlett et al. 1992). Despite considerable research into SO_4^{2-} dynamics in soils (e.g. Johnson & Todd 1983; Fuller et al. 1985; Courchesne & Hendershot 1989; David et al. 1991), studies linking soil processes to SO_4^{2-} storage and flux in subsurface and surface waters are less common. Without such links, it is difficult to place studies of soil chemistry within the overall context of SO_4^{2-} dynamics at the basin scale.

This paper presents a mass balance approach to the study of SO_4^{2-} mobility in a small wetland basin during spring snowmelt, focussing on the storage and transfer of SO_4^{2-} within and between various compartments (Fig. 1). Its related objectives are: (1) to present an approach for estimating the basin-scale SO_4^{2-} flux from the unsaturated zone to underlying groundwater; and (2) to assess the hydrological controls on SO_4^{2-} dynamics in a forested wetland environment.

Methods and materials

Study area

Research was conducted on the Canadian Shield in a 2.44-ha basin near Chalk River, Ontario (46°02′ N, 77°20′ W), on the property of Atomic Energy of Canada Ltd. (A.E.C.L.). The basin contains an ephemeral wetland which supplies streamflow for two to three months in spring (Fig. 2). Granitic gneiss bedrock is overlain by ~1.5 m of glacial till, mantled in turn by fine, homogeneous Pleistocene fluvial and aeolian sands. Their porosities and bulk densities are ~45% and 1500 kg m^{-3}, respectively, and the sands are several meters thick on side-slopes near the outlet and absent on the southeast portion of the basin divide. Well-drained Humo-Ferric Podzols have developed (Gillespie et al. 1964), which typically consist of an O horizon 2–3 cm thick, a well-defined Ae horizon rarely exceeding 8 cm in thickness, and

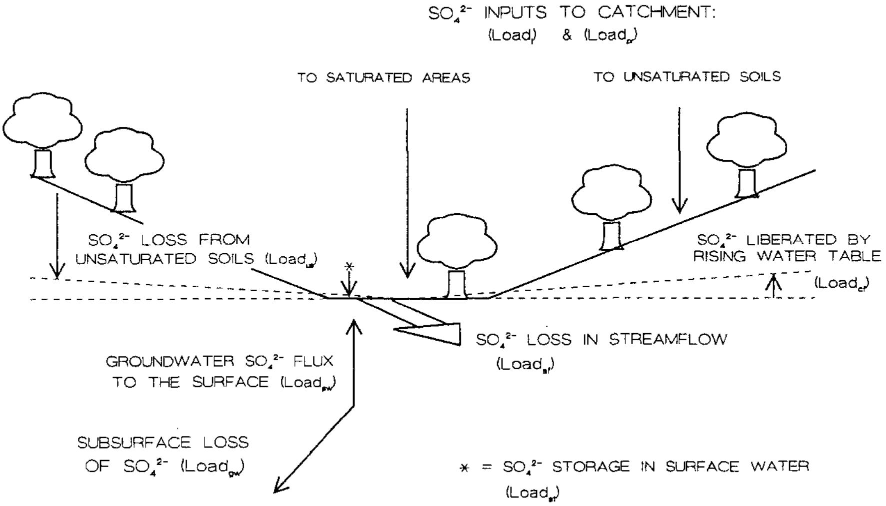

Fig. 1. Fluxes and stores of SO_4^{2-} examined in this study.

a reddish-brown B horizon at depths of between 5 and 40 cm. The basin is largely covered by aspen (*Populus tremuloides* and *P. grandidentata*), white birch (*Betula papyrifera*), and red maple (*Acer rubrum*), while fen undergrowth covers the wetland.

The area's climate is classed as Köppen DFb. Average annual precipitation is ~840 mm (Barry 1975), and the area receives moderate S inputs from atmospheric deposition relative to other sites in southern Ontario. Peak snowpack water equivalent (SWE) ranges from 100 to 150 mm (Barry & Price 1987), and snowmelt typically extends over several weeks through March and April, often accompanied by rain-on-snow events. Soils may be frozen to depths up to 0.3 m prior to melt; however, soil frost is usually loose and open textured, and does not generally restrict meltwater infiltration into the soil (Price & Hendrie 1983).

Field measurements

Water inputs to the soil during the 1989 snowmelt were estimated using a 5×5 m lysimeter lined with polyethylene sheeting prior to snowfall. The lysimeter was bounded by plywood walls extending 0.32 m above ground, preventing lateral movement of water into or out of the lysimeter along ice lenses in the snowpack. Runoff was estimated from continuous stage measurements in two 200-L drums that collected lysimeter flow. Previous work in the basin indicates that Horton flow does not occur in significant

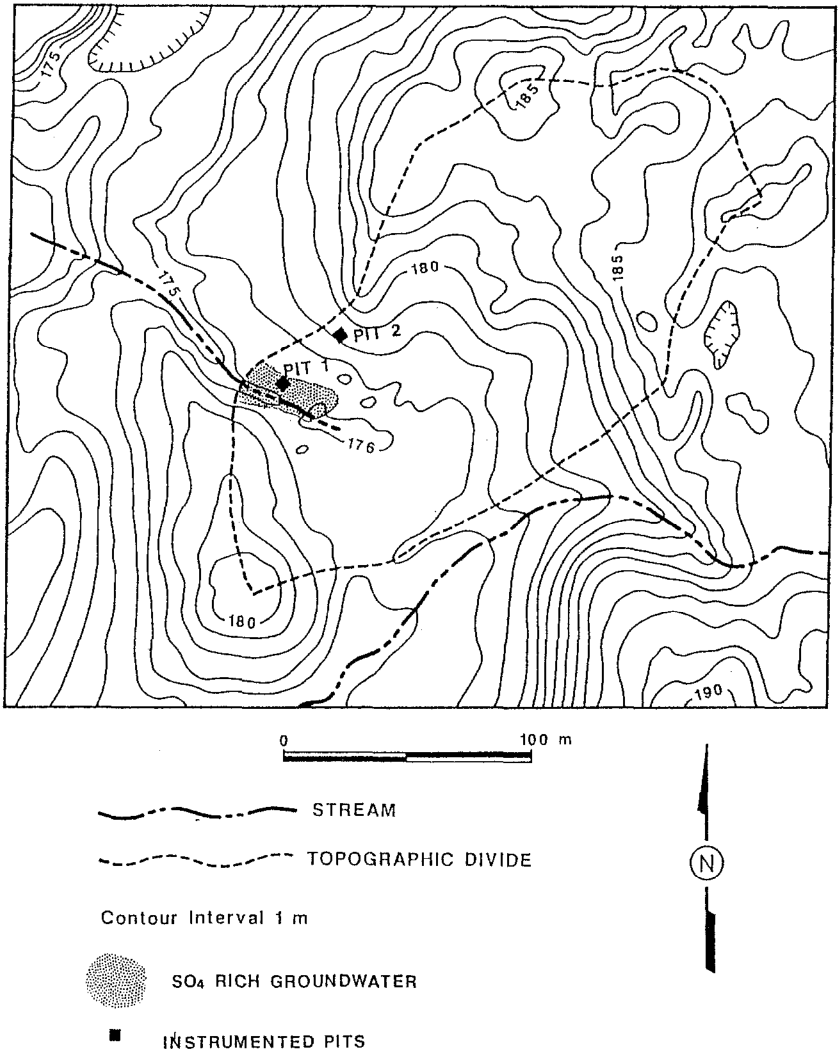

Fig. 2. Study basin topography. Locations of the two soil pits and the zone with elevated SO_4^{2-} levels in shallow groundwater are also indicated.

amounts during snowmelt (Price & Hendrie 1983; Buttle & Sami 1990a), and lysimeter runoff was assumed to represent water infiltration. Runoff depths in previous years were within 5% of average snowpack water losses determined from snow surveys (Buttle & Sami 1990b), and are representative of water inputs to the basin. Pre-melt SWE in the lysimeter was estimated from adjacent snow cores. Lysimeter runoff was sampled hourly using an automatic sampler. Precipitation was measured using a Nipher snow gauge at an open site 2 km from the basin, and individual events were sampled for chemical analysis. A manual rain gauge adjacent to the lysimeter was also monitored. Precipitation water equivalents averaged 6% < those from the Nipher gauge, but the difference was neither consistent nor significant. Therefore, Nipher gauge values were taken to represent inputs to the basin.

