SOURCES AND CONTROLS OF SULPHUR EXPORT IN PRECAMBRIAN SHIELD CATCHMENTS IN SOUTH-CENTRAL ONTARIO

By

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AUTHOR'S DECLARATION FOR ELECTRONIC SUBMISSION OF A THESIS

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ABSTRACT

A series of studies was undertaken at Plastic Lake-1 (PC1) to determine the sources and controls on S cycling in small headwater catchments on the Precambrian Shield in south-central Ontario. Two observations were made about the S cycle in this region: (1) all streams exhibit highly coherent temporal patterns in SO_4 concentrations and export, and (2) most catchments exported more SO_4 in stream water than is received in bulk deposition during the past 2 decades. Synchronous temporal patterns in annual SO_4 concentrations in both upland and wetland-draining streams were related to changes in climate, specifically those factors that determine catchment dryness. The number of days with no stream flow or stream flow below a critical threshold was a good predictor of the average stream SO_4 concentration in a particular year. Sulphate chemistry in the PC1 outflow is highly dependent on processes occurring in a conifer *Sphagnum* swamp located immediately upstream of the chemical sampling station. Hydrologic inputs to the swamp during the summer determine whether S is retained or released from peat on an annual basis. Drying and re-wetting of *Sphagnum*-derived peat caused a substantial increase in soluble SO_4 in laboratory experiments, which was slightly enhanced at higher temperature, but alternating moisture conditions had no immediate effect on *Sphagnum*. Despite large inter-annual changes in SO_4 release, over the long-term (*i.e*. 20-years) SO_4 inputs and exports from the swamp are in approximate balance. In contrast, the upland portion of PC1 (*i.e*. PC1-08) consistently exports more SO_4 than is input in bulk deposition in every year of record. Even when inputs are increased to account for potential underestimates in dry deposition or weathering, the majority of catchments in this region exhibit net export in many years. Two internal sources are suggested to account for negative budgets: desorption and mineralization. Adsorption/desorption reactions respond directly to changes in SO_4 input concentration, and lysimeter data indicate the importance of these processes for buffering short-term changes in SO_4 concentration in LFH percolate. Desorption may be the primary direct response of upland soil to decreasing SO_4 inputs

in deposition and may substantially extend the period of net SO_4 export in catchments that have large adsorbed SO_4 pools such as PC1. However, the adsorbed pool may be sustained by continuous net release from mineralization, and should also be considered in budget calculations. Mineralization was shown to be responsive to drying and re-wetting events and temperature, although results varied among different materials. Sulphate release from mineral soil did not appear to be influenced by changing moisture, temperature or deposition chemistry in laboratory experiments, although adsorption/desorption reactions may have largely masked small changes in SO_4 release *via* mineralization. The magnitude of organic S storage in mineral soil indicates that this pool could be an important source of export over the long-term. While it is unknown why (or if) mineralization is a net source of SO_4 to drainage streams, changes in climate and/or deposition could potentially influence SO_4 release from organic compounds. Soil moisture and temperature are important controls on microbial processes in soil, and changes in climate that bring about changes in soil moisture or temperature conditions could affect decomposition and mineralization processes. Similarly, historically high inputs of S and N in deposition may have brought about slow shifts in litter quality (*i.e*. decreased C:N, C:S) which could also potentially influence decomposition and mineralization rates. In order to predict the future response of surface water chemistry to changes in SO_4 (and N) deposition, it is important to consider not only the magnitude of S pools in soil, but also the potential for SO_4 cycling between pools. Likewise, models that predict changes in stream SO_4 by adsorption isotherm data alone will underestimate the importance of desorption unless the potential for continual replenishment of the adsorbed pool through the relatively slower process of mineralization is also considered. In general, predictions of recovery from S deposition can only be made from a complete understanding of S pools, transformations, and the effects of climate, which are superimposed upon the long-term trend in deposition.

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CHAPTER 1: INTRODUCTION

The atmospheric deposition of acidic sulphur (S) compounds in eastern North America has greatly declined over the past two decades in response to environmental regulations and agreements which restrict industrial emissions. Since the early 1980s, sulphate (SO_4) deposition in the northeastern United States has declined by at least 25% whereas the decrease in eastern Canada over the same time period was around 40% (EPA, 1999; Environment Canada, 1997). In the Muskoka-Haliburton region of south central Ontario, which is the location of this study, SO_4 deposition declined by around 45% between 1980 and 2000 (Watmough and Dillon, 2001).

These large reductions in SO_4 deposition were expected to bring about proportional declines in SO_4 concentrations in surface waters, and ultimately increased *p*H and alkalinity. However, a number of reports have indicated that many lakes and streams in eastern North America have not responded as expected to changes in deposition. For example, of 202 lakes considered in southeastern Canada which included 35 lakes in the Muskoka-Haliburton region, Clair *et al.* (1995) reported that 51% exhibited statistically significant decreases in SO_4 concentrations from the early 1980s to the mid 1990s, whereas 48% had no trend and 1% had increasing SO_4. In contrast, only 33% of lakes had increased *p*H or ANC, whereas 56% were stable, and 11% had acidified further. Similarly, although SO_4 concentrations in many surface waters in the northeastern United States have decreased in recent decades, the rate of decline has not been proportional to the change in deposition (Driscoll *et al.*, 1998; Stoddard *et al.*, 1999).

The covered catchment studies in Norway (RAIN) and Sweden (Gårdsjőn) also reported a delay (up to 8 yr) in the response of SO_4 concentrations in runoff following the installation of roofs that completely excluded anthropogenic deposition (Skeffington *et al.*, 1998). Results from these studies suggested that delayed responses in percolate chemistry were due to the release of SO_4

stored in soil and highlighted the importance of internal processes for determining the response of catchments to changes in deposition.

Similar net SO_4 release has been reported at a number of sites in southeastern Canada and the northeastern United States, where mass budgets indicate that catchment export of SO_4 exceeds inputs in deposition (Hornbeck *et al*., 1997; Houle and Carignan, 1995; Mitchell *et al*, 1996; Rochelle *et al*., 1987). A number of sources have been proposed to account for catchment S imbalances including underestimated inputs through weathering or dry deposition, or release of SO_4 from internal pools through desorption, mineralization or oxidation (Driscoll *et al*., 1998; Houle *et al*., 2001; Likens *et al*., 1996). Dry deposition was originally suggested as the cause of budget imbalances at the Hubbard Brook Experimental Forest (HBEF, Likens *et al*., 1990), although more recent reports suggest net mineralization might be a more important source of SO_4 export at the HBEF (Alewell *et al*., 1999; Mitchell *et al*., 2001).

Dry deposition is a notoriously difficult parameter to quantify but can be a large source of SO_4 input, particularly in high elevation catchments, and at sites located close to SO_2 emission sources (Baumgardner *et al*., 2002; Lovett *et al*., 1997; Sirois *et al*., 2002). However, at sites that are remote from point sources of emissions, S inputs *via* dry deposition are generally low compared to wet inputs. For example, Baumgardner *et al*. (2002) recently estimated that dry deposition contributed 7% and 22% of total SO_4 deposition at forested sites in New Hampshire and Maine, respectively, which are located relatively distant from major SO_2 emission sources. Similarly, Sirois *et al*. (2002) recently estimated that dry deposition constituted approximately one-third of total S inputs at the Turkey Lakes watershed in central Ontario.

Weathering inputs are also difficult to quantify on a catchment-scale but are generally considered to be small in catchments with slowly weathered igneous or metamorphic rock that has a low S-content (Mitchell *et al*., 1992a). Such rock types characterize much of the Canadian Shield region of southeastern Canada and the northeastern United States where net catchment export has been reported. For example, weathering was estimated to contribute approximately 4% (0.62 kg S/ha/yr) of S export in stream water at the Hubbard Brook Experimental Forest, NH (Alewell *et al*., 1999). Similarly, Houle and Carignan (1995) estimated that SO_4 release due to weathering constituted only a small (~ 0.05 kg S/ha/yr) portion of annual S losses in stream flow (9-15 kg S/ha) in the Lac Laflamme catchment, QC. Nevertheless, weathering can be an important source of SO_4 in catchments that have metal sulphide, gypsum or carbonate mineral deposits, and weathering inputs should always be considered when evaluating S mass budget data.

Net SO_4 losses from catchments that are both remote from SO_2 emission sources, and have negligible weathering inputs must therefore be due to release from internal pools. Driscoll *et al.* (2001) reported a strong positive relationship between wet SO_4 deposition and total S concentrations in the forest floor of red spruce stands, and suggested that net SO_4 losses are a legacy of past decades of atmospheric S deposition and resultant S accumulation in forest soils. The release of SO_4 that was previously accumulated in catchments will delay the recovery of surface waters in response to SO_2 emission controls (Driscoll *et al*., 1998). It is imperative to quantify the processes that govern SO_4 generation and SO_4 retention in catchments in order to predict the response of catchments to future changes in deposition, and to evaluate whether further reductions in emissions are necessary.

Mechanisms of S retention in catchments

While SO_4 is considered a ‘mobile anion’ and its movement through soil drives the leaching of base and acid cations, SO_4 may also be retained in soil through both biotic and abiotic processes. Biological mechanisms of SO_4 retention include vegetation uptake and microbial immobilization (assimilatory SO_4 reduction) in upland soil, and microbial dissimilatory SO_4 reduction (DSR) in lowland regions. In anaerobic zones, such as saturated riparian areas and wetlands, SO_4 reducing bacteria transform SO_4 into the highly reactive H_2S, which may then degas to the atmosphere, or react with available iron (Fe) and organic matter to form relatively immobile iron sulphide or organo-sulphide compounds (Spratt and Morgan, 1990; Wieder and Lang, 1988). Sulphate may also be assimilated by wetland vegetation such as *Sphagnum* mosses, and thereby accumulate in slowly decomposing peat deposits (Urban *et al*., 1989). However, uptake and metabolism of dissolved SO_4 (*i.e. via* DSR) and subsequent reaction with organic matter is the major route of S incorporation into peat (Brown and MacQueen, 1985).

Soil is the dominant site of S storage in most upland forested systems, and vegetation constitutes only a small (<12%) fraction of the total S content of the ecosystem (*e.g*. Mitchell *et al*., 1992a). The majority of total S in forest soil (>75%) generally is present in organic forms. Carbon-bonded S compounds (C-S) constitute the majority, and ester sulphates (C-O-S) normally account for less than 25% of total organic S (David *et al*., 1983; Mitchell *et al*., 1992c). Annual S uptake by vegetation generally is balanced by SO_4 return to the forest floor in litter and root exudates on an annual scale, and so forest vegetation is not considered to be an important net source or sink for S except in actively harvested stands (Johnson, 1984; Reuss and Johnson, 1986). However, sulphate uptake by trees and transformation to organic-S compounds and subsequent return to the forest floor in litter and roots (exudates/sloughing) may be an important source of organic-S compounds to soil. Microbial immobilization is also an important biological mechanism of SO_4 retention in well-aerated upland forest soil, and may account for a large fraction of total ecosystem retention in some catchments. For example, at the Coweeta Experimental Watershed in North Carolina, it was estimated that as much as 30 kg S/ha could be microbially incorporated into organic forms annually (Swank & Fitzgerald 1983). Immobilization of added SO_4 is apparently rapid, and may be proportional to SO_4 concentrations in soil solution (Fitzgerald *et al*., 1982; Strickland and Fitzgerald, 1984). Therefore, microbial retention of S in soil may also be responsive to changes in deposition. In addition, the balance between SO_4 immobilization and mineralization may be influenced by the S content of soil, such that SO_4 is accumulated when the S content of soil is low, whereas net mineralization occurs in soils rich in S (Chapman, 1997; Scherer, 2001). The total C:S ratio provides a rough guide to the S status of organic soil, with a C:S > 400 generally indicating S limiting conditions which favour net immobilization, whereas net mineralization predominates at a C:S < 200; apparently, either process can occur when the ratio falls between 200 and 400 (Freney, 1986). Other authors have suggested that the C:S ratio of recently added organic matter (*i.e*. litter), is a more important determinant of the potential for immobilization or mineralization than the C:S ratio of the soil itself (Chapman, 1997; Eriksen, 1997).

In acidic soils, the primary abiotic controls on SO_4 retention are adsorption and precipitation, although precipitation of SO_4 minerals (generally with Al) is apparently only important in extremely acid soils (*p*H <3) that have high inorganic Al concentrations (Khanna *et al*., 1987). Sulphate adsorption is the primary abiotic mechanism of inorganic SO_4 retention in most forest soils in eastern North America (Fuller *et al*., 1985; Neary *et al*., 1987). Hydrous oxides of Fe and Al and edges of aluminosilicate clays are generally believed to be responsible for SO_4 adsorption in soil (Bohn *et al*., 1986; Johnson and Todd, 1983). Hydrous oxides may occur freely in soil or as coatings on clay minerals, and SO_4 adsorption to oxides is related to their specific surface area and density of surface OH groups (Bohn *et al*., 1986). Iron and Al in mineral soil are generally found in one of 3 operationally defined forms including organically bound, amorphous and crystalline. A number of reports have attempted to relate adsorbed SO_4 to a specific form of Fe or Al in soil; however, results have been variable (*e.g*. Fuller *et al*., 1985; Harrison *et al.*, 1989; Johnson and Todd, 1983). Amorphous forms of Fe and Al might be expected to have greater adsorption capacity due to their higher specific surface areas, although Johnson and Todd (1983) reported that crystalline Fe was most highly correlated with adsorbed SO_4 in a survey of soil at various sites in the US.

The majority of catchments in the northeastern US and southeastern Canada that have exhibited net SO_4 losses are dominated by soils of the podzolic soil order (Rochelle *et al*., 1987). The process of podzolization results in the dissolution and leaching of Fe and Al down the soil profile to lower mineral soil where they are subsequently deposited. As podzolization continues, Fe and Al hydrous oxides become relatively enriched in subsurface soil, and as a consequence older, more weathered soils of the southeastern US (oxisols/ultisols) have higher Fe and Al oxide contents than the northeastern US and southeastern Canada, where glaciation has "reset the pedogenic clock" (Rochelle *et al*., 1987; Shanley, 1992). Sulphate adsorption is therefore considered a more important mechanism of retention in the southeastern US, and input-output budgets for these catchments are typically positive (*i.e*. net SO_4 retention) despite high rates of SO_4 deposition (Johnson *et al*., 1982; Shanley, 1992).

Sulphate adsorption is also influenced by the SO_4 concentrations in soil solution, *p*H and organic matter content. For example, a negative relationship exists between SO_4 adsorption and both soil *p*H and organic matter content. As *p*H decreases, protonation of negative functional groups on organic acids (*i.e*. hydroxyl, carboxylic, phenolic) and clays results in the creation of additional sites for anion adsorption and greater SO_4 retention. Increased nitrification due to forest harvesting and a subsequent decline in soil *p*H was shown to increase SO_4 adsorption at the HBEF (Mitchell *et al*., 1989; Nodvin *et al*., 1988). Organic acids generally decrease SO_4 adsorption by coating adsorption surfaces in soil, or by competing with SO_4 for anion adsorption sites (Courchesne and Landry, 1994; Gobran and Nilsson, 1988).

The concentration dependency of SO_4 adsorption has been described mathematically using isotherm equations. The two most commonly used equations to describe adsorption are the Langmuir and Freundlich equations. The principal difference between the two is that the latter does not have an adsorption maximum. Both generally demonstrate that SO_4 adsorption increases with increased SO_4 concentration, but that the rate of SO_4 adsorption declines at higher concentrations (Chao *et al*., 1962). In contrast, Nodvin *et al*. (1986) found that at the SO_4 concentration range normally observed in soil solution, adsorption is best described by a simple linear partitioning model, or the IM (initial mass) isotherm. The slope of the IM isotherm is indicative of the ability of a soil to retain SO_4, with a slope of 1.0 indicating complete or 100% retention, and values close to 0 suggesting negligible SO_4 adsorption (Shanley, 1992). The x-intercept of the SO_4 adsorption/desorption curve indicates the SO_4 concentration in soil solution at which SO_4 is neither adsorbed nor desorbed and therefore provides information on the potential for SO_4 release or retention under current or predicted conditions.

Mechanisms of S release in catchments

It is becoming increasingly apparent that S storage in catchment soil is not necessarily a permanent phenomena, and SO_4 that had been previously retained may be gradually released to surface waters, delaying their response to changing deposition (Driscoll *et al*., 1998; Harrison *et al*., 1989). Mineralization and desorption are the primary mechanisms by which stored S is released from upland forest soil. In wetlands, declines in water table level can result in the exposure and mineralization of organo-S compounds in peat and oxidation of metal sulphides, and subsequent release of SO_4 from wetlands (Bayley *et al*., 1986; Dillon *et al*., 1997; LaZerte, 1993).

Adsorbed SO_4 is in kinetic equilibrium with SO_4 in soil solution, and therefore a decrease in SO_4 inputs to soil through declining deposition is expected to cause the release of SO_4 from soil surfaces given enough time for reaction (Chao *et al*., 1962; Reuss and Johnson, 1986). Studies that have examined desorption from soil using soil leachate or de-ionized water amended with varying concentrations of SO_4 have shown that more SO_4 is released from soil at lower SO_4 concentrations in solution (Gobran *et al*., 1998). Hern (1994) for example, showed that nearly 3-times as much SO_4 was released from Plastic Lake soil (equilibrium *p*H of ~ 5) at an initial SO_4 concentration of 5 mg/l compared to 10 mg/l.

While many soils appear to contain some 'irreversibly adsorbed SO_4' (*i.e*. adsorbed SO_4 that is not liberated in H_2O extractions), Chao *et al*. (1962) demonstrated that as much as 45% of SO_4 that was initially adsorbed could be recovered in a single water extraction. Similarly, Harrison *et al*. (1989) found that while 29 out of 36 North American forest soils exhibited some irreversible adsorption, up to 2/3 of the initially adsorbed SO_4 could be recovered quantitatively by water extraction. Generally, soils that have a greater adsorption capacity contain more irreversibly adsorbed SO_4; however, Shanley (1992) found that even soils which exhibit 100% SO_4 adsorption (*i.e*. slope of IM isotherm of 1.0) release considerable SO_4 (~30%) in water extractions. Alewell and Matzner (1993) suggest that soils with large adsorbed SO_4 pools will respond more slowly to decreases in deposition because of their large potential for release. Accordingly, thin, organic-rich soils with low initial storage of adsorbed SO_4 should therefore respond more rapidly to changes in deposition, as has been demonstrated at the covered catchment studies in Norway and Sweden (*e.g*. Hultberg *et al*., 1998; Wright *et al*., 1988). Similarly, Prechtel *et al*. (2001) recently reported that German catchments which have deeply weathered soils and high SO_4 storage capacity responded more slowly to deposition decreases over the past decade than catchments in the Czech Republic/Slovakia and Scandinavia, respectively which have thin soils and relatively small SO_4 storage. Net release of SO_4 from soil in German catchments maintained relatively high SO_4 fluxes in stream water despite large decreases in deposition, and therefore 'delayed' their response to changes in deposition.

Model simulations indicate that discrepancies in catchment S budgets and patterns in surface water SO_4 concentrations cannot be entirely explained by soil desorption (Driscoll *et al*., 1998a; Houle and Carignan, 1995). However, these simulations have considered the adsorbed SO_4 pool to be independent of other S pools in soil, which is unlikely since SO_4 released through mineralization or weathering could also be retained or subsequently released through adsorption/desorption reactions (Bohn *et al*., 1986).

Several recent studies have discussed the potential contribution of mineralization to net SO_4 export from catchments (*e.g*. Driscoll *et al*., 1998; Houle and Carignan, 1995; Zhang *et al*., 1997). The mechanisms involved in the mineralization of S are less well understood than for desorption. It has been suggested that the microbial release of S from organic matter may be either coincident to decomposition (biological mineralization), or it may occur to satisfy microbial requirements for that element (biochemical mineralization; McGill and Cole, 1981). Mineralization rates are highest in the forest floor and decrease with depth in mineral soil, as might be expected from the distribution of soil microbes and organic matter (Atlas and Bartha, 1993). The involvement of soil microbes is indicated by studies that demonstrate the inhibition of SO_4 mineralization by the addition of antimicrobial agents such as sodium azide or erythromycin to soil. However, opposing results have also been reported (Strickland *et al*., 1984), likely due to the ubiquitous presence of sulphatase (sulphohydrolase) enzymes in soil, which are produced extracellularly by microbes and plant roots and are therefore not directly affected by antimicrobial chemicals. Synthesis of sulphatase enzymes however, may be inhibited by the addition of SO_4 to soils (end-product inhibition) (Fitzgerald, 1976); it is unknown whether the opposing process also holds true, but if so, decreasing deposition could influence mineralization rates by enhancing sulphatase enzyme production.

It is generally believed that approximately 1-3% of the total organic S in agricultural soil is released through mineralization each year (Freney, 1986), and presumably a smaller fraction would be released annually in undisturbed forest soil. However, given the size of the organic S pool in most forest soils (generally > 1000 kg S/ha; Mitchell *et al*., 1992a), even a small annual turnover could account for the magnitude of net S losses measured in some catchments. For example, Houle and Carignan (1992) calculate that only a small annual loss of 0.4% of the organic S reservoir (1230 kg S/ha) would be sufficient to explain annual net SO_4 losses from the Lac Laflamme catchment. In order for net export of S from the organic pool to occur, net accumulation of S in soil organic matter must have occurred at some point in the past. Mitchell *et al*. (1989) suggested that the large organic S reservoir in B-horizon soil may have accumulated slowly over time through the deposition of soluble organic S compounds originally leached from the forest floor. Indeed organic matter leaching appears to be an important mechanism for the translocation of S to mineral soil (Schoenau and Bettany, 1987).

Few studies have investigated the potential shift from net S accumulation to net loss that must have occurred if mineralization is now sustaining net SO_4 export from catchments. However, Bailey *et al*. (2001) calculated S budgets for the entire country of Northern Ireland between 1940 and 1990, and found that while S initially accumulated in soil (1940-1965), budgets became negative from the late 1970s onwards. Reduced S inputs in fertilizers and deposition were suggested to have stimulated organic matter decomposition and subsequent release of SO_4 through mineralization (Bailey *et al*., 2001). Eriksen (1997b) similarly found that S budgets in Danish soils shifted from positive to negative between the 1960s and 1980s, which coincided with a period of dramatic decrease in S inputs in both deposition and fertilizer. Increased mineralization in response to decreased S input is contrary to previous laboratory studies, which have shown that S mineralization is generally inhibited under conditions of low S availability (Chapman, 1997; Scherer, 2001). While the above studies were conducted in predominantly grassland catchments, similar processes may occur in forested catchments; although, further work would be required to determine the potential effects of changing S deposition on immobilization and mineralization in undisturbed forest soil. Factors that affect the biological cycling of S are of critical importance due to the large size of the organic S pool in soil (*i.e*. potential source of net export), and the magnitude of biological transformations (*e.g*. David and Mitchell 1987). Furthermore, while SO_4 deposition has declined in recent decades, nitrogen (N) deposition has remained unchanged (Stoddard *et al*., 1999). Nitrogen is normally considered the limiting nutrient in terrestrial systems, and the addition of N may act as a fertilizer in some systems, stimulating rates of organic matter breakdown and possibly the release of SO_4 through mineralization (Berg and Matzner, 1996). Therefore, the potentially stimulatory effect of N deposition should also be considered in S budget studies.

Climate effects on S release

The 1980s and 1990s were 2 of the warmest decades on record, and were also marked by a number of extreme climatic events (NOAA, 2000). Since the mid-1970s for example, El Niño events have been both more frequent and more persistent (Francis and Hengeveld, 1998). El Niño episodes are normally associated with dry, mild winters in continental Canada; however, in the Muskoka-Haliburton region El Niños are linked with warm, dry summer conditions and reduced stream flow. Elevated stream SO_4 concentrations are also associated with El Niño years, particularly in wetland-draining streams (Dillon *et al*., 1997). It has been suggested that reductions in wetland water table levels during summer droughts allow the exposure and oxidation of reduced S compounds in peat. When normal hydrologic conditions resume, newly produced SO_4 is flushed into drainage streams producing spikes in SO_4 concentration (Bayley *et al*., 1986; Devito *et al*., 1999; Dillon *et al*., 1997). In contrast, SO_4 tends to be retained in wetlands during intervening wet years, when water tables remain at or above the peat surface

(LaZerte, 1993). Similar patterns of SO_4 release have been reported in European wetlands and ponds following drought (Van Haesebroeck *et al*. 1997, Van Dam, 1988).

Changes in climate may also affect mineralization rates, and laboratory and field studies have demonstrated a stimulatory effect of both temperature and drying on SO_4 release from soil (David *et al*., 1983; Foster, 1989; Jaggi *et al*., 1999; Williams, 1967). The balance between SO_4 immobilization and mineralization may be influenced by changes in temperature and precipitation, which affect soil moisture and microbial activity. Changes in climate might affect S release from catchments in other ways; for example, higher inputs of SO_4 to a high-altitude lake were attributed to temperature-related increases in the weathering of S-bearing minerals (Sommaruga-Wögrath *et al*., 1997). Webster *et al*. (2001) reported that SO_4 concentrations in Wisconsin lakes were higher in warm dry years when reduced stream flow into lakes and greater evaporation resulted in elevated concentrations of SO_4 (and other chemicals). Finally, Wilby (1994) reported higher SO_4 concentrations in a British stream during a 3-year dry period and attributed these to an intensification of the existing hydrological regime, which likely altered flow paths and may have also enhanced oxidation of sulphides in dry soils.

Most long-term monitoring stations in North America which have reported net SO_4 export, have data sets extending back to the late 1970s or 1980s, which coincides with a period of relatively extreme weather (Francis and Hengeveld, 1998; Wilby, 1994). While climate appears to be responsible for part of the inter-annual variability in surface water SO_4 concentrations, it is unclear whether climatic variations alone can explain negative S budgets on a regional scale. In order to reduce the uncertainty in the predicted response of SO_4 to changes in atmospheric deposition, it is therefore necessary to consider a number of interrelated biological, physical and chemical processes, as well as the overriding influence of climate.

Study Site

This project was designed to investigate S cycling in catchments located in the Muskoka-Haliburton region of south-central Ontario (Figure 1). This region has received historically high inputs of SO_4 deposition, and is also characterized by acid sensitive terrain (Dillon *et al*., 1987; 1988). A long-term monitoring programme to assess the affects of acid deposition was initiated in a number of catchments in this region in the late 1970s by the Ontario Ministry of Environment (OMOE). Data collected through this program indicated that surface waters had higher SO_4 concentrations than predicted, and that SO_4 export in catchment drainage waters generally exceeded inputs in bulk deposition. Furthermore, it was also apparent that wetland-draining streams exhibited large inter-annual changes in SO_4 concentration that appeared to be climate related (Devito *et al*., 1999; Dillon *et al*., 1997). The goal of this project was therefore to investigate the response of this region to changes in deposition by examining S cycling in an individual catchment.

The Plastic Lake-1 (PC1) catchment (45˚11’N 78˚50’W) was chosen for this study because it has been the focus of a number of previous biogeochemical and hydrological investigations, which have produced a wealth of background data. Furthermore, the catchment is well instrumented for further study. The 23.3 ha PC1 catchment (Figure 1) contains a relatively large (2.2 ha) conifer-*Sphagnum* swamp directly upstream of the catchment outflow where stream chemistry is monitored. More than 80% of the runoff from the catchment drains through this wetland before discharging to Plastic Lake. Stream flow at PC1 has been continuously gauged since 1980, and stream chemistry was measured at least weekly or more frequently during periods of high flow over the same time period. An entirely upland 3.45 ha sub-catchment of PC1 (PC1-08) drains into the swamp from the northeast (Figure 1). Stream chemistry and stream flow have been measured in the PC1-08 catchment since 1983 and 1986, respectively. Soil percolate has been collected for chemical analyses at 3 zero-tension (ZT) lysimeters located in the hillslope adjacent to the PC1-

08 stream channel, and an additional 3 ZT lysimeters are located immediately outside of the PC1-08 sub-catchment (Figure 2). All lysimeters were installed in 1986/87, and percolate was collected when sample was available between 1987 and 1995. Similarly, monitoring of PC1-08 stream flow and chemistry was temporarily halted in 1995, but both lysimeter and stream flow measurements were reinitiated in the spring of 1999 for this project. Bulk deposition, precipitation depth and other climate variables have been continuously monitored at a site just outside of the PC1 catchment since the late 1970s.

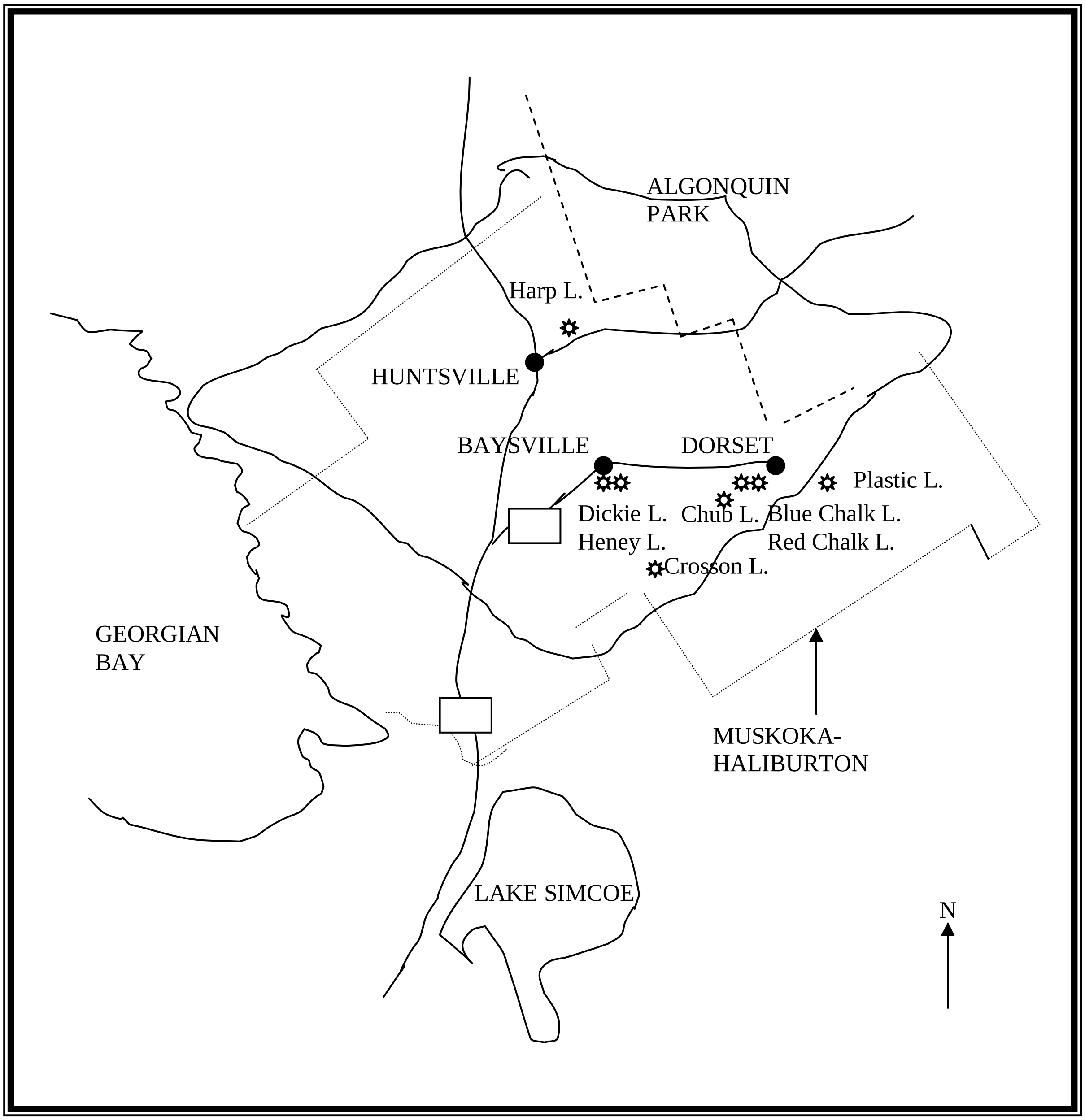
Time-averaged deposition and climate parameters are calculated as the mean of data collected at 4 (until 1995), or 3 (from 1996 to present) meteorological stations that are located within a 50 km radius of Plastic Lake. Methods of deposition collection and meteorological measurements are described in detail in Dillon *et al*. (1988) and Scheider *et al*. (1983).

Study design

A number of experiments and data analyses were performed to further examine 2 initial observations:

1. Patterns of SO_4 concentration are similar among a number of physiographically different catchments in the Muskoka-Haliburton region (*i.e*. both upland and wetland)
2. Sulphate export in stream water generally exceeds input in bulk deposition and this apparent net export is particularly great in certain years

Figure 1. Location of the study site (not to scale).



The remainder of this thesis is organized into a series of chapters which each describe a specific hypothesis related to the 2 observations above. The final chapter provides a synopsis of relevant results and general conclusions.

Chapter 2 describes the similar patterns of annual SO_4 chemistry and export observed in 8 headwater streams and discusses the apparent influence of climate (specifically temperature and precipitation) on temporal patterns of SO_4 release. In addition, SO_4 input/output budgets are calculated for the 8 catchments, and potential causes of net export are discussed.

Chapter 3 compares long-term decreases in SO_4 deposition with SO_4 concentrations in lakes and their inflows. Higher than expected SO_4 concentrations in lakes are attributed to net SO_4 export from the surrounding catchment, and the importance of catchment processes for determining the chemistry of drainage waters is highlighted.

Chapter 4 describes S cycling in an upland, forested catchment that exhibits net S export. Imbalances in the catchment S budget are investigated, and patterns of SO_4 chemistry in soil percolate and upland streamwater are compared with patterns in deposition and climate.

Chapter 5 describes a laboratory experiment which tested directly the effects of increased temperature and changing moisture conditions on SO_4 release from upland (mineral soil, organic soil) and wetland (*Sphagnum*, peat) material. The purpose of this study was to determine whether climate-related changes could explain inter-annual variations in SO_4 concentrations observed in upland and wetland-draining catchments.

Chapter 6 describes the results of laboratory experiments that investigated the importance of SO_4 adsorption and desorption reactions in mineral soil. The potential for increased SO_4 desorption in response to declining SO_4 inputs in deposition is discussed, as well as the potential contributions of desorption to negative S budgets.

Chapter 7 describes variations in the natural abundance of S isotopes in SO_4 inputs and exports from the PC1 catchment over a 2-year period, and discusses possible biological processes involved in S cycling. A second part of this chapter describes a stable S isotope addition experiment, which involved application of ^{34}S to various parts of the catchment in order to determine the transit time of S and factors affecting its retention or release.

Chapter 8 describes a laboratory experiment that tested the effect of changing deposition chemistry (SO_4 and N concentrations) on SO_4 release or retention (*i.e.* mineralization or immobilization) from organic and mineral soil.

Chapter 9 describes the elements of the sulphur mass balance calculation, and discusses the complexities in estimating specific inputs and outputs. Budget calculations are presented for a number of catchments in the Muskoka-Haliburton region.

Chapter 10 provides a summary of important results and general conclusions.

CHAPTER 2: CLIMATE EFFECTS ON SULPHATE FLUX FROM FORESTED CATCHMENTS IN SOUTH-CENTRAL ONTARIO

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ABSTRACT

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

INTRODUCTION

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

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

Mass balance measurements from a number of long-term studies of whole catchments have indicated a net imbalance between sulphur inputs and exports (*e.g*. Alewell *et al*. 1999; Driscoll *et al*. 1998; Feger *et al*. 1990; Houle *et al*. 1997; Mitchell *et al*. 1996a), such that many catchments are currently acting as a S source to drainage waters. A number of sources may account for this additional S output, including desorption from soils of sulphate that had been adsorbed when anthropogenic deposition was higher (Driscoll *et al.* 1995; Mitchell *et al.* 1996a), weathering of

S-containing minerals (Baron *et al*. 1995), mineralization of S in soil organic matter (Driscoll *et al*. 1998), underestimation of dry deposition (Edwards *et al*. 1999; Likens *et al*. 1990), and drought-related oxidation and release of S stored in wetlands (Dillon and LaZerte 1992, Dillon *et al*. 1997). Identification of the sources of S contributing to export is necessary for the prediction of ecosystem response to changes in sulphate deposition. The wide variety of explanations suggested previously would suggest that sources of S export are catchment-specific; however, the potential for regional trends or patterns to exist in sulphate export and retention should also be considered (Driscoll *et al*. 1998).

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

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

In this paper, we have compared sulphate export patterns among 8 physiographically- distinct catchments located within a ~30 km radius of the Dorset Environmental Science Centre (DESC). Trends in sulphate export over time were compared among catchments in order to determine whether regional patterns in sulphate retention exist and to identify some of the factors contributing to sulphate loss from catchments. Sulphate retention is defined here as the fraction of sulphate input to the catchment that was retained and not lost *via* stream discharge in a given year. In addition, we compared sulphate retention in individual catchments over time to determine whether sulphate export was greater than input in certain years and to identify potential relationships with climate.

METHODS

Study Site

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

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

Chemical sampling and analysis

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

Table 1: Description of the eight study catchments (From Jeffries and Snyder, 1983 and *Dillon et al*. 1991). Shallow surficial deposits (glacial till + soil) are < 1m in depth, deep surficial deposits are > 1m depth.

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

Hydrology

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

Meteorological data

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

(1980-1995) or 3 (1995-1998) bulk deposition collectors located at the meteorological stations. Details on methods and instrumentation used for the collection of bulk deposition are given in Scheider *et al*. (1979). Although bulk collectors may underestimate total sulphate deposition in some regions (*e.g.* Likens *et al*. 1990; Edwards *et al*. 1999; Novak *et al*. 1996), bulk deposition collectors are generally suitable in areas remote from point sources. Furthermore, comparisons of wet-only, and bulk sulphate deposition in the Muskoka-Haliburton area, indicated that wet sulphate deposition measurements were approximately 15-20% less than bulk estimates, a difference that was similar to dry deposition estimates from modelling calculations (Dillon *et al*. 1988). Therefore, for the purpose of this analysis we assume that sulphate deposition measured in collections of bulk deposition adequately represents total (*i.e*. wet + dry) sulphate deposition.

Statistical comparisons among streams

The degree of similarity in year-to-year patterns among streams (synchrony or coherence) was quantified as the Pearson product-moment correlation coefficient (r), with observations paired by year (Webster *et al*. 1999). Sulphate retention, or the fraction of sulphate input to the catchment that was retained and not lost *via* stream discharge in a given year was calculated as input in bulk deposition ($meq/m^2/yr$) minus stream export ($meq/m^2/yr$), expressed as a fraction of input. Pearson correlation and linear regression analyses were used to compare annual sulphate export and mean concentrations (volume-weighted) among streams, and to investigate relationships with climate (temperature, precipitation) and hydrologic variables (zero-streamflow). In addition, annual sulphate export and stream sulphate concentration were standardized using Z-scores (annual observation minus the 18-year mean, all divided by the standard deviation) in order to facilitate comparisons among the 8 streams. In order to determine whether organo-sulphur compounds contributed to net sulphur export in streams, inorganic sulphate and total-S concentrations measured in each stream over an 11-month period were compared using a paired 2-sample t-test for means. Differences between means at $p<0.05$ were considered significant.

RESULTS

Atmospheric Deposition

Bulk sulphate deposition in the Muskoka-Haliburton region decreased substantially between 1976/77 and 1997/98, although the greatest decrease in deposition occurred at the beginning of the monitoring period, between 1976/77 and 1983/84, and since then deposition has declined more gradually (Figure 1). For example, after 1993 sulphate deposition to the area has been relatively constant (between 40 and 50 meq/m^2/yr). Extremely low deposition measured in 1997/98 (~30 meq/m^2) is a result of unusually low precipitation (786 mm) in that year (Figure 1).

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

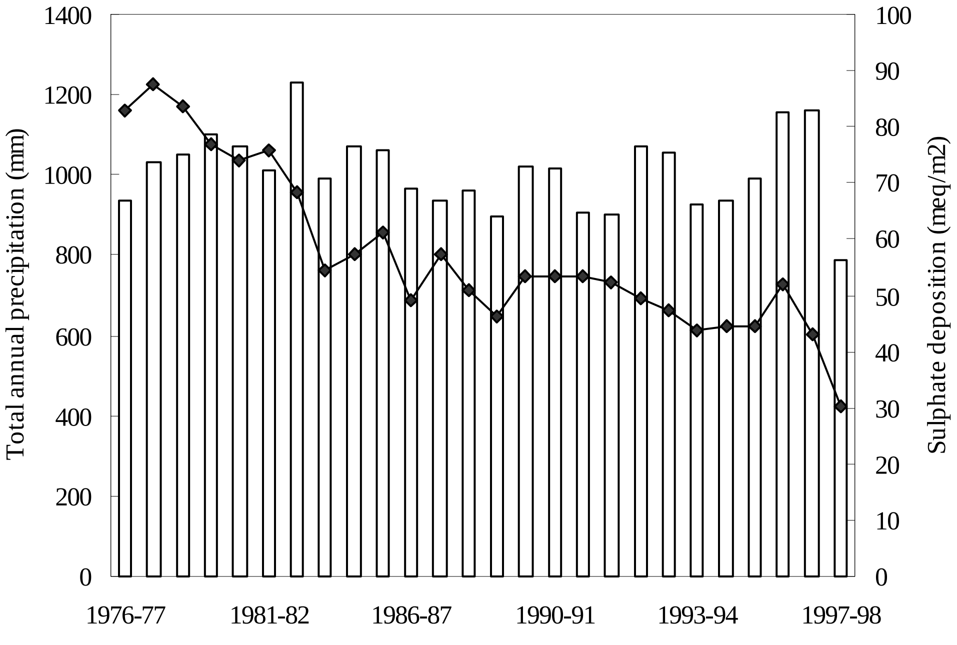


Figure 2. Mean annual discharge weighted sulphate concentration in each of the 8 study streams: 1980-81 through 1997-98.

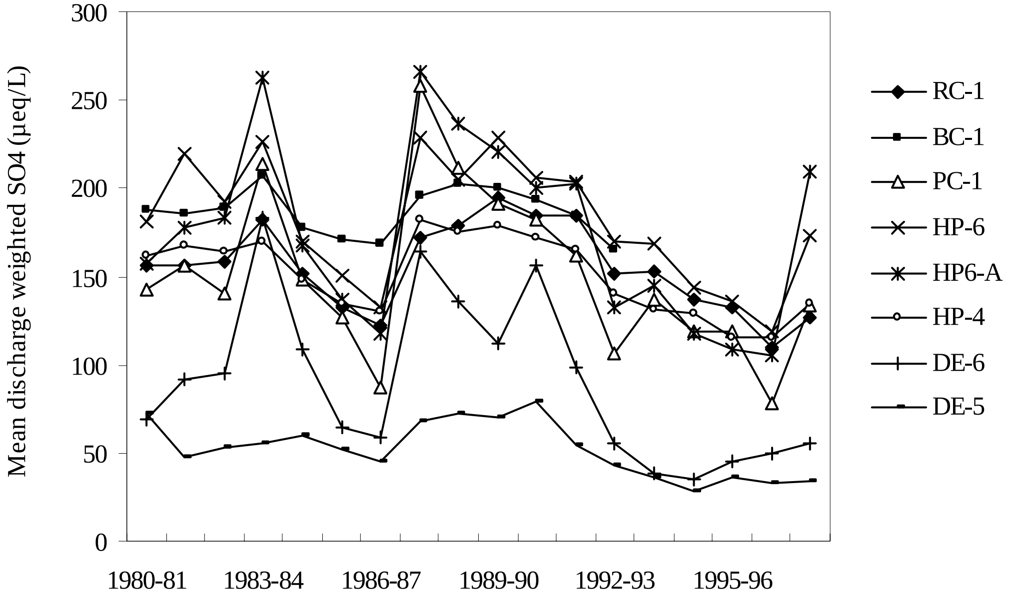
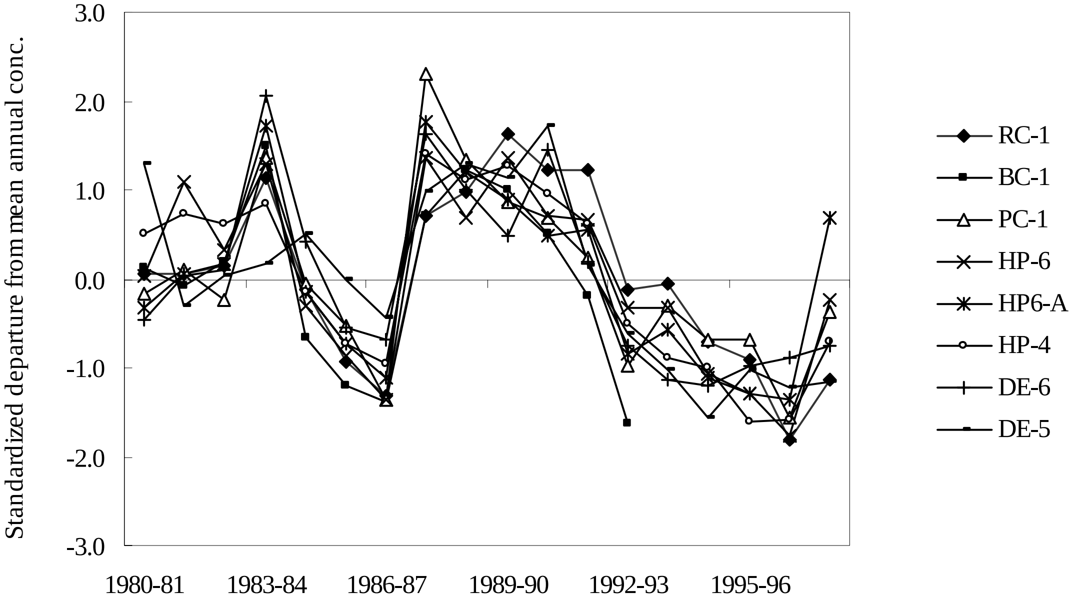


Figure 3. Annual sulphate concentration expressed as a Z-score (annual observation minus the 20-year mean, all divided by the standard deviation) in each of the 8 study streams.



Sulphate concentration patterns in streams

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

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

There was a tendency for sulphate concentrations in streams to decline over the study period, although large peaks in concentration were observed in certain years. For example, peaks in sulphate concentration in the majority of streams occurred in 1983/84 and 1987/88, whereas the lowest mean sulphate concentrations occurred in 1986/87 (Figure 2). The general decline in sulphate concentration, which occurred in all streams between 1983/84 and 1986/87 was reversed in 1987/88, when concentrations rose to levels that were in some cases more than double the previous year (*e.g*. PC1, HP6-A, DE6). Sulphate concentrations in most streams declined steadily between 1987/88 and 1996/97, but in 1997/98 sulphate levels in many streams increased once more (Figure 2). For example, in HP6-A the mean volume-weighted sulphate concentration in 1997/98 was 210 µeq/L compared with 105 µeq/L in 1996/97. Sulphate concentrations in DE5 (range 30 - 80 µeq/L) were always lower than the other 7 streams (range 35 – 265 µeq/L), and year-to-year changes were less pronounced. However, when sulphate concentrations were standardized among streams (Z-scores), the temporal pattern in sulphate concentration in DE5 was similar to the other streams (Figure 3).

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

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

Total (UV-digested) and inorganic sulphate concentrations were measured concurrently in each stream between March 1990 and January 1991 in order to determine the importance of organic-S export. Average concentrations of total-S in DE5, DE6, RC1 and HP6-A were significantly greater than the level of inorganic sulphate (Table 3). While the difference between total-S and sulphate concentrations was minor (<5%) in RC1 and HP6-A, organo-sulphur export may account for as much as 15% (DE6) to 23% (DE5) of total S export in the Dickie streams. Greater export of S in organic forms may also account for the generally poorer relationships observed between sulphate concentrations in DE5 and DE6 and the 6 remaining streams (Table 2).