A number of methods have been employed to estimate solute storage and fluxes in the unsaturated zone, including use of tension (Foster et al. 1989) and zero-tension lysimeters (Findeis et al. 1993). The former only sample soil water chemistry, and must be combined with independent estimates of water volumes passing the sample depth in order to obtain solute flux. Tension lysimeters may be difficult to operate during spring snowmelt, since they cannot sample water from frozen soils (Peters & Healy 1988). In addition, interactions between solutes and ceramic lysimeter bulbs have been reported (Beier et al. 1992). Raulund-Rasmussen (1989) found significantly lower SO_4^{2-} concentrations in tension lysimeter samples relative to those obtained from centrifugation, which was attributed to adsorption to the lysimeter bulb. Zero-tension lysimeters give representative samples of soil water chemistry along with the volume of water reaching the sample depth; however, they require saturation of soil immediately above the lysimeter before water can enter it. This distorts the hydraulic potential above the lysimeter relative to that in the lysimeter's absence (cf. Atkinson 1978). Thus, the surface area contributing solutes to the lysimeter is not necessarily equal to the lysimeter's collecting area, introducing an uncertainty to areal flux estimates (e.g. Price & Watters 1988). Use of zero-tension lysimeters at this site is particularly problematic, since the sandy soils rarely approach saturation during spring melt (Buttle & Sami 1990a).

Given these constraints, volumetric soil water (Θ) and SO_4^{2-} storage in the unsaturated zone were monitored by sequential extraction of soil cores adjacent to two pits in the basin (Fig. 2). Pit 1 (1 m deep) was 8 m from the stream and overlies a zone that displays high groundwater SO_4^{2-} levels relative to other areas in the basin (Barry & Robertson 1988). Pit 2 was located further upslope (35 m from the stream) and was 1.75 m deep. Samples were obtained by hammering a 4.6 cm I.D. aluminum pipe to depths of 0.9 m and 1.2 m at pits 1 and 2, respectively. The pipe was thoroughly cleaned with acetone prior to sampling. Soil compaction within the cores was determined during insertion, and cores were sectioned into 0.06-m segments immediately after sampling and sealed to prevent moisture loss. Cores were extracted daily for four days following the start of melt and every three days for the remainder of the study. The method provides a simple and appropriate means of estimating Θ and SO_4^{2-} changes in soils at this site, given the thick unsaturated zone, lack of significant lateral flow, and restriction of macropore flow to near-surface

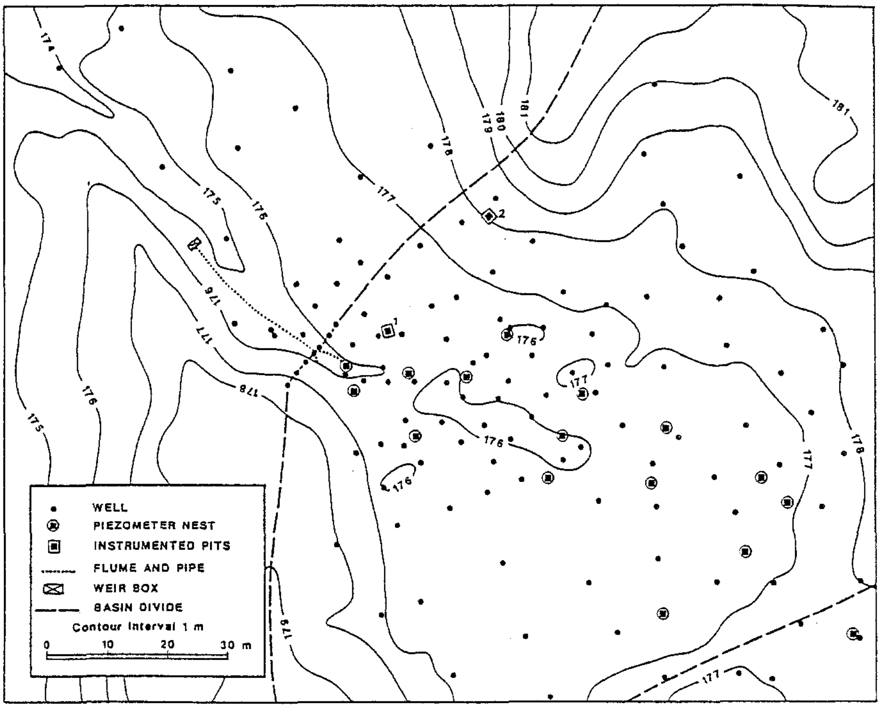

Fig. 3. Instrumentation in the lower portion of the basin.

soil (Buttle & Sami 1990). Storage changes estimated from sequential coring are complicated by soil heterogeneity, and it is impossible to demarcate the influence of recharge processes, initial conditions and textural variations upon changes in Θ and SO_4^{2-} concentration (Buttle & Sami 1990). Nevertheless, Barry et al. (1984) contend that it provides a reliable means of estimating solute fluxes in soils during snowmelt.

Water table elevations and hydraulic heads were monitored in 130 shallow wells and 18 piezometer nests installed in and around the wetland (Fig. 3). Wells were screened for a length of 1 m and were installed to depths up to 5 m, in most cases down to the underlying till. Wells in the wetland were installed up to 2 m below ground surface, and piezometer nests were installed to depths of up to 2 m. Water table levels were monitored periodically before melt, and daily after the start of melt. Results were used to estimate the extent of surface saturation in the wetland. Piezometric head was measured twice daily during peak melt. All measurements were made with a portable well logger accurate to ±0.005 m. Groundwater samples were collected from piezometer nests prior to, during, and following melt. Piezometers were pumped out 20 hours prior to sampling using a peristaltic pump. Samples for chemical analysis were taken on 19 days, with all piezometers being sampled on four of these days. Redox measurements were made concurrent with sample collection from selected piezometers on six occasions during the melt.

Discharge was monitored continuously at a flume at the basin outflow. Streamflow samples were collected at hourly intervals using a sequential sampler during the first few days of melt, and then every two hours for the remainder of the study. All samples were kept discrete.

Sample analysis

Soil water samples were obtained from core sections by centrifugation at 500 G. Each section contained ~0.1 to 0.15 kg of soil (dry weight), and yielded solutions retained with tensions of ~0–15 m H_2O. This is equivalent to soil water held in macro-, meso-, and larger (dia. >0.002 μm) micropores (Luxmoore 1981). Centrifugation was repeated at 10-minute intervals until water recovery ceased. Remaining water content was determined gravimetrically (oven drying), allowing calculation of Θ for each section. Use of centrifugation to obtain soil water samples for chemical analyses is open to criticism, since samples contain contributions from micropore water which may not move under ambient hydraulic gradients and whose chemistry may differ from water moving in macro- and mesopores. However, tracer studies in these soils indicate that micropores *do* conduct flow during snowmelt (Buttle & Sami 1990a). In addition, the time between sampling and centrifugation ranged from several hours to days. This may have allowed SO_4^{2-} concentrations in the various pore sizes to equilibriate, as suggested by Zabowski & Ugolini's (1990) study of the influence of centrifugation speed upon soil water chemistry sampled from a subalpine Spodosol. Thus, soil water samples are felt to represent the chemistry of infiltrating water. Sulphate and NO_3^- concentrations were determined for all samples by eluent-suppressed ion chromatography (sensitivity <1 μg mL^{-1}) Calcium and Mg^{2+} were determined by atomic absorption (sensitivity of 10 μg L^{-1}). Lanthanum was added to samples and standards to reduce spectral interference from other species in solution, and N_2O was used as an oxidant. Aliquots (25 to 50 mL) of all groundwater and 50 stream samples were titrated with a Mettler DL25 titrator to determine alkalinity (sensitivity of 10 μg HCO_3^- L^{-1}). A modified Gran analysis (Kramer 1980) was employed for 12 samples to confirm low alkalinity values obtained from the titrator. Alkalinity was not determined for soil water because of insufficient water volumes.

Load estimates

Sulphate inputs to the soil were estimated using lysimeter ($LOAD_l$) flows and chemistry (period-weighted method) plus precipitation inputs ($LOAD_{pr}$) once snowcover disappeared. Total SO_4^{2-} flux to the basin was separated into deposition on saturated and unsaturated areas. Sulphate outputs in streamflow ($LOAD_{sf}$) were determined using the period-weighted method (Dann et al. 1986).

Sulphate transport in the unsaturated zone was determined from Θ and SO_4^{2-} concentrations in soil cores extracted at Pits 1 and 2. Unsaturated zone thickness varies considerably in the basin, from ~0 m adjacent to the wetland to several meters on the basin divide. Johnson & Todd (1983) observed decreased SO_4^{2-} flux with depth in soil at the Walker Branch watershed in Tennessee, which they attributed to SO_4^{2-} adsorption. Organic matter content also appears to influence a soil's ability to retain SO_4^{2-}, implying that near-surface horizons may not respond similarily to deeper mineral soil. The present approach estimates SO_4^{2-} transfer to groundwater by combining SO_4^{2-} fluxes at various soil depths with estimates of the spatial variability of unsaturated zone thickness in the basin. The method is based on the soil water budget and the assumption that water motion in the unsaturated zone is via translatory flow, where infiltration into a section of soil results in downward displacement of stored water. Buttle & Sami (1990a) showed operation of translatory flow at this site, and that a small amount of stored water (3% of total soil volume) is essentially immobile during infiltration. Water flux from the soil column (O_w) during a defined interval is first calculated:

$$O_w = I_w - (M_2 - M_1) \tag{1}$$

where I_w is melt and precipitation added at the surface (L), and M_1 and M_2 are mobile water contents [$(\Theta - 0.03) \times$ soil volume] held in the soil column above the flux plane on the two occasions. O_w is assumed to be extruded from the core across the flux plane by entry of an equivalent amount of water from above. Soil column height above the flux plane required to provide this water is estimated by summing mobile water volumes in the core at time 1, beginning at the flux plane and moving up the core until the running total equals the mobile water lost, thus:

$$\sum_{k=1}^{o} = O_w \tag{2}$$

where $k = 1$ is the core's bottommost section. The interval between the flux plane and section o is assumed to have provided the water (and therefore the

SO_4^{2-}) that passed the flux plane. Sulphate transport across the flux plane (O_{SO_4}) is then

$$O_{SO_4} = \sum_{k=1}^{o} M_{1k} \cdot C_{1k} \tag{3}$$

The water table rose within 0.75 m of the surface during melt at Pit 1. Since capillary fringe thickness for these soils ranges from 0.2 to 0.4 m (Steele unpubl. data), SO_4^{2-} flux calculations at Pit 1 were restricted to the top 0.5 m of soil to avoid complications from capillary fringe waters. This method was used at Pit 1 with flux planes at 0.2 and 0.5 m below the surface, and at Pit 2 with flux planes at 0.2, 0.6 and 1.0 m. Fluxes from the pits were averaged for the 0.2 and 0.6 m flux planes to account for soil heterogeneity. For simplicity, fluxes at the 0.5 m plane at Pit 1 were assumed to equal those at 0.6 m. Mean fluxes were applied to areas of the basin with specific unsaturated zone thicknesses to estimate SO_4^{2-} fluxes from the unsaturated zone to groundwater ($LOAD_{us}$), such that fluxes determined at the 0.2, 0.6 and 1.0 m flux planes were assumed to represent those from unsaturated zones with thickness of <0.4 m, >0.4 m and <0.8 m, and >0.8 m, respectively. Basin areas corresponding to these unsaturated zone thickness intervals were estimated using surface elevation and water table data for days when cores were extracted.

Sulphate can also be transferred to the saturated zone during water table rise and conversion of vadose water to phreatic water, as distinct from SO_4^{2-} advection below the unsaturated zone (discussed above). Water table measurements were used to estimate total rise over the study. Pre-melt Θ was obtained at both pits, and SO_4^{2-} concentration in the capillary fringe was assumed to equal that in near-surface groundwater. Thus, groundwater samples taken prior to melt from shallow piezometers on the hillslopes and in the two pits were used to estimate SO_4^{2-} load immediately above the phreatic zone that was transferred to groundwater as a result of water table rise ($LOAD_{cf}$).

Groundwater flux from the basin was calculated using Darcy's Law. Five pairs of wells located in the lower basin were used to determine a range of hydraulic gradients normal to the basin boundary. Saturated hydraulic conductivities were measured using a constant head permeameter with samples from Pit 2. Cross-sectional flow area was estimated using the width of the lower end of the basin (75 m) and a mean saturated zone thickness of 1.5 m. Sulphate concentrations obtained from pit piezometers were multiplied by groundwater flow rates to estimate SO_4^{2-} flux from the basin via groundwater ($LOAD_{gw}$). The area of high SO_4^{2-} concentrations in groundwater near Pit 1 comprised ~25% of the aquifer width, and groundwater SO_4^{2-} concentrations used for these flux calculations were weighted accordingly.

Discharge and recharge areas in the wetland were identified in order to estimate groundwater SO_4^{2-} loading to surface water, initially by examining hydraulic gradients at each piezometer nest. Groundwater chemistry assisted in the identification of discharge areas in some cases, since groundwater advection in discharge areas caused the concentration of conservative solutes to remain constant with depth, whereas in recharge areas dilute surface waters cause solute concentration to increase with depth (Siegel 1988). Seepage areas around each nest were estimated from Thiessen polygons and extent of surface saturation. Groundwater discharge and recharge associated with each nest was determined from Darcy's Law. Sulphate concentrations in groundwater from the shallowest piezometer samples were multiplied by net daily discharges to determine SO_4^{2-} load to surface water ($LOAD_{sw}$). Redox measurements were used in conjunction with NO_3^- determinations to assess the potential for SO_4^{2-} reduction during passage of groundwater from the shallowest piezometers to the surface.

Water held in surface storage in the wetland prior to streamflow was estimated from surface elevations and water table data. This volume was multiplied by SO_4^{2-} concentrations in groundwater discharging to the wetland during initial melt in order to estimate SO_4^{2-} retained in surface storage ($LOAD_{st}$).