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

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

Sulphate export

Changes in stream sulphate concentration were reflected in changes in catchment export. A high degree of synchrony was observed in year-to-year patterns of sulphate export in many of the streams (Table 4), although patterns were generally less clear (Figure 4) as export is also a function of streamflow, which varies considerably from year-to-year. Again, when sulphate export is standardized among streams the similarity in their patterns becomes clear (Figure 5). All 8 catchments exhibited minimum sulphate export values in 1986/87 and 1997/98, which were generally more than 1 standard deviation less than average (Figure 5). In contrast, sulphate export in 1987/88 was substantially greater, and was in some cases more than double the previous year. For example, sulphate export in PC1 increased from 40 meq/m^2 in 1986/87 to 120 meq/m^2 in 1987/88 (Figure 4).

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

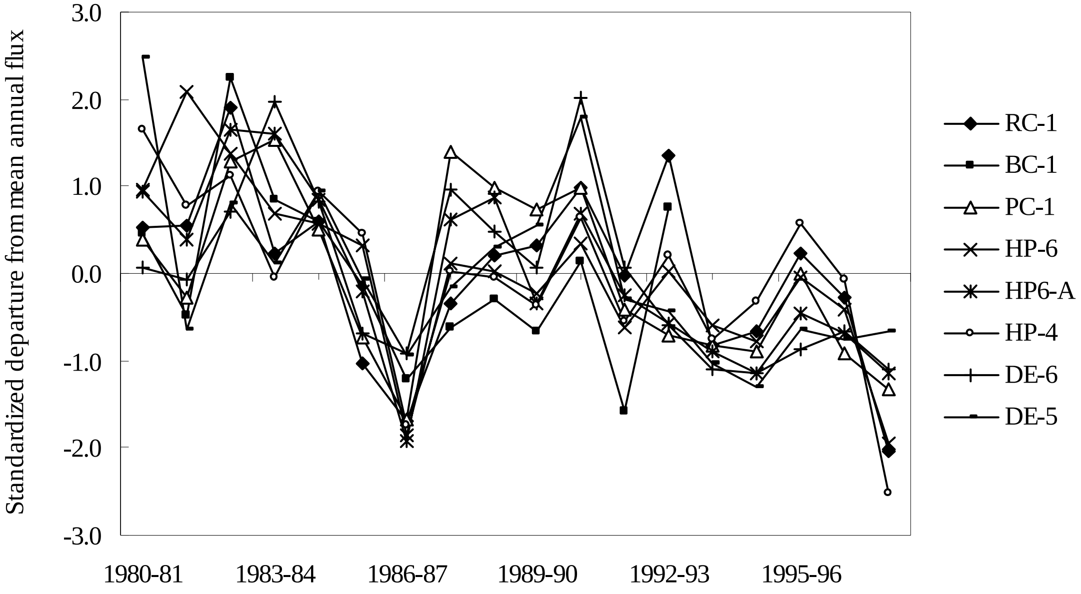


Figure 5. Annual sulphate export expressed as a Z- score (annual observation minus the 20-year mean, all divided by the standard deviation) in each of the 8 study catchments.

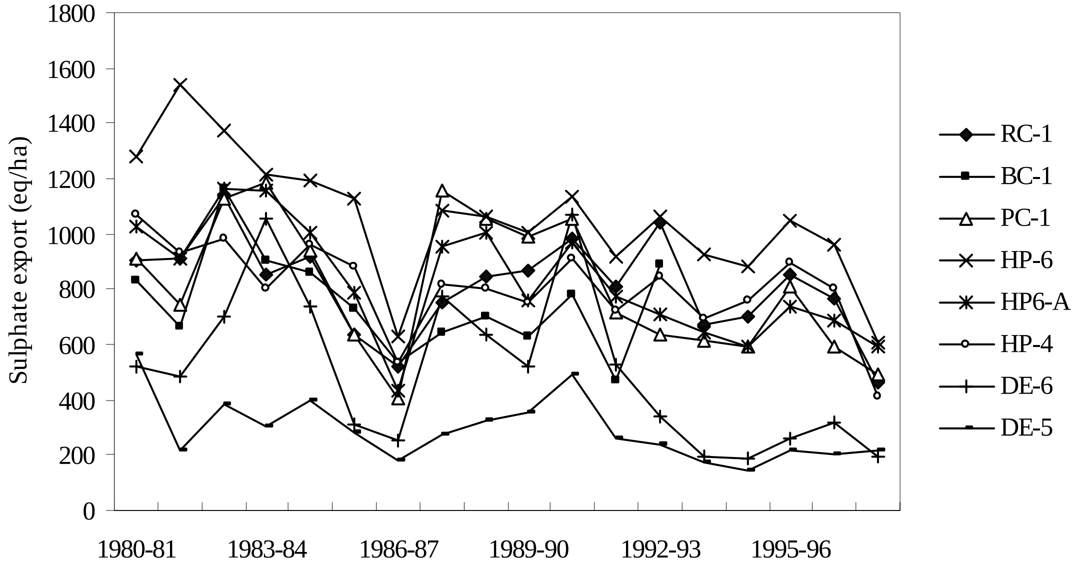


Figure 6. Annual sulphate retention in the 8 study catchments. Sulphate retention is defined as the proportion of sulphate input to the catchment in deposition that is not exported via streamflow.

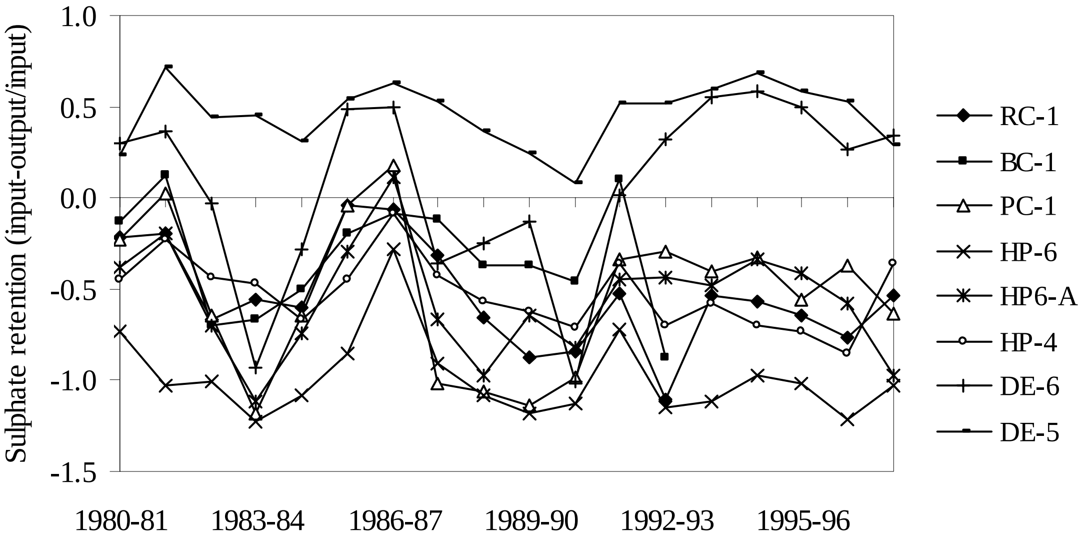
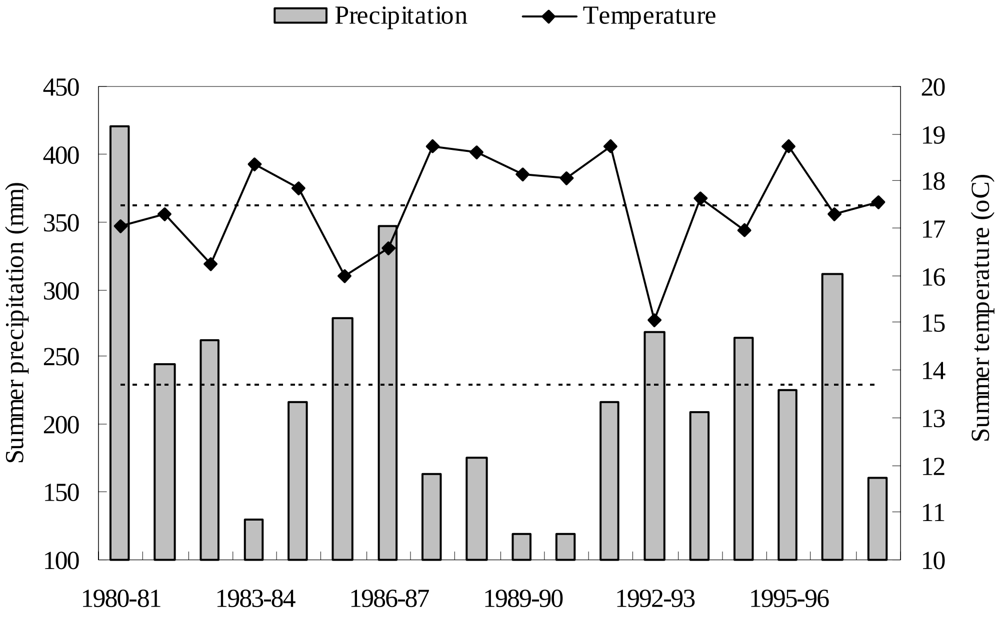


Figure 7. Total summer (June – August) precipitation and mean summer temperature in the Dorset region: 1980-81 through 1997-98. Dashed lines represent the 18-year average summer precipitation and temperature, respectively.



Although stream export of sulphate was quite variable over time, in most years sulphate export from catchments exceeded input *via* bulk deposition. Sulphate retention (defined as input from the atmosphere minus stream export expressed as a proportion of input) in most catchments was therefore negative or near zero (Figure 6). For example, in 1983/84 and between 1987/88 and 1990/91, sulphate retention in most catchments was between –0.5 and –1.0 (Figure 6), indicating that catchments exported between 1.5 and 2-times more sulphate than was input *via* bulk deposition. Only in the DE5 catchment, and occasionally DE6, was sulphate export continually less than input, and there was net retention within the catchment. However, export of sulphur in organic forms was not included in budget calculations because total S concentrations in streams were only measured over an 11-month period. In the majority of the long-term monitored streams in this region, inorganic sulphate is the dominant form of S export (Dillon, unpublished), and so measurement of sulphate concentrations in streams is adequate for determining S-export from most catchments. However, measurement of total-S concentrations may be necessary in order to approximate the magnitude of S flux in high DOC streams that drain wetland-dominated catchments such as DE5 and DE6.

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

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

Climate effects

The potential relationship between climate (precipitation and temperature) and sulphate flux from catchments was explored using linear regression analysis. The best predictors of annual sulphate concentrations in streams were summer (Jun-Aug) precipitation and temperature (Table 5).

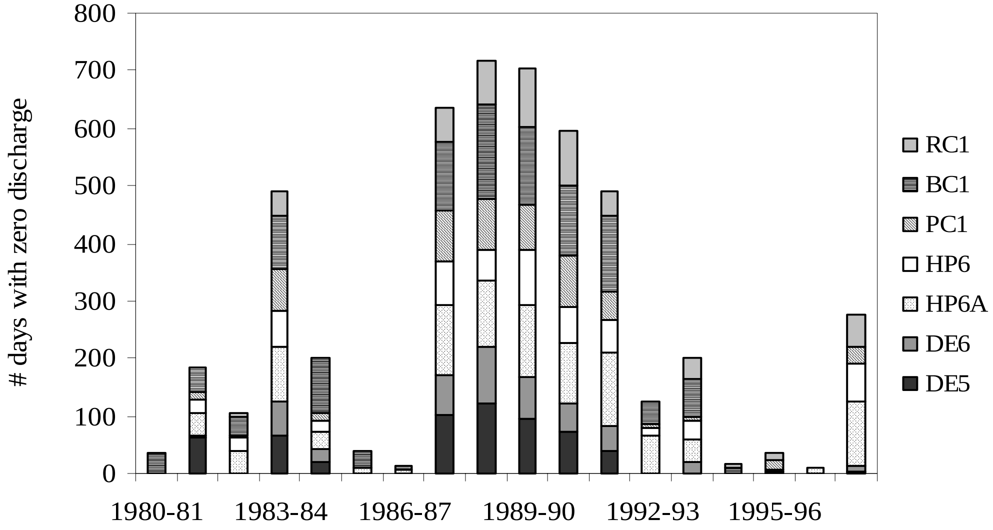
Table 5. Correlation coefficients (r) for the relationship between mean annual volume weighted sulphate concentration in each of the 8 study streams and average summer (June-August) precipitation and temperature. Correlations marked with an asterisk are significant at $p<0.05$.

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

Correlations were not very strong for some streams; however, this is likely partly a function of comparing annual average sulphate concentrations with precipitation and temperature averages for a 3-month period. Catchments generally exhibited greater net sulphate export, or more negative retention (Figure 6) in years having summers that were drier and warmer than average (18-year mean) (Figure 7).

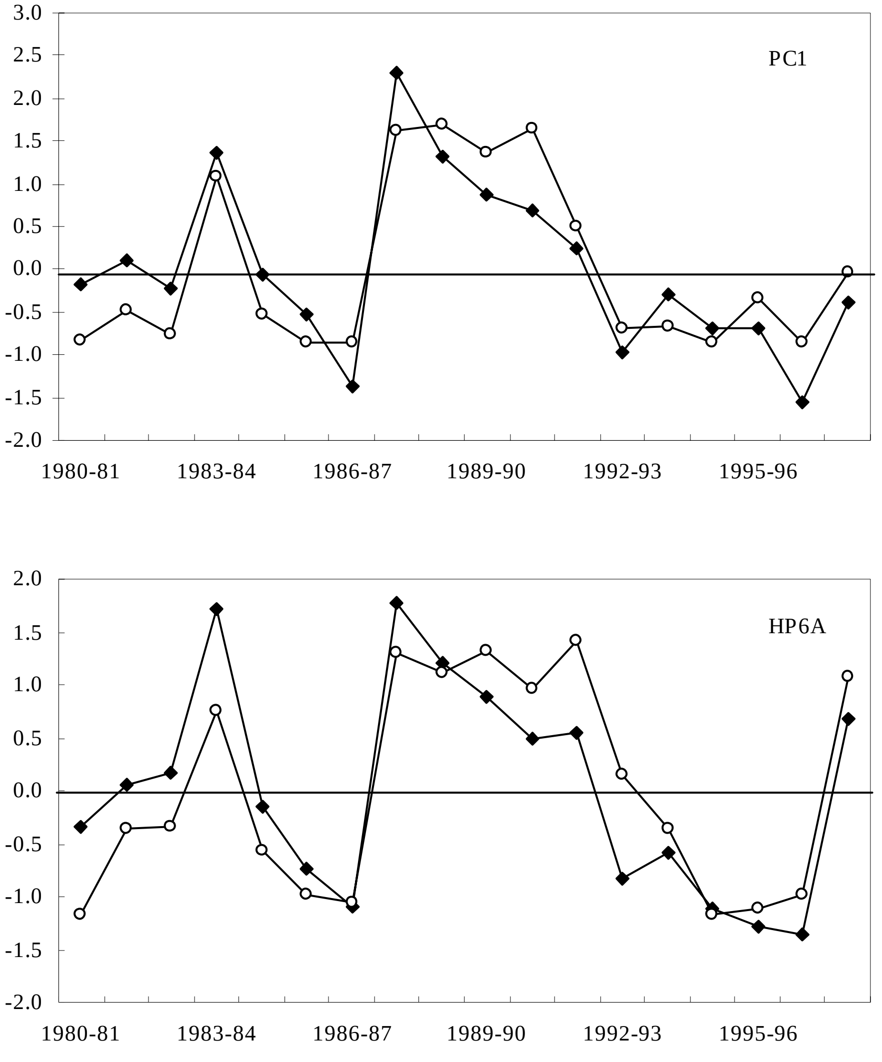
Streamflow, however, is a better indicator of dry conditions in catchments than either precipitation or temperature. Due to the predominantly thin till which dominates most of the catchments (Table 1), the majority of streams cease to flow for variable lengths of time during the summer months when conditions are generally warmer and drier than other months (Figure 8). Of the 8 catchments considered in this study, streamflow is only continuous year-round in HP4, which has significant glacial till deposits that maintain elevated groundwater levels adjacent to the stream (Hinton *et al*. 1993). The other 7 streams tended to be dry (zero discharge) for a greater number of days in years with warmer and drier than average summers (Figures 7 & 8).

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



Correlation coefficients between zero-streamflow and sulphate concentration in these 7 streams ranged from r = 0.69 (DE5) to r = 0.87 (PC1) (all at *p*<0.05). For example in the PC1 and HP6-A catchments, standardized average sulphate concentrations and zero-streamflow followed very similar patterns over time (Figure 9). In contrast, there was no significant relationship between zero discharge and sulphate concentration in HP4 (r = 0.13, *p*>0.05) because groundwater connections maintain continuous baseflow in this stream (Hinton *et al*. 1993). Nevertheless, it is likely that dry conditions similar to the other catchments existed in much of the HP4 catchment in 1983/84 and from 1987/88 through 1990/91, and temporal patterns of sulphate concentration were similar in HP4 compared to the other streams (Table 2).

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



DISCUSSION

Patterns in stream chemistry

The fact that all 8 streams exhibited similar patterns in both sulphate concentration and export, despite their physiographic differences, suggests that large-scale, or basin-wide processes such as climate are involved. Although specific regions may be characterized as having a particular climate type (*e.g*. Köppen Climatic Classification System) based on their long-term patterns in average temperature and precipitation, climate over the short-term (year-to-year) may be very variable. For example, El Niño events occur with a frequency of approximately 4 to 7 years, and can significantly affect global precipitation and temperature (see Philander 1990).Four of the strongest El Niño events since 1900 occurred during the monitoring period (1982/83, 1986/87, 1991/92 and 1997/98). In our study area, summers following El Niño events generally had lower than average precipitation, and temperatures that were higher than average, which often results in complete cessation of stream flow. The summer of 1992/93 did not follow this pattern, however, possibly due to the eruption of Mount Pinatubo in the Philippines in June 1991, which had globe-wide effects on climate (Hansen *et al*. 1996). Dry conditions persisted between 1987 and 1990, as both total annual and summer precipitation depths (892 - 949 mm, and 119-175 mm, respectively) in each of these 4 years were below the 18-year averages (1015 and 230 mm, respectively). Drought conditions during this period were also reported in England (Wilby 1994), Europe (Van Dam 1988) and much of the northeastern United States (Webster *et al*. 2000), and were related to changes in surface water chemistry. For example, Wilby (1994) reported a substantial increase in surface water acidity between 1988 and 1990, a period which was ranked as having the 3rd most severe drought since records began in 1698. They further noted that a major effect of the extreme climate experienced during this period was an enhancement of the existing hydrologic regime, such that summer low- and zero-flow periods were extended (Wilby 1994).

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

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

mg/L; DE6 18.7 – 26.1 mg/L). Houle *et al*. (1995) found that the contribution of dissolved organic sulphur (DOS) to total S concentrations in Quebec lakes was greater in lakes having higher DOC concentrations, as DOS is part of dissolved organic matter. Export of S in organic forms may therefore be important in the DE streams.

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

Other possible sources of net S-export

Although weathering may be an important source of S in some catchments (*e.g*. Turk *et al*. 1992), and temperature-related increases in mineral weathering have been reported (Sommaruga-Wögrath *et al*. 1997), weathering is unlikely to be a significant source of S to catchments in the Muskoka-Haliburton region due to very low S concentrations in bedrock and soils (Jeffries and Snyder 1983; Neary *et al*. 1987). The other possible source of additional S is dry deposition, however the contribution of dry deposition to total S-input in Muskoka Haliburton is likely very low given its remote location. Furthermore, sulphur dioxide (0.75-2μg/m^3) and particulate sulphate concentrations (1-2μg/m^3) measured in this region are low relative to areas in the eastern United States, where many of the previous studies on dry deposition were conducted (Environment Canada 1997; USEPA 1999). Dry deposition is a notoriously difficult parameter to measure, and rather than increase our bulk deposition estimates by some arbitrary enrichment factor, we justified the use of bulk deposition as a surrogate of total sulphate deposition based on previous measurements and modelling calculations which took into account the low SO_2 and particulate SO_4 levels measured in this region (Dillon *et al*. 1988). Furthermore, the amount of additional dry deposition that would be required to balance the magnitude of net sulphate export would be unrealistically high (*i.e*. bulk deposition would have to be doubled in some years; see Figure 6). At most, Sirois and Barrie (1988) estimated that dry deposition could constitute 22% of the total sulphur deposition in southeastern Ontario, and their estimates were made using data collected between 1979 and 1982 - a time period when deposition was notably higher.

Furthermore, the magnitude of dry deposition would have to vary greatly between years in order to account for the large differences measured in net retention between contiguous years. These reasons combined suggest that dry deposition alone cannot explain either the magnitude of net export, or the variations in net export over time.

Conclusions

The possible linkage between sulphate export and climate conditions has a number of important implications. Firstly, the net export of sulphate following summer droughts is substantial, and represents a major increase in sulphate input to downstream lakes. As many of the lakes in the Muskoka-Haliburton region are currently acid-stressed (Dillon *et al*. 1987; McNicol *et al*. 1998), large changes in sulphate input to these lakes could have serious consequences for both their chemical and biological recovery. Secondly, changes in industrial emissions and subsequent acid deposition under conditions of varying climate may not be directly translated into changes in stream and lake chemistry. Sulphate concentrations in a number of long-term monitored surface waters have not decreased as much as predicted given recent reductions in industrial emissions, nor have measurable improvements in *p*H and alkalinity been achieved (Driscoll *et al*. 1998; McNicol *et al*. 1998; Stoddard *et al*. 2000). While many catchments may currently be exhibiting some form of ‘delayed response’ to reductions in acid deposition due to the time required for soils to achieve a new equilibrium with lowered inputs (Reuss and Johnson 1986; Driscoll *et al*. 1998), in this region climate conditions appear to have an important influence on S-retention and export. Thus, predicted future changes in climate including a greater frequency of extreme events such as drought (*e.g*. IPCC 1995) may have important implications for S biogeochemistry, and for the recovery of acid-impacted terrestrial and aquatic systems.

CHAPTER 3: LONG-TERM (18-YEAR) CHANGES IN SULPHATE CONCENTRATIONS IN 2 ONTARIO HEADWATER LAKES AND THEIR INFLOWS IN RESPONSE TO DECREASING DEPOSITION AND CLIMATE VARIATIONS

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ABSTRACT

Sulphate concentrations in two headwater lakes and their major inflows were evaluated over an 18-year period (1980-1998) during which time sulphate bulk deposition declined by approximately 43%. The two lake catchments represent either end of the spectrum of acid sensitivity in the Muskoka-Haliburton region of Ontario. Between 1980 and 1998, SO_4 concentrations in Harp and Plastic lakes decreased, but the decrease was much less than expected (28 and 21%, respectively) given the magnitude of change in deposition. Sulphate export in streams draining into the lakes greatly exceeded SO_4 deposition to catchments in most years, and quantitatively explains the response of lake-SO_4 concentration. Furthermore, temporal patterns in mean annual SO_4 concentrations in streams were similar, and appeared to be related to climate factors. Specifically, catchment export of SO_4 was greater, and stream-SO_4 concentrations were higher, in years that had warm, dry summers, when stream flow in many catchments ceased for up to several weeks. Increased SO_4 export from catchments resulted in higher SO_4 concentrations in lakes, but the response of lake SO_4 was not as immediate or dramatic as the response of stream SO_4 to changes in catchment dryness due to the effect of the lake water residence time. Factors that affect SO_4 retention or export in catchments exert a strong influence on SO_4 concentrations in lakes and streams and need to be considered when evaluating the response of surface water chemistry to changes in sulphate deposition.

INTRODUCTION

Recently, a number of reports have suggested that widely observed delays in the response of SO_4 concentrations in surface waters to changes in SO_4 deposition (Jeffries *et al.* 1995; Dillon *et al.* 1997) may be due to the net export of SO_4 from the terrestrial catchment (Driscoll *et al.* 1995; Mitchell *et al.* 1996; Houle *et al.* 1997; Alewell *et al.* 1999). Net export of SO_4 from catchments could delay the chemical and biological recovery of acid-impacted lakes and streams and lead to continued soil acidification. Therefore factors affecting SO_4 export from catchments must be considered when making predictions of the response of surface waters to further decreases in SO_4 deposition.

Sulphur may be retained in catchments through either biological uptake or chemical adsorption and precipitation reactions in the soil. Adsorption is an important mechanism of sulphate retention in soils rich in Fe and Al hydrous oxides (Johnson *et al.* 1982), however, adsorbed sulphate generally comprises less than 30% of the total S pool in soils located north of the most recent continental glaciation (Rochelle *et al.* 1987; Mitchell *et al.* 1992; Houle *et al.* 1995). Precipitation of aluminum hydroxy sulfate minerals may also be an important means of SO_4 retention in extremely acidic soils subject to high levels of S-input (Adams and Rawajfih 1977; Khanna *et al.* 1987). The dominant form of S in most soils however, is organic (>75% of total S) (Mitchell *et al.* 1992). For example, at the Plastic Lake catchment in the Muskoka-Haliburton region, the total S pool in soil is approximately 910 kg S/ha, of which 67% is organic and the remainder is adsorbed SO_4 or soluble SO_4 (33%) (Neary *et al.*, 1987). Sulphate is incorporated into soil organic matter through both microbial assimilation and by plant uptake *via* the roots or stomata. While total S concentrations are usually greatest in the forest floor (LFH) (Neary *et al.* 1987), the mineral soil constitutes the largest S pool in soil due to its greater mass (Houle and Carignan 1992; Mitchell *et al.* 1992). Wetlands are also important storage sites for S within catchments (Devito 1995), and wetlands are a common feature on the Precambrian Shield. The generally anoxic conditions in wetlands favour microbial reduction of SO_4 to sulfide species, which may then react with iron or humic material to form relatively stable organic-S or Fe-S compounds (Urban *et al.* 1989; Wieder and Lang 1988).

Sulphate retention, however, is not always a permanent phenomenon, and S may be released from internal catchment sources through desorption from mineral soil (Fuller *et al.* 1985; Harrison *et al.* 1989), mineralization of organic-S compounds (David and Mitchell 1987), or in response to declines in wetland water tables which allow oxidation of reduced S compounds (Bayley *et al.* 1986; Devito and Hill 1999; LaZerte 1993). Release of stored sulphate may prevent the recovery of acid-impacted soils and drainage waters, especially if the S-content of soil is high (Alewell and Matzner 1993).

The Muskoka-Haliburton region is an important tourist and cottage district in south-central Ontario located on the Canadian Shield. Although this region is relatively remote from S-emission sources, bulk deposition measurements since the late 1970s indicated that SO_4 deposition to the area was high (peak 87 meq/m^2 in 1977/78) and prompted the initiation of a number of long-term surface water monitoring projects by the Ontario Ministry of Environment (OMOE). Of the 33 lakes included in the OMME monitoring program, Harp Lake (HP) and Plastic Lake (PC) are considered to be one of the least sensitive, and most sensitive to acid deposition respectively. The terrestrial catchment draining into Harp Lake contains variable amounts of relatively thick glacial till deposits, and the lake is consequently moderately well buffered relative to other lakes in the region (alkalinity ~70µeq/l). In contrast, soils in the PC catchment are generally thin (average ~40cm) and till is either absent, or is present in thin localized deposits (<1m) (Jeffries and Snyder 1983). During the late 1970s and the 1980s, the alkalinity of Plastic Lake declined to almost zero (Dillon *et al.* 1987), and is currently less than 20 µeq/l. Extensive negative chemical, and biological effects of acidification have been documented in Plastic Lake (Dillon *et al.* 1987; Stephenson and Mackie 1989). The objective of this study was to evaluate changes in SO_4 concentrations in HP and PC over an 18-year period during which SO_4 deposition declined, and to compare trends in lake water chemistry with those in major inflow streams to better understand the effect of catchment processes on lake response.

METHODS

Site Description

Harp (45˚23'N 79˚07'W) and Plastic (45˚11'N 78˚50'W) lakes are headwater lakes located in the Muskoka-Haliburton District of south central Ontario near the southern edge of the Boreal ecozone (Fig. 1, Table 1). The current (1999/2000) volume weighted average *p*H of HP is approximately 6.3, whereas the *p*H of PC is around 5.8.

Harp Lake is fed by 6 inflows (Fig. 1) that drain catchments ranging in size from 10 ha (HP6) to 191 ha (HP5) (Table 2). In total, runoff from 80% of the terrestrial catchment draining into Harp Lake is continuously measured. Sugar maple (*Acer saccharum* Marsh), beech (*Fagus grandifolia* Ehrh.) and eastern hemlock (*Tsuga canadensis* L.) generally dominate upland parts of the catchments, whereas in lowland regions, black spruce (*Picea mariana* Mill.), yellow birch (*Betula alleghaniensis* Britt.) and white cedar (*Thuja occidentalis* L.) are more common. Wetlands, including swamps, beaver ponds and riparian wetlands are present in all of the HP catchments (Table 2). Soils are underlain by Precambrian metamorphic silicate bedrock, containing variable amounts of biotite, hornblende gneiss, amphibolite and schist. Till deposits, which vary in thickness are the dominant surficial characteristics of the HP catchment (Table 2). Soils are mainly brunisols and podzols, of variable thickness, although soils in the HP catchment are significantly deeper (up to 2 m depth) than those at Plastic Lake.

Figure 1. Map of Harp and Plastic Lake catchments. Shaded areas indicate wetlands (not to scale).

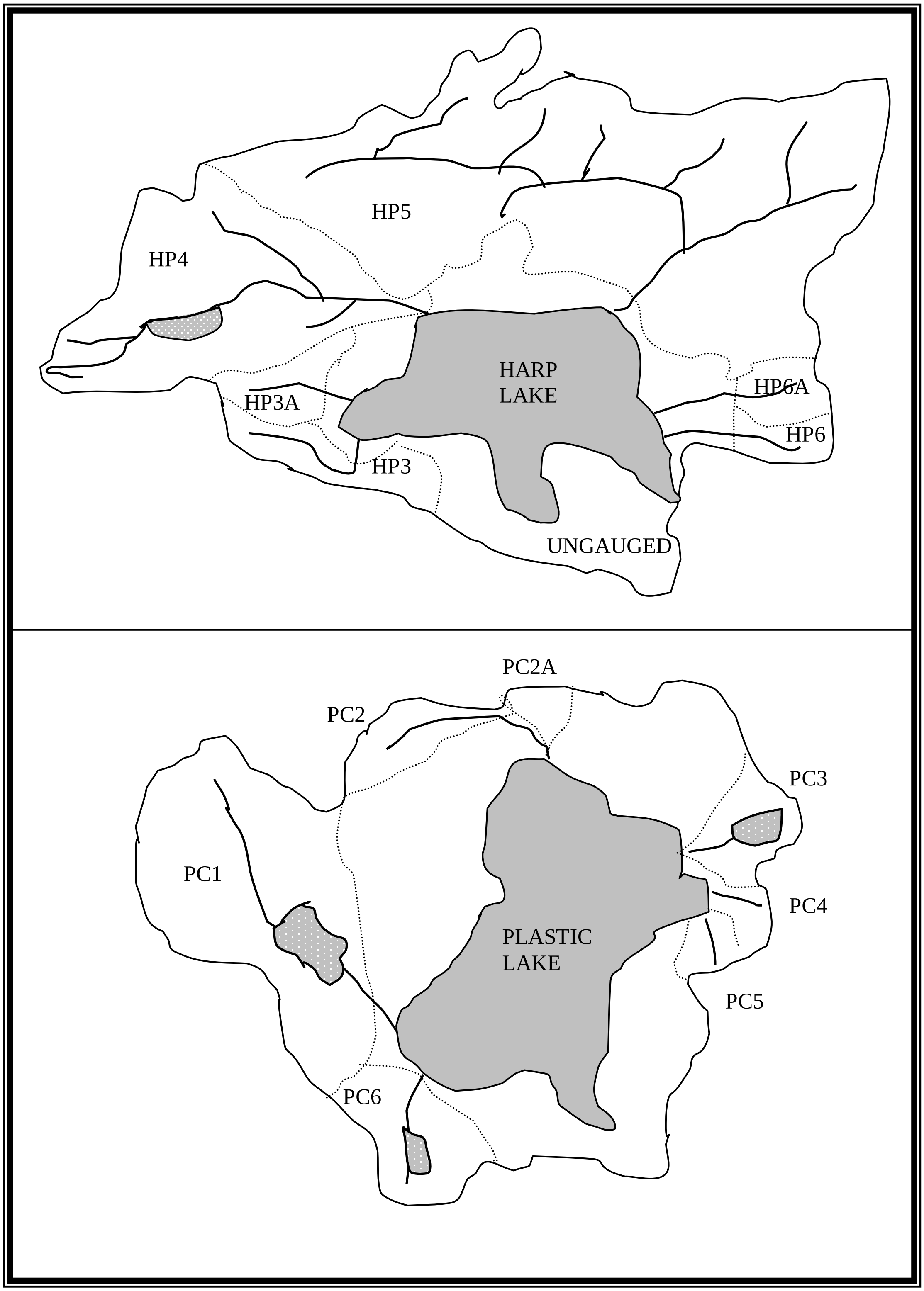


Table 1. Selected physical characteristics of Harp and Plastic Lakes.

	Lake area (ha)	*Catchment area (ha)*	*Mean, max. depth (m)*	*Flushing time[1] (yr)*
Harp Lake (HP)	71	471	13, 38	3.4
Plastic Lake (PC)	32	93	8, 16	4.1

[1] Flushing time is calculated as lake volume/lake outflow

Table 2. Characteristics of the 6 sub-catchments of Harp Lake, and of the PC1 sub-catchment of Plastic Lake. Data are from Dillon *et al*., 1991 and Devito *et al*.,1999.

	Sub-catchment area (ha)	*Avg. slope (%)*	*Dominant vegetation*	*Wetland coverage (%)*	*Area with minor till (>1m) (%)*
Harp-3 (HP3)	26	4	M	13	76
Harp-3A (HP3A)	20	8	M	3	97
Harp-4 (HP4)	119	5	M	15	56
Harp-5 (HP5)	191	3	M	13	35
Harp-6 (HP6)	10	8	M	10	34
Harp-6A (HP6A)	15	10	M	8.5	7
Plastic-1 (PC1)	23	6	WP, H	9	10

M = Maple spp., B= beech, WP = white pine, H = hemlock

Plastic Lake is fed by 7 small streams, 6 of which flow intermittently. Stream flow is continuously gauged at the base of the largest (23 ha) sub-catchment (PC1; Figure 1) which flows year-round except in very dry years. PC1 represents approximately 25% of the total catchment area draining into Plastic Lake. Twelve years of monitoring data (1980 – 1992) from all 7 of the inflows to Plastic Lake showed that SO_4 concentrations and temporal variations in SO_4 concentration measured in PC1 were similar to levels in the other 6 streams, indicating that chemical changes measured in PC1 were representative of the entire terrestrial catchment (Dillon, unpublished). In contrast to HP, the forest at PC is primarily coniferous, and is dominated by white pine (*Pinus strobus* L.) and eastern hemlock. Swamps and beaver ponds are common in all of the PC sub-catchments, and white cedar, black spruce and alder (*Alnus* spp.) generally dominate swamps. *Sphagnum* species are common groundcover. Metamorphic silicate bedrock (biotite hornblende gneiss) is overlain by thin, discontinuous sandy basal till; bedrock outcrops are common. Soils are generally shallow (< 1m), weakly developed acidic podzols and brunisols.

Sampling Methods

Bulk deposition, precipitation depth and other climate variables were measured at 4 (until 1995), then 3 (from 1996 to present) meteorological stations during the study period; all are located within a 50 km radius of the lakes. Methods of deposition collection and meteorological measurements are described in detail in Dillon *et al.* (1988).

Lakes and streams were sampled weekly, or bi-weekly, or more frequently during spring snow melt, and SO_4 concentrations were determined by ion chromatography (Ontario Ministry of Environment 1983). Lake sampling was done using peristaltic pumps or Van Dorn bottles. During the period of thermal stratification, lake water was sampled from different strata in each thermal layer (epi-, meta- and hypolimnion) in proportion to the volume of lake water in those strata. Whole-lake, composite concentration data were then obtained by combining results from the 3 different layers in proportion to each layer's total volume. During the spring and fall overturn periods, sub-samples collected from all strata were combined to produce a single sample for analysis.

Stream water level or stage was monitored continuously at V-notch or H-flume weirs located at the catchment outflows, and stage was converted to flow using established stage-discharge relationships (Ontario Ministry of the Environment 1994). Annual data were calculated for the hydrologic year (June 1 to May 31). Sulphate fluxes in stream water were calculated by multiplying the concentration for each sample interval (generally <7d) by the stream discharge for that interval, and these were expressed as areal fluxes (Dann *et al.*, 1986). Annual average volume-weighted stream SO_4 concentrations were obtained by dividing total annual flux of SO_4 by annual stream discharge.

Sulphate Budgets

Sulphate input-output budgets were calculated for each of the 7 study catchments. Sulphur input *via* weathering was assumed to be negligible given the low S content and low-weathering capacity of bedrock in the region (Jeffries and Snyder 1983; Kirkwood and Nesbitt 1991; Watmough and Dillon 2001). Therefore for the purpose of this analysis, SO_4 input to catchments was assumed to be derived entirely from atmospheric deposition. We estimated SO_4 input to catchments using measurements of bulk deposition, which in some cases can greatly underestimate total deposition (Dillon *et al.* 1982; Lindberg *et al.* 1986). However, in regions that are remote from point sources of pollution, such as the Muskoka-Haliburton region of central Ontario, the contribution of dry deposition to total deposition is generally less (Sirois and Barrie 1988). Furthermore, Dillon *et al.* (1988) compared wet-only and dry-only measurements of deposition with bulk values and found that bulk deposition of SO_4 was approximately 15-20% greater than wet-only, a difference that was similar to modeling estimates of dry deposition (17-18%). Therefore, in order to calculate SO_4 retention in each catchment we assumed that measured bulk deposition was representative of total SO_4 input to the catchment. As such, net SO_4 retention (or export) in each catchment was calculated for each hydrologic year using the following formula:

$$[(\text{bulk deposition} - \text{stream export})/\text{bulk deposition}] \times 100\%$$

Negative numbers imply net SO_4 export and positive numbers reflect SO_4 retention in the catchment.

Data analysis

In order to facilitate the comparison of temporal trends in discharge and SO_4 concentration, respectively among streams that drain catchments that vary greatly in size (*i.e.* 9 ha to 191 ha) annual average data were standardized as Z-scores. For example, $Z_t = (x_t - x_x) / SD_x$, where t = hydrologic year, x_x = 18-year average flow or SO_4 concentration, respectively and SD_x = standard deviation around the long-term average value. Pearson correlation analysis of Z-scores was used to evaluate coherence in stream flow and SO_4 concentrations, respectively among catchments.

RESULTS & DISCUSSION

Deposition

Sulphate deposition declined substantially during the study period from an average of 75 meq/m^2 in the early 1980s (1980/81-1982/83) to an average of 42 meq/m^2 in the late 1990s (1995/96-1997/98), a decrease of approximately 43% (Fig. 2). Deposition was particularly low in 1997/98 (30 meq/m^2) due to extremely low precipitation in that year (1997/98 = 786mm, long term average = 1010mm). Sulphate deposition has increased since then (data not shown), and was between 40 and 45 meq/m^2 in the last 2 years of measure (1998/99-1999/00). The greatest decline in SO_4 deposition occurred before 1983/84, and after this time year-to-year variations in SO_4 deposition were generally less than 20% (Fig. 2).

Figure 2. Bulk sulphate deposition (meq/m^2) in the Muskoka-Haliburton region, 1980-1998.

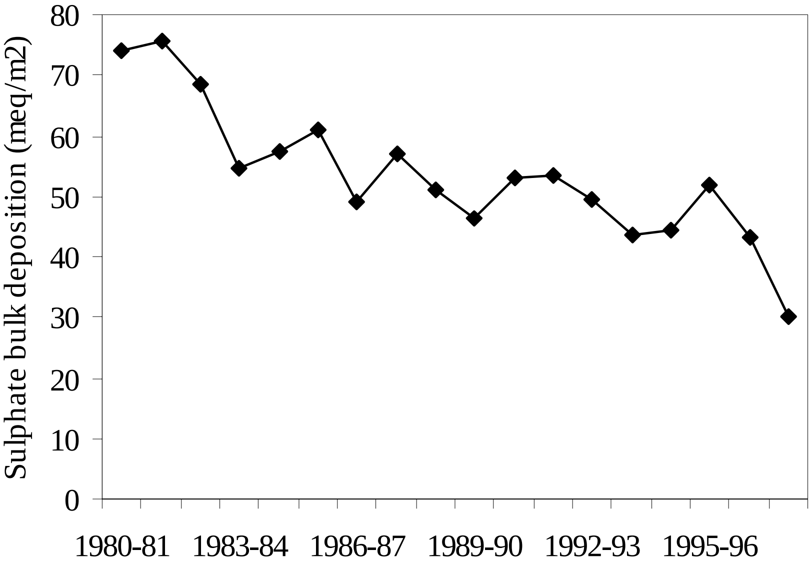
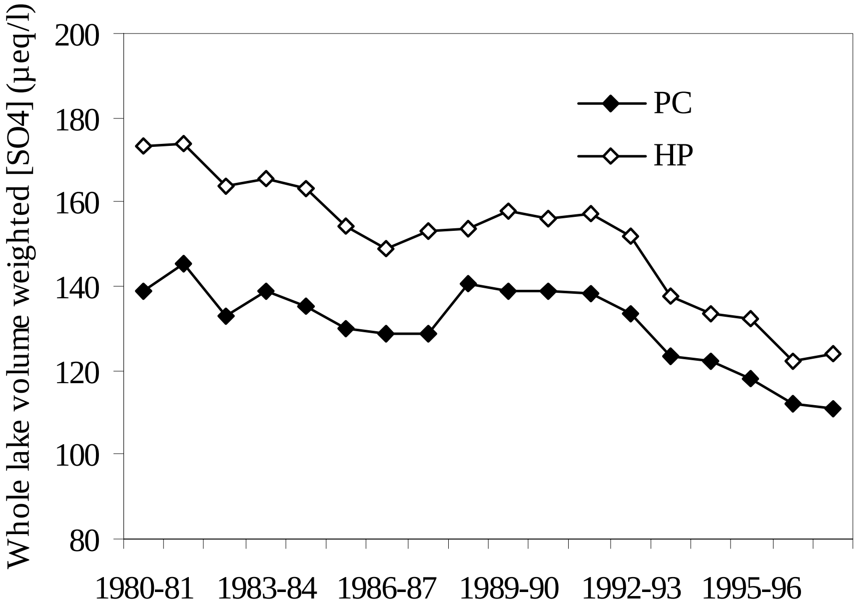


Figure 3. Whole-lake, volume-weighted average SO_4 concentrations (µeq/l) in Harp, and Plastic Lakes: 1980-1998.



Lakes

Sulphate concentrations in Harp (HP) and Plastic (PC) lakes decreased over the study period (Fig. 3). The SO_4 level in HP declined from a high of 173 µeq/l in 1981/82 to 124 µeq/l in 1997/98, whereas in Plastic Lake SO_4 concentrations decreased from 139 µeq/l in 1980/81 to 110 µeq/l in 1997/98 (Fig. 3). However the magnitude of decline in lake SO_4 concentration over the 18-year period in both of the lakes (HP 28%, PC 21%) was less than predicted given the magnitude of decline in deposition over the same time period and the flushing rates of the 2 lakes (Table 1). For example, using a steady state mass balance model that assumes SO_4 input is from bulk deposition only and that SO_4 behaves conservatively in the catchments, SO_4 concentrations in HP and PC in 1997/98 were predicted to be 102 and 82 µeq/l, respectively, compared to their measured values of 124 and 110 µeq/l. Furthermore, the temporal pattern of SO_4 concentration in lakes did not follow changes in deposition. In both lakes, SO_4 concentrations increased during the mid-1980s as SO_4 deposition declined, and remained elevated until the early 1990s, after which time they declined once more, although sulphate concentrations in both lakes rose slightly in 1997/98 (Fig. 3). In HP for example, SO_4 concentrations increased from 149 µeq/l in 1986/87 to a high of 157 µeq/L in 1991/92. A slightly different pattern in SO_4 concentration was observed in PC (Fig. 3). Sulphate concentrations began to increase after 1987/88, peaked in 1988/89 and remained high through 1991/92.

Streams

Harp Lake Inflows

Sulphate concentrations were quite variable among HP streams over time, although all streams exhibited similar highs and lows in SO_4 concentration in certain years (Fig. 4a). For example, SO_4 concentrations generally decreased between 1983/84 and 1986/87, but then increased markedly in 1987/88 by as much as 125% (HP6A) relative to the previous year.

Figure 4a. Annual average volume-weighted SO_4 concentrations (μeq/l) in 6 inflows to Harp Lake (HP3, HP3A, HP4, HP5, HP6 and HP6A): 1980-1998.

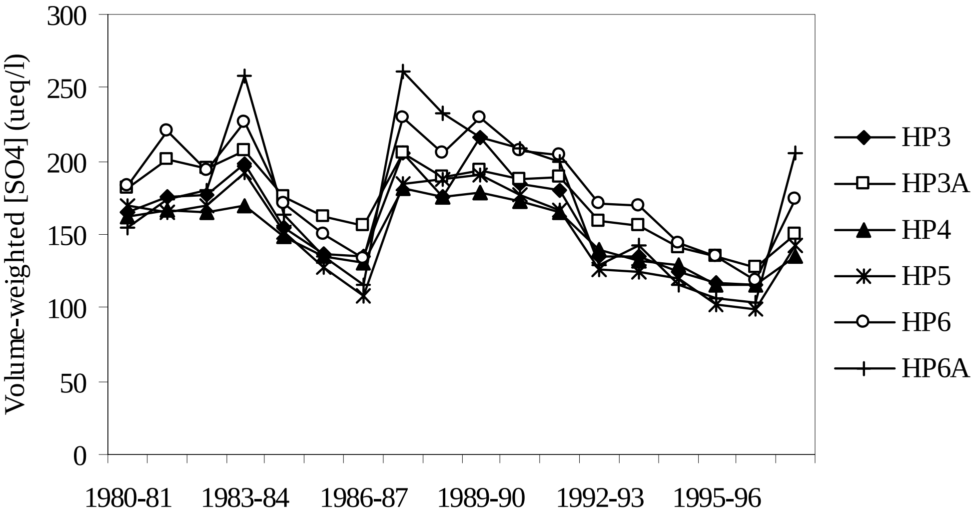


Figure 4b. Annual average volume-weighted SO_4 concentration (μeq/l) in PC1: 1980-1998.