Sulphate flux via streamflow was estimated assuming that all groundwater inputs to the wetland mixed with meltwater and precipitation contributions before leaving as streamflow. This estimate was compared with observed exports ($LOAD_{sf}$).

Fractional errors (S) associated with each SO_4^{2-} load estimate were approximated by the probable error associated with the sum of independent variables X and Y (Davidson 1978) or with their product (Devito et al. 1989):

$$S_{(X+Y)} = (S_X^2 + S_Y^2)^{0.5} \tag{4}$$

$$S_{X \cdot Y} = (X^2 \cdot S_Y^2 + Y^2 \cdot S_X^2 + S_Y^2 \cdot S_X^2)^{0.5} \tag{5}$$

Fractional errors for components employed in the load calculations are given in Table 1.

Results and discussion

Lysimeter ($LOAD_l$) and precipitation ($LOAD_{pr}$) loading

Snowmelt began on Julian Day (JD) 83, and 137 mm of water infiltrated the basin's soils by JD 100, when the lysimeter was free of snow (Fig. 4).

Table 1. Fractional errors associated with various components used in determination of SO_4^{2-} loads. Fractional error associated with SO_4^{2-} concentrations in all loads except $LOAD_{st}$ was taken from Devito et al. (1989); the fractional error associated with SO_4^{2-} concentrations in $LOAD_{st}$ was based on observed variability in SO_4^{2-} concentrations in groundwater entering the wetland during the initial stages of melt. Fractional error associated with soil water content in $LOAD_{us}$ was based on Θ variability in the upper 1 m of Perch Lake soils (Price & Bauer 1984). All other fractional errors were taken from Winter (1981) or were based on variations in components observed in the field.

Load	Components	Assumed fractional error
$LOAD_{lp}$	runoff volume	0.05
	SO_4^{2-} concentrations	0.10
$LOAD_{sf}$	streamflow volume	0.05
	SO_4^{2-} concentrations	0.10
$LOAD_{pr}$	precipitation depth	0.10
	SO_4^{2-} concentrations	0.10
$LOAD_{us}$	soil water content	0.50
	SO_4^{2-} concentrations	0.10
	areas with given thicknesses of unsaturated soil	0.05
$LOAD_{cf}$	porosity	0.05
	soil water content	0.10
	SO_4^{2-} concentrations	0.10
	capillary fringe thickness	0.20
$LOAD_{gw}$	hydraulic conductivity	0.40
	hydraulic gradient	0.10
	cross-sectional area of flow	0.25
	SO_4^{2-} concentrations	0.10
$LOAD_{sw}$	hydraulic conductivity	0.40
	hydraulic gradient	0.50
	cross-sectional area of flow	0.05
	SO_4^{2-} concentrations	0.10
$LOAD_{st}$	saturated area	0.05
	standing water depth	0.50
	SO_4^{2-} concentrations	0.44

Combination of pre-melt SWE and precipitation during this period gave a value within 3% of the lysimeter's output. Sulphate concentrations in initial lysimeter runoff were up to 8 mg L^{-1}, and declined as melt progressed. A

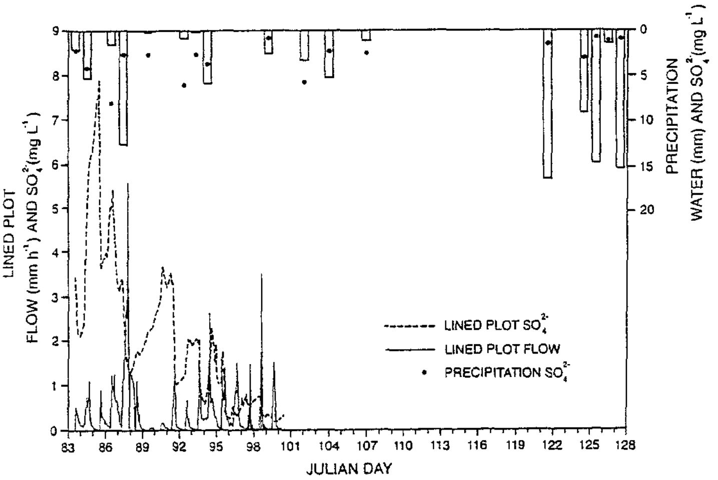

Fig. 4. Lined plot runoff, precipitation depths, and associated SO_4^{2-} concentrations.

similar pattern was observed in lysimeter runoff in previous melts (Barry et al. 1984; Barry & Price 1987), and in meltwater in the Turkey Lakes Watershed in northern Ontario (Hazlett et al. 1992). Total lysimeter output between JD 83 and JD 100 was 2.5 ± 0.3 kg SO_4^{2-} ha^{-1}. When combined with total SO_4^{2-} input in precipitation from JD 100 to JD 127 (1.0 ± 0.1 kg SO_4^{2-} ha^{-1}), 3.5 ± 0.4 kg SO_4^{2-} ha^{-1} was deposited on the basin. This compares closely with the SO_4^{2-} loading of 3.1 kg ha^{-1} observed by Barry et al. (1984) in this area during the 1983 melt. Nevertheless, it is likely less than the 'true' SO_4^{2-} loading, due to the tendency of bulk precipitation collectors to underestimate SO_4^{2-} dry deposition (cf. Cryer 1986).

Unsaturated zone ($LOAD_{us}$)

Higher Θ and SO_4^{2-} concentrations were observed at Pit 1, corresponding to its proximity to the wetland, thinner unsaturated zone, and location above the zone of elevated groundwater SO_4^{2-} concentrations (Fig. 5). Buttle & Sami (1990a) also noted higher Θ near the stream channel relative to further upslope during snowmelt on an instrumented slope beside the flume. There was little change in Θ profiles at the pits throughout the study, and SO_4^{2-} concentrations generally declined with time. Nevertheless, soil water SO_4^{2-} concentrations tended to exceed those of infiltrating meltwater and precipitation, and were highest in near-surface soils. There was no apparent relationship between SO_4^{2-} concentration and Θ in the unsaturated zone.

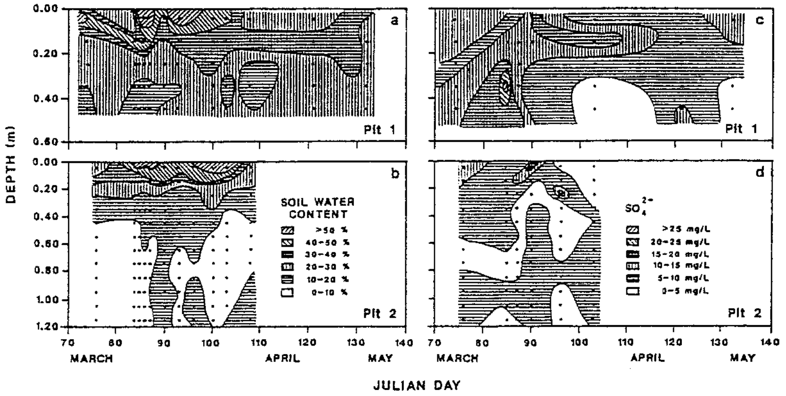

Fig. 5. Soil water contents (a and b) and SO_4^{2-} concentrations in soil water (c and d) observed at Pits 1 and 2 during the study.

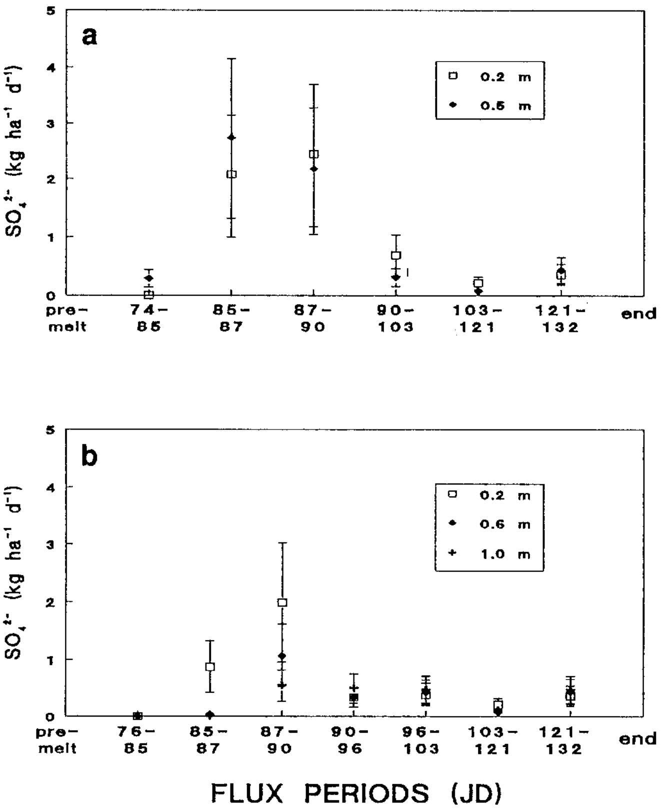

Fig. 6. Estimated SO_4^{2-} fluxes passing different flux plane depths for various periods, Pit 1 (a) and Pit 2 (b).

Table 2. Estimated and observed total streamflow and SO_4^{2-} export from the basin via streamflow.

	Total flow (m^3)	Standard error (m^3)
Estimated streamflow		
Component:		
Meltwater supplied directly to wetland	70	5
Precipitation supplied directly to wetland	26	3
Groundwater inputs to wetland	1280	822
$\sum$	1376	903
Observed streamflow	1406	70
	Total load (kg)	**Standard error (kg)**
Estimated $LOAD_{sf}$		
Component:		
Meltwater supplied directly to wetland	0.13	0.02
Precipitation supplied directly to wetland	0.05	0.01
Groundwater inputs to wetland	25.5	16.6
$\sum$	25.7	18.0
Observed $LOAD_{sf}$	17.3	1.9

Sulphate fluxes (Fig. 6) suggest that mean values at Pit 1 were consistently larger than at Pit 2 due to higher Θ and SO_4^{2-} concentrations (Fig. 5). Fluxes were generally higher at the 0.2-m flux plane than at greater depths in both pits for the same reason. However, fluxes had large relative errors, mainly due to the assumed horizontal variability in Θ on a given sampling day (Table 2), and were essentially uniform with depth and between pits for most flux periods. Nevertheless, there were significant temporal changes in SO_4^{2-} fluxes, with a general increase during initial melt followed by a decrease after JD 90. This suggests flushing of most available SO_4^{2-} from the unsaturated zone within seven days of melt initiation. Seventy-two mm of water had infiltrated the basin's soils by this date (Fig. 4), representing 52% of the lysimeter's total flow. No soil cores for SO_4^{2-} analysis were extracted from pit 2 following JD 103, and subsequent fluxes were estimated using the pattern observed at Pit 1.

Total flux from the unsaturated zone was 14.1 ± 7.3 kg SO_4^{2-} ha^{-1}, which is consistent with other snowmelt studies. Barry et al. (1984) determined SO_4^{2-} loss below 2 m at a nearby site of 10 kg ha^{-1} during the 1983 melt, Foster et al. (1989) observed a mean SO_4^{2-} flux of 17.6 kg ha^{-1} for the period January to early May at the 0.6-m depth in till at Turkey Lakes Watershed, and Stottlemyer & Toczydlowski (1991) estimated a total SO_4^{2-} flux through mineral soil in northern Michigan over winter/spring of 13 kg ha^{-1}. The estimated $LOAD_{us}$ is four times the estimated SO_4^{2-} input in meltwater and precipitation. Mineralization of organic S compounds likely dominates production of soluble SO_4^{2-} during the winter months prior to springmelt. Hazlett et al. (1992) report that over-winter mineralization could produce ~0.7 and 5.4 kg SO_4^{2-} ha^{-1} in the organic layers and upper mineral horizons, respectively, of forest soils near Sault Ste. Marie, Ontario. These mineralization rates would account for 43% of SO_4^{2-} lost from the unsaturated zone during the melt period, while desorption of previously adsorbed SO_4^{2-} may account for the remainder. Infiltration of water with relatively high SO_4^{2-} concentrations during the growing season should favour adsorption; in turn, recharge of relatively dilute spring meltwater could desorb some of this SO_4^{2-} from Fe and Al hydrous oxides in the soil (Foster et al. 1989).

Water table rise ($LOAD_{cf}$)

As infiltrating water transported SO_4^{2-} from the unsaturated to the saturated zone, the rising water table liberated SO_4^{2-} contained within and immediately above the capillary fringe. The water table rose 0.42 m at pit 1 and 0.47 m at pit 2 between JD 75 and JD 127 (Fig. 7). A 0.4–0.5 m rise was representative of other hillslope wells, although a few had increases of up to 0.7 m. It was estimated that 10336 m^3 of soil was saturated by water table rise. After subtracting the mean saturated area (513 m^2) from the total basin area (24400 m^2), the volume of saturated soil represented an average depth of 0.43 m, consistent with water table observations. Assuming a mean porosity (and thus Θ) of 0.43 in the tension-saturated zone, 2538 m^3 of water was held in a 0.25 m thick capillary fringe prior to melt. Sulphate concentration in the capillary fringe was 16 mg L^{-1}, using the mean SO_4^{2-} concentration observed in shallow piezometers from all nests located outside the wetland (Fig. 8), which gives 16.5 ± 3.8 kg SO_4^{2-} ha^{-1} in the pre-melt capillary fringe. Mean

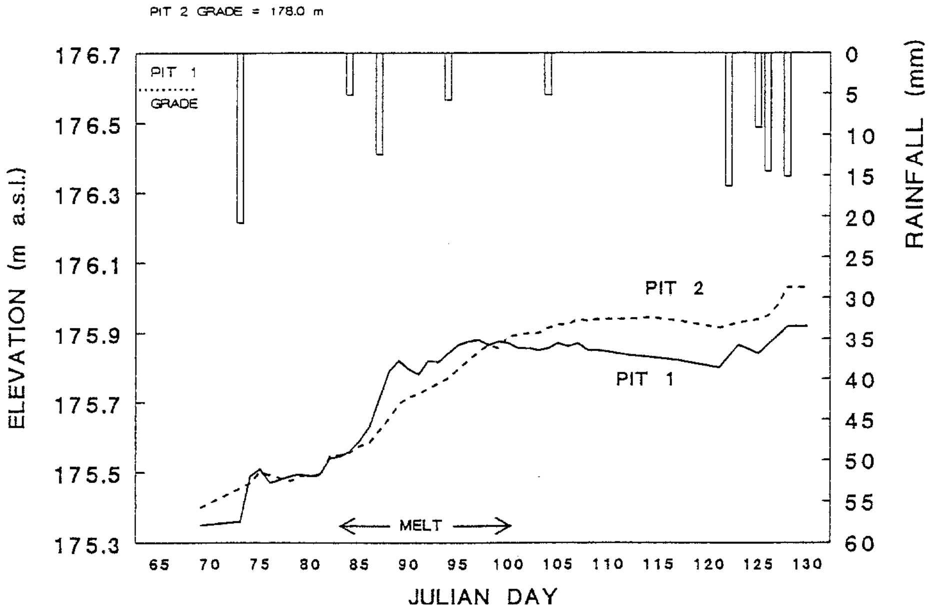

Fig. 7. Changes in water table elevation recorded at Pits 1 and 2.