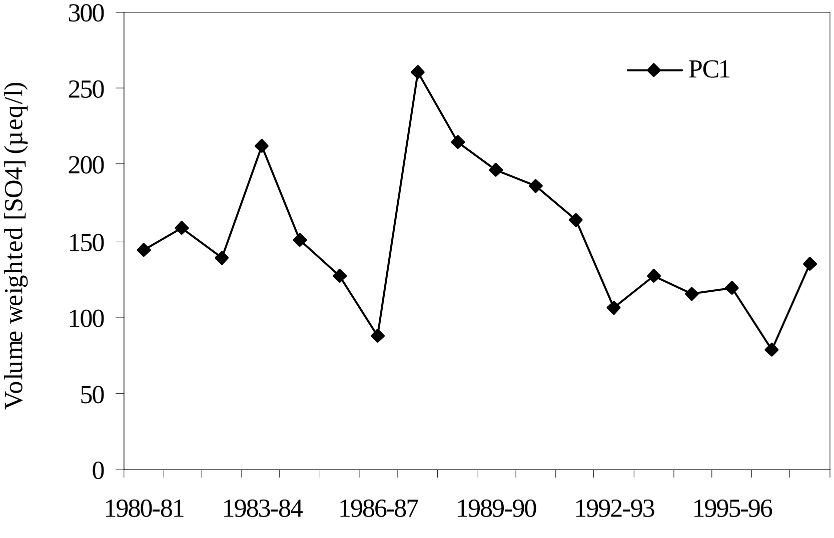
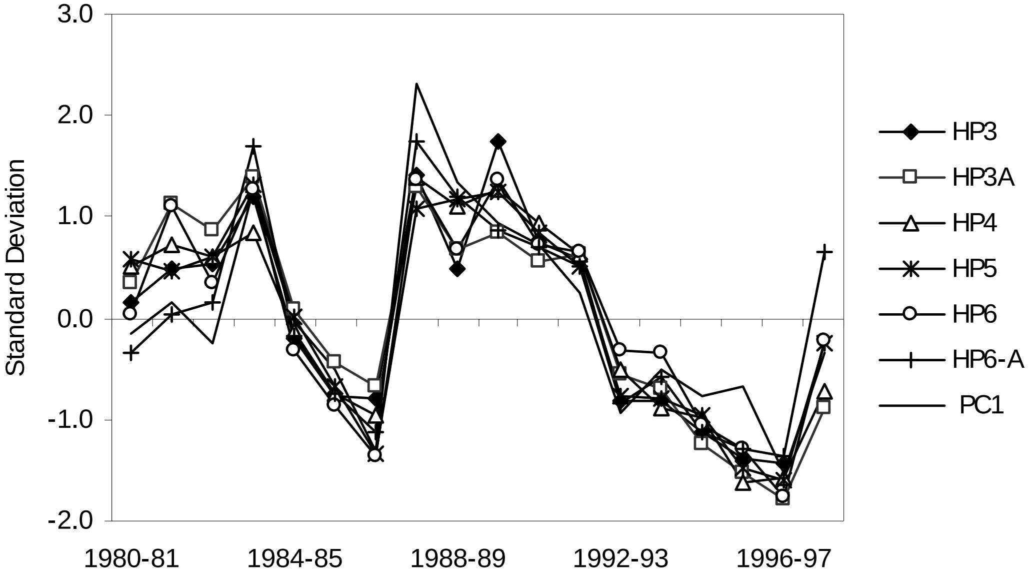


Figure 4c. Standardized annual average SO_4 concentrations (Z-scores) in the 6 HP inflows and PC1: 1980-1998. The y-axis is in units of SD relative to the 18-year mean annual SO_4 concentration in each stream.



In comparison, SO_4 concentrations in HP5, the largest inflow to Harp Lake increased by 72% between 1986/87 (107 µeq/l) and 1987/88 (185 µeq/l). Sulphate concentrations in all streams remained high until 1991/92, but then tended to decline through 1996/97. Sulphate levels increased again in all streams in 1997/98.

Plastic Lake Inflow

Sulphate concentrations in PC1 were extremely variable over time, however PC1 exhibited distinct high and low SO_4 concentrations in the same years as inflows to HP (Fig. 4b). For example, the low SO_4 level of 88 µeq/l measured in 1986/87 was followed by a large increase in concentration in the following year (261 µeq/l) - a difference of almost 200%. The only HP inflow that increased by a similar magnitude (125%) was HP6A, a relatively minor inflow (15.3 ha) to HP. Sulphate concentrations in PC1 generally began to decline following 1987/88, but like the HP streams, rose slightly in 1997/98. The similarity among streams is even more evident when SO_4 concentrations are standardized as Z-scores, and temporal patterns in standardized annual average SO_4 concentrations among all 7 streams were highly coherent ($r=0.83$ to $r=0.97$, $p<0.01$) (Fig. 4c). For example, all 7 streams had SO_4 concentrations that were at least 0.5 standard deviations (SD) below the long-term average in 1986/87, and concentrations were at least 1 SD greater than the 18-year average in the following year (Fig. 4c).

While SO_4 concentrations in all streams increased drastically in 1987/88, the response in lake chemistry was not as immediate. In PC, SO_4 levels increased in 1988/89, whereas in HP the increase was more gradual, although SO_4 concentrations in both lakes remained high until 1991/92 (Fig. 3). In order to understand the effect of changes in stream SO_4 concentration on the magnitude of SO_4 inputs to the lake, and therefore lake-SO_4 concentrations, it is necessary to evaluate SO_4 export from each of the catchments.

Sulphate Export

Export of SO_4 from each of the 6 HP catchments and from PC1 generally declined between 1980 and 1998 (Fig. 5). Temporal patterns in stream export of SO_4 did not completely mirror changes in SO_4 concentration because export is a function of both SO_4 concentration and stream discharge. Stream flow was synchronous among all catchments (Fig. 6), and all catchments exhibited low flow during the mid- to late 1980s. For example, between 1986/87 and 1989/90, flow in each of the HP catchments was between 0.5 and 1.5 standard deviations less than the 18-year average value.

Figure 5. Annual stream export of SO_4 (meq/m^2) in the 6 HP inflows and PC1: 1980-1998.

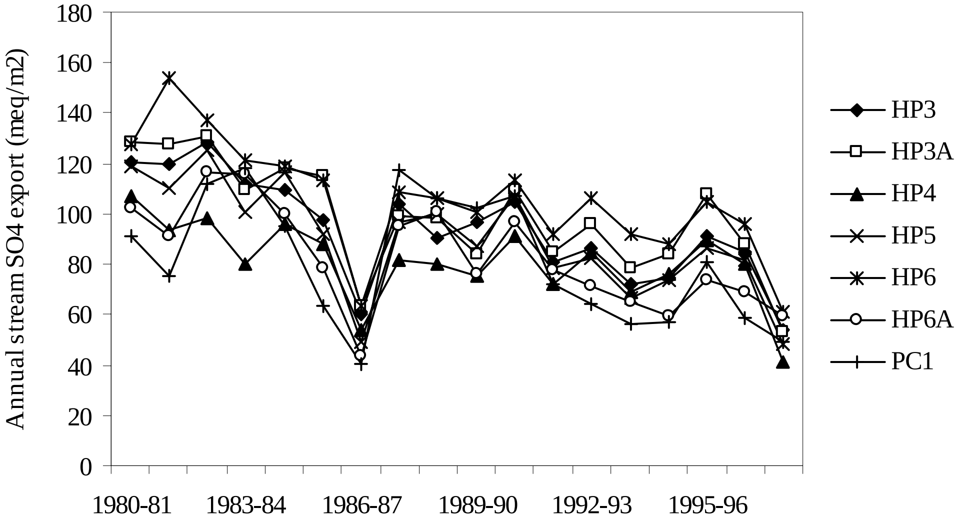
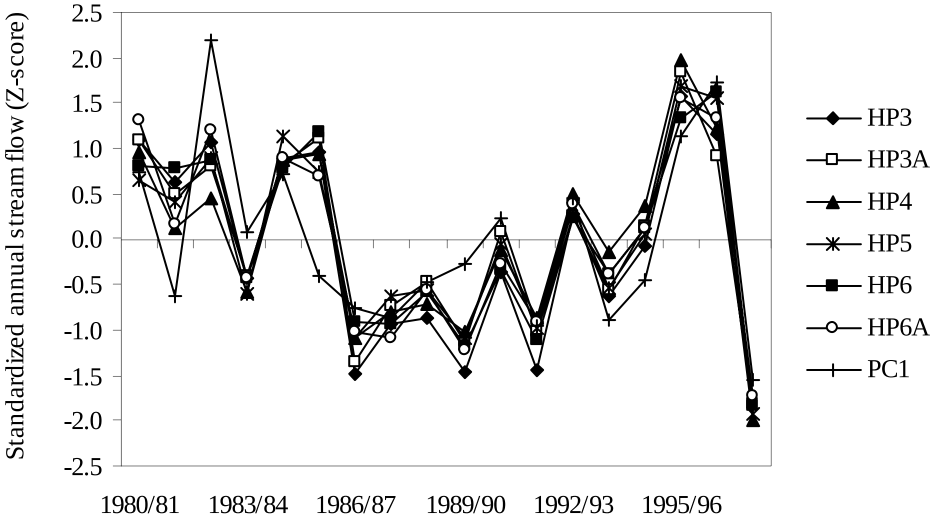


Figure 6. Standardized annual stream flow (Z-scores) in the 6 HP inflows and PC1: 1980-1998. The y-axis is in units of SD relative to the 18-year average of annual flow in each stream.



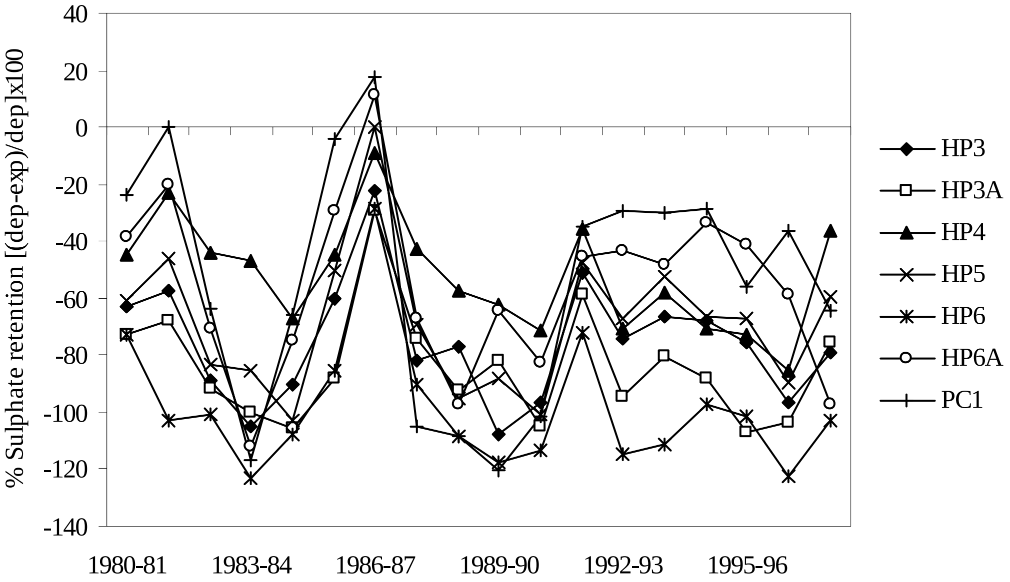
Particularly low stream flow during the period in which SO_4 concentrations were elevated (late 1980s; Fig. 4a, 4b) explains why export patterns were not as pronounced as patterns in SO_4 concentration. Nevertheless, the increase in stream export of SO_4 between 1986/87 and 1987/88 represents a substantial increase in SO_4 input to the lakes. However due to the lakes' flushing times (Table 1), year-to-year differences in catchment export should not cause immediate and dramatic changes in lake SO_4 concentrations. Sustained high SO_4 concentrations in stream outflows and consequently greater sulphate export between 1987/88 and 1990/91 resulted in higher SO_4 concentrations in HP and PC until 1991/92. Furthermore, these data suggest that temporal variations in catchment export of SO_4, particularly net export can have significant effects on long-term lake chemistry.

Sulphate Retention

Sulphate input-output budgets were calculated to assess the difference in retention (or net export) both among catchments and over time. Weathering inputs of S are negligible in this region and so deposition is the only external source of SO_4 to these catchments (Jeffries and Snyder 1983). Sulphate retention was generally negative in all 7 of the study catchments in most years, indicating that catchments were exporting more SO_4 in stream flow than they were receiving in bulk deposition (Fig. 7).

Only in 1986/87 when SO_4 export was extremely low, did most of the HP catchments appear to be in approximate balance between SO_4 input and stream export (<30% net export) (Fig. 7). Of the 6 HP catchments, HP4 exhibited the least amount of year-to-year variation in SO_4 retention, whereas HP6A had the greatest year-to-year fluctuations, varying from net retention (12%) in 1986/87 to 112% net export in 1983/84 (Fig. 6a). Similarly, SO_4 retention in the PC1 catchment was extremely variable over time, ranging from net retention of SO_4 in 1986/87, to 120% net export in 1989/90 (Fig. 7).

Figure 7. Sulphate retention (%) in the 6 HP sub-catchments and in PC1: 1980-1998. Sulphate retention, or net export in each year is calculated as: [(export – bulk deposition)/bulk deposition)] x 100%.



Explanation of patterns in stream [SO_4]

The fact that temporal patterns in SO_4 concentration were very similar among the inflows to both PC and HP, two lakes that differ greatly in their catchment physiography (Table 2) and acid sensitivity, suggests that geographically-broad scale factors are involved. Two factors that act on a wide geographic scale and might influence SO_4 chemistry are deposition and climate. Although the general decline in SO_4 concentration and export from catchments is almost certainly related to decreasing deposition, the between-year variations in stream SO_4 concentration are both too large in magnitude, and of a completely different pattern to be related to deposition. Instead, we suggest that variations in climate, specifically those that determine catchment dryness are influencing SO_4 levels in streams. A number of studies have suggested that drought events can influence the acid-base chemistry of surface waters (Wilby 1994; Webster & Brezonik 1995;

Dillon *et al.* 1997; Dillon and Evans 2002). Indeed, SO_4 concentrations in all catchments were highest in years with low stream flow (Fig. 8a). For example, the concentration of SO_4 in PC1 was greater in years in which stream flow ceased completely and the number of days with zero stream- flow (Q=0) was highly correlated with annual average SO_4 concentration (Fig. 8a; r = 0.86, $p<0.05$). A very similar relationship was found in the HP3, HP6 and HP6A catchments, where zero-stream flow is strongly correlated (r=0.78 to r=0.85, $p<0.05$) with annual stream SO_4 concentration (Fig. 8a). These 4 catchments have little groundwater supply to maintain flow during warm dry summers, which characterized the late 1980s. Specifically, 1987/88 through 1991/92 inclusive had summers that were on average 1°C higher than the 18-year average temperature of 17.5°C, and summer precipitation in these years was as low as 118mm (1990/91), compared to the 18-year average of 230mm. Wetting and drying events are known to stimulate both the decomposition of organic matter (Kirschbaum 1995; Leiros *et al.* 1999) and mineralization of sulphur in soil (Williams 1967; Foster 1989). Warmer temperatures may enhance mineralization rates through stimulation of enzyme activity (Strickland *et al.* 1984; Kirschbaum 1995), and drying and re-wetting of organic soil can result in a flush of microbial activity (Davidson *et al.* 2000) and release of organic S, C and N-compounds (Williams 1967; Ryan *et al.* 1998; Pulleman and Tietema 1999). Furthermore, water table levels in wetlands with weak groundwater connections decline during dry periods, allowing exposure and oxidation of reduced sulphur compounds, and consequent release of SO_4 upon resumption of normal hydrologic conditions (Bayley *et al.* 1986; Devito and Hill 1999).

Although the relationship between catchment dryness and SO_4 production appears clear in PC1, HP3, HP6 and HP6A, the remaining three streams, HP3A, HP4 and HP5 rarely cease to flow, even under extremely dry conditions. In these catchments, groundwater supply from deep till sustains flow during all seasons (*e.g.* Hinton *et al.* 1997), and continuous flow at the weir is not indicative of moisture conditions in the entire catchment. For example, year-round stream flow in HP4 is sustained by groundwater reservoirs in particularly deep glacial till deposits (up to 15 m) upstream of the catchment outflow. Similarly, the HP3A stream is ephemeral through the majority of its reach, but groundwater flow from an area just 100m upstream of the catchment outflow maintains continuous flow at the weir (Hinton *et al.* 1997). Year-round flow in the large HP5 catchment is likely maintained in a similar way - *via* multiple source areas that include relatively deep till deposits (Fig. 1).

In order to make a comparison between catchments exhibiting continuous flow and the ephemeral catchments described earlier, we chose a critical value of daily summer flow for each stream, and selected the number of days with stream flow less than the critical value as an indicator of catchment dryness. A critical level of daily flow for each stream was chosen by comparing summer hydrographs for each stream between 1988/89 and 1995/96, two years that had the lowest, and highest summer flow, respectively during the study period.

In this way, cutoff values of daily summer flow of 50, 100 and 10m^3/day were selected for HP5, HP4 and HP3A, respectively. These values of daily stream flow were commonly exceeded in wet summers, such as occurred in 1995/96, but were frequently not met in the particularly dry summers that typified the late 1980s. The choice of a critical daily summer flow value was obviously arbitrary, but allowed us to obtain an indicator of catchment dryness, and to examine the possible relationship between moisture conditions in the catchment and SO_4 production in streams with continuous groundwater connections.

Figure 8a. Annual average SO_4 concentration (lines) and number of days with zero-stream flow (bars) in HP6A, HP6, HP3 and PC1: 1980-1998.

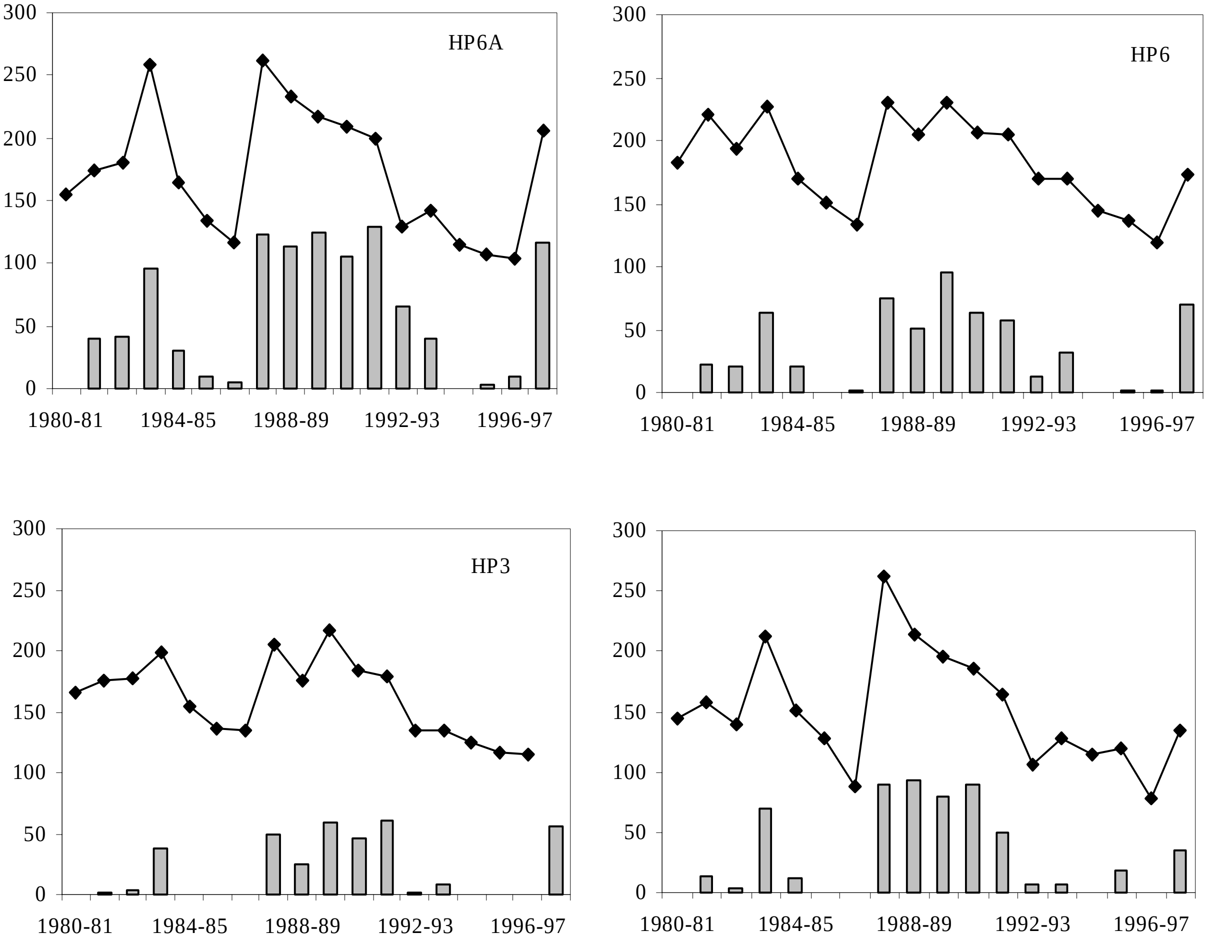
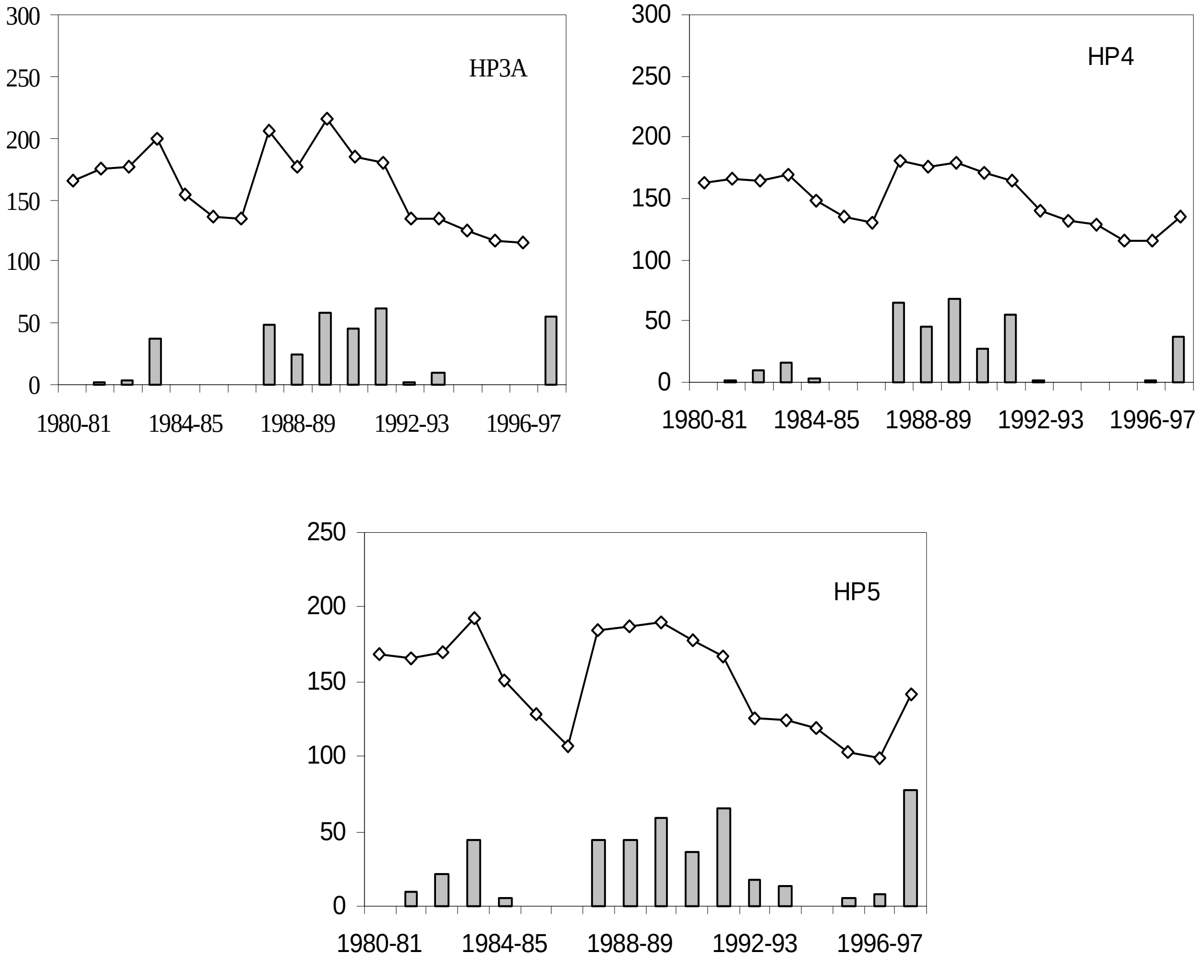


Figure 8b. Annual average SO_4 concentration (lines) and number of days with stream flow less than the critical value (bars) in HP3A , HP4 and HP5.



Stream flow in HP3A, HP4 and HP5 never ceased completely through the dry years of the late-1980s, however temporal patterns of SO_4 concentration in these streams were very similar to those in HP3, HP6 and HP6A, as well as in PC1 (Fig. 4c). Stream flow in HP3A, HP4 and HP5 was also less in these years, and the number of days that had flow less than the critical value was significantly related (r=0.43 to r=0.67, $p<0.05$) to annual SO_4 concentration in each of these catchments (Fig. 8b). The relationship between the number of days with flow less than the critical value and SO_4 concentration was not as strong as that between days with zero-flow and average SO_4 levels in PC1, HP3, HP6 or HP6A - likely due to the arbitrary choice of a critical flow value chosen to reflect catchment dryness, and the fact that some parts of the catchment will not dry completely. Nevertheless, we hypothesize that while groundwater supply may have sustained flow in these streams, that dry conditions within the catchment as a whole would have created conditions that were favourable for SO_4 production (greater frequency of drying and re-wetting events, declines in wetland water tables *etc.*).

Summary

Release of SO_4 from internal pools within catchments likely explains why lakes have not responded to changes in deposition as expected. Sulphate export from catchments is a function of both SO_4 concentration and flow, although SO_4 levels in stream water appear to be strongly related to climate variables. High annual average SO_4 concentrations in streams were associated with warm, dry summer conditions that caused flow to cease completely in streams with negligible groundwater inputs. The size of the organic S pool compared to the adsorbed SO_4 pool, and the relationship with climate suggests that release from organic forms is contributing to the net export of SO_4 from catchments. Furthermore, climate related export of SO_4 must be considered when predicting the response of surface waters to declining sulphate deposition.

CHAPTER 4: SULPHATE FLUX FROM AN UPLAND FORESTED CATCHMENT IN SOUTH-CENTRAL ONTARIO, CANADA

ABSTRACT

Net SO_4 export from forested catchments will delay the response of downstream surface waters to changes in S-deposition. In the Muskoka-Haliburton region of south-central Ontario, net SO_4 export from wetland-dominated catchments is largely explained by release of stored S from swamps. Similar net export from upland catchments requires an alternate explanation. To investigate possible sources and controls of SO_4 export in upland systems, SO_4 input-output budgets were calculated for a small (3.45 ha) upland, forested catchment in Haliburton County over an 8-year period. Temporal patterns of SO_4 concentrations in soil percolate were significantly correlated with patterns in stream water, but expected relationships with deposition were weak. Instead, SO_4 concentrations in surface soil percolate (LFH) appeared to be related to changes in soil moisture, and SO_4 concentrations in LFH percolate increased dramatically in the summer, when warm dry periods were broken by rainstorms. Higher SO_4 concentrations in organic surface soils were translated vertically down the soil profile; however, SO_4 concentrations at the base of the soil profile (B-horizon) were much less variable than in the LFH, and appear to be modified by processes occurring in the mineral soil, likely adsorption/desorption reactions. Deposition is the major source of SO_4 to catchments in this region, but SO_4 export in stream water exceeded input *via* bulk deposition by at least 40% in every year of record. Net SO_4 export from upland catchments appears to be a result of SO_4 release through mineralization of organic compounds and desorption from subsurface mineral soil.

INTRODUCTION

Sulphate (SO_4) deposition has declined in many regions in response to decreased emissions from industrial and power generation sources (Driscoll *et al.* 2001). Long-term monitoring data from a number of catchments located in acid-sensitive areas in eastern North America indicate that SO_4 concentrations in surface waters are declining, although the rate and magnitude of decline have not been as great as anticipated given the change in deposition (Driscoll *et al.* 1998; Jeffries *et al.* 1995). Furthermore, a number of catchments appear to be exporting more sulphate that is received *via* deposition (Eimers & Dillon 2002; Hornbeck *et al.* 1997; Houle *et al.* 1997; Mitchell *et al.* 1996). A number of sources may account for this apparent net export, including desorption of SO_4 that had previously been adsorbed when deposition was higher (Mitchell *et al.*, 1996); weathering of S-bearing minerals (Baron *et al.* 1995), underestimated dry deposition (Likens *et al.* 1990, Edwards *et al.* 1999) or mineralization and release of SO_4 from organic forms (Alewell *et al.* 1999; Houle & Carignan 1995). In regions that are remote from point sources, dry deposition of SO_4 often accounts for only a small (<20%) part of total deposition (Sirois *et al.* 1988), and release of SO_4 from weathering is generally only important in areas with significant mineral S-deposits (Fitzhugh *et al.* 2001; Mitchell *et al.* 1992). Most recent reports of net SO_4 export have pointed to either SO_4 desorption or organic-S mineralization as probable internal sources of SO_4 to drainage waters (Driscoll *et al.* 1998; Houle *et al.* 2001; Mitchell *et al.* 2001). However, the relative importance of these two processes and the factors that influence net SO_4 release are still not completely understood.

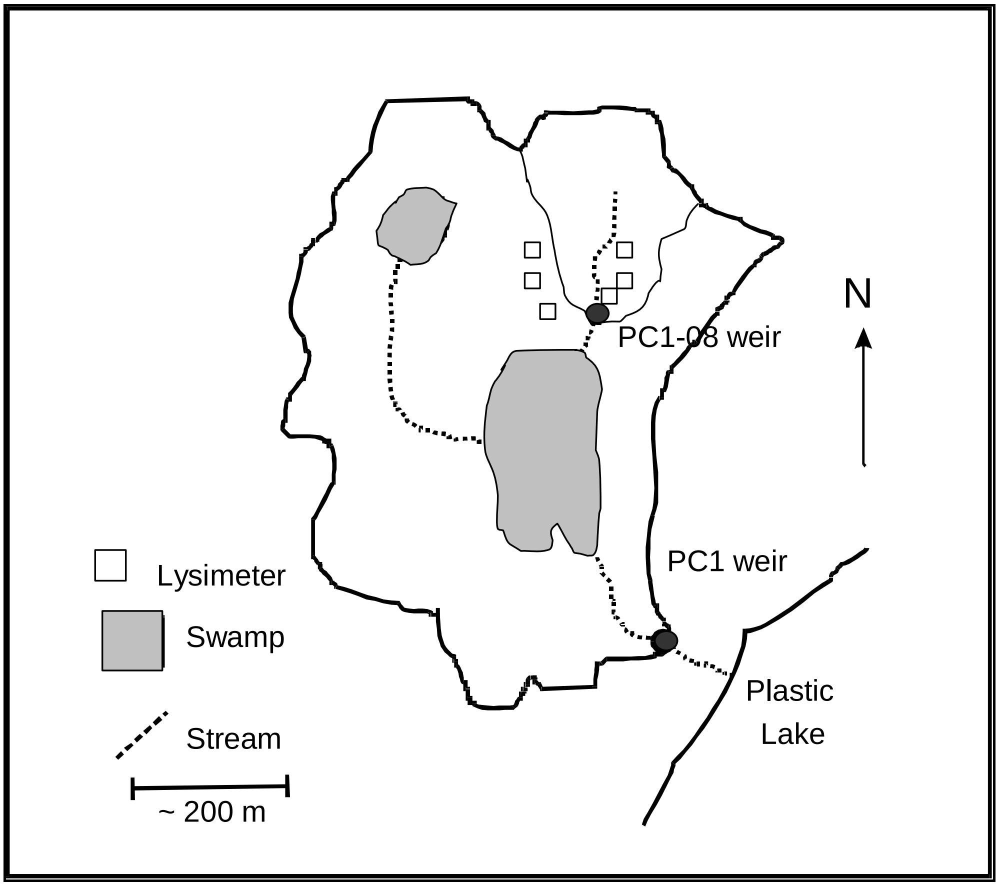
Sulphate deposition in the Muskoka-Haliburton region of south-central Ontario, Canada has declined markedly since the late 1970s, although SO_4 concentrations in many lakes and streams are currently higher than predicted given the change in deposition. Previous reports have indicated that many catchments in this region are currently exporting more sulphate than they receive, as measured by bulk deposition (Eimers & Dillon 2002), and this net export may explain why SO_4 levels in surface waters are higher than expected. Furthermore, temporal patterns of stream SO_4 concentrations and export are synchronous among a range of physiographically different catchments, and this synchrony has been related to climate factors (Eimers & Dillon 2002). In wetland-dominated catchments, SO_4 concentrations and export in drainage streams were greater in years with prolonged summer droughts, and this was attributed to the re-oxidation of stored S compounds in wetland soil when water tables declined (Devito *et al.* 1999, Dillon & LaZerte 1992; Dillon *et al.* 1997). However, temporal patterns of stream SO_4 concentrations and export are synchronous between both upland *and* wetland-dominated catchments, and therefore other factors must be invoked to explain climate-related patterns of SO_4 concentration in streams draining uplands. In this study, S cycling in a representative upland forested catchment in the Muskoka-Haliburton region was examined in detail, in order to determine both the source(s) of net SO_4 export, and the possible climate controls on SO_4 generation in an upland system.

METHODS

Study Site

Plastic Lake (45˚11'N 78˚50'W) is a 32 ha Precambrian Shield headwater lake located in Haliburton County, south-central Ontario, at the southern edge of the Boreal ecozone. The lake is fed by 1 major stream (PC1), and 6 ephemeral streams, which together drain an area of approximately 90 ha. PC1 (Plastic Lake-1) is the largest sub-catchment (23 ha) in the watershed (Figure 1). The forest at PC1 is primarily coniferous, dominated by white pine (*Pinus strobus*, 43% of total basal area) and eastern hemlock (*Tsuga canadensis*, 19% of total basal area) in the upland part of the catchment, and by white cedar (*Thuja occidentalis*) and black spruce (*Picea mariana*) in the swamp regions (Watmough and Dillon 2001).

Figure 1. Plastic Lake-1 (PC1) catchment.



A large (2.2 ha) conifer-*Sphagnum* swamp is located approximately 50 m above the catchment outflow and more than 85% of runoff from the PC1 catchment drains through the swamp before discharging to Plastic Lake. As a consequence of its location, processes occurring in the swamp strongly affect the chemistry of PC1. A short (<250 m) ephemeral stream (PC1-08) drains the northeastern part of PC1 before discharging into the swamp, and data for this study were collected from this upland sub-catchment (PC1-08; 3.45 ha). Soils in PC1-08 are generally thin (average ~40 cm), acidic ferro-humic and humo-ferric podzols, developed over granitic gneiss bedrock; shallow (<1 m) sandy basal till deposits are present in some low lying regions. Average annual precipitation to the catchment over the last 20 years was ca. 1000 mm (±130 mm), of which approximately 30% falls as snow. The mean air temperature for the same time period was 5°C; July is the warmest month (20-year average, 18.6 °C), and January has the lowest average temperature (-11.1 °C).

Hydrology

Stream stage in PC1-08 is continuously monitored at a V-notch weir using a Leopold Stevens A-71 water level recorder, and stage measurements are converted to hydrologic flow using established stage-discharge relationships (Scheider *et al.* 1983). The weir was installed in 1986 and stream flow was monitored continuously until 1995, at which time hydrological monitoring of the stream ceased, but was reactivated in the spring of 1999. The PC1-08 stream flows semi-continuously; on average, the stream is dry 95/365 days of the year, mainly during the summer months.

Lysimeters and tensiometers

Soil percolate chemistry is monitored at 3 zero-tension lysimeters in the PC1-08 catchment (ZT05, ZT06, ZT07), and at 3 additional lysimeters located just outside of the catchment (ZT01, ZT02, ZT04) (Figure 1). Lysimeters were installed beneath the LFH, Ae and B-horizons (B1, B2) in areas with maximal soil development (Findeis *et al.* 1993), and soil percolate was collected between 1987 and 1995, and again starting in the spring of 1999. Depth ranges of the LFH, Ae, B1 and B2 horizons (if all are present) at PC1-08 are generally from 0-8 cm, 8-11 cm, 11-30 cm and 30-60 cm, respectively (Findeis *et al.* 1993; LaZerte & Scott 1996). In many areas, one or more of the above horizons are not present, and bedrock outcrops cover approximately 10% of the catchment area (Lozano *et al*., 1987). Drainage water from the sandy Ae horizon was also collected, but will not be discussed here because there was little difference in SO_4 concentrations between the LFH and the thin Ae horizons. The chemical data for lysimeter samples presented here are the averages of 6 zero-tension lysimeters. Lysimeter pits were heated during the spring melt period to prevent freezing and blockage of drainage tubes. Details of lysimeter plate construction and installation can be found in Findeis *et al.* 1993. Tensiometer nests were also installed in 1986 at 3 depths (15cm, 30cm and 45cm) near each of the lysimeter stations, and measurements of soil tension (KPa) were recorded whenever lysimeters were sampled; however, only monthly average soil tension data are available between 1986 and 1992 (Findeis *et al.* 1993). Soil tension data were used to investigate possible relationships between average monthly soil moisture conditions and SO_4 concentrations in LFH and B-horizon percolate, respectively.

Sample collection and chemical analysis

Stream and soil percolate samples were collected approximately weekly, or when sample was available between 1987 and 1995, although samples were collected more frequently during periods of high discharge. Sampling was re-initiated in the catchment in 1999. All water samples were filtered (80 µm Nitex mesh) into pre-rinsed bottles, and transported to the laboratory in insulated containers. Water samples were analyzed for sulphate and chloride by ion chromatography (Ontario Ministry of Environment 1983). On average, 35, 25, 30 and 10% of lysimeter samples were collected in the spring, summer, autumn and winter seasons, respectively and 37, 13, 27, 23% of PC1-08 stream samples for chemical analysis were collected in the same seasons. Stream flows in the spring, summer, autumn and winter seasons comprise 59, 1, 23 and 16% of total annual flow in PC1-08, respectively.

Stream and hillslope SO_4 export

Sulphate fluxes in stream water were calculated by multiplying daily discharge (l/day) by weekly concentration values (mg/l), and were summed for each hydrologic year (June 1 – May 31). Export (flux per unit area; kg/ha) was calculated from the annual data.

Meteorology and deposition

Bulk deposition and meteorological variables (temperature and precipitation depth) are measured continuously at 3 stations located within a 30 km radius of the Dorset Research Centre (DESC). Average SO_4 deposition (kg/ha) to the region was calculated using SO_4 concentrations in bulk deposition and deposition volume measurements.

Statistical analyses

The degree of similarity in year-to-year patterns in SO_4 concentrations among stream water, soil percolate and deposition was quantified as the Pearson product-moment coefficient (Benson *et al.*, 2000; Webster *et al.* 2000). Pearson correlation and linear regression analyses were used to investigate relationships between SO_4 concentrations in drainage waters (stream and soil percolate) and climate variables (mean summer and annual precipitation and temperature) or soil moisture. In addition, SO_4 concentrations were standardized using Z-scores (annual observation minus the long-term mean, all divided by the standard de*via*tion) in order to facilitate comparisons among different stations (lysimeters, stream water, deposition). Data from 1999-00 to 2000-01 were not included when calculating standardized concentrations because of the length of the interval between the 2 monitoring periods (1995-1999) which lacked data.

RESULTS & DISCUSSION

Temporal patterns

- *Deposition*

Annual SO_4 deposition varied greatly during the monitoring period from a minimum of 15.1 kg SO_4/ha in 2000/01 to a maximum of 27.4 kg SO_4/ha in 1987/88, largely as a function of changes in precipitation (Figure 2). Between 1986/87 and 2000/01 there was a general decline in deposition of approximately 30%, however, during the period of lysimeter operation (1986/87 – 1994/95), SO_4 loads were relatively constant and fluctuated around 24 kg/ha/yr (Figure 2). Sulphate concentrations in deposition ranged from a high of 2.9 mg/l in 1987/88 to a low of 1.8 mg/l in 1996/97.

- *Soil Percolate*

LFH

Annual average SO_4 concentrations in percolate from the surface organic horizon (average of 6 zero-tension lysimeters) varied greatly between years, but were generally higher in the late 1980's (Figure 3). The highest average concentration of 10.5 mg/l occurred in 1987/88 whereas 1993/94 had the lowest annual SO_4 concentration of 5.1 mg/l (Figure 3).

Standardized annual SO_4 concentrations in LFH percolate were significantly related to annual average SO_4 concentrations in deposition ($r = 0.74$, $p<0.05$; $r_{crit} = 0.71$), since deposition is the primary source of SO_4 to catchments in this region (Figure 4).

Figure 2. Annual bulk SO_4 deposition (kg/ha) and precipitation (mm), 1986/87 – 2000/01.

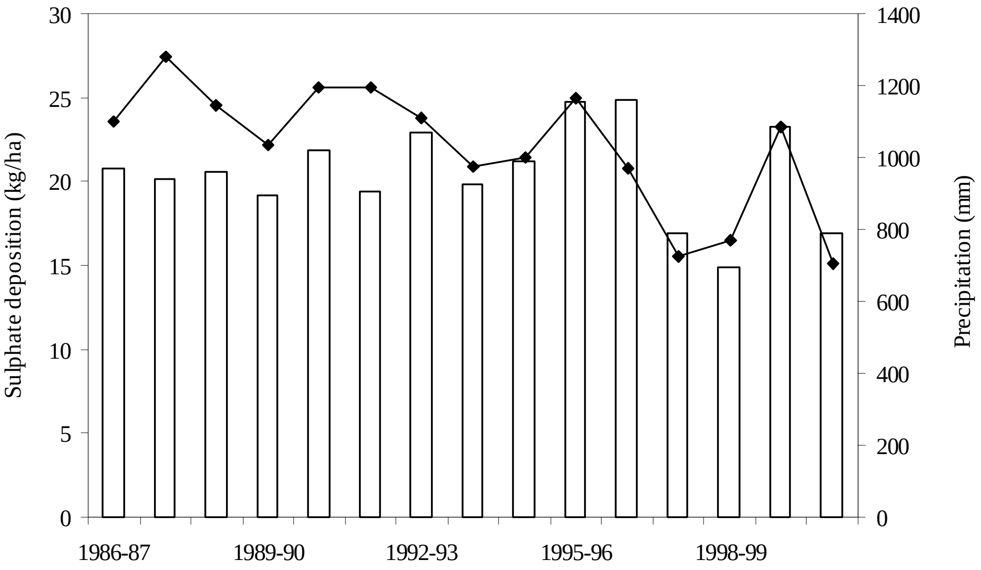
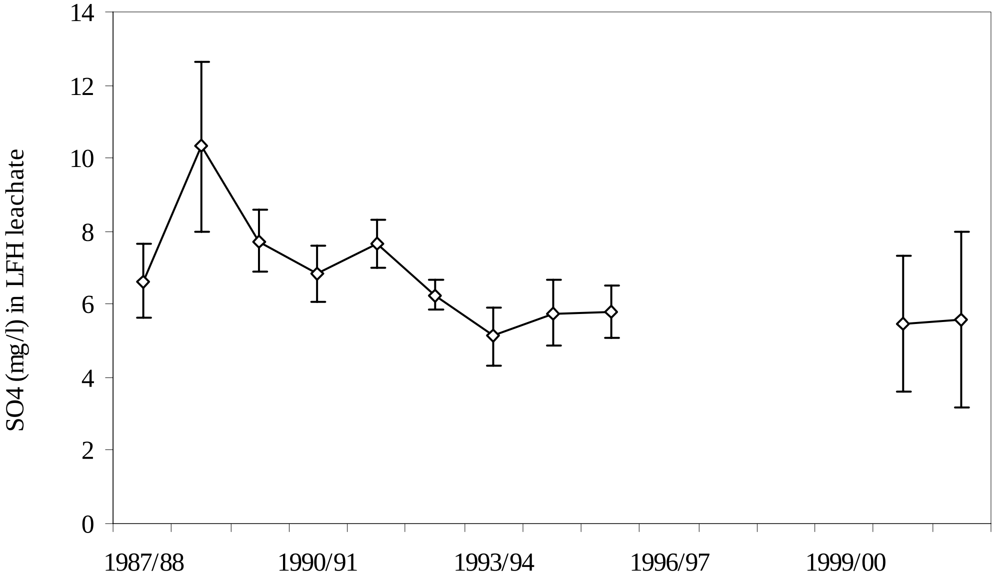


Figure 3. Annual average SO_4 concentration (mg/l) in LFH lysimeter percolate. Bars indicate ± SD.



B-horizon

Annual average SO_4 concentrations in B-horizon percolate (average of 6 lysimeters), collected near the base of the soil profile did not vary greatly between consecutive years, although concentrations were generally higher in the late 1980's and were lowest in the last 2 years of measure (Figure 5a). Temporal patterns of average annual SO_4 concentrations in B-horizon percolate were significantly correlated with patterns in the LFH (r = 0.80, $p<0.05$), but not with deposition (r = 0.57; Figure 4). Mean annual SO_4 concentrations in B-percolate were more variable than in the LFH (CVs varied from 24% to 35% compared to 7% to 22%), likely due to differences in plate depth among lysimeters, which varied from 24 cm in ZT07 to 65 cm in ZT05. Soil depth can affect SO_4 adsorption if physical (*e.g.* soil texture) and chemical parameters (*e.g.* organic matter or Fe and Al-oxide content) vary with depth (Hern 1990; Singh 1984). The distribution of macropores, roots and stones above B-horizon plates also likely varies among lysimeters, and could affect the movement of soil water and consequently percolate chemistry. In contrast, the LFH lysimeter plates were located immediately below the forest floor which did not vary greatly in depth and so the chemistry of leachate among the 6 LFH lysimeters was expected to be more similar. Annual average SO_4 concentrations in B-percolate were higher than in the LFH in all years except 1987/88 (10.3 mg/l in LFH compared to 9.7 mg/l in B-percolate), although this was not significant due to high variability among B-horizon lysimeters (Figures 3 and 5a).

- *PC1-08 Stream*

Average SO_4 concentrations in stream water were very similar to concentrations measured in B-horizon percolate in each year of record (Figure 5a). Chloride concentrations were also very similar between B-horizon percolate and stream water, suggesting that little evapoconcentration occurs between the hillslope and the stream channel and that SO_4 concentrations measured in B-horizon percolate are representative of subsurface discharge to the stream channel (Figure 5b).

Table 1. Selected physical characteristics of soil at PC1-08. Data are from Lozano *et al*., 1987 and Neary *et al*., 1987.

	LFH	*B*
%Sand	0	90
%Silt	0	9
%Clay	0	1
%Organic carbon	41	5
Bulk Density (g/cm^3)	0.014	0.67-0.87
Porosity	0.86	0.40
Average Depth (range; cm)	10 (5-15)	24 (0-60+)
Total S (mg/kg)	1000-2000	300-600
Adsorbed S-SO_4 (mg/kg)	0-20	100-200

Due to the thin, sandy nature of soils at PC1-08 (Table 1) and moderate slopes (<10%), the majority of rainfall that reaches the forest floor passes vertically through the soil profile and then laterally over the impermeable bedrock surface to the stream channel (Renzetti *et al.* 1992; Peters *et al.* 1995; Buttle and Turcotte 1999). Previous hydrologic studies have demonstrated that macropore flow along the soil/bedrock interface is a major contributor to stream flow at PC1-08 (Renzetti *et al.* 1992; Peters *et al.*1995), and it is therefore not surprising that stream and B-horizon SO_4 and Cl concentrations are similar. However, similar SO_4 concentrations in stream water and soil percolate respectively, indicate that SO_4 export calculated using stream flow and stream SO_4 measurements is representative of export from upland soil.

Temporal patterns of SO_4 concentrations in PC1-08 were synchronous with patterns of SO_4 in both LFH (r = 0.89, $p<0.01$) and B-horizon percolate (r = 0.77, $p<0.05$) but were not significantly related to changes in deposition loads (r = 0.69) (Figure 4). Standardized annual SO_4 concentrations in the wetland-draining PC1 stream were also synchronous with patterns in soil percolate (LFH: r = 0.95, $p<0.01$; B: r = 0.75, $p<0.05$), but not with deposition (r = 0.67) (Figure 4).