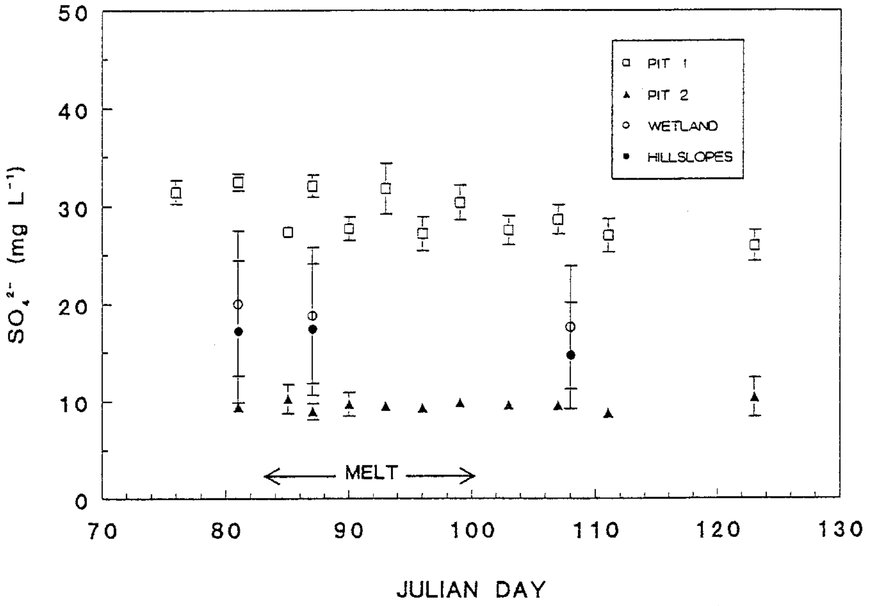

Fig. 8. Mean SO_4^{2-} concentrations (±1 s.d.) observed in samples taken from piezometers at Pits 1 and 2, all wetland piezometers and all piezometers located on hillslopes surrounding the wetland.

water table rise above the capillary fringe was 0.18 m. This layer had a mean Θ of 0.19 and a SO_4^{2-} concentration of 15 mg L^{-1} (based on soil core samples); thus, an additional 5.0 ± 1.3 kg SO_4^{2-} ha^{-1} was transferred to groundwater as a result of water table rise.

Subsurface loss ($LOAD_{gw}$)

Steep down-valley gradients dominated subsurface flow before melt in the upper basin, while the wetland displayed more gradual water table slopes (Fig. 9). Subsurface flow was normal to the basin divide at the outflow. Groundwater was directed to the wetland and stream by JD 105. Water table gradients at the outflow averaged 0.021 ± 0.002, and mean saturated conductivity was $5.2 \times 10^{-5} \pm 2 \times 10^{-5}$ m s^{-1} (Steele unpubl. data). Weighted mean groundwater SO_4^{2-} concentration was obtained using SO_4^{2-} levels in groundwater at both pits, which averaged 28.9 ± 2.7 and 9.6 ± 1.1 mg L^{-1} over the study for Pits 1 and 2, respectively (Fig. 8). Estimated groundwater flux from the basin was 3.0 ± 1.5 kg SO_4^{2-} ha^{-1}. This was probably an overestimate since Fig. 9 indicates groundwater inputs to the basin's upper area. However, these inputs were assumed to be negligible due to the minimal thickness of the saturated zone at this location.

Groundwater flux to the surface ($LOAD_{sw}$)

Hydraulic gradients showed that seven of the wetland nests acted as discharge zones at some time during melt. Vertical hydraulic gradients greatly exceeded horizontal ones; however, since hydraulic head differences between the surface water and the piezometers were usually quite small (0–0.02 m), it was sometimes difficult to distinguish discharge and recharge zones. Assistance was provided by alkalinity and cation concentrations in surface water and in groundwater sampled from piezometers (Siegel 1988). Groundwater discharge was assumed for nests where alkalinity, Ca^{2+} and Mg^{2+} concentrations were similar at all three depths and were consistently higher than surface water values (Fig. 10a). A number of nests had piezometric heads inconsistent with water table elevations (e.g. Fig. 10b). Piezometric heads at this nest indicated possible groundwater discharge, but this was contradicted by infiltration of dilute surface water to the middle piezometer. This nest was assumed to be located in a transmission zone.

Sulphate fluxes from recharge and discharge zones gave a net contribution of 10.5 ± 7.2 kg SO_4^{2-} ha^{-1} to the wetland. The accuracy of this value depends on hydrometric estimates as well as factors influencing groundwater SO_4^{2-} concentration as water moves from the shallowest piezometer to the surface. Connell & Patrick (1968; 1969) showed that SO_4^{2-} becomes unstable

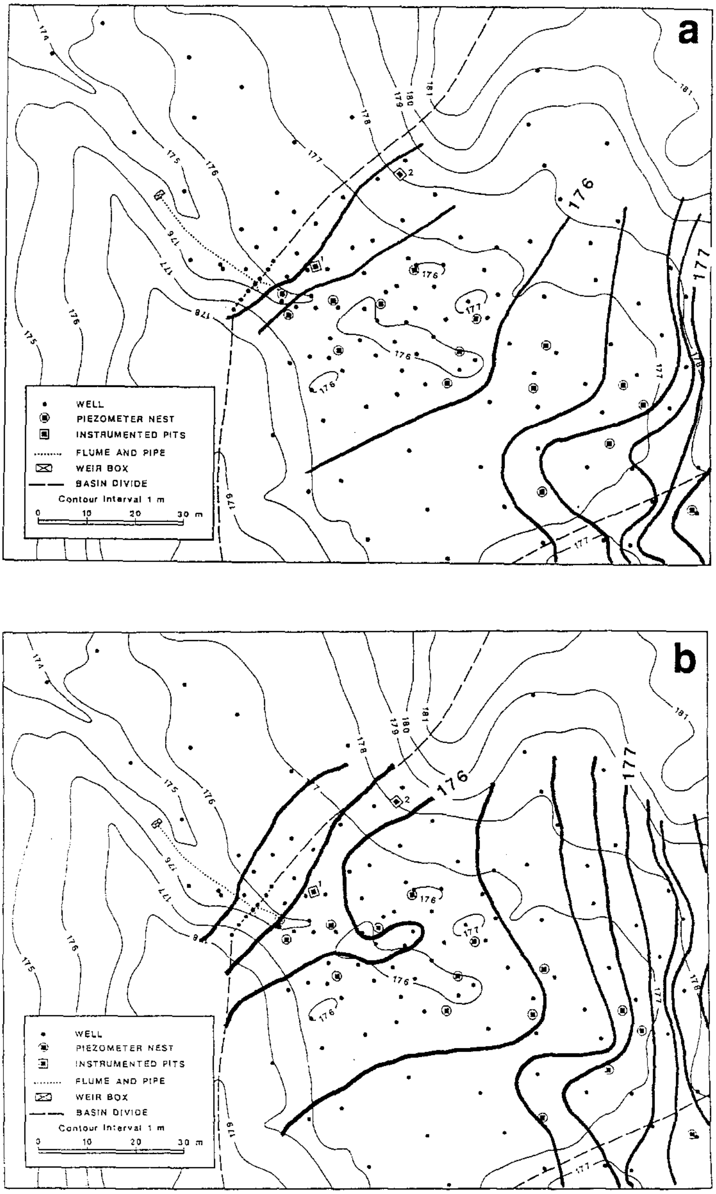

Fig. 9. Spatial patterns of water table elevations in the lower portion of the basin: (a) JD 83; (b) JD 105. Water table elevations are expressed in m a.s.l., with a contour interval of 0.25 m.

at redox potentials below −150 mV, and that NO_3^- was completely reduced prior to any SO_4^{2-} reduction. Groundwater redox measurements failed to detect potentials <−150 mV, and traces of NO_3^- in groundwater existed at

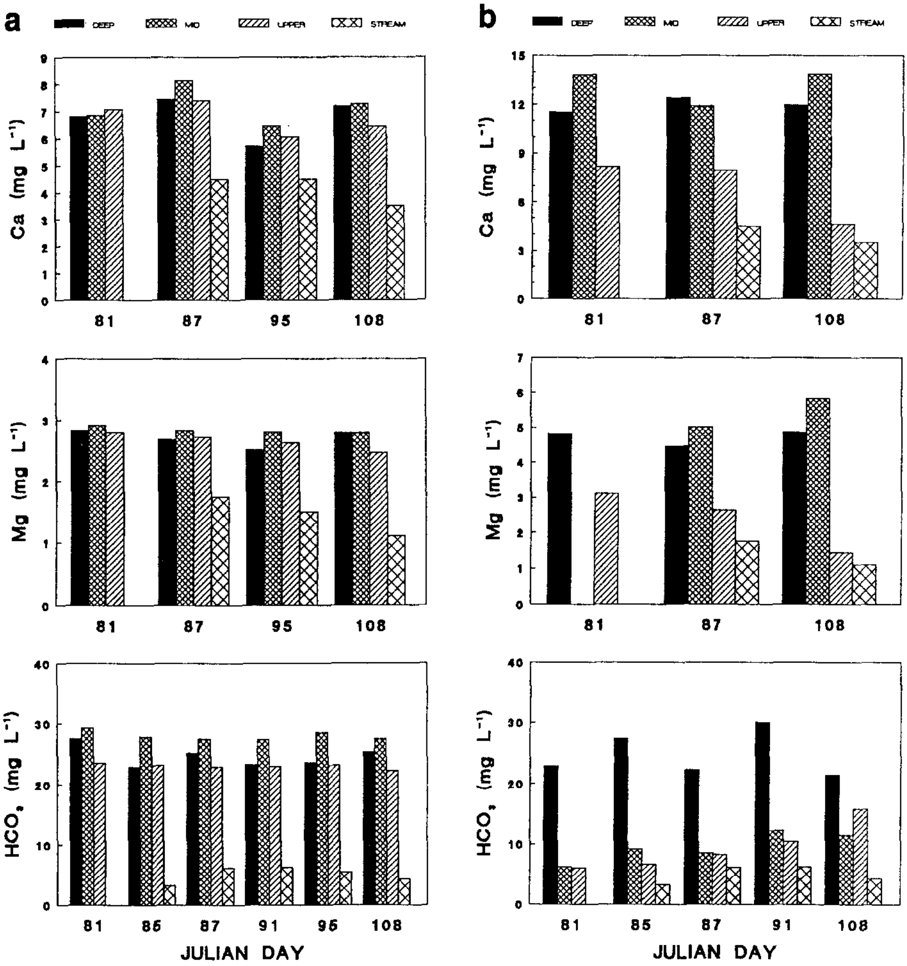

Fig. 10. Groundwater chemistry from wetland piezometer nests indicating (a) groundwater discharge, and (b) zone of transmission. 'DEEP', 'MID' and 'UPPER' indicates the relative position of the piezometers in the nest, while 'STREAM' indicates the chemistry of streamflow samples obtained at the same time as the groundwater samples.

most sites early in the melt and persisted at some discharge sites throughout the period. Thus, redox values do not support SO_4^{2-} reduction in near-surface groundwater.

Surface storage ($LOAD_{st}$)

Groundwater flux to the wetland began before JD 84, but streamflow did not start until depression storage was satisfied later that day. The wetland was near saturation before the main melt as a result of rain-on-snow on JD

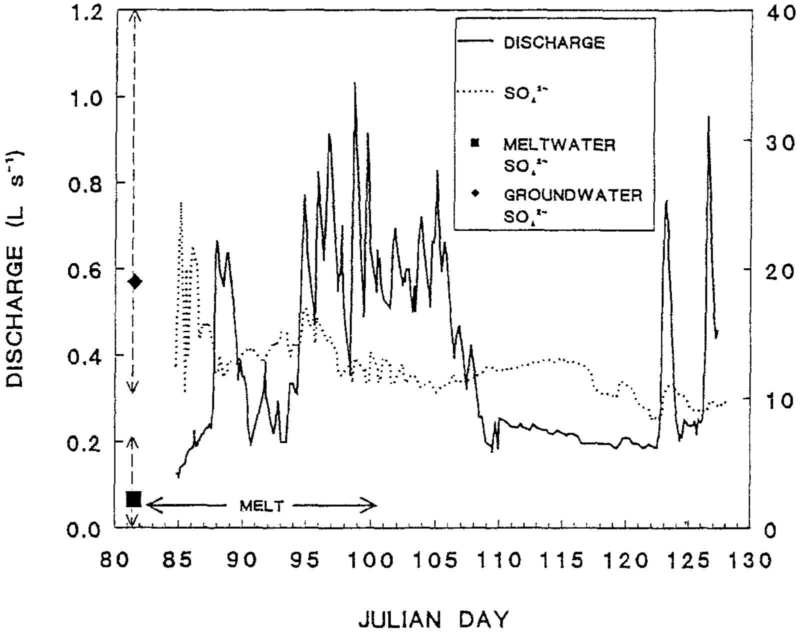

Fig. 11. Streamflow and SO_4^{2-} concentrations during the study. Means and ranges of SO_4^{2-} concentrations in meltwater and groundwater are also indicated.

73–74,and the mean depth of standing water prior to streamflow was ~0.025 ± 0.012 m. Lysimeter results indicate ~0.01 m of water left the snowpack before streamflow began, suggesting that most surface storage was supplied by groundwater. Piezometric data indicated groundwater discharge at four wetland nests on JD 83, with a mean SO_4^{2-} concentration of 20.4 ± 4.5 mg L^{-1}. Therefore the estimated surface storage prior to streamflow was 0.1 ± 0.07 kg SO_4^{2-} ha^{-1}, with 70% supplied from groundwater and the remainder from initial melt.

Streamflow ($LOAD_{sf}$)

Streamflow sulphate concentrations (Fig. 11) followed a trend similar to that noted by Barry & Robertson (1988) during the 1987 melt at this site. Stream SO_4^{2-} levels increased from 12 mg L^{-1} to a maximum of 25 mg L^{-1} within 12 hours of the start of flow. Concentration subsequently fluctuated between 12 and 17 mg L^{-1} until snowpack loss 16 days later, and thereafter stabilized between 10 and 13 mg L^{-1}. According to Barry & Robertson (1988), SO_4^{2-}-rich groundwaters from the lower wetland discharge to the surface during initial flow, and reach the flume prior to dilution by upper wetland waters with lower SO_4^{2-} concentrations. Streamflow SO_4^{2-} levels begin to fall when upper wetland waters mix with groundwater discharging in the lower basin.