Synchronous patterns in SO_4 concentrations and export among both upland and wetland-draining catchments in the Muskoka-Haliburton region were previously related to inter-annual variations in summer precipitation and temperature (Dillon *et al.* 1997; Chapter 2). In wetland-draining catchments, such as PC1, changes in summer precipitation and temperature influence wetland water table levels, and SO_4 concentrations and export are greatest in years with warm dry summers, when wetland water tables are low allowing exposure and re-oxidation of stored S compounds in organo-S rich peat sediment (Devito *et al.*, 1999; Dillon and LaZerte 1992). Conversely, in years with average or wet summers SO_4 concentrations and export are lower, and net SO_4 retention or an approximate balance between inputs and outputs occurs (Devito and Dillon 1995; LaZerte 1993). However, while the wetland was identified as the source of higher SO_4 concentrations in PC1, the relationship between summer precipitation and temperature and SO_4 levels in the upland PC1-08 stream is less clear. In order to investigate the possible relationship between moisture conditions and SO_4 concentrations in upland soil percolate (and consequently stream water), we compared soil tensiometer data with SO_4 concentrations in LFH and B-horizon percolate.

Figure 4. Standardized annual average SO_4 concentrations in deposition, B-horizon percolate, LFH percolate, and PC1-08 and PC1 stream water.

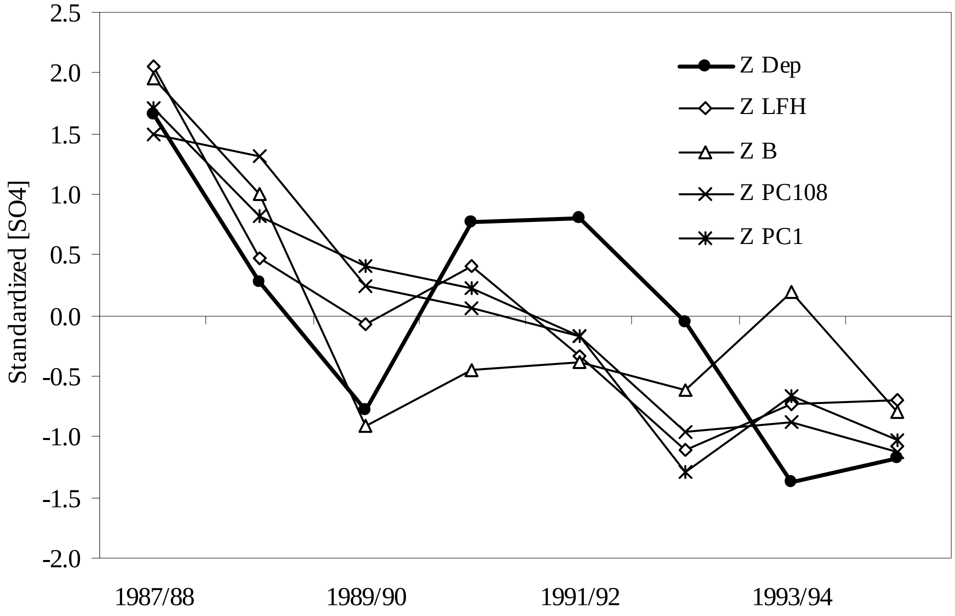


Figure 5a. Annual average SO_4 concentrations (mg/l) in B-horizon percolate and PC1-08 stream water. Bars indicate ± SD.

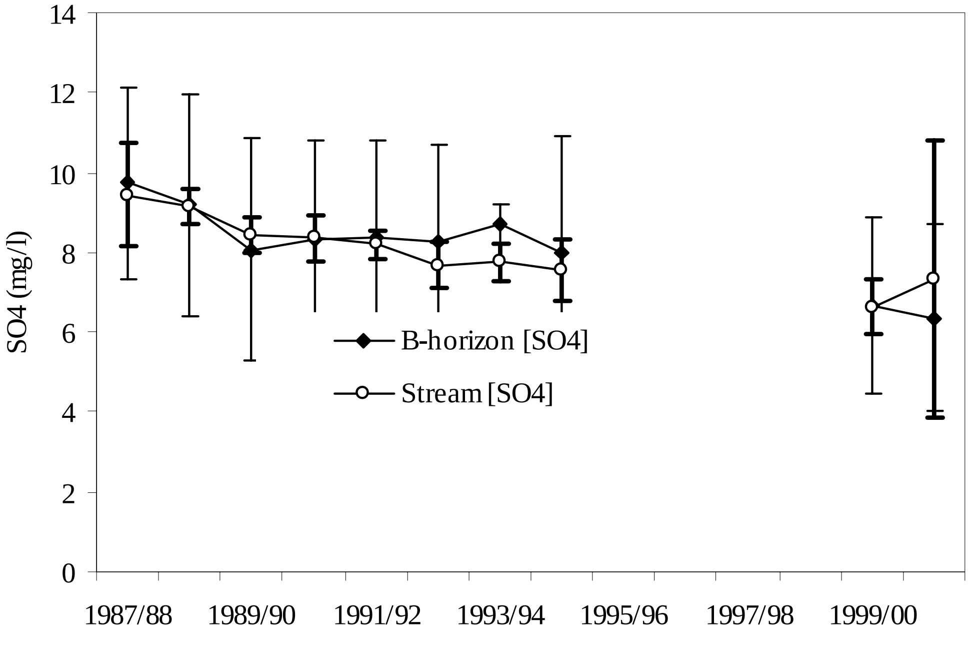


Figure 5b. Average annual Cl concentrations (mg/l) in B-horizon percolate and PC1-08 stream water. Bars indicate ± SD.

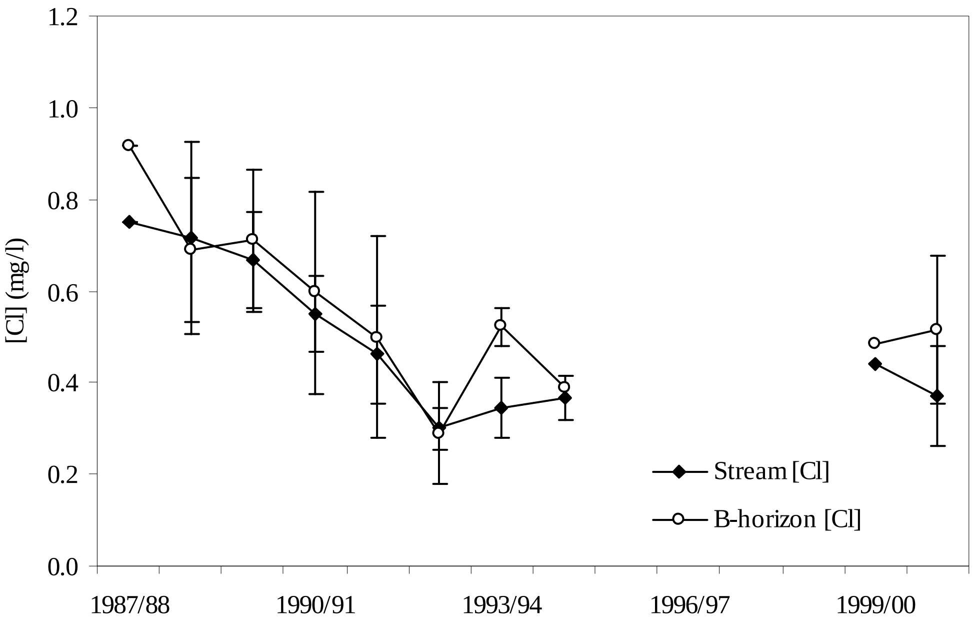


Figure 6a. Average monthly SO_4 concentration (mg/l) in LFH percolate and soil tension at 15 cm (KPa).

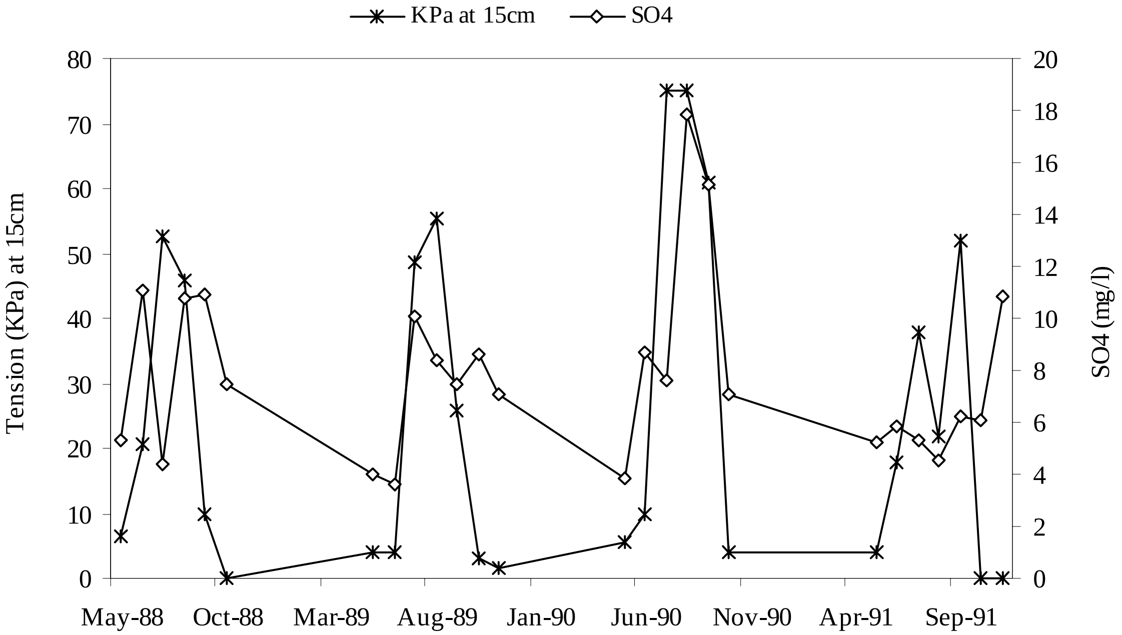


Figure 6b. Ratio of monthly average SO_4 and Cl concentrations in LFH percolate and soil tension at 15cm.

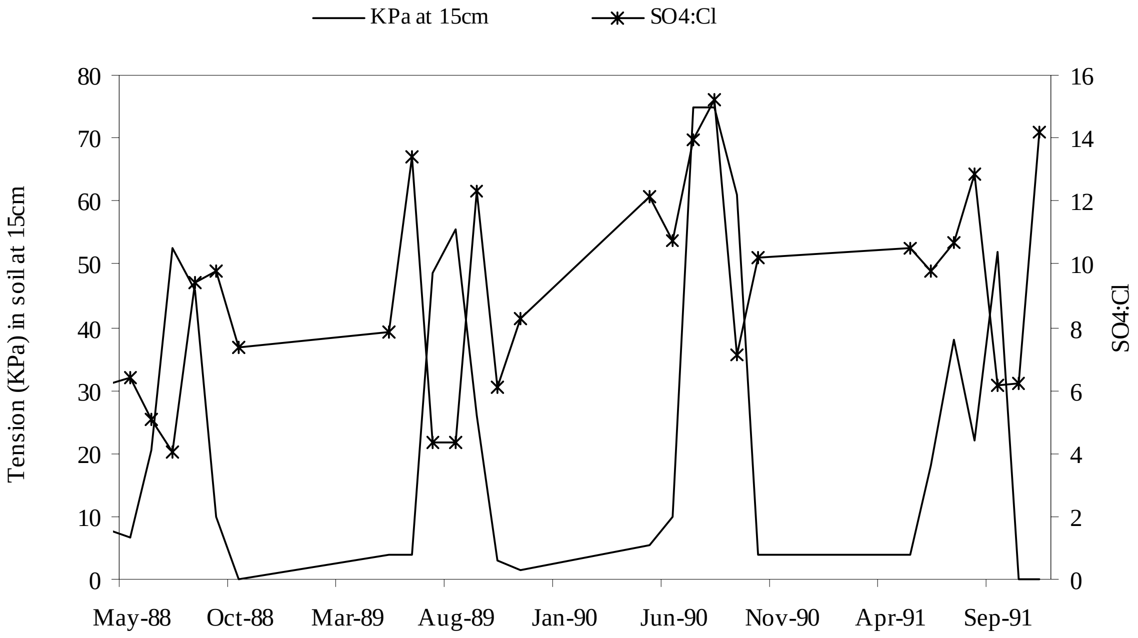
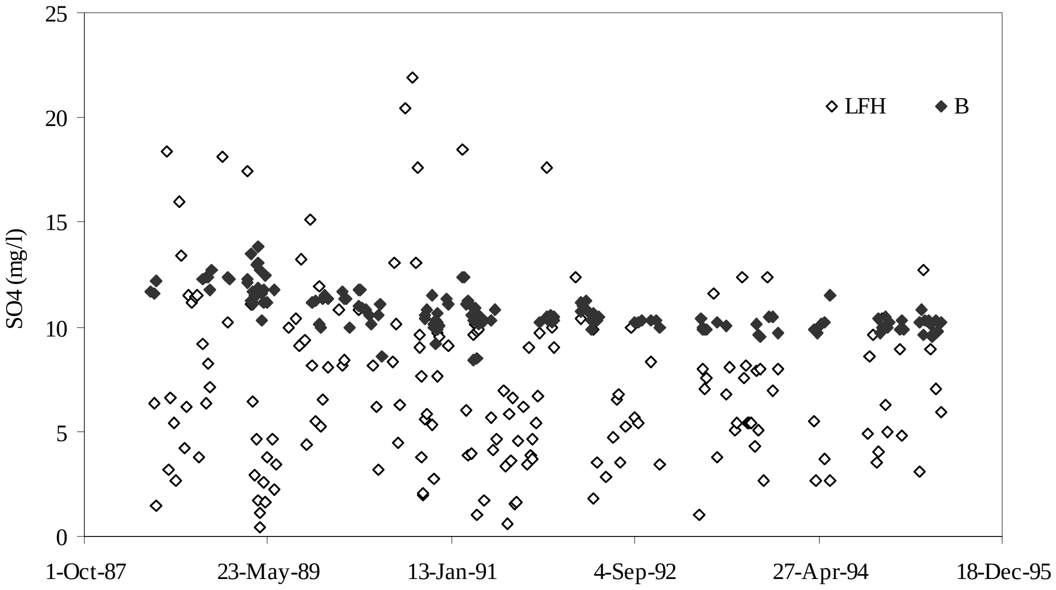


Figure 7. Daily SO_4 concentrations (mg/l) in LFH and B-horizon percolate, respectively at a zero-tension lysimeter in the PC1-08 sub-catchment.



Soil percolate chemistry and soil moisture – LFH

Sulphate concentrations in LFH percolate were highest immediately following periods of elevated soil tension (*i.e*. dry soil conditions), when soils were re-wet (Figure 6a). While no information on the variability in monthly tensiometer data is available (*i.e*. standard deviations were not published), the sandy well-drained soils in the PC1 catchment respond quickly to wetting and drying forces, and so soil moisture may fluctuate widely within a given month, particularly during the summer and fall.

Part of the increase in SO_4 concentration in LFH percolate following dry periods may be due to evapoconcentration effects, particularly in months when peaks in SO_4 concentration coincided with peaks in soil tension (Figure 6a). However, the increase in SO_4 concentration between a consecutive wet and dry month (range 0.1 – 42 mg/L) was always greater than the relative increase in Cl concentration (0.1-7.4 mg/L), and the association between soil moisture and SO_4 in LFH percolate is evident even when SO_4 is weighted by Cl (Figure 6b). The relationship between SO_4 release in LFH percolate and changes in soil moisture would be clearer if we had daily measurements, rather than monthly means to compare. Annual average SO_4 concentrations in LFH percolate were always 2.3 (1991/92 or 1992/93) to 3.6 (1987/88) times greater than the concentration of SO_4 in deposition in the same year. In this region approximately 50% of the total annual precipitation is evapo-transpired and the remainder is manifested as runoff; therefore on an annual scale, SO_4 concentrations in LFH percolate should be a maximum of 2 times greater than deposition, given that evapoconcentration effects extend deeper than the surface organic horizon. Sulphate concentrations in LFH percolate that are greater than predicted from evapoconcentration effects could be due to mineralization and release of SO_4 from organic S compounds, or to unmeasured dry deposition.

Similar increases in SO_4 concentration have been reported in PC1 following dry periods and these were inferred to be due to release from peat (Dillon *et al.* 1997). High SO_4 concentrations in LFH percolate following dry conditions may similarly be explained by release of SO_4 through mineralization. The sandy, well-drained soils that characterize the PC1-08 catchment respond rapidly to changes in precipitation, and stream flow often ceases entirely in summer months when evapotranspiration demands exceed precipitation inputs. Summer dry periods however are often interrupted by flashy summer storms, or by the return of normal fall precipitation. A number of studies have reported an increase in microbial activity following drying events, and fluctuations in soil moisture have been shown to stimulate organic matter breakdown and induce a flush in C and N *(*Davidson *et al.* 1998; Leiros *et al.* 1999; Pulleman & Tietema 1999) and P (Grierson *et al.* 1998) mineralization. Peaks in SO_4 concentration may reflect the immediate response of the microbial community to available moisture, greater surface area of detritus due to physical and invertebrate breakdown of dry litter, or to turnover of the dead microbial biomass produced during the dry period (Grierson *et al.* 1998; Magid *et al.*, 1999; Pulleman & Tietema 1999). Drying alone was shown to cause SO_4 mineralization and conversion of carbon-bonded forms of S to ester SO_4 (David *et al.* 1982). However, increases in SO_4 concentrations in soil percolate following drying and re-wetting have been demonstrated in both field and laboratory experiments, suggesting that dry deposition is not the sole contributing factor.

The relationship between SO_4 concentrations in LFH percolate and soil moisture may explain why SO_4 concentrations in PC1-08 stream water follow the same temporal pattern as PC1, a wetland-draining stream. However, SO_4 produced in upland surface soil must first pass through the underlying mineral soil before reaching the stream, and therefore processes occurring in the B-horizon must also be considered when interpreting patterns of SO_4 chemistry in stream water.

Soil chemistry and soil moisture – B-horizon

While inter-annual changes in SO_4 concentrations are synchronous among LFH and B-horizon percolate, daily SO_4 concentrations in LFH percolate are highly variable compared to concentrations in percolate collected at the base of the soil profile. For example, daily SO_4 concentrations measured in water draining the B-horizon in ZT04 over the entire period of record were remarkably constant and ranged from 7.5 to 11.7 mg/l (Figure 7). In contrast, daily SO_4 concentrations in the LFH were extremely variable and ranged from 0.45 to 22 mg/l in ZT04, and the majority of LFH samples had lower SO_4 concentrations than the respective B-horizon sample from the same day (Figure 7). However, both high and low SO_4 concentrations in LFH percolate were accompanied by relatively constant levels in B-percolate (Figure 7), indicating that processes occurring in the B-horizon, possibly adsorption/desorption reactions are modifying the magnitude of SO_4 release from organic surface soil. Houle and Carignan (1995) similarly found that SO_4 concentrations in soil solution were strongly buffered during percolation through the B-horizon at the Lac Laflamme catchment in Quebec. Sulphate adsorption at mineral soil surfaces is known to buffer drainage waters to high SO_4 inputs in deposition (Fuller *et al.* 1987; Rochelle *et al.* 1987).

However, SO_4 adsorption is not always a permanent phenomenon, and a number of researchers have suggested that soils may release previously adsorbed SO_4 in response to decreasing inputs in deposition (*e.g*. Harrison *et al.*, 1986). These suggestions are based on the premise that SO_4 concentrations in soil solution tend toward equilibrium with the adsorbed pool (Reuss and Johnson, 1986). Thus if SO_4 concentrations in soil solution decrease, adsorbed SO_4 may be released from soil particles to compensate, and *vice versa*. This reversal between adsorption and desorption may explain why SO_4 concentrations in B-horizon percolate are so constant over time relative to concentrations in the LFH (Figure 7).

Table 2. Sulphate input in bulk deposition, gross export in stream water and net export: 1987/88-1994/95 and 1999/00-2000/01

Hydro. year (Jun1-May31)	*Bulk dep. (kg/ha)*	*Flow (m^3/y)*	*Gross SO_4 export (kg/ha)*	*Net export (gross-dep.)(kg/ha)*	*% Net export (gross-dep./dep. x 100)*
1987/88	27.4	16,300	44.8	17.3	63.1
1988/89	24.5	16,864	45.6	21.1	86.1
1989/90	22.2	17,621	43.7	21.5	96.7
1990/91	25.6	21,713	53.0	27.5	107.5
1991/92	25.6	16,174	38.7	13.1	51.1
1992/93	23.8	21,290	47.4	23.6	99.3
1993/94	20.9	12,729	28.6	7.6	36.4
1994/95	21.4	16,604	36.4	15.0	70.1
1999/00	23.3	22,476	43.24	19.9	85.6
2000/01	15.1	11,830	25.2	10.1	66.6

Sulphate Mass Budget for PC1-08

Net SO_4 release through either mineralization or organic S compounds and/or desorption from subsurface mineral soil may explain why SO_4 export in PC1-08 stream water greatly exceeds input in bulk deposition, in every year of record (Table 2). Net export (as a proportion of input) varied from as much as 108% in 1990/1991 to 36% in 1993/94. There was no clear trend in net export over time, and the amount of excess SO_4 export in stream water varied greatly between years, primarily due to changes in stream flow (Table 2). Clearly, the magnitude of annual net export from PC1-08 and variability in net export among years is too great to be explained by unmeasured dry deposition. Additional dry deposition to at least double bulk deposition inputs would be required to balance the magnitude of net SO_4 export from PC1-08 measured in certain years. However, we acknowledge that dry deposition may contribute to some of the calculated net export, and Sirois *et al.* (2001) recently estimated that dry deposition could account for as much as one-third of the total S deposition at the Turkey Lakes Watershed (TLW) - a site that has similar annual bulk deposition to PC1. Although Beall *et al.* (2001) found that SO_4 concentrations in wet-only deposition reported by Sirois *et al.* (2001) were 85% of their values in bulk deposition, suggesting that bulk deposition collectors did measure a portion of dry deposition at TLW. Assuming wet deposition ≈ 0.66(total) (Sirois *et al.*, 2001), and wet = 0.85(bulk) (Beall *et al.*, 2001), then bulk = 0.78(total), and bulk deposition estimates should be increased by an additional 22% to account for unmeasured dry deposition. Dillon *et al.* (1988) similarly found that SO_4 inputs in wet-only deposition were approximately 85% of inputs in bulk deposition in the Muskoka-Haliburton region. Another possible source of SO_4 to stream water is mineral weathering, and weathering can be an important source of S in regions with significant deposits of S-bearing minerals (Fitzhugh *et al.* 2001; Mitchell *et al.* 1992). However S-levels in granitic gneiss bedrock in this region are negligible (Jeffries & Snyder 1983) and Houle & Carignan (1995) estimated that weathering of granite in Quebec would only supply around 0.15 kg SO_4/ha to annual export. Bulk deposition, therefore was considered to be the dominant source of SO_4 to the PC1-08 catchment. The magnitude of annual net export calculated in this study (7.6 – 27.5 kg SO_4/ha/yr) is indicative of net export from a number of catchments in this region, including Lac Clair, QE (13 kg SO_4/ha/yr) (Houle *et al.* 1997), Huntington Forest, NY (14 kg SO_4/ha) (Mitchell *et al.* 1996) and Hubbard Brook, NH (10-15 kg SO_4/ha/yr) (Hornbeck *et al.*, 1997).

Possible source(s) of net sulphate export at PC1-08

The adsorbed SO_4 pool in upland soils at PC1-08 is around 290 kg S-SO_4/ha, which is large enough to sustain net SO_4 export of the magnitude currently measured (average 18 kg SO_4/ha/yr) for almost 50 years. However, the organic S pool in mineral soil at PC1-08 is even larger, and is estimated to be around 580 kg S/ha, and net losses of 18 kg SO_4/ha/yr would constitute only a 3% loss from the organic S pool per year. Further work is required to determine the relative importance of desorption compared to mineralization for net SO_4 export from upland soils. Results of this study suggest that the processes of adsorption-desorption and mineralization-immobilization may in fact work together, such that higher SO_4 concentrations in LFH percolate (because of greater mineralization/less immobilization or root uptake and/or higher deposition) are balanced by increased adsorption in underlying mineral soil. Similarly, when SO_4 levels in LFH percolate are lower due to decreased inputs in deposition or less microbial mineralization (or greater immobilization), then SO_4 may be desorbed from mineral soil until a new equilibrium is reached. Obviously the relative importance of biological *versus* abiotic retention may vary seasonally, and will depend on factors such as temperature and hydrology. For example, if periods of high microbial mineralization are followed by flashy summer storms, released SO_4 may bypass adsorption sites in the mineral soil due to primarily overland flow or macropore routing through the soil.

Summary

In summary, changes in soil moisture, brought about by variations in precipitation and temperature appear to be responsible for similar temporal patterns of SO_4 chemistry between upland-draining and wetland-draining streams. However, unlike wetland-draining streams, such as PC1, which vary between annual net retention or net export depending on hydrologic conditions, SO_4 export from the upland PC1-08 catchment consistently exceeds SO_4 input from bulk deposition, in every year of record. The constancy of SO_4 concentrations in B-horizon percolate indicates that processes occurring in subsurface mineral soil, likely adsorption and desorption reactions, are able to modify the magnitude of SO_4 exported from surface soils, and in effect, modify the response of soil and stream waters to changes in deposition. Together, the processes of mineralization and immobilization in surface organic soil, and adsorption and desorption in subsurface mineral soil, appear to be responsible for the observed net export of SO_4 from upland forested catchments in the Muskoka-Haliburton region. Understanding both the source(s) and controls of net SO_4 losses from forest soils is necessary to predict the response of catchments to future changes in deposition and climate.

CHAPTER 5: THE EFFECTS OF DRYING AND RE-WETTING AND INCREASED TEMPERATURE ON SULPHATE RELEASE FROM UPLAND (FOREST FLOOR, MINERAL SOIL), AND WETLAND (PEAT, *SPHAGNUM*) MATERIAL

ABSTRACT

Long-term catchment studies in south central Ontario have shown that SO_4 concentrations in upland and wetland-draining streams are elevated following summer droughts. The objective of this laboratory study was to determine the effects of drying and re-wetting and temperature, respectively on the release of SO_4 from wetland (*Sphagnum* and peat) and upland (LFH and mineral soil) material collected from the PC1 catchment in Haliburton County, and from catchment S50 in the Turkey Lakes Watershed. Soil or plant material was either air-dried and subsequently re-wet or was kept at its initial moisture content, and samples were incubated at 18°C and 25°C, respectively for 30 d with periodic sampling for SO_4 (24 h, 48 h, 7 d, 14 d, 21 d, 30 d). Peat exhibited the most marked response to drying of the 4 materials considered, and within 24 h of re-wetting dried peat from both catchments released 3 to 4 times more $SO_{4(NH4Cl)}$ (0.13-0.36 mg g^{-1}) than continuously moist peat (0.050 mg g^{-1}), although temperature had only a marginal effect on SO_4 concentrations. There was no immediate response of *Sphagnum* to either drying or temperature, and although SO_4 concentrations in *Sphagnum* tended to increase from initial levels (~0.060 mg g^{-1}) over the 30-d incubation (maximum 0.13 mg g^{-1}), they were generally less than concentrations in dried peat. Sulphate concentrations in LFH material from both catchments were highest at the start of the incubation (24 h) in all treatments, although LFH material that was dried and/or incubated at 25°C tended to show the largest increase over background levels. In contrast, neither temperature nor drying appeared to affect SO_4 release from mineral soil collected from either site. Results of laboratory incubations suggest that increases in SO_4 concentration that have been reported in wetland-draining streams immediately following

summer dry periods are likely explained by drying and re-wetting of peat rather than increased mineralization in *Sphagnum*. Similarly, higher SO_4 concentrations that have been measured in LFH percolate following fluctuations in soil moisture may be in part be due to drying and re-wetting of the forest floor. In contrast, while the mineral soil constitutes a large pool of total S, it does not appear to be responsive to changes in moisture or temperature in the short-term (<30 d), although small changes in SO_4 release from organic S compounds may have been partly obscured by adsorption/desorption reactions in mineral soil.

INTRODUCTION

In the Muskoka-Haliburton region of south central Ontario, increased SO_4 concentrations and export have been measured in both wetland-draining and entirely upland catchments following summer droughts (Devito *et al*., 1999; Dillon and LaZerte, 1992; Eimers and Dillon 2002). Higher SO_4 concentrations were also reported in a wetland-draining stream in the Turkey Lakes watershed (S50), north of Sault Ste. Marie following extended dry periods (Jeffries *et al*., 2001). Increased SO_4 concentrations in wetland-draining streams occurred following declines in wetland water table levels and were inferred to be due to the oxidation of reduced S compounds in wetland soil (Dillon *et al*., 1997). In uplands, SO_4 concentrations in soil percolate draining the forest floor (LFH) were highest during the summer and fall, immediately following rainstorms that broke previous dry periods, and fluctuating moisture conditions and increased mineralization were suggested as the probable cause (see Chapter 4). However, in both cases, higher SO_4 concentrations occurred in summers that were both warmer, and drier than average, and the potentially confounding effect of higher temperatures during dry periods was not considered (Davidson *et al*., 1998). Furthermore, while enhanced mineralization may explain higher SO_4 concentrations and export following dry periods, this has never been directly tested, and SO_4

mineralization rates in upland or wetland soil are not available to compare with measured export in drainage streams.

The objectives of this study were to quantify the effects of drying and re-wetting and temperature, respectively on the release of SO_4 from mineral soil, forest floor, peat and *Sphagnum*, and to determine the contribution of changes in moisture and temperature to temporal variations in stream SO_4 chemistry. Two catchments were included in this study – the extremely acid-sensitive, coniferous Plastic Lake catchment #1 (PC1), and the moderately acid-sensitive, deciduous S50 catchment, which drains into Batchawana Lake, and is part of the greater Turkey Lakes watershed. Sulphate release (mg g^{-1}) from peat, *Sphagnum*, mineral soil (B-horizon) and forest floor material (LFH), respectively that was dried and subsequently re-wet was compared to SO_4 release in continuously moist material, in a laboratory incubation experiment. Experiments were replicated at 18°C and 25°C to test separately the effect of temperature.

MATERIALS & METHODS

Material used in this study was collected from 2 headwater stream catchments - Plastic Lake #1 (PC1; 45°11’N 78°50’W) in Haliburton County, south-central Ontario, and S50 (47°04’N 84°23’W) located in the Turkey Lakes Watershed, in Algoma District north of Sault Ste. Marie, Ontario. Both catchments are undisturbed and are located on the Canadian Shield. Soils at the 23 ha PC1 catchment are generally thin (average 40 cm), acidic (Table 1), humo-ferric or ferro-humic podzols, which directly overly bedrock (granitic gneiss) or thin (<1m) sandy, basal till deposits. Soils in the 12 ha S50 catchment are generally thicker and less acidic (Table 1), poorly developed sombric brunisols and humo-ferric and ferro-humic podzols (Canadian System of Soil Classification, 1998). White pine (*Pinus strobus*) and hemlock (*Tsuga canadensis*) dominate the upland forest at PC1, whereas the forest cover at S50 is primarily composed of sugar maple (*Acer saccharum*) and yellow birch *(Betula alleghaniensis*).

In each catchment, surface forest floor material (LFH: litter, fermentation and humus horizons) and underlying mineral soil (B-horizon) was collected from 3-4 upland sites, and samples from the same horizon from the individual pits were combined in the field. Soil from the B-horizon was collected from a depth range of 10-30 cm beneath the base of the LFH (Table 1).

Both PC1 and S50 contain *Sphagnum*-dominated swamps, which have previously been identified as probable sources of SO_4 peaks measured in stream water following summer droughts (Devito *et al*., 1999; Dillon *et al*., 1997; Jeffries *et al*., 2001). Similar to upland sites, peat and *Sphagnum* samples (entire live plants plus associated fibric material) were collected at 3-4 sites in each swamp and pooled in the field. Completely humified peat was sampled at a depth of 20-40 cm beneath the base of *Sphagnum* plants. Water level fluctuations of at least 20-40 cm relative to the peat surface are common in the PC-1 swamp during dry summers (Devito and Hill, 1997). Similar detailed hydrologic studies have not been conducted in the S50 swamp, but it was assumed that similar changes in water table height could occur in dry summers, due to reported peaks in SO_4 concentration in the S50 stream following dry periods (Jeffries *et al*., 2001).

All upland and wetland samples were sealed in plastic bags for transport to the laboratory. Samples were sorted in the laboratory, and rocks (>5mm), twigs, roots and other debris were removed by hand, because moist soil could not be easily sieved without physical disturbing the samples. After sorting, soils were stored at 4°C prior to the start of experiments, which occurred within 1 week of sample collection.

Experimental design

In the laboratory, mineral soil, LFH, peat and *Sphagnum* collections were divided in two, and one half was left open to air dry while the other half was kept sealed in plastic bags to preserve its initial moisture content. Prior to dividing materials into dry and wet treatments, sub-samples of each material were removed for the determination of initial SO_4 concentrations and moisture content. Both continuously wet soil and soil that was air-dried were kept in a constant temperature 18°C incubator for up to 1 week, or until soils in the dry treatment were visibly dehydrated – which generally corresponded to a decrease of 20% - 40% of their initial moisture contents (Table 1). Mineral soil, LFH and *Sphagnum* material tended to lose moisture more rapidly than peat, which required the full 1-week period to lose sufficient moisture (Table 1). Air-dried soils were subsequently re-wet with deionized-H_2O to increase their water contents to approximately their initial values (hereafter referred to as DRY) (Table 1). Both continuously moist (hereafter referred to as WET) and DRY samples were divided into 4 (PC) or 3 (S50) replicates per temperature treatment. Individual replicates were placed in clear, plastic 1.2-l stand-up Zip Lock bags. In total, 16 bags (2 temperature treatments x 2 moisture treatments x 4 replicates) were prepared for each material (LFH, mineral soil, peat and *Sphagnum*) from PC1, and 12 bags were similarly prepared for materials collected in S50. Bags were not sealed to allow air exchange, but were placed in closed cardboard boxes with a humidity source to reduce moisture losses. Half of the replicates of each material were then transferred to either a 25°C incubator, or an 18°C incubator, respectively, where they were kept in darkness for the duration of the 30-day experiment. Soils were sampled at 6 times over the 30-day period, at 24 h, 48 h, 7 d, 14 d, 21 d and 30 d, following re-wetting of the air-dried samples. Bag weights were recorded prior to incubation, and at each time of sampling to monitor weight changes due to moisture loss. If necessary, slight moisture loss during incubation was corrected by additions of water to the original weight. Initial SO_4 concentrations in materials prior to incubation (T=0) are indicated as dashed line on figures, and net SO_4 mineralization at each time interval was assessed as the difference in SO_4 concentration from the beginning of the incubation (*i.e.* $C_T - C_0$). The 4 temperature/moisture treatments are labeled as HD (25°, dry), LD (18°C, dry), HW (25°C, wet) and LW (18°C, wet) on all figures.

Table 1. Moisture contents and *p*H [initial/pre-drying (WET), post-drying and post re-wetting (DRY)] in peat, *Sphagnum,* LFH and mineral soil. Range in total S concentrations in PC1 material also given.

	PC peat			PC *Sphagnum*			PC LFH			PC mineral soil		
	Init	air dry	Rewet	Init	air dry	Rewet	Init	air dry	Rewet	Init	air dry	Rewet
% H_2O	89	70	84	94	75	94	80	60	79	37	25	36
*p*H	3.5		3.5	3.5		3.5	3.4		3.4	4.0		4.0
Tot. S (mg/kg	2000-6000			1000-1400			1100-1700			350-500		
	TL peat			TL *Sphagnum*			TL LFH			TL mineral soil		
	Init	air dry	Rewet	Init	air dry	Rewet	Init	air dry	Rewet	Init	air dry	Rewet
% H_2O	85	68	84	92	75	92	84	66	84	40	25	36
*p*H	4.0		3.8	4.0		4.1	4.0		3.9	4.0		

Analysis

Sulphate was extracted from organic material (LFH, *Sphagnum* and peat) using 0.01 M NH_4Cl and from mineral soil (B-horizon) using 0.03 M NaH_2PO_4 (1000 mg P l^{-1}) in a 1:5 soil-to-solution ratio. Maynard *et al*. (1987) recommend using a weak salt such as NH_4Cl instead of H_2O for extracting soluble SO_4 from organic material because H_2O may liberate some organic SO_4 (*i.e*. ester sulphates) and produces inconsistent results. Samples were shaken with the appropriate extraction solution in 250-ml Erlenmeyer flasks for 1 hour, and were then centrifuged and filtered (Whatman 42). Extracts were further syringe filtered (0.45 μm) prior to analysis for SO_4 by ion chromatography (Dionex). All samples were extracted ‘field’ moist, and were not air- or oven-dried prior to analysis to avoid changes in SO_4 release due to additional drying. To correct for differences in soil moisture between replicates additional sub-samples were removed at each time of sampling for determination of moisture content. All SO_4 concentrations are presented per gram dry weight of material.

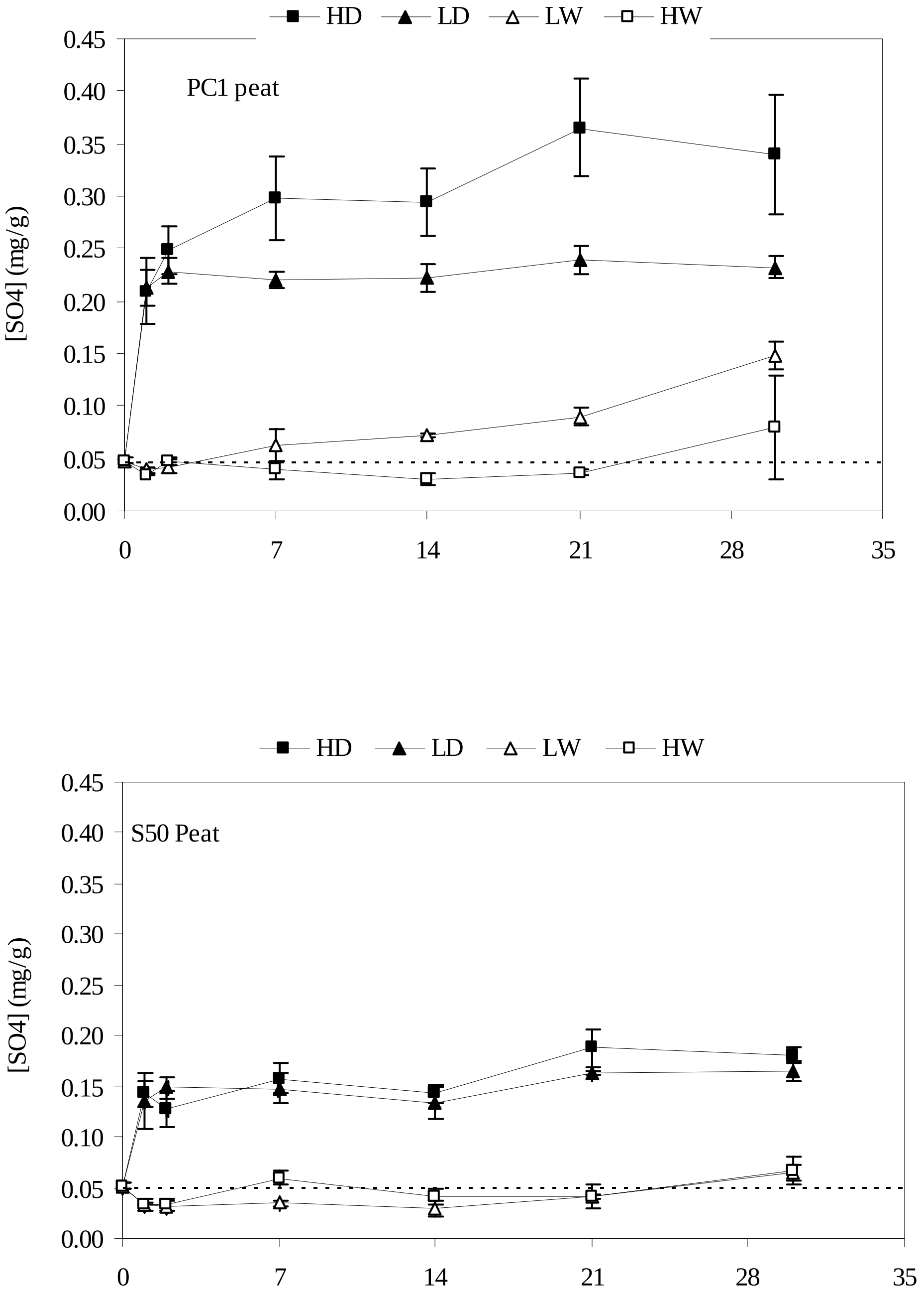
RESULTS

Peat

Sulphate release from peat increased markedly following drying, and the effect of drying was immediate (24 h) (Figure 1). Sulphate concentrations in peat increased from initial values of ~0.05 mg g^{-1} at T_0 to between 0.14 mg g^{-1} (S50) and 0.21 mg g^{-1} (PC1) within 24 h of re-wetting (Figure 1). Sulphate concentrations continued to generally increase in DRY PC1 peat incubated at 25°C, indicating an additional stimulatory effect of temperature, whereas SO_4 concentrations in DRY peat incubated at 18°C were relatively constant over the entire incubation period (Figure 1). In contrast, temperature exhibited a negligible effect on SO_4 release from S50 peat, as SO_4 concentrations were similar in the HD and LD, and HW and LW treatments, respectively (Figure 1). Drying appeared to be the dominant control on SO_4 release from S50 peat, however SO_4 concentrations in DRY S50 peat (0.13-0.19 mg g^{-1}) were always less than in DRY peat from PC1 (0.21– 0.37 mg g^{-1}).

Sulphate concentrations in continuously moist peat were similar to or less than initial levels in S50 peat throughout the 30-d incubation, potentially indicating some immobilization or SO_4 reduction had occurred. Similarly, SO_4 concentrations in WET peat from PC1 did not differ significantly from initial levels (HW) or increased slowly over time (0.003 mg $g^{-1}day^{-1}$) to a maximum concentration of 0.15 mg g^{-1}on the final day of incubation (LW).

Figure 1. Sulphate concentrations (mg/g) in peat from PC1 (upper) and S50 (lower) in the 4 temperature/moisture treatments (HW, HD, LW and LD) over a 30-d incubation period.



Sphagnum

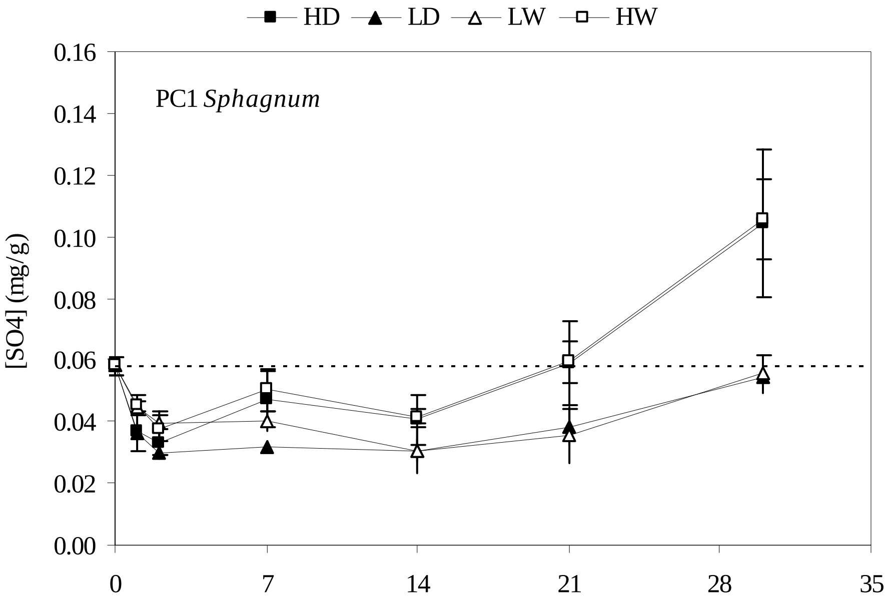
There was no immediate effect of drying or temperature on SO_4 release from *Sphagnum* in either catchment (Figure 2). In fact, SO_4 concentrations in *Sphagnum* decreased from initial levels (~0.060 mg g^{-1}) during the first 7 (S50) to 14 d (PC1) of incubation, indicating some potential immobilization or plant uptake of initially present SO_4 (Figure 2). *Sphagnum* plants in the WET treatments appeared healthy and maintained their initial turgor and colour throughout the incubation. In contrast, *Sphagnum* plants in the DRY treatments generally became more wilted and less green over time. Nevertheless, SO_4 concentrations in both WET and DRY *Sphagnum* increased after 1 (S50) or 2 weeks (PC1) incubation, to maximum SO_4 concentrations of 0.13 mg g^{-1} (S50) and 0.11 mg g^{-1} (PC1) at 30 d.

Temperature appeared to be the primary cause of increased SO_4 over time in *Sphagnum* from PC1. For example, SO_4 concentrations remained at or below their original levels in the LD and LW treatments, but were approximately double their initial concentrations in the HD and HW treatments after 30 d incubation (Figure 2). In contrast, the highest SO_4 concentrations in S50 *Sphagnum* occurred in the HD and LD treatments, indicating drying had a more important influence on SO_4 release from *Sphagnum* at the Turkey Lakes catchment.

LFH

Initial SO_4 concentrations were slightly less in coniferous forest floor material from PC1 (0.036 ± 0.004 mg g^{-1}) compared to deciduous LFH from S50 (0.048 ± 0.005 mg g^{-1}). Within 24 h of incubation, SO_4 concentrations in LFH material in all treatments increased markedly from their initial levels in both catchments, however the relative magnitude of increase was much larger in deciduous forest floor material from S50. For example, after 24 h SO_4 concentrations in PC1 LFH increased to a maximum of ~0.091 mg g^{-1} (HD), compared to 0.36 mg g^{-1} (HW) at S50 (Figure 3). The initial increase in SO_4 concentration measured after 24 h of incubation in all treatments may

Figure 2. Sulphate concentrations (mg/g) in *Sphagnum* from PC1 (upper) and S50 (lower) in the 4 temperature/moisture treatments (HW, HD, LW and LD) over a 30-d incubation period. Bars indicate SD.



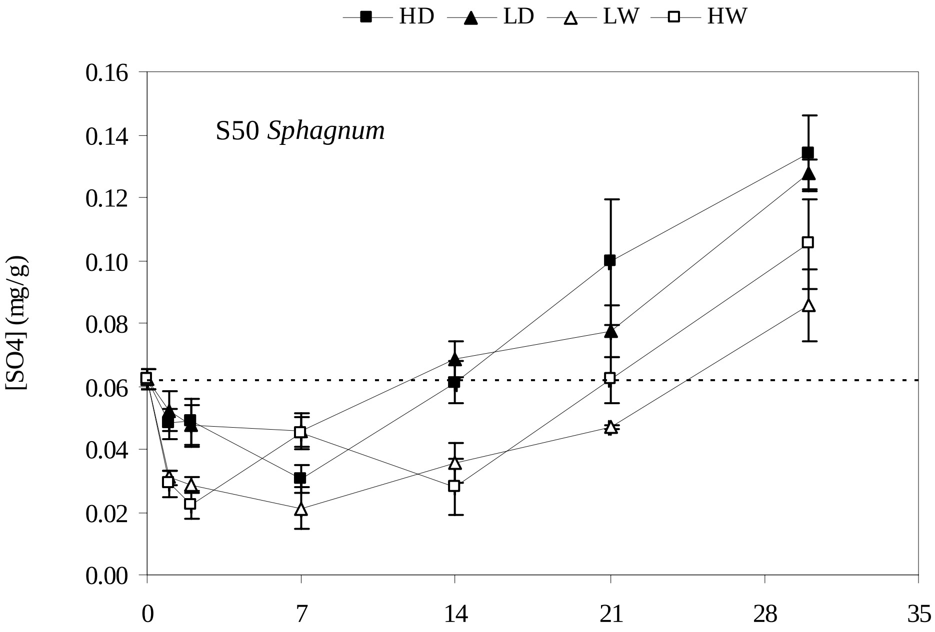
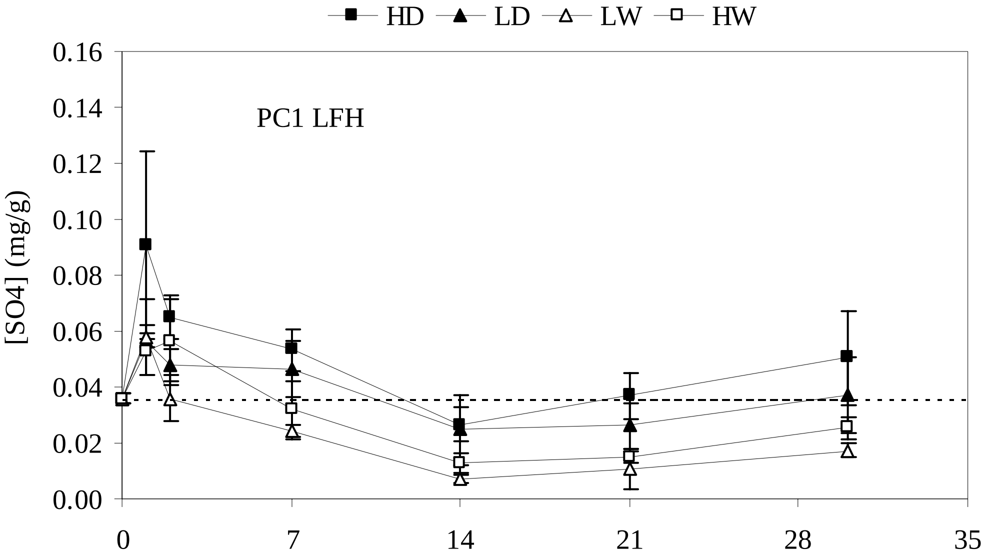
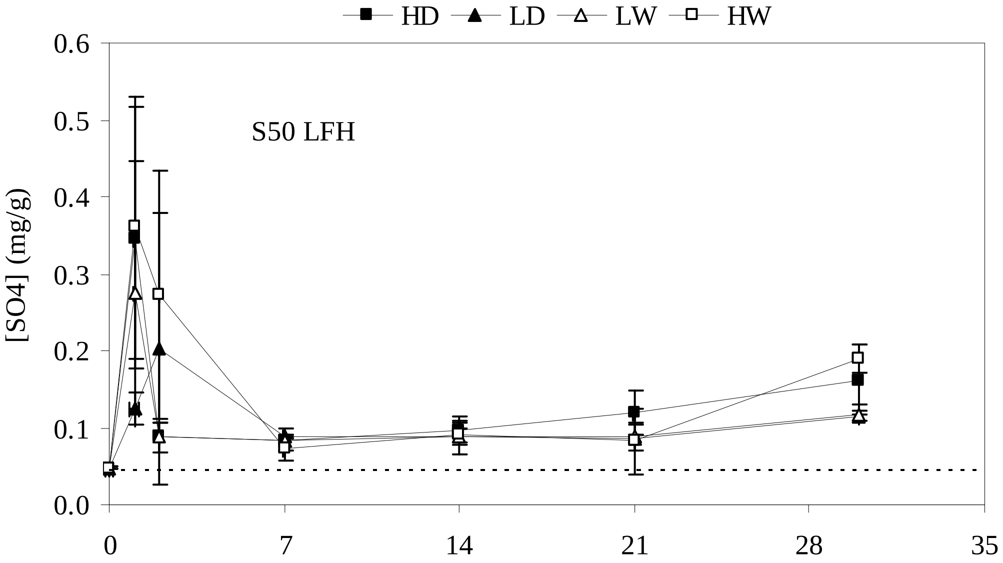


Figure 3. Sulphate concentrations (mg/g) in LFH from PC1 (upper) and S50 (lower) in the 4 temperature/moisture treatments (HW, HD, LW and LD) over a 30-d incubation period. Bars indicate SD.



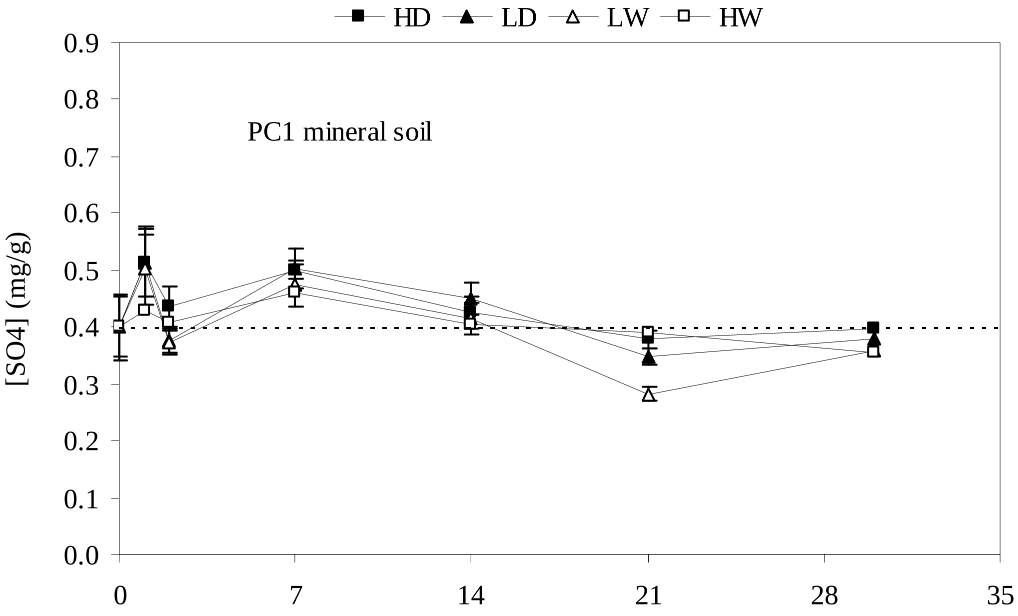


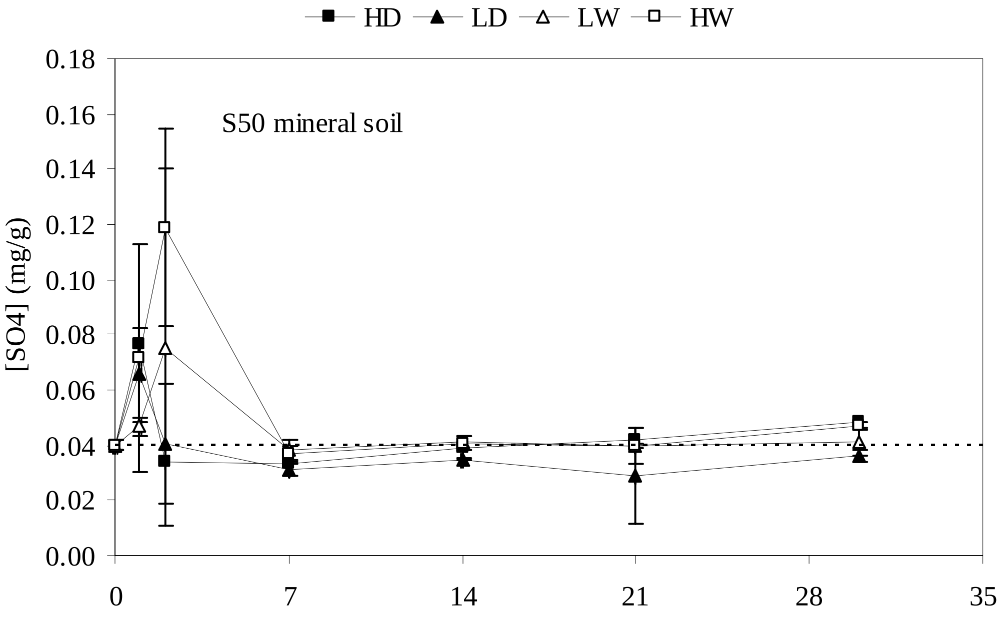
have been partly due to physical disturbance of LFH material during handling. However, SO_4 concentrations were consistently highest in the HD treatment at PC1, and were significantly higher (t-test, $p<0.05$) than concentrations in the LW and HW treatments at most sample times (*i.e*. 24 h, 7d-30d). Furthermore, SO_4 concentrations in PC1 LFH in the HD and LD treatments were consistently between 0.01 and 0.02 mg g^{-1} greater than concentrations in the HW and LW treatments, respectively after 48 h incubation (Figure 3). Sulphate concentrations in LFH from S50 were highest in the HD and HW treatments during the first 48 h, perhaps in part due to a temperature effect, although differences were not statistically significant (Figure 3).

The initial increase in SO_4 concentration in LFH material was brief, and concentrations decreased between 24 h and 48 h, and were slightly higher than (S50) or in some cases less than their initial levels (PC1) after 7+d incubation (Figure 3). Similar to *Sphagnum*, a decrease in SO_4 concentration in LFH material must have been due to microbial immobilization, as plant uptake would be negligible since living plants were not present in LFH samples. Sulphate immobilization was apparently greater in continuously moist PC1 LFH material, since SO_4 concentrations in LFH extracts generally increased in the order of HD>LD>HW>LW after 7 d incubation. While SO_4 concentrations declined between 24 h and 7 d incubation in S50 LFH, they increased again after 7 d to values that were 2- (LD) to 4-times (HD) higher than initial concentrations at 30 d (Figure 3).

Patterns in SO_4 concentration over time were generally similar in LFH material from S50 and PC1, respectively, although SO_4 concentrations were always higher in deciduous, compared to coniferous LFH, respectively during the entire incubation period (Figure 3). In addition, S50 LFH always showed net mineralization (*i.e*. concentrations were consistently greater than initial levels), whereas SO_4 concentrations in PC1 LFH were occasionally less than initial levels, indicating SO_4 immobilization in forms that could not be liberated by NH_4Cl.

Figure 4. Sulphate concentrations (mg/g) in mineral soil (B-horizon) from PC1 (upper) and S50 (lower) in the 4 temperature/moisture treatments (HW, HD, LW and LD) over a 30-d incubation period. Bars indicate SD.





Mineral soil

Neither temperature nor drying had a marked effect on $SO_{4(NaH2PO4)}$ concentrations in mineral soil from either catchment. At PC1, SO_4 concentrations in all treatments increased slightly over initial levels (0.40 mg g^{-1}) during the first 24-h of incubation to between 0.43 mg g^{-1} (HW) and 0.51 mg g^{-1} (HD, LD). In contrast, SO_4 concentrations in mineral soil from S50 increased greatly during the first 24 h (HD, LD) or 48 h (HW, LW) of incubation, by approximately 50% (LD) to 300% (HW) over initial levels. After some initial variability, SO_4 concentrations were relatively constant over time in mineral soil from both PC1 and S50 and were similar to initial levels (Figure 4). The decrease in SO_4 concentration measured in S50 mineral soil after 48-h suggests that initially released SO_4 was subsequently retained in forms that could not be liberated by NaH_2PO_4 extraction.

Mineral soil at PC1 had substantially higher SO_4 concentrations than soil at S50, and at any one sample-time concentrations in a respective temperature/moisture treatment were between 3.5 and 13-times greater in PC1 soil compared to S50 (Figure 4). Adsorbed SO_4 concentrations measured in this study are similar to those reported earlier for both catchments. For example, Neary *et al* (1987) found adsorbed SO_4 concentrations at PC1 to be between 0.30 and 0.50 mg g^{-1}, and Foster *et al*. (1986) reported adsorbed SO_4 concentrations of 0.014 to 0.056 mg g-1 in B-horizon soil at the nearby S31 catchment in the Turkey Lakes Watershed. Sulphate concentrations in mineral soil at PC1 (0.28 - 0.51 mg g^{-1}) were generally greater than in PC1 peat, which released the most SO_4 post-drying of the 3 organic materials tested. However, LFH material generally had the highest SO_4 concentration of the 4 materials considered at S50.

DISCUSSION

Temperature & moisture effects on SO_4 release from wetland soil

Drying had a large effect on SO_4 release from peat, supporting earlier suggestions that higher SO_4 concentrations in wetland-draining streams following summer droughts are due to release from peat (Devito *et al*., 1999; Dillon *et al*., 1997; Jeffries *et al*., 2001). Of the 4 materials considered in this study, peat exhibited the largest, most consistent and immediate response to drying. At a given temperature, the relative increase in SO_4 release from DRY *versus* WET peat at PC1 was between 150% and 900%, and in S50 peat the difference was around 300%. At the PC1 catchment, SO_4 release from dry peat was further stimulated by increased temperature, although ultimately, drying was a more important and immediate control on SO_4 release. Similarly, drying enhanced SO_4 release from S50 peat, although temperature had no effect, which suggests that post-drought increases in SO_4 in S50 stream water are likely due to drying of peat and are probably not a direct function of increased temperature. However, in the field situation, higher temperatures could enhance moisture losses through evapotranspiration, and so temperature could contribute indirectly to SO_4 release from peat. Furthermore, this experiment only considered a maximum temperature of 25°C, whereas in central Ontario maximum daily temperatures may reach 30°C or higher in the summer (OMOE, unpublished data).

Relatively low SO_4 concentrations in the WET peat treatments, which were generally similar to initial levels (*i.e.* T_0) indicate that SO_4 was neither released nor retained from continuously moist peat. The WET treatments were intended to replicate field moisture conditions that would occur when the water table is at or above the wetland surface. Under wet conditions, SO_4 is known to be retained in wetlands through microbial SO_4 reduction (Bayley *et al*., 1986; LaZerte 1993; Urban *et al*., 1989). For example, SO_4 is retained in the PC1 swamp in years that have average or high summer precipitation, when stream flow from the swamp is continuous and the water table is maintained near the wetland surface (Devito *et al*., 1999; LaZerte 1993). However, peat in the

WET treatments had a moisture content of 85-89% and was not completely saturated (Table 1). Stable or marginally increasing SO_4 concentrations in the WET treatments may therefore be explained by slightly aerated conditions in peat that did not favour SO_4 reduction.

In contrast, the initial response of *Sphagnum* to incubation appeared to be SO_4 retention, through either immobilization or plant uptake, since SO_4 concentrations were actually less than initial levels during the first 1-2 weeks of incubation. Sulphate concentrations in *Sphagnum* gradually increased over time, but even the maximum concentration observed after 30 d incubation was less than concentrations measured in DRY peat after 24 h in either catchment. The gradual increase in SO_4 concentration over time that occurred in both PC1 and S50 *Sphagnum* may have been due to the progressive breakdown of plant material and release of associated SO_4. Rates of *Sphagnum* decomposition are known to be extremely slow due to the presence of readily leached phenolic compounds in *Sphagnum* cell wall material, that are extremely resistant to decomposition and also have antibiotic properties (Verhoeven and Toth, 1995). However, SO_4 concentrations increased at similar rates in both DRY and WET *Sphagnum*, despite the fact that WET *Sphagnum* appeared healthy throughout the incubation, whereas DRY *Sphagnum* became progressively more brown and wilted over time. Nevertheless, results of this study indicated that SO_4 release from *Sphagnum* could potentially approach levels measured in peat over a sufficient length of incubation. However, the length of time required for SO_4 release from *Sphagnum* to reach levels that were measured in dried peat within 24 h of re-wetting suggests that SO_4 peaks observed in PC1 and S50 stream water immediately following dry periods are primarily due to release from peat, rather than *Sphagnum*.

Temperature & moisture effects on SO_4 release from upland soil

Sulphate concentrations in upland-draining streams may also increase following summer dry periods, and lysimeter measurements in the upland part of the PC1 catchment have shown that SO_4 concentrations in LFH percolate are higher during rain events that follow periods of low soil moisture (*see Chapter 4*). A number of studies have shown that C, N and P mineralization rates in forest floor material are sensitive to changes in soil moisture, and increase following drying and re-wetting (Davidson *et al*., 1998; Grierson *et al*., 1998; Pulleman and Tietema, 1999). Results from this laboratory study generally confirm field measurements, and indicate greater SO_4 release from dried coniferous LFH (PC1) compared to continuously moist LFH, which is slightly enhanced at higher temperatures. In contrast, deciduous LFH from S50 did not respond consistently to either drying or temperature, and while SO_4 concentrations were highest in the HW and HD treatments within the first 48 h of incubation, there was little difference among treatments throughout the remainder of the study. In an earlier laboratory study using material from the Turkey Lakes watershed, Foster (1989) reported a significant increase in S-mineralization in F material of the LFH horizon with temperature, which was manifested early in the incubation (<7 d). The use of entirely F material, as opposed to a mixture of L, F and H material consisting of litter in various degrees of decomposition, may explain part of the difference between these two studies. Nevertheless, the average SO_4 concentration in S50 LFH after 30 d incubation at 25°C (0.19 mg g^{-1}), was identical to that reported by Foster (1989) for F material that was incubated at 20°C for the same length of time (~0.19 mg g^{-1}). It is also possible that the difference between temperatures that were considered in this study (7°C), was not large enough to elicit the same clear response as reported by Foster (1989), who compared SO_4 mineralization rates at 10°C, 20°C and 30°C. We chose 18°C and 25°C because they fall within the range of summer temperatures commonly experienced in the Muskoka-Haliburton region. A number of studies have shown that decomposition processes are sensitive to changes in temperature. For example, Kirschbaum (1999) used the Q_{10} function to summarize literature reports of the temperature dependence of soil organic matter decomposition, and found that decomposition rates in upper latitudes (north of 40°latitude) more than double with a 10°C increase in temperature. Presumably a 7°C difference in temperature should have been large enough to effect measurable changes in SO_4 release, and indeed, SO_4 concentrations in dry peat, *Sphagnum* and coniferous LFH at PC1 were generally significantly higher in the 25°C treatments. It should also be noted that differences in SO_4 release between 18°C and 25°C were likely easier to detect in coniferous LFH, which had substantially lower SO_4 concentrations than deciduous LFH from S50.

Temperature & moisture effects on SO_4 release from mineral soil

Sulphate release from mineral soil showed no consistent response to drying or temperature at either study catchment. This was not surprising, since microbial activity is highest in the top 10 cm of soil where organic matter is most concentrated (Atlas and Bartha, 1993), and B-horizon soil was sampled at a depth of 10-30 cm. However, the majority (~2/3) of total S in mineral soil at PC1 consists of organic S compounds (Neary *et al*., 1987), as is the case for most upland forest soils (Mitchell *et al*., 1992). Therefore it was expected that SO_4 release from organic-S compounds in mineral soil would respond to changes in moisture and/or temperature. Instead, the lack of response to either temperature or drying suggests that biological processes are not important controls of short-term (*i.e*. daily) SO_4 dynamics in mineral soil. However, the initial flush in SO_4 concentration, which occurred in S50 mineral soil and to a lesser extent PC1 mineral soil during the first 24 h of incubation may indicate a brief release of SO_4 from organic sources, likely due to soil handling (Magid *et al*., 1997). Similarly, the subsequent decrease in SO_4 concentration must have been due to biological immobilization, since the NaH_2PO_4 extract would have liberated all subsequently adsorbed SO_4 from mineral soil (*e.g*. Fuller *et al*., 1985; Johnson and Todd, 1983). While the mineral soil appears to be biologically active, the majority of organic S compounds in mineral soil may be relatively recalcitrant, and therefore less readily mobilized in short-term incubations. Certainly, a number of studies have shown that carbon-bonded S compounds account for the bulk (>75%) of organic S in mineral soil (Mitchell *et al*., 1992). Carbon-bonded S compounds are apparently associated with humic substances, and are relatively resistant to degradation as indicated by their resistance to chemical extractants (David *et al*., 1982; Freney 1986; McGill and Cole, 1981). Houle *et al*. (2001) recently proposed that the large accumulation of organic S in mineral soil at Lac Laflamme, QC, is due to incomplete decomposition of LFH material and subsequent translocation of soluble organic S compounds down the soil profile to where they are adsorbed by mineral soil particles. Again, this study would suggest that the mineral soil is more important for S storage than for S immobilization or mineralization, at least in the short-term, however, over the longer term), net SO_4 release from mineral soil could provide an important source of SO_4 to drainage waters.

A lack of response in SO_4 release from mineral soil to changes in moisture or temperature may also in part be an artifact of the method of SO_4 extraction from mineral soil. A salt (NaH_2PO_4) rather than a water extract was used to remove all inorganic SO_4 from soil, including any newly released SO_4 that may have been subsequently re-adsorbed by soil minerals. However, adsorbed SO_4 is present in large excess of soluble SO_4 (~20:1) in mineral soil at PC1 (Neary *et al.*, 1987). Therefore small changes in soluble SO_4 due to release from organic S compounds may have been difficult to detect by monitoring changes in the relatively large adsorbed pool. Nonetheless, adsorbed SO_4 concentrations in S50 soil are relatively low, and are similar to H_2O-soluble SO_4 concentrations (see also Foster *et al*., 1989), yet there was no significant effect of either temperature or drying on SO_4 release from S50 soil over the 30-d incubation.

Comparison of laboratory results with field measurements

Previous reports have indicated substantial net SO_4 export occurs from both upland and wetland-draining catchments in the Muskoka-Haliburton region, and that net export is particularly large following dry summers (Eimers and Dillon, 2002). However, the source(s) and controls of net export or the causes of inter-annual variations in SO_4 export have never been directly determined. Annual net SO_4 export from the 23.3 ha wetland-draining PC1 catchment ranges from –4.3 to +31 kg ha^{-1} yr^{-1}. Net SO_4 retention generally occurs in years with wet summers, and highest net export occurs following particularly dry summers, although between 1980 and 1999, only 3 years showed a net retention of SO_4 (Dillon *et al*., 1997; Eimers and Dillon, 2002).

In an effort to place laboratory results in quantitative perspective with annual catchment flux, the average net SO_4 concentration measured after 24 h in DRY peat (*i.e*. 0.16 mg g^{-1}) from PC1 was extrapolated to the field situation. The following assumptions were made for this calculation: (i) the 1-week drying period corresponded to a water table decline of 40 cm in the PC1 swamp (depth of peat exposed in a typical dry summer), (ii) the re-wet phase corresponded to a 40 cm rise in water table height (iii) the entire 2.2 ha swamp contributes to SO_4 cycling. Using these assumptions and a peat bulk density of 0.12 g cm^{-3} (Lozano *et al*., 1987), it was calculated that ~250 kg SO_4 would be released from peat that was dried to a moisture content of 70% and subsequently re-wet. To put this number in perspective, LaZerte (1993) reported that the PC1 swamp exported ~370 kg SO_4 during a 6 month period (September-February) that followed a particularly dry summer in 1987 when stream flow ceased for 89 contiguous days. These results indicate that a seemingly small decline in peat moisture content of ~20% can result in substantial SO_4 release from peat upon re-wetting. In addition, total S storage in the PC1 swamp is large compared to the magnitude of net SO_4 export following dry periods. For example, assuming an average S concentration in peat of 4000 mg kg^{-1} and a peat depth of 2 m (LaZerte 1993), total S storage in the 2.2 ha PC1 wetland was estimated to be at least 9500 kg S ha^{-1}. Therefore a net export of 250 kg SO_4 (83 kg S) as was calculated for dried peat at PC1, would only correspond to a 0.4% loss from the total S pool in the wetland.

In contrast to the wetland, which exhibits net SO_4 retention or export depending on the hydrologic conditions, the upland part of the PC1 catchment (PC1-08; 3.45 ha), consistently exports more SO_4 in stream discharge than is input to the catchment in bulk deposition in every year of record, in the range of 10 to 28 kg SO_4 ha^{-1} yr^{-1} (see Chapter 4). A number of long-term monitored catchments have been reported to show net SO_4 export, and mineralization has been proposed as a potential source (*e.g.* Alewell *et al*., 1999; Hornbeck *et al*., 1997; Houle and Carignan, 1995; Mitchell *et al*., 1996; Prietzel *et al*., 2001). However, results of this study indicated that following an initial flush in SO_4 release, SO_4 was actually retained in PC1 LFH material, whereas SO_4 release from mineral soil was not affected by changes in moisture or temperature. However, if the maximum net SO_4 concentration measured in LFH material (HD: 0.055 mg g^{-1}) is extrapolated to the catchment scale, assuming an average depth of 10 cm and bulk density of 0.014 g cm^{-3}, then a total of 2.7 kg SO_4 could be released from dried LFH within 24 h of re-wetting (at 25°C). Presumably more than 1 cycle of drying and re-wetting of the forest floor would occur at PC1-08 each year, and so over an annual cycle, drying and re-wetting of the forest floor could contribute to net SO_4 release from the catchment. Sulphur storage in the forest floor at the 3.45 ha PC1-08 catchment amounts to approximately 20 kg S/ha (at 1400 mg S kg^{-1}) and therefore a release of 2.7 kg SO_4 (0.9 kg S) corresponds to a loss of 4.5% from the total S pool in the LFH horizon. Given the magnitude of net export normally measured in PC1-08 and the relatively small S pool in the forest floor, it is unlikely that SO_4 release from LFH material is the sole source of net catchment export. However, the magnitude of SO_4 release following drying of LFH material is large enough to explain increases in SO_4 concentration that have been measured in LFH percolate immediately following periods of low soil moisture, and therefore SO_4 release from surface organic soil may contribute to inter-annual differences in SO_4 export in the PC1-08 stream (see Chapter 4).

The other possible source of net SO_4 export in upland stream water is desorption from mineral soil, which may increase in response to declining SO_4 inputs in deposition (Harrison *et al*., 1989; Reuss and Johnson, 1986). The adsorbed SO_4 pool in upland soil is certainly large enough to sustain the magnitude of net SO_4 export that is measured in PC1-08. For example, assuming an average depth of 25 cm, a bulk density of 0.77 g cm^{-3} (Lozano *et al*., 1987), and an average

$SO_{4NaH2PO4}$ concentration of 0.45 mg g^{-1}, then the adsorbed SO_4 pool in B-horizon soil at PC1-08 is approximately 290 kg S-SO_4/ha. Total S storage in the B-horizon is even larger (~870 kg S/ha), and although results of this 30-d incubation study showed that SO_4 release from mineral soil was not responsive to changes in moisture or temperature, the organic S pool in mineral soil is large compared to annual net export, and may therefore be an important source of SO_4 to drainage waters over the long-term. Additional work would be required to investigate the potential importance of organic-S in mineral soil as a source of net SO_4 export in drainage water, and the controls on net release.

Conclusions

Results of this laboratory study indicated that cycles of drying and re-wetting have a substantial effect on SO_4 release from organic material, particularly peat. Increases in SO_4 concentration that have been reported in wetland-draining streams immediately following summer dry periods are likely explained by drying and re-wetting of peat rather than increased mineralization in *Sphagnum*. Similarly, higher SO_4 concentrations that have been measured in LFH percolate following fluctuations in soil moisture may be in part be due to drying and re-wetting of the forest floor. Although mineral soil constitutes a large pool of total S, it does not appear to be responsive to changes in moisture or temperature in the short-term (<30 d), although small changes in SO_4 release from organic S compounds may have been partly obscured by adsorption/desorption reactions in mineral soil. Furthermore, over longer time periods, SO_4 release from mineral soil may become important, particularly given the large pool of organic S storage in mineral soil.

CHAPTER 6: SULPHATE ADSORPTION AND DESORPTION IN TWO ACIDIC PODZOLS IN THE MUSKOKA-HALIBURTION REGION, SOUTH-CENTRAL ONTARIO

ABSTRACT

The short-term effect of increasing and decreasing soil-solution sulphate (SO_4) concentration on 2 podzolic mineral soils was examined in a laboratory batch experiment using forest floor percolate amended with varying amounts of SO_4. Soil from Plastic Lake (PC1-08) had a substantially higher native adsorbed SO_4 concentration (~650 mg SO_4/kg) compared to Harp 6 (HP6; 16 mg SO_4/kg). However, both soils were capable of adsorbing additional SO_4 when the SO_4 concentration in a forest floor percolate was increased, and both released SO_4 at lower SO_4 concentrations. For PC1-08, the critical SO_4 concentration at which SO_4 was neither retained nor released occurred around 19 mg/l, whereas for HP6 the concentration was much lower at 5 mg/l. These results suggest that SO_4 should be consistently released from soil at PC1-08 at SO_4 concentrations that are currently (1999-01) measured in forest floor percolate in the field (range 0.3 – 10.4 mg/l), whereas SO_4 adsorption and desorption should be in approximate balance at HP6. The observed relationship between initial SO_4 concentration and retention or release could be described equally well by both a Langmuir and Initial Mass isotherm. According to the Langmuir formulation, soil from PC1-08 had a greater potential for additional SO_4 adsorption ($K_{max} \approx 360$ mg/kg) than soil at HP6 ($K_{max}= 125$ mg/kg). Initial Mass isotherm calculations indicated that 33% of SO_4 inputs should be retained through adsorption reactions in PC1-08 soil compared to only 13% at HP6. These results suggest that streamwater draining upland catchments that have high native adsorbed SO_4 concentrations may take longer to respond to changes in SO_4 deposition, than catchments with less strongly adsorbing soils. However, a number of other factors may influence SO_4 retention or release in catchments, and adsorption/desorption results

should be put into context by considering soil depth and primary hydrologic pathways as they determine the ‘horizon of last contact’ for soil drainage water prior to entering the stream channel. Other internal sources of SO_4 such as mineralization should also be considered when inferring the potential contribution of desorption to net catchment SO_4 export, since SO_4 generation from organic S compounds may continuously replenish the adsorbed pool.

INTRODUCTION

Sulphate adsorption in soil can ameliorate the effects of S deposition by decreasing the amount of H^+ and cations leached from soil in drainage waters. The reversibility of SO_4 retention has become a question of concern, since desorption of SO_4 that was adsorbed when deposition was higher may delay the response of downstream surface waters to recent decreases in S deposition. Studies in Europe where deposition has been historically higher, but where recent declines in emissions have been much larger compared to North America have highlighted the importance of adsorption in soil as a temporary sink for SO_4. The covered catchment studies in Norway and Sweden, for example showed that SO_4 levels in soil drainage water and streams remained high for several years following installation of roofs which completely removed anthropogenic SO_4 inputs (Hultberg *et al*., 1998; Wright and Jenkins, 2001). These studies demonstrated that SO_4 release from soil could delay the response of catchments to decreases in deposition.

In addition, a number of catchments in both Europe and eastern North America have reported SO_4 losses in drainage water that exceed inputs in deposition (*i.e.* net export) and have suggested the presence of an internal, as yet unaccounted for S source (Driscoll *et al*., 1998; Feger 1995; Houle and Carignan, 1995; Mitchell *et al*., 1996). A number of possible sources have been proposed to account for net SO_4 losses, including the adsorbed SO_4 pool in mineral soil (*e.g.* Lofgren *et al*., 2001; Mitchell *et al*., 1996).

Sulphate that is adsorbed to soil particles is in equilibrium with SO_4 in soil solution (Chao *et al*., 1962). It has been suggested that if SO_4 concentrations in soil solution decline in response to lower deposition, then SO_4 may be released from mineral soil to compensate until a new equilibrium between adsorbed and solution SO_4 is achieved (Reuss and Johnson, 1986). In the Muskoka-Haliburton region, SO_4 concentrations in deposition declined by almost 50% between the start of monitoring in the late 1970s and the present time, 2002.

A number of studies have attempted to determine the reversibility of SO_4 adsorption in mineral soil, and to assess the potential for SO_4 desorption due to decreased deposition (*e.g*. Harrison *et al*., 1989). The majority of these studies have treated mineral soil with varying concentrations of SO_4 in distilled water, or simulated rainfall (*e.g*. Fuller *et al*., 1985; Harrison *et al*., 1989). However, in natural systems, soil percolate that comes into contact with subsurface mineral soil contains organic acids (among other chemicals), due to the passage of deposition through the forest floor. The presence of organic acids is known to decrease SO_4 adsorption, through either competition for binding sites or by altering the nature of Fe and Al oxides (Gobran and Nilsson, 1988). Soil *p*H may also affect SO_4 adsorption, and adsorption is generally greater at lower *p*H due to increased protonation of hydroxyl sites on Fe and Al oxides (Chao *et al*., 1962; Kaiser and Kaupenjohann, 1998).

In this study, the potential for SO_4 adsorption and desorption in acidic podzols was determined using a forest floor percolate that was amended with varying concentrations of SO_4. Soils from 2 catchments were considered in this study – PC1-08, and HP6, because earlier reports indicated that soils from PC1-08 and another sub-catchment of Harp Lake, HP4 had adsorbed SO_4 concentrations that differed by a factor of 10 (Neary *et al*., 1987). The objective of this study was to determine whether SO_4 release from mineral soil occurs at SO_4 concentrations that are currently measured in forest floor percolate, and to speculate on the potential contribution of SO_4 desorption to apparent net SO_4 losses (*i.e*. stream export > bulk deposition) in these 2 catchments.

METHODS

Study sites

Soils used in adsorption/desorption experiments were collected from the Plastic Lake 1-08 (PC1-08; 3.4 ha) and Harp Lake-6 (HP6; 10 ha) catchments, respectively located in the Muskoka-Haliburton region, south-central Ontario. Soils in these Precambrian Shield catchments are classified as orthic humo ferric or orthic ferro humic podzols, according to the Canadian soil classification system (Agriculture Canada Expert Committee on Soil Survey, 1998). Further details on the soil profiles and physiography at PC1-08 and HP6 can be found in Devito *et al*. (1999), Dillon *et al*. (1991) and Neary *et al*. (1987). The forest at PC1-08 is dominated by white pine (*Pinus strobus*; 43% basal area) and eastern hemlock (*Tsuga canadensis*; 19% BA), whereas sugar maple (*Acer saccharum*; 41% BA) and eastern hemlock (23% BA) are more common at HP6 (Watmough and Dillon, 2002). Sulphate deposition in the Muskoka-Haliburton region is currently around 20 kg/ha/year (~2 mg/l), but was greater than 40 kg/ha/year (~4 mg/l) in the late 1970s (Dillon *et al*., 1988).

Sampling

At PC1-08, B-horizon mineral soil was collected from a depth of 10-20 cm (B1) and 30-40 cm (B2), respectively beneath the base of the Ae horizon. Soil was collected in this manner from 3 adjacent pits and soils from individual pits from the same depth were combined. At HP6, B-horizon soil was similarly collected from 3 pits, but from one depth only: 10-15 cm beneath the base of the H or Ae horizon. In the lab, soils were coarse sieved (5 mm), and roots, pebbles and other debris were removed. Sub-samples of each soil were removed at this time and dried at 65°C for 48 h to determine the moisture content. Soils were stored at 4°C in the dark prior to use in experiments. The *p*H (0.01 M $CaCl_2$) of the different soils was determined using a 1:5 soil:solution ratio.

Table 1. Selected chemical properties of the 6 SO_4 treatment solutions

	*p*H	*SO_4 (mg/l)*	*DOC (mg/l)*
Treatment 1-FFL	4.7	0.77	9.8
Treatment 2	4.7	1.7	9.8
Treatment 3	4.7	7.5	9.8
Treatment 4	4.7	32.5	9.8
Treatment 5	4.7	42.0	9.8
Treatment 6	4.7	65.2	9.8

Sulphate treatment solution

Forest floor leachate (FFL) was used as the base for SO_4 treatment solutions. Organic leachate was obtained by shaking field-moist coniferous litter material (LFH) from PC1-08 in de-ionized water for 2 hours (1:10 ratio). The leachate obtained was filtered (Whatman 1) and then amended with varying amounts of Na_2SO_4 to produce 5 different SO_4 concentrations (Table 1). The same leachate (*i.e*. from PC1-08 LFH) was used in experiments with both PC1-08 and HP6 soil. The range in concentrations used in experiments was chosen to cover the range in SO_4 concentrations measured in LFH percolate at lysimeters in PC1-08 and HP4 (0.2 - 42 mg/l) (LaZerte and Scott, 1996). All 5 SO_4 solutions were adjusted to *p*H 4.7 using HCl (Table 1), which is typical of forest floor percolate at PC1-08, whereas the *p*H of LFH percolate at HP4 (and presumably HP6) is slightly higher (average *p*H at 6 zero-tension lysimeters: 5.1 ± 0.3, n=944; Findeis *et al*., 1993). The dissolved organic carbon (DOC) content was measured using a Shimadzu total organic carbon analyzer (TOC-5000). The DOC concentration in FFL (Table 1) was less than the average DOC concentration measured in LFH percolate at PC1-08 (35 ± 17 mg/l; 1999-01); however, DOC concentrations in water draining the LFH horizon are highly variable and range from 2 to 70 mg/l (LaZerte and Scott, 1996).

Adsorption/Desorption experiments

In order to measure the amount of SO_4 released or retained by mineral soil, 25 ml of the appropriate FFL-SO_4 solution was shaken for 1-hour with a mass of field moist mineral soil that was equivalent to 5 g dry-weight. Experiments were conducted in quadruplicate. Field-moist soils were used in all experiments in order to prevent unintentional SO_4 release due to drying, and experiments were performed in the dark at 4°C to limit the potential for biological activity. After shaking, soil slurries were centrifuged and *p*H (glass electrode) of the supernatant was recorded. Supernatants were then sequentially filtered through Whatman 42 disks, followed by 0.45 μm syringe filters prior to analysis by ion chromatography (Dionex 600). Net SO_4 retained or released was calculated by subtracting the amount of SO_4 added in FFL solutions from the amount of SO_4 remaining in soil solutions after shaking for 1 hr and SO_4 concentrations in soil were expressed per unit dry weight. Native adsorbed concentrations in soils were determined in a similar manner by shaking the equivalent of 5 g (dwt) soil with 25 ml 0.03 M NaH_2PO_4 for 1 hr. Water-soluble SO_4 was measured in PC1-08 soil only, by substituting de-ionized water for NaH_2PO_4 in the procedure above. The functional relationship between solution and adsorbed SO_4 is known as the sulphate adsorption isotherm (Reuss and Johnson, 1986). Langmuir (*e.g*. Chao *et al*., 1962) and Initial Mass (*e.g*. Nodvin *et al*., 1986) adsorption isotherms for PC1-08 and HP6 soil were calculated using STATISTICA 5.1 (StatSoft, Inc.).

RESULTS & DISCUSSION

PC1-08 - Sulphate fractions

Water soluble SO_4 concentrations in B1 and B2 soil were 42 ± 3 and 30 ± 4 mg SO_4/kg, respectively, and were less than 10% of native adsorbed SO_4 concentrations (669 ± 43 and 631 ± 34 mg SO_4/kg, respectively). Adsorbed SO_4 concentrations in PC1-08 soil used in this experiment were higher than the maximum concentration reported by Hern (1990) of 300 mg SO_4/kg. Neary *et al*. (1987) determined an average adsorbed SO_4 concentration of 331 ± 200 mg SO_4/kg in 8 profiles they examined at PC1, although concentrations ranged from 23 to 660 mg SO_4/kg. Soil chemistry is highly spatially heterogeneous, and soils used in these experiments were collected from 3 adjacent pits. Therefore, adsorbed SO_4 concentrations measured in this study are not representative of the entire catchment, and high values in this analysis relative those obtained by Neary *et al*. (1987) should not be interpreted as evidence of increased adsorption over time. Indeed, a survey of soil chemistry at various sites within the PC1-08 catchment in 1999 indicated that the average adsorbed SO_4 concentration in B-horizon soil was 278 ± 203 mg SO_4/kg (range 74 to 743 mg/kg; n=20). Given the high degree of variability associated with soil measurements it is impossible to assess temporal changes in the adsorbed SO_4 pool. In order to evaluate potential changes in adsorbed SO_4 over time, the original soil pits that were investigated by Neary *et al*. (1987) would have to be re-visited and sampled in an identical manner, so that data could be analyzed using a repeated-measures test.

Adsorbed SO_4 may also vary with depth, and Hern (1990) found that adsorbed SO_4 concentrations in mineral soil 10-20 cm beneath the base of the LFH were ~25-30% greater than those in soil 30-40 cm beneath the organic horizon. In contrast, the difference in adsorbed SO_4 between upper and lower B-horizon soil used in this experiment was only 5% over the same depth interval. Sulphate adsorption within a podzol profile depends on the distribution of Fe and Al oxides and organic matter with soil depth, as well as *p*H, which normally increases toward the bedrock interface (Johnson and Todd, 1982). However, we did not evaluate the Fe or Al oxide or organic matter content of B1 and B2 soil, and Hern (1990) did not present these data. The *p*H of B1 and B2 soil was similar (4.4 and 4.6, respectively), although due to the logarithmic *p*H scale, a difference of 0.2 *p*H units corresponds to a 1.6X increase in H^+ concentration. Therefore slightly higher adsorbed SO_4 concentrations in B1 compared to B2 soil (1.1X) may in part be due to the creation of additional sites for anion adsorption through increased protonation (Hern 1990; Singh 1984).

Despite the large degree of variability in adsorbed SO_4 estimates, NaH_2PO_4-extractable SO_4 concentrations in soil at PC1-08 are relatively high compared to other catchments in southeastern Canada and the northeastern US that have the same soil type. For example, adsorbed SO_4 levels in podzols at Lac Laflamme, QC are on average 25 mg SO_4/kg (Houle and Carignan, 1995), and are less than 100 mg/kg at the Hubbard Brook, NH (Fuller *et al*., 1985). Foster *et al*. (1986) reported adsorbed SO_4 concentrations of 14 - 56 mg SO_4/kg in B-horizon soil at the Turkey Lakes Watershed. In the northeastern US and southeastern Canada, where recent glaciation has "reset the pedogenic clock" (Shanley, 1992), catchments are generally considered to have a low SO_4 adsorption potential due to their relatively unweathered profiles with low Fe and Al concentrations and high organic content (Rochelle *et al*., 1987). Nevertheless, adsorbed SO_4 concentrations at PC1-08 are similar to values reported at sites in the unglaciated southeastern US, where oxisols (ultisols) retain the majority of SO_4 in deposition (*e.g.* Harrison *et al*., 1989). For example, Shanley (1992) reported adsorbed SO_4 concentrations in oxisols at Panola Mountain, GA to be less than 265 mg SO_4/kg. However, soil depth also affects total SO_4 retention by adsorption on a watershed scale, and soils in the southeastern US generally have thicker mineral soil horizons compared to more recently de-glaciated sites of the northeastern US and southeastern Canada (Rochelle *et al*., 1987). The total pool of adsorbed SO_4 at sites in the southeastern US is therefore likely to be substantially greater than that at PC1-08 (average soil depth ~37 cm), and accounts for their generally positive SO_4 budgets (*i.e*. net retention). Using adsorbed SO_4 concentrations and bulk densities reported by Neary *et al*. (1987), the adsorbed SO_4 pool in soil at PC1-08 was estimated to be around 290 kg S-SO_4/ha, which is equivalent to approximately 36 years of bulk deposition (@8 kg S/ha/yr).

Differences in adsorbed SO_4 concentrations among catchments in the same climatic and geologic zone may also be attributed to differences in forest type. Coniferous litter is more acidic than deciduous litter, and greater leaching and eluviation of Fe and Al is observed under coniferous canopies (Brady, 1990). Subsequent illuviation of Fe and Al oxides in subsurface soil results in the creation of anion adsorption sites. Fuller *et al*. (1985) found that soil at a coniferous site had 3-times higher adsorbed SO_4 concentrations than soil at a neighbouring deciduous site at the Huntington Forest, NY.

HP6-Sulphate fractions

Mineral soil from HP6 had a native adsorbed SO_4 concentration of 16 mg SO_4/kg, which is substantially less than at PC1-08. However, previous surveys of soil chemistry at another sub-catchment of Harp Lake - HP4, indicated that adsorbed SO_4 concentrations in HP soils are low, and are on average 65 mg SO_4/kg, although a minimum of 13 mg/kg was measured in one profile (Neary *et al*., 1987). Adsorbed SO_4 concentrations at HP6 are comparable to concentrations reported in podzols at sites in the northeastern US and southeastern Canada (Fuller *et al*., 1986; Johnson and Todd, 1983), which are purportedly less efficient at retaining SO_4 *via* adsorption reactions. Assuming a constant SO_4 concentration of 16 mg SO_4/kg over the entire ~1m depth of the B-horizon (Watmough and Dillon, 2002), the adsorbed pool at HP6 is estimated to be around 43 kg S-SO_4/ha, which is equivalent to approximately 5 years of bulk deposition.

PC1-08 - Sulphate adsorption

The addition of SO_4 to soil in FFL at concentrations greater than 18-20 mg SO_4/l resulted in the net retention of SO_4 by PC1-08 soil, whereas SO_4 was released from soil at lower concentrations (Figure 1). Adsorption/desorption reactions are the most plausible explanation for changes in SO_4 retention or release from soil at varying levels of SO_4 input. Biological activity would have been low under the conditions of the experiment (4°C, complete darkness), and therefore biological retention (immobilization) or release of SO_4 (mineralization), were likely not important factors.

In addition, results from HP6 (see below) indicated that soil acidity was constant among the 5 FFL-SO_4 treatments following equilibration with soil, and soil *p*H was therefore not responsible for the relationship between SO_4 retention and the amount of SO_4 applied. Another factor that may influence SO_4 retention or release is DOC. The effect of DOC in FFL on SO_4 adsorption could not be determined because only one concentration of DOC was considered in this experiment (Table 1). Gobran and Nilsson (1988) found that SO_4 adsorption was completely inhibited at SO_4 concentrations in FFL that were less than 750 mg SO_4/l, whereas SO_4 retention increased linearly at SO_4 concentrations in distilled water that were between 0 and 1500 mg SO_4/l. However, the DOC concentration in FFL used in the aforementioned experiment was very high (728 mg/l) compared to this study (10 mg/l). If DOC in FFL used in this experiment had a negative effect on SO_4 adsorption, then the effect of the added DOC may have been to shift the x-intercept to a higher SO_4 concentration; whereas the limit between adsorption and desorption may have occurred at a lower SO_4 concentration in a distilled water solution. However, the purpose of using FFL in this experiment was simply to provide a more realistic base solution for SO_4 treatments. Since the DOC concentration in FFL used in this experiment (~10 mg/l) was low compared to average concentrations in LFH at PC1-08 or HP4 (2-70 mg/l), it is likely that the actual limit between SO_4 adsorption and desorption occurs at a higher SO_4 concentration than that determined here.

Figure 1. Relationship between SO_4 (mg/l) in treatment solution and SO_4 removed or released (mg/kg) in PC1-08 upper and lower B-horizon mineral soil, respectively (Langmuir adsorption isotherm).