Between JD 84 and JD 127, 7.1 ± 0.8 kg SO_4^{2-} ha^{-1} left the basin in streamflow, twice the input in meltwater and precipitation (3.5 ± 0.4 kg SO_4^{2-} ha^{-1}). Comparable input:output ratios have been observed by Stottlemyer (1987) and Stottlemyer & Toczydlowski (1991) during snowmelt in northern Michigan. Mean daily SO_4^{2-} flux in streamflow was 0.17 kg ha^{-1} d^{-1}, similar to the 0.18 kg ha^{-1} d^{-1} measured by Barry et al. (1984). It also falls within the range of 0.05–0.64 kg ha^{-1} d^{-1} reported by Lynch & Corbett (1989) for spring months at the Leading Ridge Experimental Watersheds in Pennsylvania (1978–83). However, total flux was less than that observed by Stottlemyer & Toczydlowski (1991) during the 1988/89 winter (13.2 kg ha^{-1}), which may reflect greater SO_4^{2-} deposition in northern Michigan (9.2 kg ha^{-1}).

Total SO_4^{2-} export via streamflow was estimated by combining meltwater and precipitation SO_4^{2-} loads to the saturated area with groundwater SO_4^{2-} flux to the wetland (Table 2). Evapotranspiration was assumed to be minimal during the study. Calculated water flux essentially equalled observed streamflow, supporting the estimated groundwater discharges as well as the assumption that SO_4^{2-} export via streamflow is the sum of groundwater and melt/precipitation inputs to the wetland. Predicted SO_4^{2-} input to the wetland was 50% > observed stream export, although the large error associated with the estimated flux means this difference is not significant at the p = 0.05 level. Water table elevations indicated that standing water depth in the wetland increased by ~0.085 m (44 m^3) after streamflow began, and some of the estimated SO_4^{2-} load went into surface storage rather than leaving as streamflow. Therefore the predicted SO_4^{2-} flux from the basin is likely to be slightly overestimated; nevertheless, the large discrepancy between observed and estimated exports suggests that SO_4^{2-} concentrations in groundwater discharging to the wetland decreased between the shallowest piezometers and the wetland surface, despite lack of evidence of SO_4^{2-} reduction from redox measurements. Such reduction may be due to bacteria in sediment pellets or detrital particles in the uppermost wetland soils (Jorgensen 1977), the effect of which could not be detected through redox measurements in water sampled ~0.2 m below the wetland surface.

SO_4^{2-} fluxes and stores

The dominant SO_4^{2-} flux in this basin was from the unsaturated zone to groundwater (Fig. 12) as a result of leaching and capillary rise, such that the saturated zone experienced a net gain of SO_4^{2-} during melt. Net loss of SO_4^{2-} from the unsaturated zone during melt is probably satisfied by atmospheric

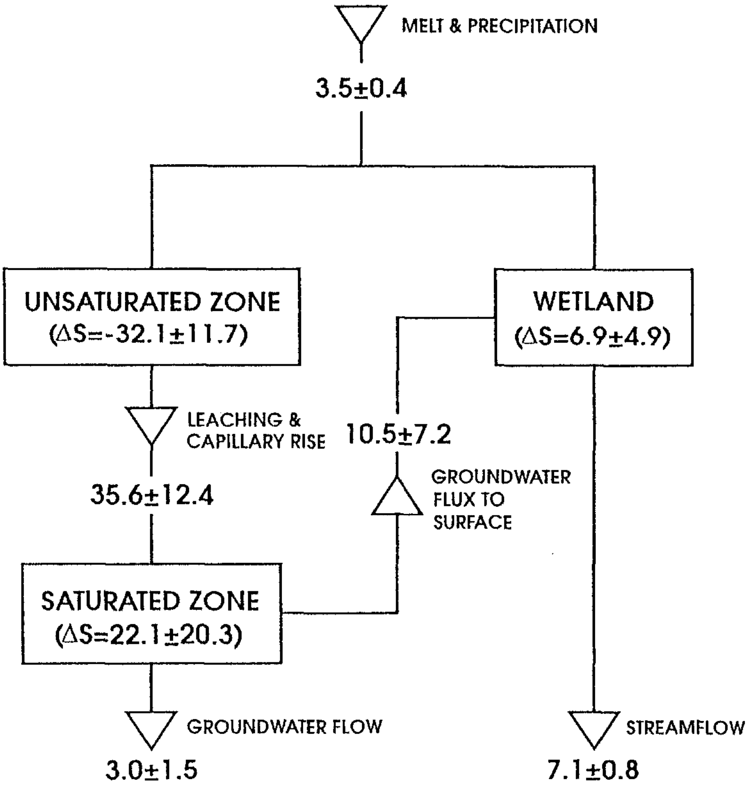

Fig. 12. Transfers and stores of SO_4^{2-} within the basin during the 1989 melt, with associated probable errors. All units are in kg SO_4^{2-} ha^{-1}. Fluxes were measured or estimated; ΔS values were derived.

inputs and oxidation of sulphides during the summer and fall. In addition, the pattern of SO_4^{2-} loss from the unsaturated zone and gain by the saturated zone is reversed by redevelopment of the capillary fringe during water table decline in the summer, leaving residual SO_4^{2-} in the unsaturated zone. Therefore some SO_4^{2-} may undergo repeated transfer between the unsaturated and saturated zones prior to export from the basin, and such a hypothesis could be tested by tracers studies using radiolabelled SO_4^{2-}. Sulphate storage in the saturated zone will also be depleted by subsurface and surface flow from the basin following the study period, as well as by transformation and uptake. The largest relative errors in the flux calculations are for the groundwater terms, and an even more intensive hydrometric network than that reported here may be required to reduce these errors significantly.

Summary

Significant net export of SO_4^{2-} occurred during snowmelt, as noted in other basin-scale mass balance studies. This reflects SO_4^{2-} release from the unsaturated zone, where $LOAD_{us}$ was four times that supplied in meltwater and precipitation. The unsaturated zone apparently contained a large supply of soluble SO_4^{2-} that was flushed from organic and upper mineral soil layers early in the melt; however, this supply was only partially depleted almost one month after melt. Any horizontal or vertical variations in SO_4^{2-} fluxes in the unsaturated zone were overwhelmed by the large relative error associated with these fluxes estimates. Minor changes in groundwater SO_4^{2-} levels during melt suggest that SO_4^{2-} release from the unsaturated zone counteracted any dilution expected to result from large water inputs to the basin. Conversion of the tension-saturated zone to phreatic water due to water table rise was at least as important as vertical fluxes from the unsaturated zone in supplying SO_4^{2-} to groundwater.

Of the 35.6 ± 12.4 kg SO_4^{2-} ha^{-1} supplied to the saturated zone, only 10.1 ± 2.3 kg ha^{-1} was exported from the basin via surface and shallow subsurface flow during and immediately following snowmelt. Remaining SO_4^{2-} may be retained in the basin's groundwater and soil water, may continue to leave the basin via surface and subsurface flow during the following spring and summer, may be lost as a result of deep groundwater flow, or may undergo transformation or uptake. Shallow subsurface flow accounted for up to 30% of total SO_4^{2-} export from the basin during the period. Groundwater contributions also dominated streamflow and SO_4^{2-} flux from the basin (Table 2).

Sulphate fluxes to and from the saturated zone are the dominant transfers of SO_4^{2-} with this basin; they also possess large uncertainties. Further research should concentrate on processes affecting SO_4^{2-} behaviour as it moves through soils into groundwater and thence to surface water, as well as improved methods of estimating these fluxes.

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