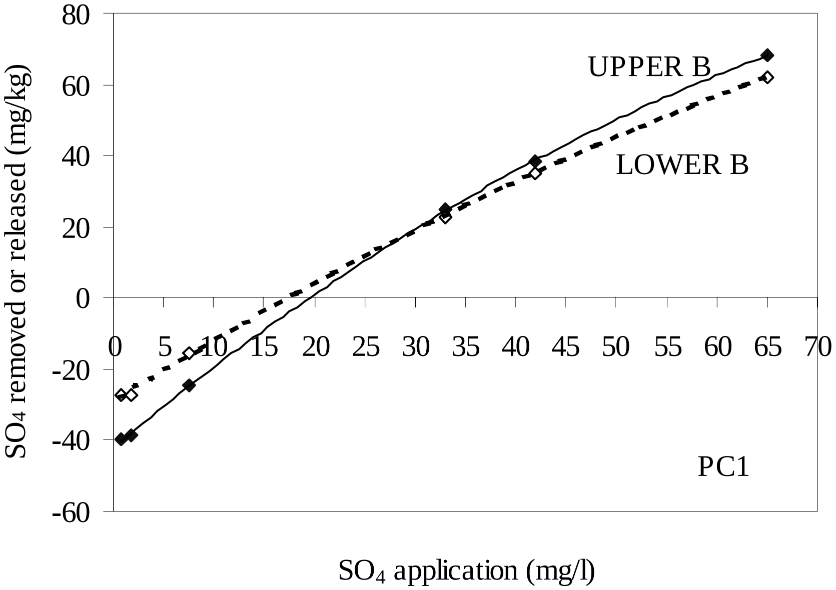
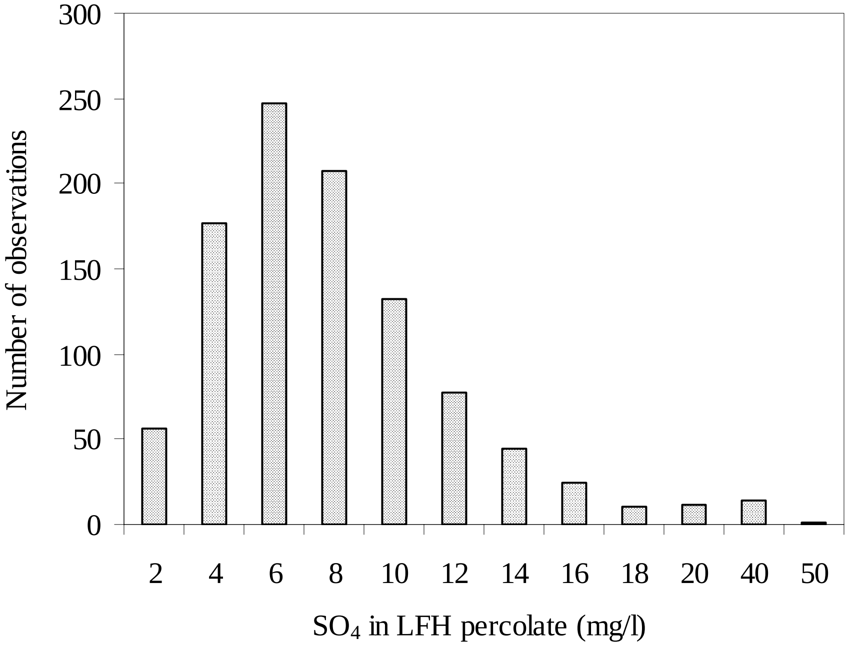


Figure 2. Histogram of SO_4 concentration (mg/l) in LFH percolate at PC1-08. Data collected between 1987 and 1995 (OMOE, *unpublished*).



Both the Freundlich and Langmuir adsorption isotherms are commonly used to describe the relationship between concentrations of an adsorbate and adsorption by an adsorbent. If the data indicate an adsorption maximum, then the Langmuir equation is more appropriate, whereas the Freundlich isotherm is suitable in the absence of a maximum (Chao *et al*., 1962). Because of the logarithmic form of the Freundlich relationship, negative values of SO_4 desorption could not be modeled using the Freundlich equation (*e.g.* Nodvin *et al*., 1986), and so we instead applied the Langmuir isotherm to soil data from PC1-08. Furthermore, the slightly curvilinear relationship between SO_4 adsorption/release and SO_4 concentration in FFL indicated the potential for an adsorption maximum in PC1-08 soil (Figure 1). The form of the Langmuir equation is:

$$C_a = \frac{K_{\max} \times C_s}{K_s + C_s}$$

where C_a is the adsorbed SO_4 concentration (mg/kg) and C_s is the SO_4 concentration in solution. K_{max} and K_s are constants, representing the maximum adsorption (mg/kg) (additional to native adsorbed SO_4) and the concentration at which C_s is equal to one-half K_{max}, respectively. The maximum amount of additional SO_4 (K_{max}) that could be adsorbed in PC1-08 soil was calculated to be 388 mg/kg in B1 (upper B) and 338 mg/kg in B2 (lower B), and the half-saturation constants (K_s) were 211 mg/l and 134 mg/l in B1 and B2, respectively. Since the maximum SO_4 concentration measured in LFH percolate at PC1-08 is less than 50 mg SO_4/l (Figure 2), the adsorption maximum would likely never be reached in PC1-08 soil. However, these results indicate that there is a substantial capacity for additional SO_4 adsorption in PC1-08 soil.

While the Langmuir function appeared to statistically fit adsorption data from PC1-08, Nodvin *et al*. (1986) explain that at low concentrations, such as those used in this experiment, the Langmuir relationship between adsorption and adsorbate concentration is linear. Linear 'initial mass' isotherms (IM) are consistent with the Langmuir isotherm at low adsorbate concentrations, and are useful for describing systems where removal and release processes occur in one experiment (Kaiser and Kaupenjohann, 1998; Nodvin *et al*., 1986). Likewise, there was a statistically linear relationship between SO_4 retention/release and SO_4 concentration in B1 and B2 soil at the low SO_4 concentrations used in this experiment (Figure 3). The slope of the IM isotherm reflects the ability of a soil to retain SO_4 (*i.e*. % of input SO_4 retained by adsorption), and can be used to compare SO_4 adsorption potentials among soils.

In general, despite a high native adsorbed SO_4 concentration, the slope of the initial mass isotherm for PC1-08 (0.29-0.35) was slightly less than that published for podzols at Hubbard Brook, NH (slope = 0.51) (Nodvin *et al*., 1986), but was similar to podzolic soil in NE Bavaria, Germany (0.10-0.49) (Kaiser and Kaupenjohann, 1998). In contrast, deeply weathered soils (oxisols) in the southeastern US have IM isotherm slopes that are close to unity, indicating almost 100% adsorption (Rose 1996; Shanley 1992).

HP6 - Sulphate adsorption

Similar to PC1-08, the amount of SO_4 removed from solution increased as the concentration of SO_4 in FFL increased, whereas SO_4 was released from soil at lower concentrations (Figure 4). However, the limit (x-intercept) between net adsorption and release was substantially lower in HP6 soil compared to PC1-08, and occurred at around 5 mg SO_4/l (Figure 4). Greater SO_4 retention at higher SO_4 additions in the HP6 experiments was not a result of increased soil acidity, because soil *p*H following equilibration with SO_4 solutions was similar among all 5 treatments (Table 2). Gobran and Nilsson (1988) similarly found that the addition of SO_4 to soil at concentrations as high as 1500 mg SO_4/l did not affect soil *p*H likely due to strong buffering by Al and organic acids.

Figure 3. Relationship between SO_4 applied (mg/kg) and SO_4 removed or released (mg/kg) in PC1-08 upper (solid) and lower (dashed) mineral soil, respectively (Initial Mass isotherm).

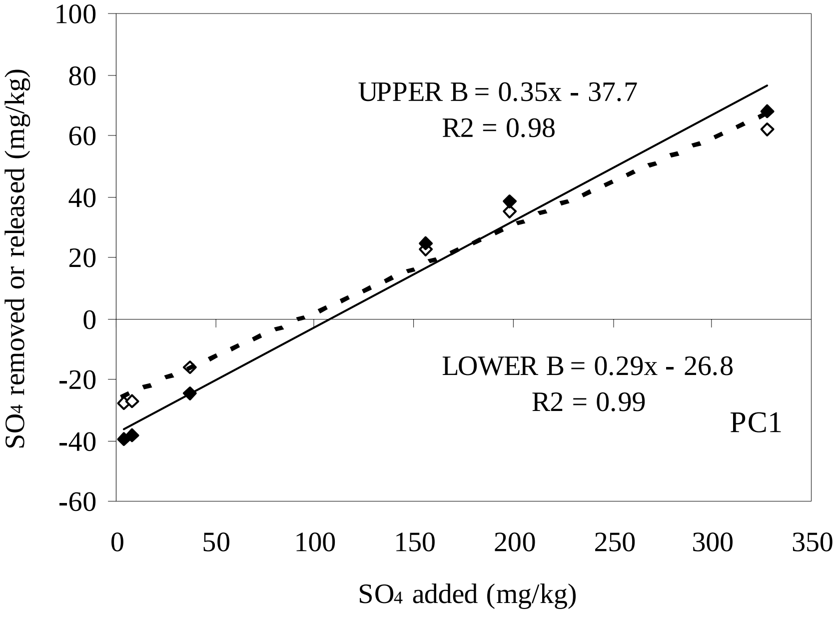


Figure 4. Relationship between SO_4 (mg/l) in treatment solution and SO_4 removed or retained (mg/kg) in HP6 mineral soil (Langmuir adsorption isotherm).

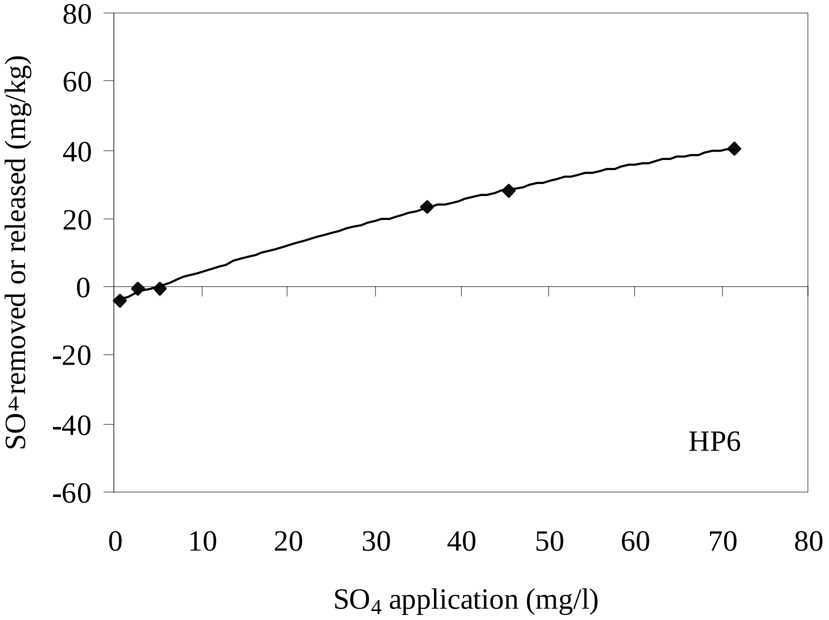


Figure 5. Relationship between SO_4 applied (mg/kg) and SO_4 removed or released (mg/kg) in HP6 soil (Initial Mass isotherm).

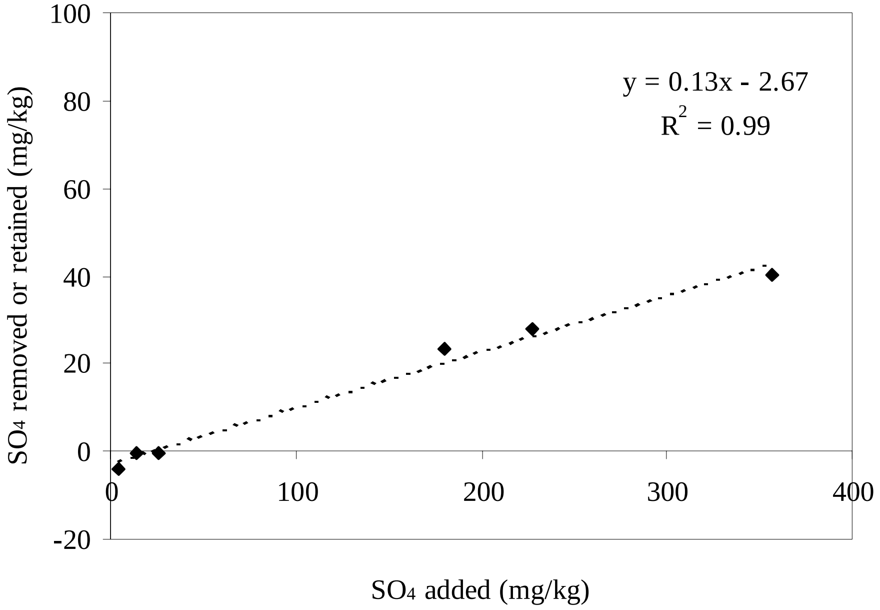
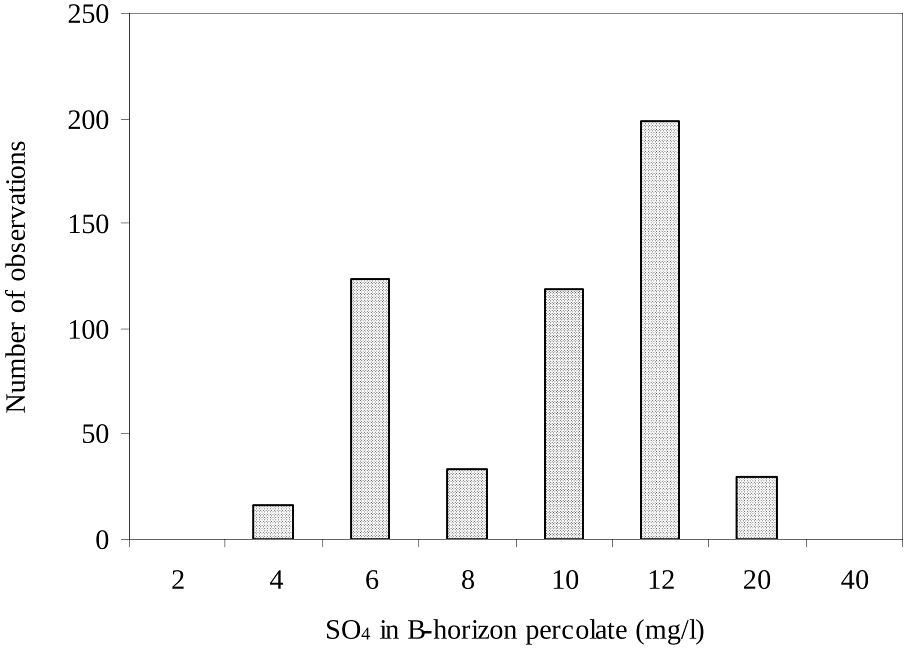


Figure 6. Histogram of SO_4 concentration (mg/l) in B-horizon percolate at PC1-08. Data collected between 1987 and 1995 (OMOE, *unpublished*).



Application of the Langmuir adsorption isotherm to HP6 soil yielded estimates of K_{max} and K_s of 125 mg/kg and 129 mg/l, indicating that similar to PC1-08, soil at HP6 is capable of adsorbing more SO_4 if inputs were to increase. The adsorption maximum at HP6 is approximately 1/3 of that at PC1-08, but both PC1-08 and HP6 have substantially higher adsorption maximums than soil at Lac Laflamme, QC (K_{max} = 45 mg/kg) (Houle and Carignan 1995). The slope of the initial mass isotherm for HP6 soil (0.13) was lower than at PC1-08, indicating that despite a potentially high capacity for additional SO_4 adsorption that the proportion of SO_4 retained by soil at HP6 per unit SO_4 addition (*i.e*. 13%) is relatively small (Figure 5).

Table 2. Measured *p*H in HP6 soil filtrates. Soils were shaken for 1-h with SO_4 solutions of varying concentration, centrifuged and then filtered. Averages are of 4 replicates, +/- SD.

	pH of filtrate
Treatment 1-FF	4.44 ± 0.05
Treatment 2	4.43 ± 0.01
Treatment 3	4.53 ± 0.09
Treatment 4	4.41 ± 0.01
Treatment 5	4.42 ± 0.09
Treatment 6	4.32 ± 0.02

PC1-08 - Sulphate desorption

The limit between adsorption and desorption in soil at PC1-08 (x-intercept) occurred at 18 mg/l in the lower B (B2) and at 20 mg SO_4/l in the upper B (B1) (Figure 1). In comparison, the average current (1999/00-2000/01) SO_4 concentration in LFH percolate at PC1-08 is 5.3 ± 2.8 mg/l, with a range over this period of 0.3 to 10.4 mg/l. In previous years of monitoring (1987-1993), a maximum of 42 mg SO_4/l in LFH percolate was measured, although concentrations were generally less than 20 mg/l (Figure 2). According to these results, SO_4 should be consistently released from B soil at SO_4 concentrations that are currently measured in LFH percolate. For example, at an input SO_4 concentration of ~ 6 mg/l in LFH solution, approximately 19 mg SO_4/kg should be released from the lower B (B2), and ~ 30 mg/kg should be released from B1 (Figure 1). These values constitute approximately 4 and 3% of their respective adsorbed levels in lower and upper B soil. Hern (1990) similarly found that SO_4 was consistently released from PC1-08 soil at SO_4 additions less than 10 mg SO_4/l, and Foster (1986) reported that an input SO_4 concentration of >12 mg/l was required to initiate SO_4 retention in Bhf1 soil (4-7 cm beneath the LFH) at the Turkey Lakes watershed.

Some authors have suggested that the y-intercept of the adsorption curve is a reflection of the amount of soluble SO_4 present in soil (Shanley 1992). Water-extractable SO_4 concentrations in B1 and B2 soil at PC1-08 were identical to the y-intercepts of the B1 and B2 adsorption curves (42 mg/kg and 30 mg/kg, respectively), because the lowest SO_4 concentration in FFL treatment solution (0.8 mg/l) was almost zero (Figure 1). However, if the amount of SO_4 released at 0 mg SO_4/l is expressed in mg/l of soil water, then an average of 89 mg SO_4/l is calculated, which is much higher than SO_4 concentrations typically measured in B-horizon percolate at PC1-08 (Figure 6). It is more likely that water liberates part of the weakly adsorbed SO_4 that is retained by electrostatic forces in soil (Fuller *et al*., 1985; Sharpley *et al*., 1992). Sulphate concentrations measured in water extracts, therefore, may not be representative of dissolved SO_4 in soil solution. Furthermore, if SO_4 measured in water extracts is indicative of native soluble SO_4, then presumably all soluble SO_4 should be liberated in a single water extraction. However, Neary *et al*. (1987) reported that SO_4 continued to be released from PC1-08 mineral soil after 6 sequential distilled water extractions, whereas SO_4 concentrations in water extracts of LFH and Ae material declined to below detection after 3 or 4 successive washes. They concluded that distilled water may be capable of removing part of what is considered to be adsorbed SO_4 (Neary *et al*., 1987). Van Stempvoort *et al*. (1992) similarly found that SO_4 concentrations calculated per liter soil water were substantially higher than SO_4 concentrations in soil percolate, and suggested that part of the 'excess' water-soluble SO_4 was non-specifically bound SO_4, which was released due to the change in ionic strength brought about by the addition of de-ionized water to soil.

HP6 - SO_4 desorption

While the chemistry of soil percolate is not currently measured at HP6, lysimeter data from the near by HP4 catchment are available from 1987-1992. The average SO_4 concentration in LFH percolate over this period was 4.9 ± 3.4 mg SO_4/l, with a maximum and minimum of 24.4 and 0.40 mg/l, respectively (Ontario Ministry of Environment, *unpublished data*). If we assume that HP4 and HP6 have similar LFH chemistry, and that the current SO_4 concentration in LFH percolate is comparable to the previous average of 4.9 mg/l, then SO_4 release from B-horizon soil should be in approximate balance with current inputs (*i.e*. no net release). It is more likely however, that SO_4 concentrations in LFH percolate at HP4 (and by inference HP6) have decreased since 1992 (see Chapter 4 for temporal trend in LFH [SO_4] at PC1-08), and are currently lower than 5 mg/l. These results predict that SO_4 is desorbed from mineral soil at HP6 at SO_4 concentrations in LFH percolate less than 5 mg/l.

Comparison of desorption results with current net export of SO_4 from catchments

Mass balance budgets for a number of catchments in the Muskoka-Haliburton region indicate that SO_4 export in drainage water exceeds input in bulk deposition in most years of record by 1 to 37 kg SO_4/ha/year (Chapter 2). Assuming that this apparent net export is at least partly from an internal S source, and is not entirely due to the underestimation of inputs through dry deposition or weathering, then SO_4 desorption is a plausible explanation. In most forested catchments, more than 90% of the total S storage is present in soil, and a substantial amount of S in soil may occur as adsorbed SO_4 (Mitchell *et al*., 1992). At PC1-08, it was estimated that adsorbed SO_4 constitutes approximately 1/3 of the total S found in the B-horizon, with the remainder present in organic forms (Neary *et al*., 1987). Given the large size of the adsorbed S pool (~290 kg S-SO_4/ha) at PC1-08 relative to annual SO_4 inputs in deposition (6-8 kg S-SO_4/ha/year), and the relationship between decreased SO_4 concentrations and SO_4 release from soil, the adsorbed pool at PC1-08 represents an important potential source of SO_4 export.

It should be noted, that PC1-08 soil used in this experiment had a native adsorbed SO_4 concentration which was at the upper limit of the range of adsorbed SO_4 concentrations previously measured in this catchment (*e.g*. Neary *et al*., 1987). In addition, samples were only collected from 3 pits and, as such, these results cannot be interpreted as representative of the entire catchment. However, it may be argued that adsorption/desorption isotherms are only useful for predicting SO_4 export in streams if soil samples are collected from the 'horizon of last contact' (O'Brien and Hendershot, 1993), and therefore represent the last horizon that soil water percolates through prior to discharging to the stream. Very few adsorption/desorption studies however, have used such as sampling strategy, making it difficult to extrapolate results published in the literature to the field situation (*e.g*. Gobran and Nilsson, 1988; Harrison *et al*., 1989; Houle and Carignan, 1995). Similarly, the sampling strategy used in this study was not structured to evaluate the adsorption/desorption properties of soils at the terminus of the soil percolate pathway. Nevertheless, in order to get a rough approximation of the magnitude of SO_4 desorption that would occur from PC1-08 soil with a high native adsorbed SO_4 content, we extrapolated the Initial Mass isotherm results to the catchment scale using the current average SO_4 concentration in LFH percolate (6 mg/l) and an annual runoff value of 0.5 m (Scheider *et al*., 1994). Assuming 100% of the runoff passes through the LFH horizon, approximately 103.5 kg SO_4 would be input to the B-horizon. If 103.5 kg SO_4 were to fully mix with soil in the B-horizon (200 kg/m^2), this would result in a SO_4 input of ~15 mg/kg. Applying this value to the Initial Mass isotherm equation for lower PC1-08 B-horizon soil (Figure 3), approximately 22.4 mg SO_4/kg should be desorbed from soil at this level of input, which translates to a flux of 45 kg SO_4/ha from the catchment. Annual net SO_4 export estimates for PC1-08 are generally less than 45 kg/ha/yr (7-28 kg SO_4/ha/yr; see also Chapter 4), and net export was 10 kg/ha in 2000/01. Differences between measured and predicted SO_4 export, respectively may in part be due to the fact that soil samples used in this study were relatively enriched in adsorbed SO_4 compared to previous reports, and likely don't represent soil from the horizon of last contact. Soil with a lower native adsorbed SO_4 content would release less SO_4 through desorption at a given level of SO_4 input.

Less is known about S storage in soil at HP6, although soils in this catchment are generally deeper than at PC1-08 (Dillon *et al*., 1991; Watmough and Dillon, 2002). Nevertheless, it was estimated that the adsorbed pool at HP6 was approximately 1/5 of that at PC1-08 although the magnitude of net SO_4 export from HP6 is similar to, or greater than that estimated for PC1-08 (Chapter 2). It should be remembered, however, that pool estimates for HP6 are based on adsorbed SO_4 measurements at only 3 pits within the 10 ha catchment, and as such are highly uncertain. Similar to PC1-08, isotherm calculations were extrapolated to the catchment scale assuming a current SO_4 concentration in LFH percolate at HP6 of 3 mg/l. Using a similar calculation to that presented for PC1-08 above, and a runoff value of 0.5 m/yr, it was estimated that ~150 kg SO_4 would be input to the B-horizon annually in LFH percolate. Assuming complete mixing with mineral soil (600 kg/m^2 -average soil depth at HP6 ≈ 3X PC1-08), 150 kg SO_4 would correspond to an input of 2.5 mg/kg to the B-horizon. Application of this value to the Initial Mass isotherm equation for HP6 (Figure 5) predicts a net release of –2.34 mg/kg from HP6 soil, which translates to an annual net export of 14.1 kg/ha. This value is substantially lower than field estimates of HP6 net export (average 25 kg/ha/yr, see also Chapter 2). Similar to PC1-08, extrapolated values from HP6 experiments do not approximate field estimates, which implies that laboratory results do not adequately describe sorption reactions likely due to simplifications associated with such extrapolations, and because soils used in experiments were not representative of the soils which affect stream chemistry. In addition, other internal sources, such as the organic-S pool, may contribute to net SO_4 export *via* mineralization reactions. Indeed, a number of authors have argued that although the adsorbed pool is responsive to changes in input SO_4 concentration, that SO_4 release through mineralization of the relatively large organic S pool is also an important long-term source of SO_4 export from catchments (*e.g*. Driscoll *et al*., 1998; Feger 1995; Houle and Carignan, 1995). Certainly at PC1-08, the organic S pool is approximately 2-times larger than adsorbed SO_4, and while we do not have any data on total S concentrations at HP6, it is assumed that organic S storage is similarly large in this catchment.

In order to achieve a more realistic assessment of the contribution of desorption to net SO_4 export from catchments, we suggest that soils should be sampled from the horizon of last contact, or the soil horizon through which percolate passes immediately prior to discharging to the stream. Previous hydrological studies in the PC1-08 upland have shown that the majority of storm flow in the late spring and fall is produced from water that passes vertically through the soil profile to the soil/bedrock interface, where it then flows laterally to the stream channel (Peters *et al*. 1995; Renzetti *et al*., 1992). As water percolates through mineral soil, SO_4 may be retained or released depending upon the physical and chemical characteristics of the particular horizon of contact. Therefore at PC1-08, soil at the bedrock interface would be the ‘horizon of last contact’ and the adsorption/desorption properties of these soils may be the most important for determining SO_4 export in drainage waters. It should be noted however, that the horizon of last contact may not always correspond to the deepest soils, but will depend on the primary hydrologic flow paths within a catchment. For example, soils located adjacent to the stream riparian zone or on lower slopes may be particularly important for determining whether SO_4 in upland soil drainage contributes to SO_4 export in stream flow (*e.g*. Dail and Fitzgerald, 1999). Furthermore, if intense storm events generate mainly surface flow - which tends to occur following dry periods when the forest floor is hydrophobic (Biron *et al*., 1999), then runoff will completely by-pass adsorption sites in the mineral soil. This discussion indicates that simple interpretation of adsorption/desorption isotherms will not be sufficient for predicting the response of mineral soil to changes in deposition, and acidification models must also consider the effect of varying hydrology (flowpaths, rainfall patterns) on chemical exports from mineral soil. Of further note, is that mineralization of organic-S compounds in both surface and mineral soil may provide a continuous input to the adsorbed SO_4 pool (Bohn *et al*., 1986), and further complicate predictions of SO_4 retention or release through adsorption/desorption reactions.

In conclusion, results of these experiments indicate that SO_4 release and retention in soil from both PC1-08 and HP6 are responsive to changes in input SO_4 concentration. According to adsorption isotherms, SO_4 should be consistently released from B-horizon soil at PC1-08 and likely also HP6 at the range of SO_4 concentrations encountered in the field, and soils are not in equilibrium with current SO_4 input (Figures 1 and 4). Furthermore, HP6 soil that has a relatively small pool of adsorbed SO_4 may release less SO_4 in response to reduced SO_4 inputs (*i.e*. through deposition), and respond more rapidly to changes in deposition than soils with a high native adsorbed SO_4 content such as PC1-08. These experiments, however, were based on a limited collection of soil that was not spatially representative of each catchment, and more sampling would be necessary to adequately characterize adsorption reactions and pools at each catchment. Nevertheless, the magnitude of potential desorption calculated for HP6 and particularly PC1-08 indicates that desorption may be an important source of SO_4 export in Muskoka-Haliburton catchments and should be considered when predicting the response of catchments to changes in deposition.

CHAPTER 7: SULPHUR ISOTOPE RATIOS IN A CANADIAN SHIELD CATCHMENT

ABSTRACT

The isotopic composition of SO_4 in bulk deposition, soil percolate and streams flowing into, and draining a conifer-*Sphagnum* swamp were monitored over a 12-month period in a forested catchment in south-central Ontario. After 12-months, a ^{34}S-enriched tracer was applied to plots within the upland and wetland parts of the catchment, and monitoring of the tracer's fate continued for another 12-months. The isotopic composition of bulk deposition did not vary greatly over the entire monitoring period and was on average, +5.2 ± 0.6‰. Prior to tracer application, the isotopic signature of soil percolate (+4.4 ± 0.4‰) was similar among horizons, and tended to be slightly lower than in deposition. Similarly, before the tracer was applied, the isotopic composition of upland-draining stream water did not vary greatly over time, but was slightly higher than in deposition or soil percolate (+5.7 ± 0.7‰). Small differences in isotopic composition among bulk deposition, soil percolate and stream water, respectively, indicate that there is little isotopic fractionation associated with S-transformations in the upland catchment. In contrast, S-isotope signatures in stream water draining the swamp were more variable over time, and were higher than in precipitation (average +8.6 ± 2.6‰). Higher $\delta^{34}SO_4$ values in the swamp outlet compared to deposition and the upland-draining inflow to the swamp are likely a result of kinetic isotope effects associated with dissimilatory sulphate reduction in peat. Consistently lower SO_4 concentrations in the swamp outflow (average 4.5 ± 1.9 mg/l) compared to the upland-draining inflow (average 7.2 ± 0.8 mg/l) are consistent with the prevalence of reducing conditions in saturated peat. The application of a ^{34}S-enriched tracer (total 1 mg ^{34}S) to plots within the swamp had no effect on the $\delta^{34}SO_4$ of the swamp outflow, likely due to isotope dilution in the large S pool in peat. In contrast, the $\delta^{34}SO_4$ signature in soil percolate and stream water increased (maximum +14.7‰) following application of ^{34}S to plots in the hillslope and streambed, although the effect was temporary, and S-isotope signatures in soil percolate returned to pre-tracer values

within 1 month of tracer application, whereas enriched $\delta^{34}SO_4$ values were measured in stream water for at least 2 months following the application.

INTRODUCTION

Stable S isotopes ratios can be used to investigate biogeochemical processes involved in S-cycling in catchments (*e.g*. Krouse and Tabatabai, 1986; Mitchell *et al*., 2001). Two types of approaches have been used; the first involves the application of S with an isotopic composition that is distinct from S sources and pools within the system of study, whereas the other involves an evaluation of changes in the natural abundance of S isotopes both among system components, or over time. Studies of the former type have generally involved the application of large quantities of isotopically distinct S, because most readily available S tracers (*e.g*. gypsum) have $\delta^{34}S$ signatures that are only ~5-25‰ higher than ambient deposition or geologic sources of S. For example, Prietzel *et al.* (1995) added S ($\delta^{34}S$ = +28‰) at a maximum rate of 87 kg S-SO_4/ha, whereas Gieseman *et al*. (1995) applied fertilizers with $\delta^{34}S$ values of +10.2 and +13.7‰ at a rate of 170 kg S-SO_4/ha to sites in southern Germany, where deposition has an average $\delta^{34}S$ of +7.4‰ (Mayer *et al*., 1995). Tracer applications have been used to evaluate the residence time of S in systems and to follow the fate of S applied in simulated deposition.

Changes in the natural abundance of S-isotopes can be used to elucidate S-transformations and sources in catchments, since the S-isotopic composition of a particular ecosystem component is a product of the isotopic composition of sources (and their mixing ratios), and fractionation processes that occur during S-transformations (Alewell *et al*., 1999; Hesslein *et al*., 1988). Some S transformations result in negligible fractionation (adsorption, desorption, precipitation) (*e.g*. Van Stempvoort *et al*., 1990), whereas others have been shown to be selective for the lighter ^{32}S. For example, plant uptake, or assimilatory sulphate reduction (ASR) might be slightly preferential to ^{32}S, resulting in $\delta^{34}S$ values in plant tissue that are 1 to 2‰ lower than the reactant SO_4 (Novak *et al*. 2001). Some studies have suggested that the microbial processes of immobilization and mineralization may also be slightly preferential to ^{32}S (Fuller *et al*., 1986; Mayer *et al*., 1995; Zhang *et al*., 1998). Immobilization and mineralization would tend to have opposing effects on the isotopic composition of SO_4 in soil solution, since immobilization should produce ^{32}S-enriched organic-S compounds in soil and leave residual reactant SO_4 in soil solution relatively enriched in ^{34}S (*i.e*. higher $\delta^{34}S$), whereas preferential mineralization of ^{32}S-enriched organic-S should release SO_4 with a lower $\delta^{34}S$ signature. However, isotopic fractionations associated with immobilization and mineralization, respectively are generally small, and differences in $\delta^{34}S$ signatures between reactants and products are normally only ~1-4 ‰ (Mayer *et al*., 1992). In contrast, dissimilatory sulphate reduction (DSR), which occurs under anaerobic conditions, results in marked isotopic fractionation between the ^{32}S-enriched product (lower $\delta^{34}S$) and ^{34}S-enriched reactant SO_4 (higher $\delta^{34}S$), because bacteria preferentially reduce the lighter ^{32}S (Krouse and Tabatabai, 1986). Therefore saturated peat generally has a lower (or more negative) $\delta^{34}S$ signature than SO_4 in bog porewaters, although substantial shifts in $\delta^{34}S$ signatures in wetland outflows may occur following periods of water table drawdown and subsequent exposure of previously submerged peat (Mandernack *et al*. 2000).

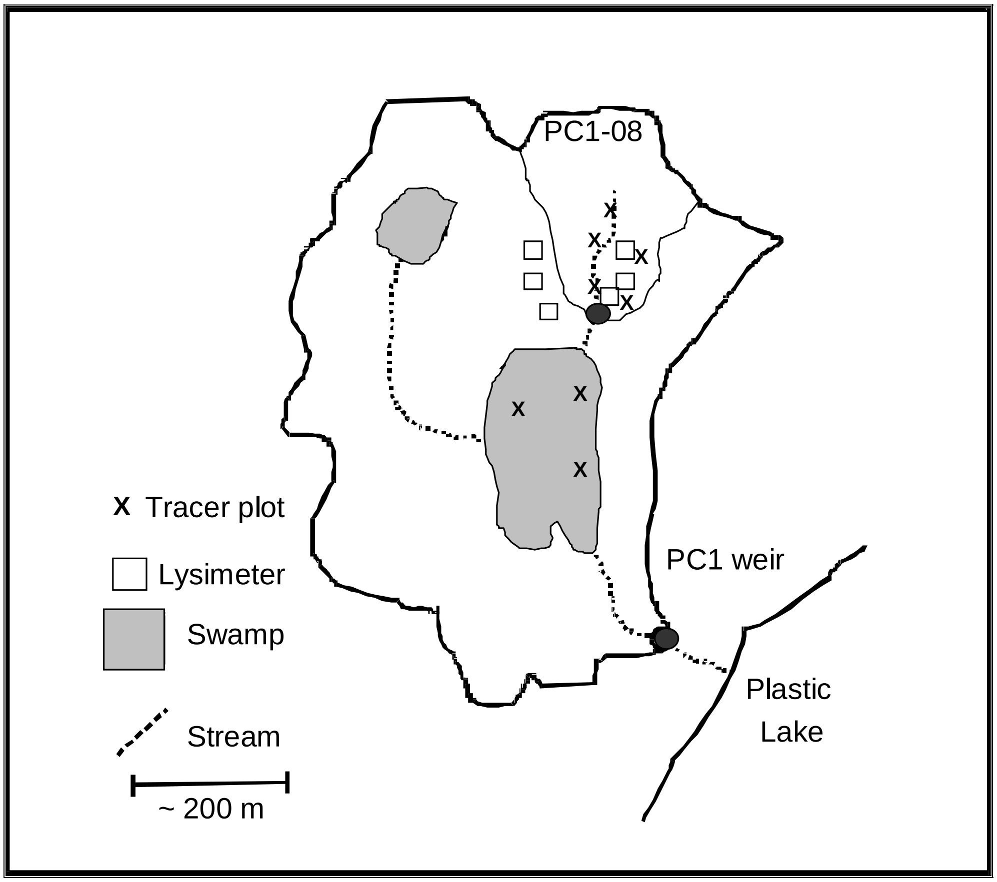
In the Muskoka-Haliburton region, S-inputs through weathering are negligible due to the low S-content of granite bedrock, and slow weathering rates (Jeffries and Snyder, 1983; Watmough and Dillon, 2001), and therefore deposition is the primary input of S to catchments. The aim of this study was to compare the isotopic composition of deposition to isotope ratios in soil percolate, upland stream water, and stream water exiting a conifer *Sphagnum* swamp in the Plastic Lake-1 catchment, to determine whether there was evidence of DSR in the upland and wetland, respectively. In addition, a ^{34}S-enriched (99.8%) SO_4 tracer was applied in simulated rainfall to plots within the upland hillslope, streambed and wetland, respectively in order to investigate the transit time for atmospherically-deposited SO_4 in different parts of the catchment. In contrast to other tracer applications, only a very small application of ^{34}S was required to alter the isotopic composition of material within plots, because the ^{34}S content of the tracer (*i.e*. 99.8% ^{34}S) was substantially higher than that of naturally present S, or of S in deposition (~4.4% ^{34}S).

METHODS

Study Site

The study was conducted in the 23.3 ha Plastic Lake-1 (PC1) catchment, located in Haliburton County, south-central Ontario. The catchment is underlain by granitic gneiss bedrock, and is covered by thin surficial deposits (<1 m) and generally thin (average 40 cm), coarse-textured (90% sand) humo-ferric and ferro-humic podzols. The forest at PC1 is primarily coniferous, and is dominated by white pine (*Pinus strobus*) and eastern hemlock (*Tsuga canadensis*). The PC1 catchment is drained by a first-order stream (PC1) which passes through a 2.2 ha swamp before discharging into Plastic Lake (Figure 1). White cedar (Thuja occidentalis) and black spruce (Picea mariana) dominate the swamp, with extensive *Sphagnum* ground cover. More than 85% of the runoff draining PC1 passes through this swamp prior to exiting into the lake, and as a consequence, within-swamp processes exert a strong control on the chemistry of the PC1 stream (Devito and Hill, 1999). A separately gauged intermittent stream drains an entirely upland sub-catchment of PC1 (PC1-08, 3.45 ha) before entering the swamp along its north-east border (Figure 1).

Figure 1. Plastic Lake-1 (PC1) study catchment. Location of lysimeters and tracer application plots are indicated.



Four, zero-tension lysimeters (installed in 1987) are located at various locations in the upland part of PC1 (Figure 1), and were used to collect soil percolate from beneath the LFH, Ae and B-horizons for chemical and isotopic analyses.

As part of a separate study, a ^{34}S-enriched tracer (99.8% ^{34}S) was applied in synthetic rainfall to 2 plots in the upland, and to 3 plots in each of the stream bed and swamp on August 15, 2000. An earlier application date was originally planned for (June), however wet conditions in the swamp and upland stream during June and July necessitated a delayed application date. The chemistry of the synthetic rainfall was similar to the current deposition at PC1, and the *p*H was adjusted with HCl to ~4.7 (Table 1). The objective of the tracer application was to assess the transit time of atmospherically deposited SO_4 at ambient levels. In total, 0.33 mg of ^{34}S was applied as SO_4 to each of 2, 2.4 m^2 plots on the hillslope, directly overlying lysimeter plates, to 2, 0.073 m^2 plots in the PC1-08 streambed, and to 2, 0.073 m^2 plots in the wetland (Figure 1). A higher dose (4.1 mg $^{34}S\text{-}SO_4$) was applied to 1 additional plot in each of the streambed and wetland (Figure 1). In total, 3L of labeled synthetic rainfall was applied to each lysimeter plot (equivalent to a 1.25 mm rain event), and 0.5L was applied to each stream or swamp plot (equivalent to a 6.8 mm rain event), containing either 0.33 mg $^{34}S\text{-}SO_4$ or 4.1 mg $^{34}S\text{-}SO_4$. Due to the very small mass of ^{34}S added relative to the size of the natural S pools in plots, the tracer was not expected to have a substantial or long-lasting effect on the $\delta^{34}SO_4$ signature of soil percolate or stream water. The range in S concentrations in forest floor (LFH), B-horizon mineral soil and peat at PC1 are 1000-2000mg S/kg, 300-600 mg S/kg and 2000-7000 mg S/kg, respectively. For example, assuming complete mixing of 0.33 mg $^{34}S\text{-}SO_4$ in the top 10cm of peat in a 0.073m^2 plot (bulk density = 0.13 g/cm^3), and a background δ^{34}S signature in peat of +2‰ at 4000 mg S/kg, the expected δ^{34}S in peat following application of the tracer would be +4.1 ‰. It was for this reason that a higher application of ^{34}S (4.1 mg) was added to 1 plot in each of the stream and wetland.

Table 1. Major element concentrations (µeq/l) in synthetic rainfall used in tracer application, compared to bulk deposition chemistry at PC1. The *p*H of synthetic rainfall was adjusted to 4.7 using HCl.

	SO_4	*Ca*	*Mg*	NH_4-N	NO_3-N	p*H*
Synthetic Rainfall	42	26	15	38	38	4.7
Bulk deposition (average 1993-1998)	42	12	3.2	28	36	4.4

Table 2. Average seasonal volume-weighted sulphate concentrations (µeq/l) in deposition at PC1

	1999-00	*2000-01*
Summer (June-August)	54	33
Fall (September-November)	46	64
Winter (December-February)	25	23
Spring (March-May)	50	52

At the time the tracer was applied to plots in the streambed, the water table in the stream was at least 19 cm below the sediment surface at the weir, and there was zero flow. In contrast, the stream exiting the swamp (PC1) flowed nearly continuously during the summer of 2000. The wetland plots were located near the swamp perimeter in order to avoid areas with ponding, or lateral flow, however the water table in the swamp plots was generally within 5-8 cm of the peat surface throughout the monitoring period.

Table 3. Mean (±SD, n) monthly $\delta^{34}S$ signatures in bulk deposition, and in soil percolate from control and treatment lysimeters. Soil percolate averages for August 2000 are for samples collected prior to application of the tracer on Aug.15.

	Bulk deposition	LFH		Ae		B	
		Treatment	Control	Treatment	Control	Treatment	Control
Jun-99	4.82 ± 0.52 (2)	4.45 ± 0.35 (2)	4.7	4.70 ± 0.21 (4)	3.75 ± 1.06 (2)	4.45 ± 0.21 (2)	na
Jul-99	4.7	4.27 ± 0.10 (2)	Na	4.41	na	4.60	na
Aug-00	5.09 ± 0.10 (3)	5.01	4.62	4.35	4.45	4.69 ± 0.69 (2)	4.31
Sept-00	4.85 ± 0.61 (5)	7.14 ± 0.86 (2)	5.79	7.85 ± 3.04 (2)	5.87	na	na
Oct-00	5.34	na	Na	na	3.02	na	na
Nov-00	5.66	4.88 ± 0.78 (5)	4.57	4.88 ± 0.45 (3)	4.65	4.3	na

Table 4. Total precipitation and average temperature in the summers (June-September) of 1999 and 2000, and number of days with zero stream flow, compared to the long-term averages at PC1 (20-year) and PC1-08 (7-year).

	1999-00	*2000-01*	*Long-term average*
Summer precipitation (mm)	274	331	235
Summer temperature (°C)	17.4	14.7	17.4
Number of contiguous days with zero stream flow at PC1 weir	8	0	30
Number of contiguous days with zero stream flow at PC1-08 weir	17	45	76*

Sample Collection and Analysis

Bulk deposition was collected less than 30 m away from the PC1 catchment boundary at a meteorological site maintained by the Ontario Ministry of Environment (Dorset), which also monitors precipitation depth and temperature. At least 2 L of deposition were required to produce enough SO_4 for isotope analysis, and samples from individual rain or snowfall events were occasionally bulked to provide sufficient sample for SO_4 extraction. Stream water samples for isotopic and chemical analyses were collected from the upland-draining PC1-08 and the wetland-draining PC1 stream, and soil percolate was collected from the 4 zero-tension lysimeters when there was sufficient sample for analysis. Water samples were analyzed for SO_4 by ion chromatography at the Ontario Ministry of Environment Dorset Research Centre.

Peat cores (60 cm) were extracted from 3 sites within the PC1 swamp in October 1999, using a Russian Peat Corer, and cores were sectioned into 10 cm depth intervals. Peat from different depth intervals was air-dried, and then ground in a Wiley Mill to obtain a fine powder. Samples were sent to the University of Waterloo Environmental Isotope Laboratory for $\delta^{34}S$ analysis.

Sulphate in filtered water samples (Whatman GF/F) was concentrated using BioRad AG 1-X8 ion exchange resin (100-200 mesh Cl^- form). Resin was first conditioned in 0.5 M NaCl and then rinsed with de-ionized water prior to packing in 2-cm diameter, 10-cm long plastic disposable columns (Evergreen Scientific Ltd.). A square of glass wool was placed at the resin surface to reduce resin dispersal and/or compaction while passing samples through the columns. Samples were poured into 2-L separatory funnels that were attached to columns *via* Tygon tubing, and a 0.45 μm filter was placed in-line between the funnel and column. Sample solutions were passed though anion exchange columns by gravity drainage, at a rate determined by filtration through the 0.45 μm filter, which was always less than 20 mL/min. Retained SO_4 was eluted from resin using 50 mL 0.5 M NaCl, followed by 100 ml de-ionized water. The eluent was acidified to *p*H<4.0

with HCl, and SO_4 was precipitated as $BaSO_4$ by the addition of excess $BaCl_2$ (0.5 M). Samples were heated and stirred for 10 minutes over a hot plate to promote precipitation of $BaSO_4$. The overlying solution was decanted to waste, and the remaining $BaSO_4$ precipitate was washed at least 3 times (ddH_2O) and oven dried (65°C) to a constant weight. All isotopic analyses were carried out at the University of Waterloo Environmental Isotope Laboratory, using a Micromass IsoChrom MG/EA isotope ratio mass spectrometer. Sulphur isotope ratios are expressed in the standard $\delta^{34}S$ notation as parts per thousand enrichment or depletion in the ratio of ^{34}S:^{32}S relative to the CDT standard:

$$\delta^{34}S_{sample}(‰) = \frac{^{34}S/^{32}S_{sample} - ^{34}S/^{32}S_{s\tan dard}}{^{34}S/^{32}S_{s\tan dard}} \times 1000$$

Monthly average $\delta^{34}S$ signals in deposition and stream water were weighted by the mass of SO_4 in deposition or stream water, respectively over the same time period. Isotope signals in soil percolate were not mass weighted since accurate estimates of percolate volume were not available.

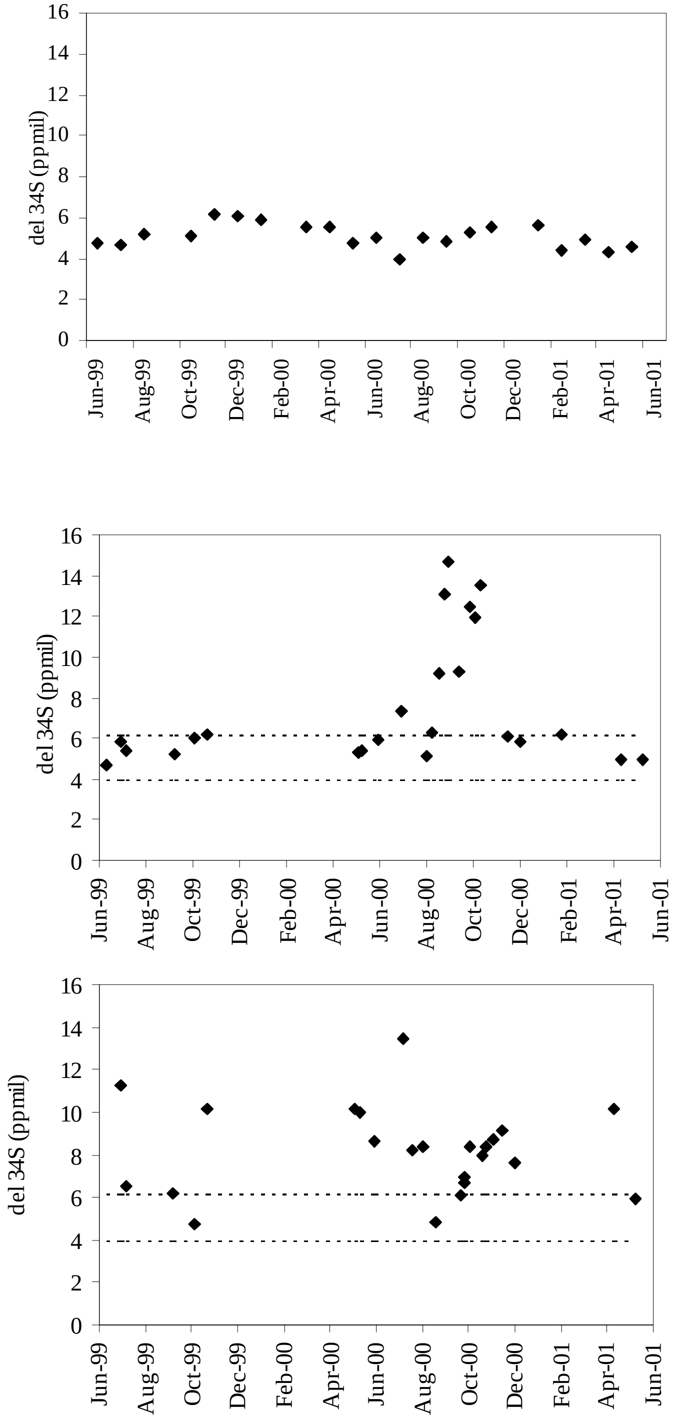
RESULTS & DISCUSSION

Bulk deposition

The S-isotopic composition of deposition at PC1 was fairly constant over the 1999/00-2000/01 monitoring period and $\delta^{34}SO_4$ ratios in individual measurements ranged from +4.0 to +6.8‰. Monthly averages varied between +4.0 and +6.2‰, with an overall mean of 5.1 ± 0.6‰ (Figure 2). Deposition $\delta^{34}SO_4$ ratios measured in this study were similar to those reported by Van Stempvoort *et al*. (1991), who measured $\delta^{34}SO_4$ values of +3 to +5‰ in precipitation at PC1 between 1986 and 1988. The isotopic composition of deposition appears to be fairly consistent in areas of eastern North America that are not influenced by marine sources. For example Hesslein *et al.* (1988) reported that the 3-year mean $\delta^{34}SO_4$ in precipitation at the Experimental Lakes Area in northwestern Ontario was +4.8‰, and the mean $\delta^{34}SO_4$ signature of deposition at the Hubbard Brook watershed in New Hampshire is around +4.4‰ (Alewell *et al*. 2000). Passage of deposition through the forest canopy (throughfall) does not appear to affect the isotopic composition of SO_4 (Torssander and Morth, 1998), and $\delta^{34}SO_4$ values in deposition and throughfall at Plastic Lake are similar (Van Stempvoort *et al*., 1992).

Although monthly average $\delta^{34}S$ values in bulk deposition fell within a fairly narrow range (~+4 to +6‰), there was a tendency toward lower $\delta^{34}S$ values in summer compared to winter months (Figure 2). A similar seasonal pattern in $\delta^{34}S$ in deposition at sites in the Great Lakes basin has been reported by Nriagu and Coker (1978), who suggested that lower $\delta^{34}S$ values in summer deposition may be due to the greater relative contribution of biogenic compounds (*i.e*. reduced S gases from wetlands) during the growing season. Gaseous S emissions from the PC1 wetland have not been measured, but due to the generally wet conditions and high water table levels in the summers of 1999 and 2000, SO_4 reduction rates in the PC1 swamp and other local wetlands may have been high (see PC1 section below). Sulphate concentrations in bulk deposition at PC1 (collector located < 100 m from wetland) and at 2 other collectors in the region (Harp, Heney) were relatively constant over the 2-year period, and monthly averages (volume-weighted) ranged from 1.3 to 2.8 mg/l. Sulphate concentrations in deposition were lower in the winter of both years, but concentrations were not always highest in the summer (Table 2).

Figure 2. δ^{34}S ratios (‰) in bulk deposition (top), upland-draining PC1-08 stream water (middle) and the PC1 swamp outflow (bottom) over a 2 year period in the PC1 catchment. Dashed lines indicate the range in δ^{34}S measured in bulk deposition.



Therefore other factors might contribute to lower $\delta^{34}S$ values in summer deposition, and Alewell *et al.* (2000) suggested that the temperature dependence of the isotopic shift during SO_4 formation in the atmosphere may explain lower $\delta^{34}S$ values in summer deposition at the Hubbard Brook Experimental Forest.

Isotopic composition of upland and wetland drainage waters prior to ^{34}S- tracer application

- *Soil Percolate*

The isotopic composition of soil solution collected by lysimeters was similar among all soil horizons prior to application of a ^{34}S-enriched tracer in August 2000, and was on average +4.4 ± 0.4‰ (Table 3). Van Stempvoort *et al*. (1990) reported a similar isotopic composition of soil seepage water at PC1 (+4.8 ± 1.2‰). The range in average monthly $\delta^{34}SO_4$ ratios in soil percolate prior to application of the tracer (+3.8 to +4.7‰) was not significantly lower than the corresponding range in $\delta^{34}SO_4$ ratios in deposition (Table 3). Although the period of soil percolate monitoring prior to tracer application is too brief to allow interpretation of isotope signals, it is useful to speculate on the potential for S-isotope fractionation in upland soils. For example, previous authors have reported a slight fractionation (-1 to -2‰) in $\delta^{34}S$ due to plant assimilation (*e.g.* Novak *et al*. 2001) and Van Stempvoort *et al*. (1991) reported $\delta^{34}S$ ratios in foliage, litter and humus at PC1 of 3.7, 3.7 and 3.5‰, respectively. Assuming lower values in plant material are due to preferential uptake of $^{32}SO_4$, then residual SO_4 in soil percolate should be correspondingly enriched in ^{34}S. However, if plant (or microbial) assimilation results in slightly lower $\delta^{34}S$ ratios in organic material, then decomposition and mineralization of S in litter and soil organic matter should release SO_4 with lower $\delta^{34}S$ values, which would counter the enrichment of ^{34}S in residual SO_4 due to plant uptake. Presumably the isotopic composition of SO_4 in soil solution could vary seasonally, particularly if the magnitude of SO_4 uptake or release by plants and soil microbes is large compared to the soluble SO_4 pool in soil, which would further complicate the interpretation of isotope ratios. However, Alewell *et al.* (1999) found that $^{34}SO_4$ ratios in stream water at the Hubbard Brook Watershed were consistently at least 1‰ lower than in bulk precipitation and suggested mineralization might be responsible. While lower $\delta^{34}SO_4$ values in soil percolate compared to annual averages in deposition at PC1 may indicate that part of the SO_4 in soil water is derived from the mineralization of organic S compounds, without a longer sample record it is difficult to make generalizations. It should also be noted that $\delta^{34}S$ signals in deposition are generally lowest during the summer months when the biological processes which are reported to favour the release of ^{32}S (*i.e.* mineralization) are most active. In summary, due to the relatively small isotopic fractionations associated with immobilization or plant uptake and mineralization, S-isotope ratios appear to be unsuitable for distinguishing among S-transformations in aerobic upland soils. Van Stempvoort *et al.* (1992) came to a similar conclusion from their analyses of $\delta^{34}S$ signatures in the PC1 catchment and another site in southwestern Ontario.

- *Upland-draining stream (PC1-08)*

Prior to application of a ^{34}S tracer to plots within the hillslope and streambed, the $\delta^{34}SO_4$ signature in PC1-08 stream water ranged between +4.7 and +7.4‰, and was on average +5.8 ± 0.7‰ (Figure 2). Similarly, the concentration of SO_4 in PC1-08 did not vary greatly over time (5.0 – 8.6 mg/l), and was on average 6.6 ± 0.8 mg/l during the monitoring period. Upland stream water $\delta^{34}SO_4$ ratios were higher than in soil percolate from the B-horizon (Table 3), despite similar SO_4 concentrations in B-percolate and PC1-08 (see Chapter 4). PC1-08 stream water $\delta^{34}SO_4$ ratios were also slightly higher than in bulk deposition (+5.1 ± 0.6‰) (Figure 2). Again, due to the paucity of soil percolate samples prior to tracer application it is difficult to attribute statistical significance to differences in $\delta^{34}S$ values between percolate and upland stream water; however, they are suggestive of fractionation processes occurring in the streambed. Microbially mediated dissimilatory sulphate reduction (DSR), which favours the incorporation of ^{32}S in reduced products and leaves reactant SO_4 relatively enriched in ^{34}S could be responsible for higher $\delta^{34}S$ values in PC1-08 stream water. Furthermore, negative $\delta^{34}S$ values have been measured in subsurface stream sediment (Table 5), which is consistent with the occurrence of DSR in the streambed. Total S and organic matter concentrations in stream sediment are also high compared to upland mineral soil (Table 5).

Table 5. Loss on ignition, total carbon and sulphur concentrations and $\delta^{34}S$ ratios in upland mineral soil and stream bed sediment at PC1-08.

Site	Depth interval	OC (g/kg)	S (mg/kg)	$\delta^{34}S$ (‰)
Upland	10-30 cm beneath LFH	43	350	5.2
Stream channel	0-10 cm beneath LFH	419	900	-0.03
Stream channel	10-40 cm beneath LFH	162	680	-4.9

However, despite the prevalence of generally wet and cool conditions, stream flow in PC1-08 ceased for 17, and 45 days in the summer/fall seasons of 1999/00 and 2000-01, respectively (Table 4). Previous work has shown that the water table in the PC1-08 streambed must be *at least* 19 cm below the sediment surface at the weir before stream flow ceases. Given the average soil depth in the streambed at PC1-08 is around 60 cm, a water table decline of 19 cm amounts to a substantial exposure of stream sediment which has a low or negative $\delta^{34}S$ signature. It was therefore expected that $\delta^{34}S$ values in stream water would decrease and SO_4 concentrations would rise following dry periods because of the release of ^{32}S-enriched SO_4. However, this was not the case, and $\delta^{34}S$ values in PC1-08 stream water were fairly consistent over time despite large variations in flow and there was no apparent relationship between $\delta^{34}S$ and stream SO_4

concentration (Figure 3a). For example, following a 9-day dry period in July 1999 with zero flow, the $\delta^{34}SO_4$ in PC1-08 immediately following resumption of flow was +5.2‰. One possible explanation for these inconsistencies is that DSR occurs primarily in pockets of deep sediment that remain saturated except during extremely dry periods with large water table draw downs. However, we currently do not have the data to confirm this hypothesis.

Wetland-draining stream (PC1)

In contrast to the upland-draining PC1-08 stream, the isotopic composition of stream water draining the conifer *Sphagnum* swamp (PC1) was variable and $\delta^{34}S$ ratios in PC1 were generally higher than in deposition (Figure 2). Prior to addition of a ^{34}S enriched tracer to plots within the wetland, the $\delta^{34}SO_4$ signature in the swamp outflow ranged from +4.8 to +13.5‰, and was on average +8.6 ± 2.6 ‰ (Figure 2). The mean SO_4 concentration in the swamp outflow was 4.5 ± 1.9 mg/l and ranged from 0.45 to 8.6 mg/l over the same period. Similar to PC1-08, there was no apparent relationship between $\delta^{34}S$ ratios in PC1 stream water and SO_4 concentrations (Figure 3b).

In contrast to the upland-draining PC1-08 stream, isotopic fractionations associated with DSR can explain high $\delta^{34}SO_4$ ratios in the swamp outflow. While stream flow ceased in PC1-08 in both 1999 and 2000, flow in PC1 was maintained almost continuously except for 8 days in 1999 (Jul. 29-30, Aug. 3, Sept. 1-5) (Table 4). The relationship between water table height in the swamp and daily flow in PC1 indicates that the water table was within 6 cm of the peat surface at flow rates greater than 10,000 l/d (Figure 4a). Therefore, only the top several centimeters of peat would have been exposed to air in either year (Figure 4b), and peat would have remained saturated for the majority of time.

Figure 3a. δ^{34}S-SO$_4$ (‰) in PC1-08 stream water versus SO$_4$ concentration (mg/l)

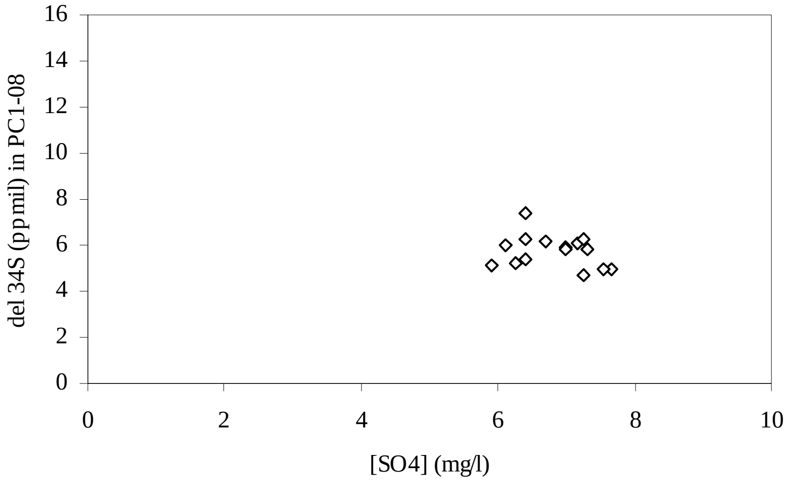


Figure 3b. δ^{34}S-SO$_4$ (‰) in PC1 stream water versus SO$_4$ concentration (mg/l)

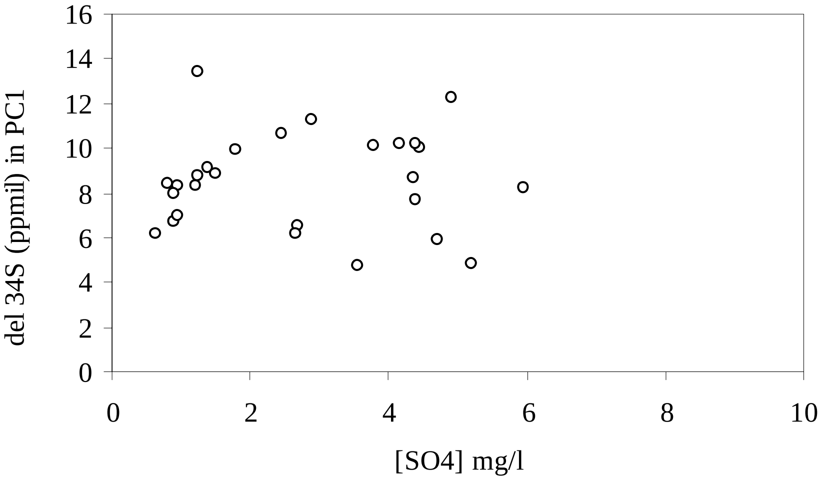


Figure 4a. Relationship between daily flow in PC1 (l/day) and water table height in the wetland relative to the peat surface (cm).

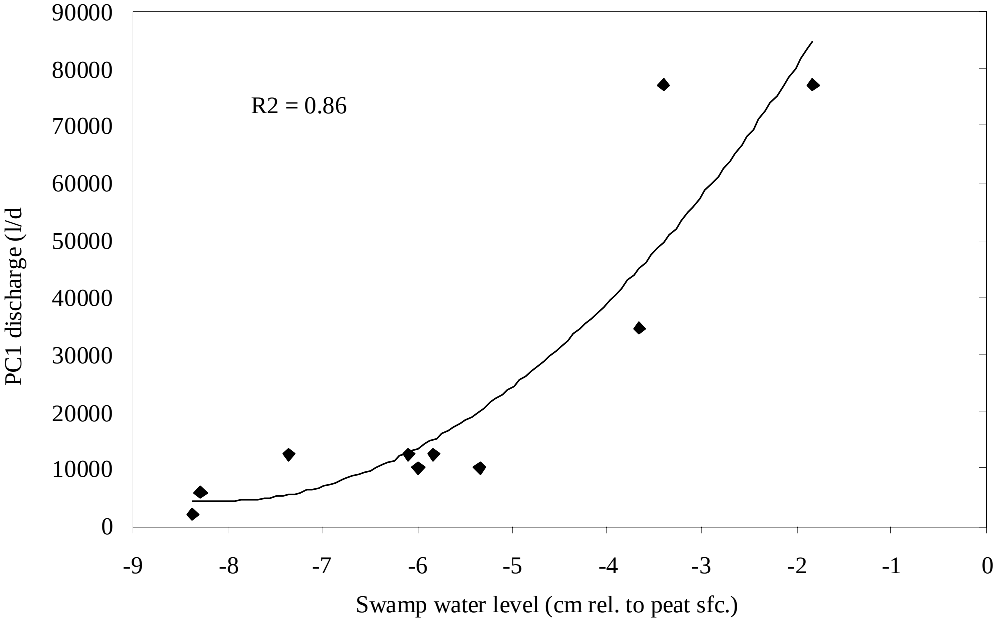
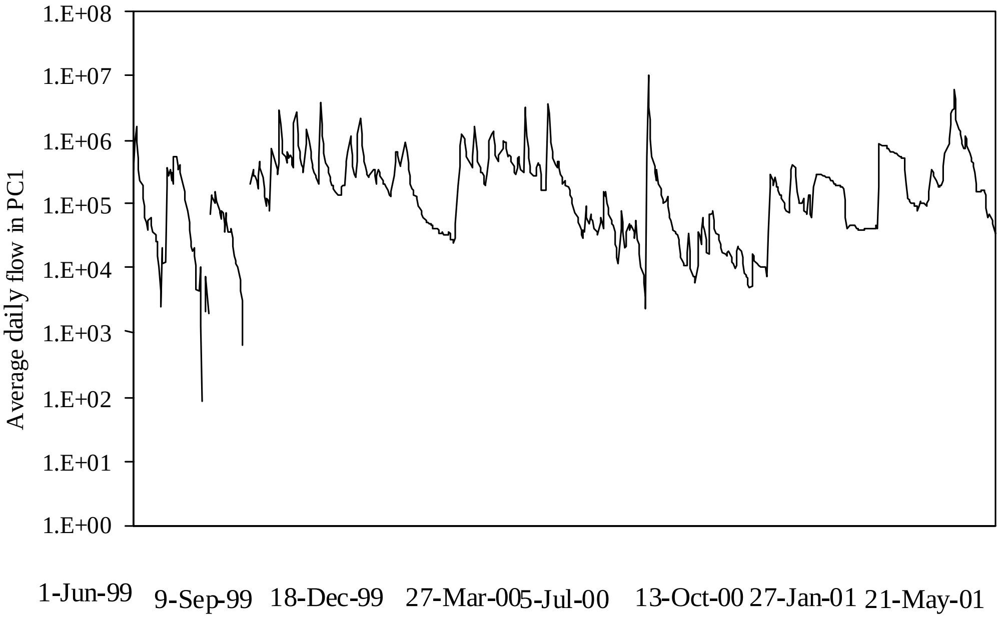


Figure 4b. Daily flow in PC1 (l/day) through the entire monitoring period.



Waterlogged conditions in the swamp that favour SO_4 reduction, likely explain the generally low SO_4 concentrations and high $\delta^{34}SO_4$ ratios in PC1 compared to PC1-08 (Figure 2). Similarly, $\delta^{34}SO_4$ ratios in the swamp outflow were consistently higher than in deposition, except for 2 specific occasions.

On Sept.7, 1999 and Aug.1, 2000, $\delta^{34}SO_4$ ratios in PC1 were less than +6‰, and were within the range measured in deposition and the swamp inlet (Figure 2). The first occasion followed a brief dry period when stream flow in PC1 ceased (Figure 4b), and the water table in the swamp may have declined to more than 8 cm below the peat surface (Figure 4a). Exposure of S-rich peat that has a generally lower $\delta^{34}S$ signature could have resulted in the export of isotopically light SO_4. For example, analysis of 3 cores within the PC1 swamp indicated that $\delta^{34}S$ ratios in the top 60 cm of peat were less than +6‰, and are between –1.5 and +3.2‰ in the top 20 cm (Figure 5a). Sulphur concentrations in peat cores were high (2180-6560 mg/kg), indicating substantial S storage in the wetland (Figure 5b). There was no apparent relationship between S isotope ratios and S concentrations in peat, which might be expected if S reduction resulted in preferential storage of ^{32}S (*e.g*. Morgan, 1995). However, cores were extracted in a hydrologically active part of the swamp, and lateral flow, as well as groundwater upwelling (Devito and Hill, 1999) would influence the pattern of isotope ratios with depth. In addition, expected decreases in $\delta^{34}S$ with depth may not occur in peatlands such as PC1 that undergo substantial changes in water table height due to variable redox conditions in surface peat (Novak *et al*., 1994). Lower $\delta^{34}SO_4$ ratios in PC1 following the Sept.1-5 period of zero stream flow were not accompanied by an increase in SO_4 concentration, which was expected had substantial S-oxidation occurred. For example, the SO_4 concentration in PC1 on Sept. 7. 99 was 3.6 mg/l compared to 6.3 mg/l in the PC1-08 inflow. However, SO_4 concentrations in PC1 were even lower (~0.8 mg/l) in the final week of August as

Figure 5a. δ^{34}S values (‰) with depth (cm) in 3 cores extracted from PC1 swamp.

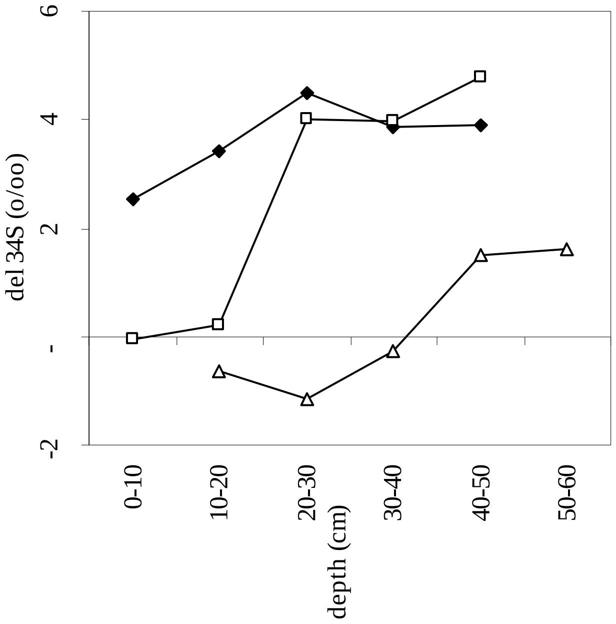
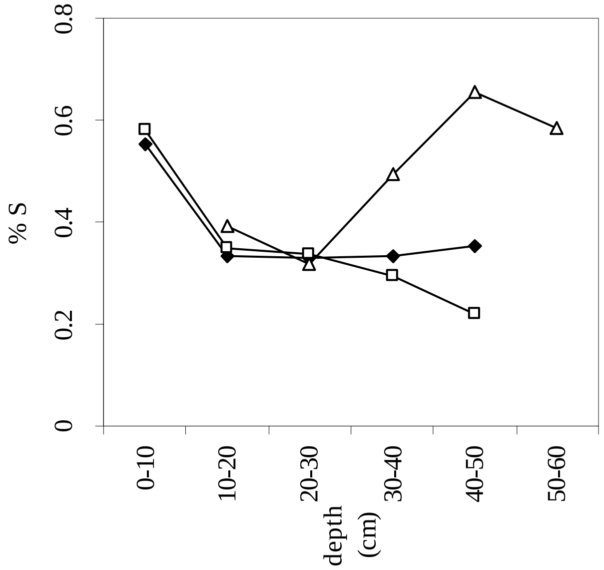


Figure 5b. Total S concentrations (%) with depth (cm) in 3 cores extracted from PC1 swamp.



stream flow declined. Therefore while the SO_4 concentration in PC1 following resumption of flow on Sept.7 was low compared to PC1-08, it was 4.5-times higher than the concentration measured prior to the dry period, possibly due to S oxidation in peat. The second occasion of a relatively low $\delta^{34}SO_4$ signature in PC1 (+4.9‰) occurred on Aug.1 2000 (Figure 2).

The previous day was marked by a particularly large storm event (116 mm), which resulted in substantial overland runoff from the catchment, and discharge in PC1 spiked to 10^6 l/d on Aug.1 (Figure 4b). The $\delta^{34}SO_4$ signatures in PC1, and also PC1-08 (+5.1‰) following this large storm event were remarkably similar to the $\delta^{34}SO_4$ of the event itself (+5.0‰), and may simply be a result of the isotopic composition of deposition dominating the signature in stream water. However, the swamp was also relatively dry prior to the Jul.31 event (Figures 4a, b), and therefore part of the decrease in $\delta^{34}SO_4$ in the swamp outflow on Aug.1 may be due to the export of isotopically-light SO_4 following S-oxidation in peat. Indeed, the 4.7-fold increase in SO_4 concentration between Jul.27 (1.1mg/l) and Aug.1 (5.2 mg/l), suggests that at least part of the decrease in $\delta^{34}SO_4$ in PC1 stream water was due to enhanced release from peat. High lateral runoff through soluble SO_4-rich surface organic horizons during this large storm event may have also contributed to higher SO_4 concentrations in storm water.

Isotopic composition of upland and wetland drainage waters following tracer application

Soil percolate

Following application of a ^{34}S-enriched tracer to soil above 2 treatment lysimeters, the $\delta^{34}S$ signal increased to more than +7‰ in LFH and Ae percolate in September 2000 (Table 3). However, by November 2000 $\delta^{34}SO_4$ signals in soil percolate from control and treatment lysimeters were less than +5‰, and were similar to values measured prior to application (Table 3). These results indicate that either, a) the tracer had been flushed from the upland plots by this time, or b) mixing of the tracer with ambient S in plots had diluted the tracer signal to below detection. Although all surface vegetation was removed from plots prior to tracer application, it is also possible that roots of trees from outside the plots could have accumulated some of the enriched $^{34}SO_4$. The most direct way to assess within-plot retention of the tracer would have been to measure $\delta^{34}S$ signals in soil samples from the treatment plots. However, this was not possible because soil could not be analyzed directly without prior extraction due its low S, and high inorganic content.

Another way of interpreting the change in $\delta^{34}S$ in soil percolate is to calculate the mass of ^{34}S that would have had to be lost from treatment plots in order to account for the relatively high $\delta^{34}S$ values measured in LFH and Ae percolate in September 2000 (Table 3). In order to do this calculation both the volume of soil percolate and the concentration of SO_4 in percolate are required. Between the time of tracer addition (August 15 2000) and the subsequent collection of soil percolate (September 11 2000), a total of 38.3 mm rain fell on the PC1 catchment. A single rain event on September 10 constituted 1/3 (13.5 mm) of this total (Figure 6). Smaller events which occurred between August 15 and September 10 were not large enough to generate soil percolate at the treatment lysimeters. LFH and Ae percolate collected on September 11 contained approximately 5 mg SO_4/l. If we assume that the entire 13.5 mm rain event of September 10 generated an equal amount of runoff (*i.e.* the unlikely situation of zero evapotranspiration or storage), and assuming only vertical flow, then a total percolate volume of ~32 L would have been produced through each plot, corresponding to a flux of 160 mg S. Given a background $\delta^{34}S$ in control percolate of +5.8‰, an additional 0.042 mg ^{34}S must have been present in percolate from treatment plots in order to increase the $\delta^{34}S$ to 7.5‰. A total of 0.33 mg ^{34}S was applied to each lysimeter plot, and so the amount of ^{34}S estimated to have been present in percolate from the Sept.10 event would account for only ~13% of the total tracer added.

Figure 6. Daily precipitation (mm) between the date of tracer application (Aug.15.00) and Nov.15.00 (first PC1-08 stream sample following tracer application which had a background $\delta^{34}S$ value).

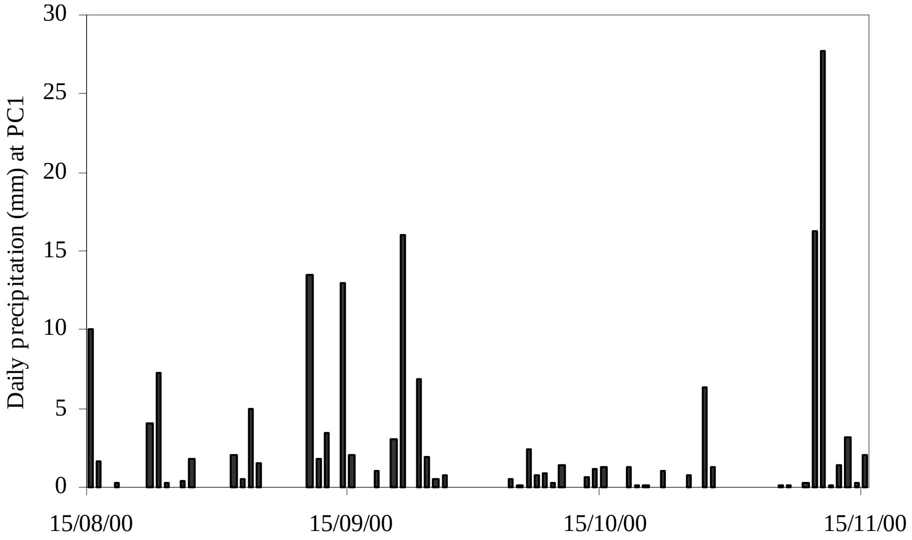
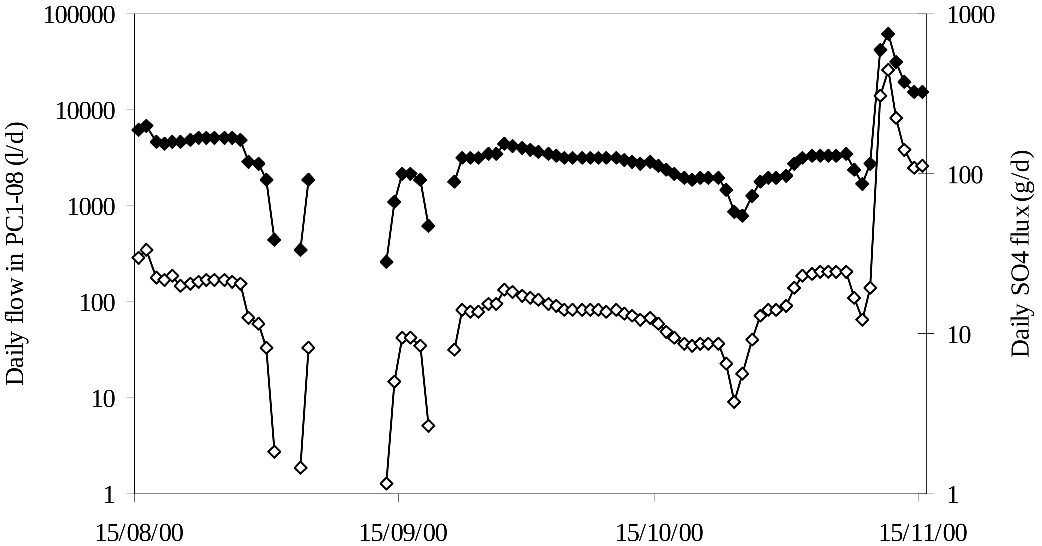


Figure 7. Daily stream flow (l/day) (solid diamonds) and SO_4 flux (g/d) (open diamonds) in PC1-08 between Aug.15.00 and Nov.15.00



Conditions were relatively dry until November (October 2000 precipitation was 24 mm compared to the 20-year average of 105 mm), and the subsequent isotope sample was collected on November 11, following a week of daily rainfall (a total of 51 mm fell between November 7 and November 15) (Figure 6).

The isotopic composition of percolate from control and treatment lysimeters was similar on this date, and values were within the range measured prior to application of the tracer (Table 3). Background $\delta^{34}S$ ratios in soil percolate from treatment lysimeters on November 7 are likely due to dilution of the tracer in ambient SO_4 in percolate and/or retention in the plots (in soil or plants) however, due to analytical limitations the latter explanation could not be assessed. Increased $\delta^{34}S$ signals in soil percolate immediately following tracer application indicated that some of the ^{34}S passed through the soil with little interaction, although the remainder may have been retained.

- *Upland-draining stream (PC1-08)*

Maximum $\delta^{34}SO_4$ values in PC1-08 were measured immediately following the application of a ^{34}S-enriched tracer to sites within the upland hillslope and stream bed (Figure 2). Elevated $\delta^{34}S$ ratios were measured in PC1-08 stream water between August 16 and October 10 inclusive, but by November 15 2000, isotope signatures had returned to pre-application values (Figure 2). Similar to upland soil percolate, it is difficult to assess whether the return of $\delta^{34}S$ ratios in stream water to pre-application values is due to the complete flushing of the tracer from the catchment, or to a gradual mixing and dilution of the isotope signal over time. However, it is possible to roughly calculate the mass of ^{34}S exported in stream water over the period during which $\delta^{34}S$ values were elevated, and to compare this estimate with the actual amount of ^{34}S added to treatment plots. Using daily flow measurements at the PC1-08 weir, and weekly SO_4 chemistry data, it was estimated that approximately 460 g SO_4 was exported from the catchment between August 16 and November 14, 2000 inclusive (Figure 7). Using an average $\delta^{34}S$ in stream water during this period of 12‰ and a pre-application $\delta^{34}S$ of +5.7‰, it was calculated that an additional 39 mg ^{34}S would have had to be present in stream water to increase the $\delta^{34}S$ from +5.7 to +12‰. However, only 5.1 mg ^{34}S was applied to stream plots, which is much less than the mass required to increase the $\delta^{34}S$ signature of 460 g SO_4 to 12‰. Even if we assume that the entire hillslope application of 0.66 mg ^{34}S was transported to the stream, the sum (5.76 mg ^{34}S) still does not approach the amount of ^{34}S estimated in stream water. However, the assumption that the $\delta^{34}S$ signature in PC1-08 was 12‰ for the entire period between August 16 and November 14 may be an overestimate, because there were no isotope measurements in PC1-08 between the last enriched sample on October 10 (+13.5‰) and the subsequent 'background' sample on November 15 (+6.1‰). The calculation of the mass of ^{34}S in stream water required to produce a signal of 12‰ is highly dependent on the estimate of SO_4 flux in stream water over the same time period (Figure 7). Furthermore, the majority of the SO_4 flux (360 g, or 80%) actually occurred during a period of high flow between November 10 and 14 (Figure 7). If we instead assume that the isotopic composition of stream water was only enriched in ^{34}S between August 16 and November 9 - which corresponds to an export of 90 g SO_4 in stream water, a much lower estimate of 7.6 mg ^{34}S is obtained. This value is much closer to the total mass of ^{34}S applied to plots in the stream and hillslope (5.76 mg ^{34}S). It is difficult to precisely identify the timing of isotope flushing (or signal dilution) in the catchment given the lack of isotope samples between October 10 and November 15, 2000. However, despite the very small addition of enriched ^{34}S to PC1-08 (total 5.76 mg ^{34}S) relative to annual S inputs in bulk deposition (~7 kg S/ha/year), the isotope signature in stream water was elevated for as long as 3 months following tracer application (Figure 2). These results may indicate that atmospherically deposited SO_4 in PC1-08 is not transported conservatively through the catchment, but is at least temporarily retained – although the mechanisms of retention could not be determined in this study.

Wetland-draining stream (PC1)

The application of a $^{34}SO_4$ tracer (5.1 mg ^{34}S in total) to plots within the swamp did not appear to affect the isotopic composition of PC1 stream water. The range in $\delta^{34}SO_4$ in PC1 prior to tracer application was similar to the range measured after August 15 (+5.9 to +12.2 ‰). This was not surprising, since the pool of soluble SO_4 in the 2.2 ha swamp is large - around 8 g S/m^2 in the top 42 cm (Lozano *et al*., 1987), which represents a substantial potential for isotope dilution. In addition, treatment plots within the swamp were at least 100 m away from the weir where isotope samples are collected, in contrast to PC1-08, where tracer plots were located immediately upstream (within 5 m) of the weir (Figure 1). Even assuming that the entire mass of ^{34}S applied in the PC1-08 streambed and hillslope was flushed into the swamp, this mass was tiny (5.76 mg ^{34}S) compared to the pool of soluble SO_4 (8 g S/m^2) or total S storage in peat (150 g S/m^2 in the top 40cm; Devito, 1995).

Conclusions

Although differences in isotopic composition among bulk deposition, upland stream water and soil percolate were not great, $\delta^{34}S$ values generally increased in the order of soil percolate<deposition<PC1-08. Isotopic fractionations associated with uptake and mineralization in upland soil, and dissimilatory sulphate reduction in stream sediment might contribute to differences in $\delta^{34}SO_4$ signatures among upland compartments. In general however, S-isotope ratios do not appear to be well suited to identifying S-transformations in upland systems. In contrast, $\delta^{34}SO_4$ ratios in stream water draining a conifer *Sphagnum* swamp were generally higher than in deposition or the inlet stream, and are likely a result of dissimilatory SO_4 reduction in peat. The application of a ^{34}S-enriched tracer to small plots within the upland and wetland had no effect on the isotopic composition of the swamp outflow, but increased $\delta^{34}SO_4$ ratios in soil percolate and upland stream water for at least 2 months, indicating that current deposition inputs are not immediately lost in upland drainage water.

CHAPTER 8: EFFECT OF SO_4 AND N (NH_4NO_3) ADDITIONS ON SOLUBLE SO_4 CONCENTRATIONS IN LFH AND MINERAL SOIL

ABSTRACT

Net S mineralization may be affected by a number of factors including changes in S and N deposition. Net mineralization may contribute to the apparent net export of SO_4 that has been observed at a number of long-term monitored catchments in eastern North America, including Plastic Lake (PC1) in the Muskoka-Haliburton region of south-central Ontario. In this study, the effect of varying concentrations of SO_4 or N (NH_4NO_3) on net SO_4 release in LFH and mineral soil was measured in a laboratory incubation experiment using material collected from the PC1 catchment. Soluble SO_4 concentrations in LFH and mineral soil were measured before and after incubation with varying concentrations of SO_4 (0 to 417 µeq/l) or N (NO_3 + NH_4; 0 – 607 µeq/l), respectively at 18°C for 24 h. Soluble SO_4 concentrations in LFH increased in all SO_4 treatments following incubation; however, the magnitude of increase was greatest in LFH incubated with low SO_4. For example, soluble SO_4 concentrations increased from 0.61 meq/kg to between 1.1 and 1.3 meq/kg following incubation with SO_4 at a concentration less than 42 µeq/l, which is the current level of SO_4 in bulk deposition in Muskoka-Haliburton. In contrast, soluble SO_4 concentrations were between 0.86 and 0.93 meq/kg in LFH incubated with high SO_4 (>190 µeq/l). These results indicate that SO_4 release from LFH tended to be greater under conditions of low SO_4 availability, which may be due to either enhanced mineralization or decreased immobilization, or both. In contrast, N additions had no effect on SO_4 retention or release in either LFH or mineral soil, and soluble SO_4 concentrations in LFH treated with N-only were identical to those in LFH treated with SO_4. These results may indicate that SO_4 release from mineralization is stimulated under conditions of lower SO_4 availability, which could occur due to decreasing S deposition. However, the fact that SO_4 was released from LFH material within 24 h

incubation regardless of whether S or N was added indicates that S mineralization is rapid, and may be an important source of S to drainage waters independent of changing deposition.

INTRODUCTION

Changes in deposition inputs of S and N may affect mineralization and nutrient cycling in forest soils (Kuperman, 1999). A number of reports in eastern North America and Europe have suggested that net mineralization may account for at least part of the apparent imbalance between SO_4 input in deposition and SO_4 export in streamwater (Alewell *et al.*, 1999; Driscoll *et al.*, 1998; Houle and Carignan, 1995). However, the factors controlling net mineralization are not well defined. Net S mineralization is the difference between immobilization and gross mineralization, which occur simultaneously in soil. At steady state, immobilization will equal mineralization, however at any given point in time the relative balance between these 2 processes could change, for example due to changes in climate or management, or possibly due to changes in S availability. Sulphur deposition could affect mineralization through changes in the exogeneous supply of SO_4 (*i.e*. availability in soil solution), and/or by longer-term effects on substrate quality (*i.e*. endogeneous S concentration). Sulphate immobilization increases in response to greater SO_4 availability (Fitzgerald *et al*., 1983), and there is also evidence that S enzyme activity is inhibited at higher SO_4 concentrations (Freney *et al*., 1986). If the opposing reactions of decreased immobilization and enhanced enzyme activity under conditions of lower SO_4 availability are also true, then net SO_4 mineralization could increase in theory in response to decreased deposition. A decline in S immobilization due to lower SO_4 availability could also result in an apparent increase in net mineralization if gross mineralization rates are unchanged.

Nitrogen inputs in atmospheric deposition may have a large effect on organic matter decomposition, particularly in systems that are limited by N (*e.g*. Berg and Matzner, 1996).

Nitrogen is normally the limiting nutrient in forest systems, and catchments in the Muskoka-Haliburton region retain more than two-thirds of N-input in atmospheric deposition, indicating that their capacity for N retention has not yet been satisfied (Dillon and Molot, 1990; Watmough and Dillon, 2002). In contrast to S-deposition, atmospheric inputs of N have remained relatively constant over recent decades (Dillon *et al*., 1988; Stoddard *et al*., 1999). Some authors have suggested that as N accumulates in soil, the C:N ratio will decline possibly stimulating decomposition (Aber *et al*., 1989). Ghani *et al*. (1992) found that S mineralization was greater following additions of N, and therefore SO_4 release from organic material might respond positively to increasing N-deposition. However, both stimulatory and retarding effects of N deposition on decomposition and mineralization have been reported (Berg and Matzner, 1996; Fog 1988). Nitrogen availability might also have indirect effects on S cycling. For example, nitrification has been shown to increase SO_4 retention in mineral soil because the H^+ release that accompanies this process increases SO_4 adsorption. However, retention of SO_4 through adsorption reactions is only important in subsurface mineral soil and is not an important mechanism of SO_4 retention in surface horizons that are rich in organic acids and have low Fe and Al oxide contents (*e.g*. Neary *et al*, 1987).

The purpose of this study was to evaluate the effect of variable SO_4 and N (NH_4NO_3) additions on net SO_4 mineralization in soil collected from the PC1catchment. The effect of N-additions on SO_4 release from both forest floor material (LFH) and mineral soil (B horizon) was considered; whereas the effect of SO_4 additions was only measured in LFH, because adsorption-desorption reactions were expected to be more important short-term controls on SO_4 in mineral soil.

METHODS

Study Site

Surface organic material (LFH) and mineral soil were collected from the 23 ha PC1 catchment, which drains into Plastic Lake near Dorset, Ontario. The forest at PC1 is primarily coniferous, and is dominated by white pine (*Pinus strobus*) (42% of basal area), eastern hemlock (*Tsuga canadensis*) (19%) and red maple (*Acer rubrum*) (10%) (Watmough and Dillon 2001). The LFH horizon varies in depth, but is on average ~10 cm, and is composed of 3 visibly distinct layers: LFH (L), which contains readily identified plant material, a more decomposed F layer, and a completely humified H layer (Canadian System of Soil Classification, 1998). The average depth of the underlying B-horizon is ~ 30 cm. Soils at PC1 are classified as either ortho humo-ferric or ortho ferro-humic podzols (Lozano *et al*., 1987), and are coarse textured (~90% sand) and acidic. The *p*H ($CaCl_2$) of the LFH and B-horizons are approximately 3.5 and 4.0, respectively.

Sample collection

Forest floor (0-10 cm) and B-horizon mineral soil (collected from ~20 cm below base of LFH) were collected from 3 different plots in the upland part of the PC1 catchment in late October 2001, and materials from different plots were combined. The carbon contents of LFH and B-horizon soil were ~40% and 5%, respectively. LFH material was mixed by hand to produce a homogeneous sample containing both recently deposited foliage and more decomposed humus. Roots, twigs and stones were removed. Similarly, mineral soil from the 3 different plots was sorted and homogenized by hand, and then sieved (5 mm). LFH and mineral soils used in experiments were treated field-moist to avoid unintentional SO_4 release due to drying (David *et al*., 1983). The moisture content of soils was determined by weighing before and after drying sub-samples at 65°C for 48 h. Sub-samples of LFH and mineral soil were also removed at this time to determine initial (*i.e*. time=0) soluble SO_4, NO_3 and NH_4, and adsorbed SO_4 concentrations. Soluble SO_4 and N was extracted from field-moist LFH by shaking the equivalent of approximately 5 g (dwt) LFH with 25 ml de-ionized water for 1 hour. Initial concentrations of both adsorbed SO_4 and soluble SO_4 and N were determined in mineral soil using a similar procedure, except that 25 ml 0.03 M NaH_2PO_4 was substituted for de-ionized water to liberate adsorbed SO_4. After shaking, soil slurries were centrifuged, and supernatants were filtered (Whatman 42, followed by 0.45 µm syringe filter) and then analyzed by ion chromatography (Dionex 6000).

Experimental design

Sulphate solutions were produced by serial dilution of a stock SO_4 (Na_2SO_4) solution in de-ionized water. In this way, a series of 5 test concentrations was produced, ranging from 0 (control) to 417 µeq/l (Table 1). Similarly, 5 solutions of varying N concentration were produced by serial dilution of a stock N (NH_4NO_3) solution (Table 1). Solutions were prepared immediately prior to use in experiments.

Sets of 200 g (fresh wt.) of LFH were thoroughly mixed with 200 ml of the appropriate SO_4 solution in 10-L plastic basins. LFH in the control treatment was mixed with 200 ml of de-ionized water (DIH_2O). At the time of sampling (*i.e.* late October), a fresh weight of 200 g LFH corresponded to a dry weight of ~71 g (65% moisture), and so solutions were applied at a solution-to-LFH ratio of 2.8:1; this ratio was chosen to approximate the LFH:deposition ratio expected in a low autumn precipitation event (4 mm). Application of 200 ml solution to LFH material only increased the moisture content from 65% to 80% (dwt).

Following application of the appropriate SO_4 solution, sub-samples of approximately 50 g LFH were removed and placed in food-grade polyethylene bags, such that 4 replicates were produced per SO_4 treatment. In a similar way, 125 g (fresh wt) of mineral soil was mixed with 25 ml of each SO_4 and N solution, respectively and sub-samples of approximately 30 g were apportioned into 4 replicates per treatment. The initial moisture content of mineral soil was 28%, and so SO_4 and N solutions were applied to mineral soil at a 0.28:1 solution-to-soil ratio.

Unsealed bags (to allow air exchange) containing LFH or mineral soil were placed in a closed box containing a humidity source to maintain initial moisture conditions. The box was then placed in a temperature-controlled room (18°C) for 24 h; 18°C is the average summer (June-August) temperature in Muskoka-Haliburton. A relatively brief (24 h) incubation was used since results of the drying and re-wetting experiment (Chapter 5) indicated that variations in SO_4 release among treatments were manifested within 24 h. At the end of the incubation period, sub-samples from each treatment were removed and extracted moist in de-ionized water (1 part soil to 5 parts DIH_2O), following the same procedure as outlined above. All concentrations are expressed per unit dry weight of soil.

Data treatment

Soluble SO_4 and N concentrations in each treatment were calculated as the difference between the total measured concentration and the amount added in each treatment solution. The significance of differences among treatments ($p<0.05$) was assessed by ANOVA (Statistica), and differences among means were identified by Tukey's Honest Significance test.

RESULTS

Effect of added SO_4 on net soluble SO_4 concentrations in LFH

Soluble SO_4 concentrations in LFH prior to incubation (*i.e.* time=0) were 0.61 ± 0.05 meq/kg (Figure 1). After 24 h, net soluble SO_4 concentrations in LFH incubated with low SO_4 (*i.e.* 0-42 µeq/l) increased to approximately double their initial concentrations (1.1 – 1.3 meq/kg), indicating substantial net mineralization. For reference, 42 µeq/l corresponds to the current SO_4

concentration in deposition in Muskoka-Haliburton. However, the ultimate concentration of deposition-derived SO_4 in LFH solution is a function of both solution volume and processes that consume or produce SO_4 in the LFH horizon. For example, since approximately 50% of incoming deposition in the study region is evapo-transpired on an annual basis (*i.e*. ~0.5 m), average annual SO_4 concentrations in LFH solution should be at least double concentrations in deposition. Indeed, the initial soluble SO_4 concentration in LFH (0.61 meq/kg) was high compared to the amount of SO_4 added in treatments A through D (Table 1). Therefore, although SO_4 additions used in treatments A through D were low compared to current ambient deposition, they only corresponded to small increases over initial soluble SO_4 levels in LFH material. Small increases in SO_4 input in the 4 low treatments (A-D) relative to initial soluble SO_4 levels in LFH (<20%; Table 1) likely explains why there was no statistical difference in mean soluble SO_4 concentrations among treatments A-D (Figure 1). Specifically, SO_4 additions in these treatments may not have been large enough to effect statistically significant changes in net mineralization.
Nevertheless, these results indicate that at low SO_4 applications, net SO_4 mineralization may increase soluble SO_4 concentrations in LFH by a factor of 2.

In contrast, net mineralization was lower and soluble SO_4 concentrations were significantly less in LFH incubated with high SO_4 concentrations (>208 µeq/l), that corresponded to 5, or 10-times current deposition (Figure 1) and represented increases of 97 and 192%, respectively over initial levels (Table 1). Lower soluble SO_4 concentrations in the 2 highest treatments may be attributed to either increased SO_4 immobilization or decreased gross mineralization under conditions of greater SO_4 availability. Lower net SO_4 concentrations in the high SO_4 treatments are likely not due to increased adsorption, since SO_4 adsorption in organic horizons is negligible due to low levels of Fe and Al oxides and the interfering effect of organic acids on SO_4 adsorption (Neary *et al*., 1987).

Table 1. Sulphate and inorganic N (NO_3 + NH_4) concentrations in treatment solutions A through F (µeq/l); their corresponding soluble concentrations in LFH and mineral soil (meq/kg), and the % increase that N and S additions in treatment solutions represented over initial soluble concentrations in LFH and mineral soil.

SO_4-treatment: LFH	**A**	**B**	**C**	**D**	**E**	**F**
[SO_4] in application solution (µeq/l)	0	4	21	42	208	417
Resultant [SO_4] addition to LFH (meq/kg)	0	0.012	0.059	0.117	0.59	1.17
% increase over initial SO_4 (0.61 ± 0.05 meq/kg)	-	2	10	19	97	192

N-treatment: LFH	**A**	**B**	**C**	**D**	**E**	**F**
Inorganic [N] in application solution (µeq/l)	0	6	30	61	304	607
Resultant inorganic [N] addition to LFH (meq/kg)	0	0.017	0.085	0.17	0.85	1.70
% increase over initial inorganic N (3.4 ± 0.5 meq/kg)	-	0.5	2.5	5	25	50

N-treatment: mineral soil	**A**	**B**	**C**	**D**	**E**	**F**
Inorganic [N] in application solution (µeq/l)	0	6	30	61	304	607
Resultant inorganic [N] addition to mineral soil (B) (meq/kg)	0	0.0017	0.0084	0.017	0.084	0.17
% increase over initial inorganic N (0.080 ± 0.02 meq/kg)	-	2	10	21	105	211

Effect of added N on net soluble SO_4 concentrations in LFH

Soluble SO_4 concentrations in LFH increased over initial levels following 24-h incubation with N, however there was no significant difference among N-treatments and final soluble SO_4 concentrations in all N-treatments ranged from 1.1 ± 0.1 to 1.5 ± 0.2 meq SO_4/kg (Figure 2).

For reference, the average N concentration in current deposition in the Muskoka-Haliburton region is around 60 µeq N/l. However, similar to the argument presented above for SO_4, it may be more relevant to compare N additions to initial soluble inorganic N levels in LFH (see Table 1).

After 24h incubation, soluble SO_4 concentrations in LFH treated with N were comparable to those in LFH treated with low SO_4 and were approximately double initial soluble SO_4 concentrations in LFH (Figures 1 and 2). Soluble SO_4 concentrations appeared to be slightly higher in the maximum N treatment (1.49 ± 0.10 meq/kg); however, they were not significantly different from concentrations in treatment C (1.34 ± 0.12 meq/kg), which corresponded to a N application of only 2.5% above the initial level of soluble N in LFH (Table 1).

Fate of nitrogen added to LFH

Initial soluble inorganic N concentrations in LFH prior to incubation were around 3.4 ± 0.5 meq/kg made up of 3.1 ± 0.3 meq/kg of N-NH_4 and 0.40 ± 0.50 meq/kg N-NO_3 (Figure 3). Interestingly, soluble N concentrations in treatment A (DIH_2O) increased substantially after 24 h incubation at 18°C, whereas N concentrations in LFH that had been treated with N varied little from initial values (Figure 3). It is unknown why soluble inorganic N concentrations increased in the de-ionized water treatment, whereas any added N in treatments B through F was recovered in water-extracts following incubation, suggesting that inorganic N added to LFH was not metabolized.

Figure 1. Net soluble SO_4 (meq/kg) in LFH following 24-h incubation of LFH material with varying concentrations of SO_4 or distilled water. Dashed lines indicate initial (*i.e.* prior to incubation) soluble SO_4 levels in LFH (95% confidence interval). Error bars are the standard deviation of 4 replicates.

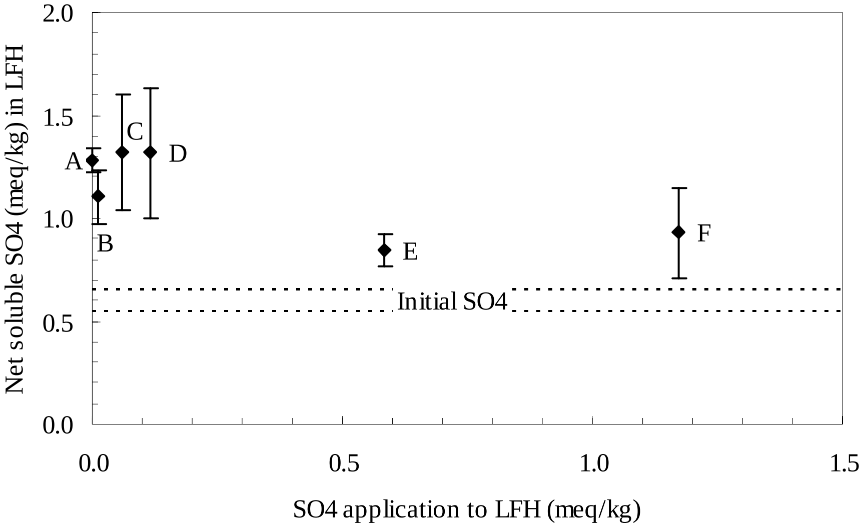


Figure 2. Net soluble SO_4 (meq/kg) in LFH following 24-h incubation with de-ionized water or varying concentrations of inorganic N. Dashed lines indicate initial soluble SO_4 levels in LFH (95% confidence interval). Error bars are standard deviation of 4 replicates.

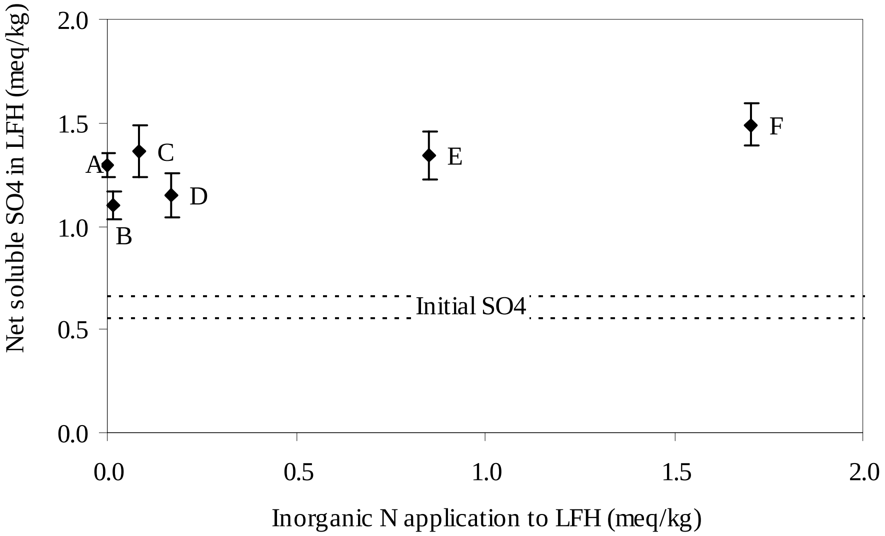


Figure 3. Net soluble inorganic N in LFH (meq/kg) following 24-h incubation with de-ionized water or varying concentrations of inorganic N (NH_4 + NO_3 added in equal proportions). The dashed lines indicate initial soluble inorganic N levels in LFH.

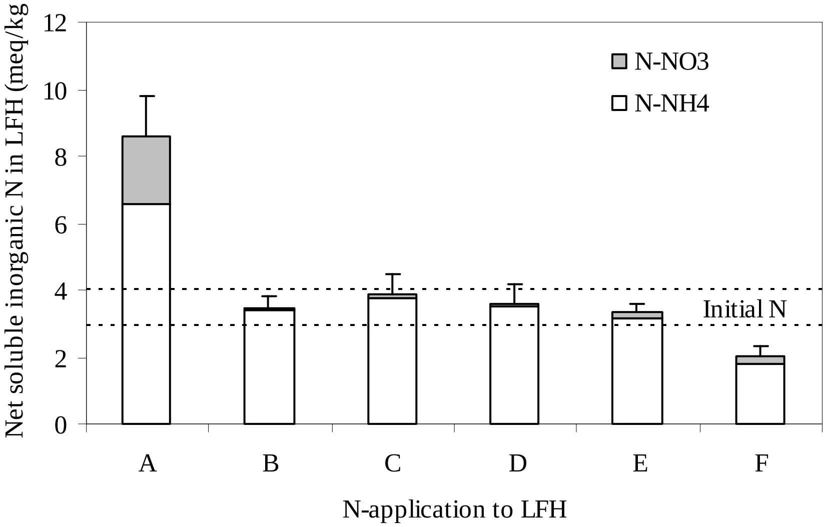


Figure 4. Net soluble SO_4 in mineral soil (meq/kg) following 24-h incubation of mineral soil with de-ionized water or varying concentrations of inorganic N. Dashed lines indicate initial soluble SO_4 levels in mineral soil (95% confidence interval). Error bars are standard deviation of 4 replicates.

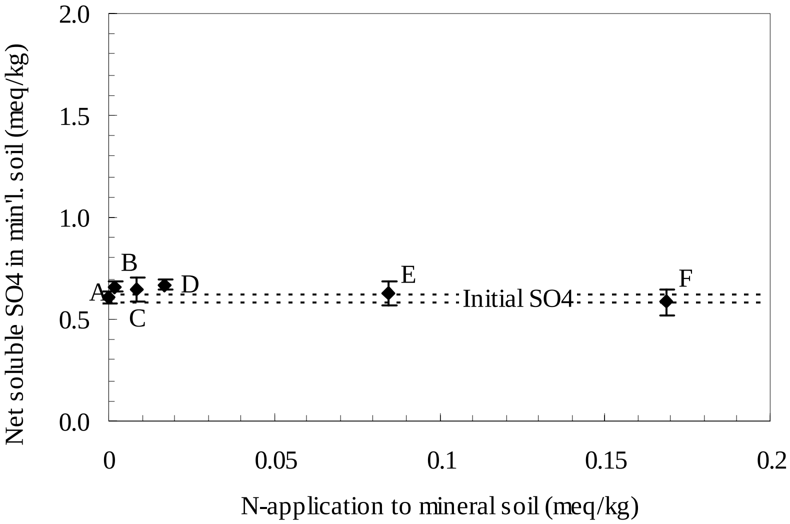
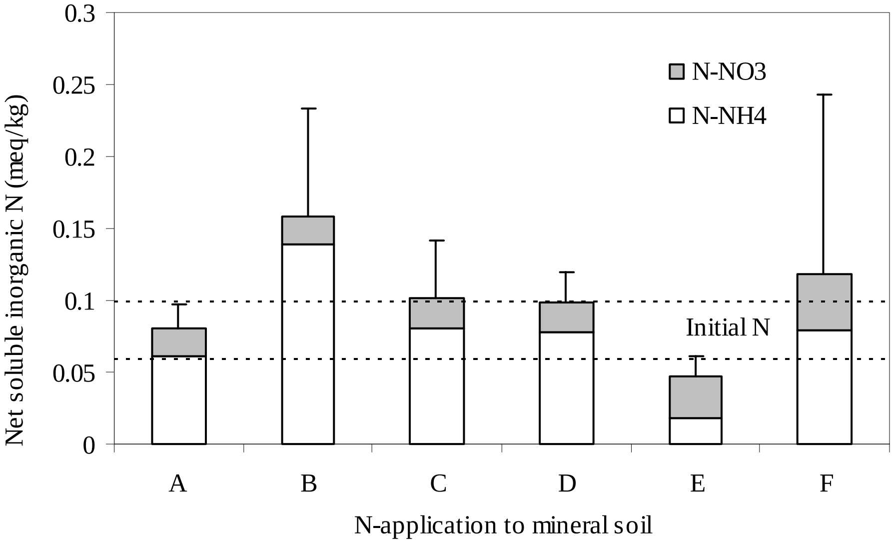


Figure 5. Net soluble inorganic N (NO_3 + NH_4) in mineral soil (meq/kg) following 24-h incubation of mineral soil with distilled water or varying concentrations of inorganic N. Dashed lines indicate initial soluble N levels in mineral soil (95% confidence interval). Error bars are standard deviation of 4 replicates.



Soluble N in the highest N treatment following incubation was significantly lower than the initial level ($p<0.05$), possibly due to greater immobilization under conditions of increased N availability (Figure 3). If inorganic N was immobilized during decomposition, this could explain why SO_4 concentrations were slightly higher in the highest N treatment (Figure 2). Changes in dissolved organic N were not measured in this experiment, but may have increased in the higher N-treatments if inorganic N additions stimulated decomposition. In comparison to the SO_4 treatments in which the maximum SO_4 addition was equivalent to a 192% increase over initial levels, N-additions corresponded to relatively smaller increases (≤50%) over initial soluble inorganic N concentrations in LFH (Table 1). This may explain in part, why inorganic N additions appeared to have little effect on net SO_4 concentrations in LFH material.

While the N application solutions were made up of equal parts of N-NH_4 and N-NO_3, following 24 h incubation at 18°C, inorganic N in LFH extracts was dominated by NH_4 (Figure 3). Nitrate-N constituted less than 6% of the total inorganic N measured in all of the treatments except the control and highest N-application where N-NO_3 amounted to 24% and 12% of total inorganic N measured, respectively (Figure 3). However, inorganic N that was present in LFH prior to incubation was also dominated by NH_4 (3.1 ± 0.3 meq/kg), whereas NO_3 (0.40 ± 0.50 meq/kg) comprised approximately 11% of total inorganic N, although initial NO_3 concentrations in LFH were extremely variable (CV 125%).

Effect of added N on net soluble SO_4 concentrations in mineral soil (B)

Soluble SO_4 levels in mineral soil prior to incubation were around 0.61 ± 0.02 meq/kg (Figure 4). Neither incubation nor the addition of N to mineral soil appeared to have an effect on SO_4 release from mineral soil, and soluble SO_4 concentrations in N-treatments A through F were similar to initial levels and ranged from 0.58 ± 0.06 to 0.67 ± 0.03 meq/kg (Figure 4). Initial soluble SO_4 concentrations in mineral soil and LFH were similar, but following incubation SO_4 concentrations in LFH were approximately double those in mineral soil.

Fate of nitrogen added to mineral soil

Initial soluble inorganic N concentrations in mineral soil were around 0.080 ± 0.020 meq N/kg, and were less than 1% of concentrations in LFH incubated with de-ionized water (8.6 ± 1.2 meq N/kg) (Figure 5). Initial soluble inorganic N in mineral soil was comprised of approximately 25% N-NO_3 and 75% N-NH_4. Nitrogen amendments to mineral soil corresponded to proportionally larger increases over initial concentrations than did N-additions to LFH (Table 1). Inorganic N concentrations in mineral soil following incubation were more variable both within and among treatments, and were comprised of relatively more N as NO_3 compared to LFH (Figure 5). For example, the proportion of N present as NO_3 in mineral soil extracts ranged from 13% in treatment B to 65% in treatment E. There did not appear to be any relationship between added N and resultant soluble inorganic N concentrations in mineral soil following incubation.

DISCUSSION

Effect of added SO_4 on net soluble SO_4 concentrations in LFH

Final soluble SO_4 concentrations in all LFH treatments were higher following 24-h incubation, indicating that net mineralization had occurred. However, LFH material incubated with low SO_4 had a higher net soluble SO_4 concentration after 24-h, indicating either increased gross mineralization and/or decreased immobilization in the presence of lower SO_4 availability. In contrast, LFH incubated with SO_4 at a concentration that corresponded to an increase of 2-4 times above initial levels had lower net SO_4 release. It is difficult to attribute these responses to changes in either immobilization or mineralization, since both processes are known to be responsive to added SO_4. For example, SO_4 that is added to forest soil is rapidly (24-h) incorporated in organic matter, and immobilization shows a positive response to added SO_4 (David and Mitchell, 1987; Strickland *et al*., 1986). The opposing process of S mineralization is also sensitive to added SO_4, and is inhibited by the addition of SO_4 at levels that exceed biological demand (Cooper 1972). Moreover, the formation of S-mineralizing enzymes (sulphatases) is sensitive to end-product concentrations, and is inhibited by the addition of SO_4 (Freney *et al*., 1986). Presumably, the opposite response of greater mineralization and/or less immobilization in the presence of reduced SO_4 availability might also occur (*e.g*. McGill and Cole, 1981). Indeed, the addition of S-poor material to low S soil caused increased mineralization, whereas immobilization occurred if S-rich material, or elemental S was added to the same soil (Chapman 1997).

In agricultural studies, the S nutritional status of soil is expressed by the C:S ratio (*e.g*. Scherer 2001). A C:S ratio greater than 400 is generally associated with S-limiting conditions and S immobilization, whereas mineralization is more common in soils with a C:S ratio of <200 (Barrow 1967; Chapman 1997; McGill and Cole, 1981; Scherer 2001). Apparently either immobilization or mineralization may occur at a C:S ratio between 200 and 400, and Chapman (1997) identified a critical C:S ratio of 340 as the limit between net mineralization and immobilization in straw residues. The relatively high S content (0.16%) and correspondingly low C:S ratio (250) of LFH used in this study suggests that mineralization may predominate over immobilization in LFH at PC1. A low C:S ratio does not imply that mineralization occurs throughout the year, or that mineralization consistently exceeds immobilization – only that mineralization might be *favoured* to occur. A host of other temporally variable environmental factors such as soil moisture, temperature, microbial status and availability of nutrients such as N, P and labile C would also affect the balance between mineralization and immobilization.

The relationship between the C:S ratio in soil and mineralization/immobilization which has been described in the agricultural literature implies that the S content of soils is responsive to changes in S-inputs. Indeed, in areas that are affected by acid deposition, the S content of soil and plant material (particularly foliage) has been related to the level of atmospheric S input on both temporal and spatial scales. For example, Pregitzer *et al*. (1992), and Kuperman (2001) found that S concentrations in foliage and surface soil increased along a S deposition gradient. Zhao *et al*. (1998) reported that the temporal trend in S-content in archived herbage samples from Rothamsted, England was very similar to the trend in SO_2 emissions in the U.K over the same time period. These reports indicate that S accumulation by plants may respond directly to greater S-availability, and therefore S inputs to soil in LFH should increase correspondingly. Because both plant uptake and microbial immobilization are responsive to changes in SO_4 inputs, in theory, the C:S ratio in soil at PC1 may have gradually decreased over time in response to historically high S-inputs in atmospheric deposition in Muskoka-Haliburton (Dillon *et al*., 1988). By comparison, weathering inputs of S would likely be small due to the low S content and slow weathering rates of silicate granite bedrock in this region (Jeffries and Snyder, 1983; Watmough and Dillon, 2001). Therefore, past SO_4 inputs in anthropogenic deposition may have accumulated in soil until the S content increased to a point that immobilization was no longer favoured, and the balance shifted to a state of net mineralization. Indeed, fertilizer studies have demonstrated that the addition of S-rich material to soil increases mineralization, whereas application of S-deficient materials stimulates immobilization (Chapman 1997; Eriksen 1997a). We do not have any archived soil or LFH samples from PC1 with which to evaluate the supposition of S accumulation over time, however the C:S ratio remains a plausible explanation for changes in immobilization and mineralization that may have occurred over the long-term (Scherer 2001).

Contrary to what was expected there was no difference in net SO_4 concentrations among the low SO_4 treatments (*i.e.* <42 μeq/l). It was hypothesized that SO_4 release from LFH would increase in response to decreased SO_4 input, possibly due to a stimulatory effect of lower SO_4 availability on S mineralization, and/or reduced immobilization. However, differences in mineralization or immobilization among SO_4 treatments may not have been manifested over the short incubation period (*i.e.* 24-h) used in this study. For example, Houle *et al.* (2001) found that SO_4 immobilization in LFH material from a balsam fir forest only reached an asymptote after 2-7 days incubation. In addition, due to the high concentration of native soluble SO_4 in LFH relative to amounts added in the low SO_4 treatments, as well as inherent variability associated with soluble SO_4 concentrations, differences among treatments would have been difficult to detect. Perhaps a better approach would have been to wash LFH prior to use in experiments in order to remove any SO_4 that was initially present. However, washing and excessive handling of LFH may have resulted in unforeseen changes in the microbial biomass, and resulted in further difficulties with data interpretation and extrapolation to the field situation. Another approach would have been to increase the volume of treatment solution applied to LFH (*i.e.* >200 ml) in order to increase the mass of SO_4 applied. However, the application of a larger volume of treatment solution to LFH could cause saturated and anaerobic conditions to develop, and lead to unexpected changes in mineralization/immobilization.

Another factor that may have influenced the results is LFH quality. Forest floor material used in this experiment was collected in the late fall and therefore included recently fallen litter (L). Had LFH been collected at the end of the summer when it contained a greater proportion of degraded material (*i.e*. no fresh L) the results might have been different.

Effect of added N on net soluble SO_4 concentrations in LFH

Mass balance budget calculations for catchments in the Muskoka-Haliburton region indicate that the majority of N in atmospheric deposition is retained in catchments and is not exported in drainage waters (Dillon and Molot, 1990; Watmough and Dillon, 2002). For example, N concentrations in stream water draining the upland part of PC1 (PC1-08) are among the lowest measured in the region (Watmough and Dillon, 2002). Low N leaching losses in stream water at PC1 suggest that soils have a high capacity to retain added N. The addition of N to PC1 LFH at concentrations that exceed current deposition was expected to affect decomposition and consequently net SO_4 release. However, there was little difference in SO_4 concentrations among N-treatments, or between LFH treated with N and LFH treated solely with SO_4. A negligible response to N-addition is likely in part due to relatively high background N levels in LFH; even the maximum N treatment only corresponded to a 50% increase over initial N levels. While changes in the exogeneous N supply did not appear to affect mineralization, this does not necessarily mean that continued atmospheric inputs of N are not affecting decomposition *in situ*. Sustained inputs of N plus negligible inorganic N leaching losses imply that the N content of soil and/or vegetation at PC1 may have increased over time. It has been suggested that a shift toward narrower C:N ratios in soil may increase rates of N leaching, and possibly decomposition and mineralization rates as well (Aber *et al*., 1989; Berg and Matzner, 1996; Kuperman, 1999).

Limited measurements (n=6) at PC1 indicate that the C:N ratio in LFH is currently (2001) between 21 and 30.

The addition of DIH_2O to LFH appeared to stimulate net N release from LFH, whereas initial and final net soluble N levels were similar in LFH that was treated with N indicating that any added N was recovered in water extracts. It is difficult to explain differences in soluble N concentrations between treatment A (DIH_2O) and LFH treated with N, but the addition of N may have stimulated N immobilization in LFH due to the generally N-limiting conditions at PC1. The slight shift in the composition of inorganic N towards greater dominance of NH_4 that occurred in treatments A through F further indicates that N-additions caused changes in the soluble N pool within 24-h incubation.

Effect of added N on net soluble SO_4 concentrations in mineral soil (B)

In contrast to LFH, there was negligible net S mineralization in mineral soil over the 24-h incubation period in any of the N-treatments. However, it is possible that any SO_4 that was released from organic S was subsequently re-adsorbed by soil particles. We did not measure changes in adsorbed SO_4 because adsorbed SO_4 concentrations at PC1 are very high (>6 meq/kg) relative to soluble SO_4 levels, and results from a previous experiment (Chapter 5) indicated that differences in S mineralization could not be assessed by monitoring the adsorbed pool.

There were negligible differences in net S mineralization among N-treatments despite the fact that N additions to mineral soil constituted relatively large increases over background values. Again, SO_4 release from organic compounds may have been partly masked by adsorption/desorption reactions. Inorganic N concentrations in mineral soil were also 30-60 times lower than in LFH, although initial soluble SO_4 concentrations were similar in the two materials. This was not expected, since most studies report higher soluble SO_4 concentrations in forest floor material compared to subsurface mineral soil (Neary *et al.*, 1987). However, soluble SO_4 concentrations in surface organic soil are both temporally and spatially variable, and depend on a number of factors including antecedent moisture conditions, temperature, plant and microbial activity, *etc*. For example, similar soluble SO_4 levels in LFH and mineral soil may have been due to the time of their collection (*i.e*. late October). Soils were collected following a week of daily rainfall (58 mm over 7 days), and continuously wet and cool conditions (average 6°C) may have resulted in a relatively constant distribution of SO_4 with depth.

The majority of the microbial biomass in soil is concentrated in the surface organic horizons (Atlas and Bartha, 1993) and so an apparently low potential for mineralization in B-horizon soil is not entirely surprising. However, total S concentrations in the B-horizon at PC1 are relatively high (~0.4%) and two-thirds of total S storage in mineral soil is organic, with the remainder present as adsorbed SO_4 (Neary *et al*., 1987). The C:S ratio in the organic fraction of mineral soil at PC1 is around 200, which is lower than in LFH, and so given adequate conditions for microbial activity (*i.e.* soil moisture, temperature and nutrients), S mineralization might be expected to occur. However, results of this and a previous study (see Chapter 5) indicated that factors which are expected to influence microbial activity in soil (*i.e*. N, temperature and moisture) had no apparent effect on SO_4 release from mineral soil. This was despite the fact that organic S compounds constitute ~67% of the total S in mineral soil at PC1, although adsorbed SO_4 accounts for the other third, and therefore adsorption-desorption reactions may have masked the release of SO_4 from organic compounds. Nonetheless, a number of reports have suggested that carbon-bonded S compounds, which constitute the majority of organic S present in mineral soil may be relatively recalcitrant to degradation (David *et al*., 1983; McGill and Cole, 1981; Mitchell *et al*., 1992a). Mineralization of organic S in mineral soil therefore, is likely not as important in the short-term (*i.e*. 24 h) cycling of S. In contrast, adsorption/desorptions respond directly to changes in SO_4 input (see Chapter 6) and may be the primary immediate controls on net SO_4 release from mineral soil. Over the long term (*i.e*. months- years) S mineralization in mineral soil could be an important source of SO_4 to drainage waters – particularly considering the relatively large pool of S in mineral soil compared to LFH at PC1 (~54 keq/ha, and 1 keq/ha, respectively). In support of this, Houle *et al*. (2001) showed that the large organic-S pool in mineral soil at Lac Laflamme, QC is only slowly cycled, but suggested that it may be an important source of SO_4 export in the long term.

Results of these experiments indicated that net SO_4 mineralization occurred in LFH in all SO_4 and N treatments. Net SO_4 mineralization was greater in the low SO_4 treatments, whereas the addition of N to LFH or mineral soil had no effect on soluble SO_4 concentrations. Greater net mineralization under conditions of reduced SO_4 availability may have been due to increased gross mineralization, decreased immobilization, or both. However, the relatively high S content and low C:S ratio in LFH at PC1 suggests that mineralization might be favoured to occur. In theory, a system could change over time from a state of net immobilization of S in organic material to a state of net mineralization. This shift could be brought about by the gradual accumulation of S (or N) in soil and a corresponding decline in C:S (or C:N) ratio, and/or it could be a more direct response of mineralization or immobilization to lower S availability in soil solution, caused by decreasing deposition. Results of this experiment were not sufficient to evaluate either hypothesis, and further work is required to assess the role of mineralization in the S-budgets of Muskoka-Haliburton catchments.

CHAPTER 9: SULPHUR MASS BUDGET CALCULATION

Mass budget calculations

As part of this study, SO_4 input-output budgets were calculated for 11 catchments (see Chapters 2 and 3) in the Muskoka-Haliburton region using long-term data collected by the Ontario Ministry of Environment and the following basic equation:

$$\text{INPUTS} - \text{OUTPUTS} = \text{NET CHANGE}$$

If inputs exceed outputs, S is being retained within the catchment, whereas if S exports exceed inputs, the catchment is releasing S from internal sources. Complete S budget equations include S inputs in deposition (wet + dry) and weathering and S removals in stream drainage water and net S accumulation in forest biomass. Most reports of catchment S budgets assume weathering inputs to be negligible, and often bulk deposition is used as a surrogate of total deposition (*e.g.* Hornbeck *et al*., 1997; Mitchell *et al*., 1996). In addition, S accumulation in biomass and removal in harvesting are generally not considered. However, the value of budget calculations is entirely dependent upon the accuracy with which the various components of the budget are estimated. In order to interpret S budget results it is first necessary to examine the methods used to estimate the various components of the basic budget equation, including any associated assumptions or errors. The mechanisms of S storage and release from internal pools will be discussed in Chapter 10.

Inputs

Negative S budgets have been occasionally attributed to underestimated inputs in deposition, specifically the dry deposition component (*e.g.* Edwards *et al*., 1999; Likens *et al*., 1990). Sulphur deposition to catchments occurs *via* three pathways: wet (rain, snow) dry (gas, particulate) and cloud (fog). Fog deposition is a particularly important source of S in high elevation and coastal regions (*e.g*. Lovett *et al*., 1997; Miller and Friedland, 1999). Wet deposition is relatively straightforward to measure using collectors that are open only during rain or snow events. In contrast, dry deposition is the transfer of gases or particles to land surfaces in the absence of precipitation, and is notoriously difficult to quantify, particularly in complex terrain (Lovett *et al*., 1997). Various methods have been used to estimate dry deposition to catchments, although the two most commonly used are the inferential method and throughfall monitoring. The inferential method involves coupling measurements of SO_2 (gas) and SO_4 (particulate) concentrations in air with velocity estimates for dry deposition, which are dependent on the dominant land-use type and aerodynamic resistances calculated at the site (Sirois *et al*., 2001). The throughfall method is based on the premise that the forest canopy is an efficient scavenger of dry deposition, and that precipitation falling beneath the canopy is thereby relatively enriched in chemicals compared to deposition in clearings. Bulk deposition collectors, which are continuously open offer a simple and economical means of assessing wet deposition plus a variable portion of the dry deposition. Bulk deposition collectors can seriously underestimate total deposition in areas that are close to emission sources, where dry deposition comprises a larger proportion of total deposition (Dillon *et al*., 1982). For example, dry S deposition accounted for 50% of total S deposition (25-30 kg S-SO_4/ha/yr; 1977/78) at the Walker Branch Watershed, TN, which is located within 20 km of 3 coal-fired power plants and within 350 km of 22 power plants (Johnson *et al*., 1982). However, at sites remote from point sources, dry deposition is small compared to wet S inputs. For example, Baumgardner *et al*. (2001) recently estimated that annual dry S inputs in Vermont and Maine were less than 1 kg S/ha, compared to total annual deposition of 6-7 kg S/ha. In contrast, dry S inputs in the Ohio River Valley, close to emission sources ranged from 3 to 8 kg S/ha/yr and total S inputs were between 12 and 17 kg S/ha/yr (Baumgardner *et al*., 2001).

Dry S deposition to the Muskoka-Haliburton region is assumed to be small, due to its remote location from major emission sources and Dillon *et al*. (1988) resolved that bulk samplers collected approximately the total (wet + dry) deposition of S. While bulk collectors are unlikely to sample 100% of the S input to forested landscapes, SO_2 and particulate SO_4 concentrations are low in the study region (maximum 1-2 ug/m^3, generally below detection limit of 1 µg/m^3) compared to the Hubbard Brook (2-3 µg/m^3) where dry deposition was estimated to be ~0.9 kg S/ha in 1993 (Lovett *et al*., 1997). By comparison, bulk deposition in the Muskoka-Haliburton region was around 7 kg S/ha in 1993. Assuming a similar rate of dry deposition in this region as at Hubbard Brook, and 0% collection of dry deposition in bulk collectors, a dry input of 0.9 kg S/ha/yr would only constitute 11% of total S inputs at Muskoka-Haliburton (*i.e*. 0.9/7.9). Recently, Sirois *et al*. (2001) estimated that dry deposition constituted approximately 1/3 of total S deposition at the Turkey Lakes Watershed (TLW). In a related report, Beall *et al*. (2001) showed that wet deposition calculated by Sirois and others was equivalent to approximately 85% of their bulk S deposition estimates, and suggested that bulk deposition included a portion of the dry S inputs to the TLW. These 2 estimates can be used to calculate the proportion of dry deposition not sampled by bulk collectors, *i.e.*:

Wet = (0.66 * total)   (Sirois *et al*. 2001)

Wet = (0.85 * bulk)   (Beall *et al*., 2001)

Therefore bulk = (0.78 * total), and an additional 22% should be added to bulk estimates to approximate total S deposition at the TLW. Annual bulk deposition at the TLW is very similar to that measured in the Muskoka-Haliburton region (Jeffries *et al*., 1997), and the contribution of dry deposition may also be comparable (Sirois and Barrie, 1988). However, forest type (coniferous *vs*. deciduous) and canopy cover (% closure) also influence dry deposition through changes in surface area and resultant scavenging of gases and particulates. Therefore dry deposition inputs may vary among catchments in the Muskoka-Haliburton region, and dry inputs could constitute a larger proportion of total deposition at coniferous catchments such as PC1.

Throughfall monitoring has also been conducted in the Muskoka-Haliburton region to approximate total S deposition. Measurements at the PC1 and HP4 catchments over a 3-year period (1983-1986) indicated that dry deposition could account for as much as 31% or 7%, respectively of total annual deposition as approximated by throughfall (Neary and Gizyn, 1994). Throughfall flux estimates assume that canopy coverage above throughfall collectors is representative of canopy coverage over the entire catchment. Treeless areas, such as stream channels and rock outcrops are not accounted for in these calculations. While regions with no tree cover may be proportionately small in many catchments, at PC1, bedrock outcrops cover 10% of the 23.3 ha catchment, and the swamp, which has a relatively low basal area (~18 m^2/ha) covers another 10% (Lozano *et al*., 1987). Throughfall collectors may also over-estimate total deposition if SO_4 is leached from foliage (Lovett *et al*., 1997).

Weathering inputs of S are also inherently difficult to assess. Sulphur concentrations in rock types that are considered representative of the catchment combined with estimates of weathering rates can provide a rough approximation of S inputs *via* weathering. Weathering can be a major source of S input in catchments with substantial S-bearing mineral deposits (Mitchell *et al*., 1986). For example, pyrite dissolution was concluded as the source of net S export in the Loch Vale watershed in the Colorado Rocky Mountains, where exposed bedrock covers 80% of the catchment area (Baron *et al*., 1995; Mast *et al*., 1990).

Isotope data can be used to infer the role of lithogenic S in catchment budgets if $\delta^{34}S$ signals in soil minerals are distinct from other S sources in the catchment. For example, Fitzhugh *et al*. (2001) interpreted low $\delta^{34}S$ ratios during base flow at a site directly downstream of a mapped coal seam to S weathering; however, only 4% of S export from the catchment could be attributed to lithogenic sources. In the upland-draining PC1-08 catchment, similarities in $\delta^{34}S$ signals among deposition, soil percolate and stream water were interpreted as evidence that deposition is the primary source of S to this catchment (Chapter 7). This interpretation relies on the assumption that $\delta^{34}S$ ratios in minerals are not coincidentally similar to ratios in deposition, and we do not have $\delta^{34}S$ data for till and bedrock in the study region to verify this assumption. However, Jeffries and Snyder (1983) summarized the geology of catchments in the Muskoka-Haliburton region and reported that total S concentrations are low (<0.01%) in the slowly weathered granitic silicate bedrock that typifies the area. Glacial tills are locally derived and have a similar chemical composition to bedrock (Jeffries and Snyder, 1983). Kirkwood (1990) reported that the major minerals at PC1 are quartz, feldspars (plagioclase, orthoclase), vermiculite, amphibole and iron oxides, none of which contain S, and S was below the limit of detection (100 mg/kg) in till at the base of the soil profile. However, the presence of minor deposits of S-bearing minerals such as pyrite cannot be discounted. In an analysis of S cycling in 20 forest systems primarily located in the northeastern US, and including 1 in Canada (Turkey Lakes) Mitchell *et al*. (1992) concluded that weathering was an insignificant source of S compared to deposition.

Houle and Carignan (1995) used a different approach to estimate S inputs *via* weathering in a Canadian Shield catchment, and suggested that SO_4 concentrations in stream water due to weathering of S-bearing minerals should be proportional to the molar Si:S concentration in granite (1196:1), assuming that both elements are weathered in this proportion. They concluded that S weathering would contribute at most 0.05 kg S/ha to annual export from the Lac Laflamme catchment. If a similar calculation is made for PC1-08, which has an average stream Si concentration of ~3 mg/l, then only 3 µg S-SO_4/l is attributable to weathering, which corresponds to an annual export of ~0.05 kg S/ha (assuming 17,000 m^3/yr), similar to Lac Laflamme. In contrast, Wilander (1994) used a charge equivalent base cation-to-sulphur ratio of 0.05 to estimate S weathering inputs to Swedish surface waters. They found that the S:Si ratio in granite published by Krauskopf (1967) and used by Houle and Carignan (1995) predicted lake SO_4 concentrations that were at least 60-times lower than measured concentrations in Swedish lakes unaffected by acid rain (Wilander, 1994). Furthermore, they state that since Si concentrations in lakes can vary seasonally due to biological processes, that the BC:S ratio provides a better estimate of background SO_4 concentrations. Following this approach, a S weathering input of ~0.3 kg S/ha/yr was calculated for PC1 using the base cation (Ca+Mg+K+Na) weathering value published by Kirkwood and Nesbitt (1991) of ~400 eq/ha/yr and a BC:S ratio of 1:0.05. A similar estimate (0.6 kg S/ha/yr) was calculated for the Hubbard Brook watershed, which accounted for less than 3% of total inputs (Likens *et al*., 1977). For reference, an annual input of 0.3-0.6 kg S/ha/yr corresponds to <5% of annual S export in the PC1 stream. It should be noted, however, that Si is not present in S-bearing minerals, and few S-minerals contain base cations, therefore the use of ratios to predict S weathering may be unfounded (Wilander, 1994). However, ratios based on the elemental content of major rock types provide a means of obtaining rough weathering estimates for mass budget calculations.

Outputs

Sulphate export from catchments occurs in stream water and through net accumulation in biomass. Gaseous losses of S may also be substantial in lowland systems. In upland systems, however, biogenic S emissions are thought to be small, and Andreae and Jaeschke (1992) estimated gaseous outputs from temperature forests to be only 0.16-0.53 kg S/ha/yr, which is minor compared to S export in stream water in most catchments (Mitchell *et al*., 1992a).

A number of different methods have been used to calculate annual fluxes in stream flow, including discharge-weighted, regression, and period-weighted calculations, although the period-weighted method is most commonly applied (Dann *et al*., 1986; Likens and Bormann, 1995). In the period-weighted method output fluxes are calculated by multiplying the stream flow between two consecutive sampling dates by the average SO_4 concentration of the two consecutive samples. This method was used to calculate SO_4 export from catchments in the Muskoka-Haliburton region, and is consistent with the method used by the OMOE Dorset Environmental Science Centre.

While continuous concentration and discharge measurements would obviously provide the most accurate estimates of nutrient export, due to the high cost of intensive sampling most monitoring programs use a less frequent sampling interval, which generally involves collection of weekly grab samples. The OMOE stream chemistry data set is of particularly high quality, since the majority of streams have been sampled on a weekly or bi-weekly basis since the late 1970s, and streams are sampled more frequently (*i.e*. daily) during periods of high flow such as the spring melt. For example, between May 1980 and May 1998, 1,342 chemical samples were collected from the PC1 stream, which corresponds to a frequency of one sample every 5 days. The period-weighted method can result in inaccuracies if discharge varies significantly between samples, however if samples are taken often enough during periods of variable flow (*i.e*. summer, spring), then this method is the most accurate method for estimating export (Dann *et al*., 1986).

The other mechanism by which S may be retained in forest ecosystems and thereby removed from stream flux measurements is net tree uptake. Sulphur is an essential plant nutrient required in the formation of amino acids, enzymes, nucleic acids and other functional groups. If trees are harvested then S may be permanently removed from the catchment, otherwise S that is accumulated in plant biomass is eventually returned to the soil when the tree dies and decays. Even so, over the relatively long life span of a typical forest, accumulation of S in biomass could be important, particularly in a rapidly aggrading stand. At PC1, total S storage in forest biomass (above + below ground) is approximately 30 kg S/ha (Table 9-1). Given the average age of the stand (80 yrs), annual S accumulation by trees was estimated to be 0.4 kg S/ha (assuming annual S uptake is constant over the tree's lifetime). This uptake rate is low compared to that reported by Johnson *et al.* (1982) for a chestnut oak stand in Tennessee (2.1 kg S/ha/yr.), but was similar to the uptake rate calculated for a balsam fir stand in Quebec (0.4 kg S/ha/yr., assuming stand age of 47 yr. at time of study) (Houle and Carignan, 1992). Compared to the magnitude of annual stream S export in catchments in this region (up to 22 kg S/ha/yr), net annual accumulation in biomass appears small.

Table 9-1. Sulphur content (kg/ha) of above and below ground biomass in the PC1 forest in 1999, and annual S input to the forest floor in litter fall (1985/86). Data from Lozano and Parton (1986) and Watmough (*unpublished*).

	S content (kg/ha)
Crown	7.5
Bark	3.7
Stem	11.6
Above	22.8
Below	6.5
Total	**29.3**
S in litter fall (kg/ha/yr); total mass of litter (kg/ha/yr)	2.4; 3934

Furthermore, the forest biomass at PC1 did not change over the period 1983-1999, possibly due to nutrient limitations to forest growth brought about by acid-induced cation depletion in soil (Watmough and Dillon, 1999). In a mature, non-aggrading stand, annual S requirements for litter production and root growth are likely supplied by internal cycling – namely litterfall and root exudates and mortality. Mitchell *et al.* (1992) reported that vegetation represented less than 12% of the total S content of 20 forested systems considered in the IFS study. At PC1, S in forest biomass is only 3% of total ecosystem storage (see Tables 9-1 and 9-2), whereas at Lac Laflamme the proportion in vegetation is just over 1% (Houle and Carignan, 1995). Therefore even if these forests were clear cut, only a small portion of total S storage in the catchment would be exported. The relatively small amount of S stored in forest biomass and low annual net requirements, indicate that S uptake by trees can largely be ignored in mass balance approximations (Johnson *et al*., 1984). However, this does not imply that trees are not important for S cycling and transformations (*i.e*. inorganic to organic forms) in catchments.

Table 9-2. Total S content of a typical podzol profile at PC1 (data from Neary *et al*., 1987 and this study).

	Depth (m)	*Bulk density (g/cm^3)*	*Organic C (mg/kg)*	*Total S (mg/kg)*	*Total S (kg/ha)*	*Adsorbed S-SO_4 (mg/kg)*	*Adsorbed S-SO_4 (kg/ha)*
LFH	0.10	0.014	290-440	920-1660	20	0	0
Ae	0.02	0.95	18-21	110	20	0.7	0.13
B	0.25	0.77	20-49	300-600	870	100-200	290
Total	**0.37**				**910**		**290**

While it is apparent that there are a number of assumptions associated with the basic mass budget equation, in many regions, such as Muskoka-Haliburton, bulk deposition appears to be a reasonable surrogate for total S input, and outputs can be approximated using stream export. Nonetheless, in order to be completely conservative in these calculations, various ‘correction factors’ can be applied to the data. For example, 22% was added to annual bulk deposition to bring S inputs in line with recent estimates for the TLW (Beall *et al*., 2001; Sirois *et al*., 2001). In addition, a further 0.6 kg S/ha/yr (estimate published for Hubbard Brook; Alewell *et al*., 1999) was added to atmospheric deposition to account for potentially unmeasured weathering inputs (Table 9-3). Even with these additions, it is apparent that S export exceeds input (negative values) in many years of record at PC1, and in nearly all years of record at HP4 (Table 9-3).

Table 9-3. Mass Balance estimates for PC1 and HP4, all units in kg S/ha/yr. Weathering was estimated at 0.6 kg S/ha/yr.

Year	*Bulk Dep.*	*Bulk*1.22*	*Total Input (Bulk*1.22 + weathering)*	*Stream export (kg S/ha/yr)*		*Input – Export (kg S/ha/yr)*	
				PC1	*HP4*	*PC1*	*HP4*
1980-81	11.8	14.4	15.0	14.6	17.1	0.4	-2.1
1981-82	12.1	14.8	15.4	12.1	14.9	3.3	0.5
1982-83	10.9	13.3	13.9	17.9	15.8	-4.0	-1.8
1983-84	8.7	10.6	11.2	19.0	12.8	-7.7	-1.6
1984-85	9.2	11.2	11.8	15.2	15.3	-3.4	-3.5
1985-86	9.8	11.9	12.5	10.2	14.1	2.3	-1.6
1986-87	7.9	9.6	10.2	6.5	8.6	3.7	1.6
1987-88	9.1	11.2	11.8	18.7	13.0	-7.0	-1.3
1988-89	8.2	10.0	10.6	17.0	12.8	-6.5	-2.3
1989-90	7.4	9.0	9.6	16.3	12.0	-6.7	-2.4
1990-91	8.5	10.4	11.0	17.2	14.6	-6.2	-3.6
1991-92	8.5	10.4	11.0	11.5	11.6	-0.5	-0.6
1992-93	7.9	9.7	10.3	10.2	13.5	0	-3.2
1993-94	7.0	8.5	9.1	9.1	11.1	0.1	-1.9
1994-95	7.1	8.7	9.3	9.2	12.1	0.1	-2.8
1995-96	8.3	10.1	10.7	13.0	14.4	-2.2	-3.6
1996-97	6.9	8.4	9.0	9.4	12.8	-0.4	-3.8
1997-98	4.8	5.9	6.5	7.9	6.6	-1.4	-0.1
1998-99	5.5	6.7	7.3	9.4	6.5	-2.1	0.8
SUM	**160**	**195**	**206**	**244**	**240**	**-38**	**-34**

Furthermore, both catchments exhibited a cumulative net export of –38 S/ha (PC1) and –34 kg S/ha (HP4) over the 20-year monitoring period. It should be noted, however, that mass balance calculations for the PC1 *Sphagnum* swamp, indicate that inputs were in approximate balance with outputs over a 7-year period (1983-1990) that included both wet and dry years. For example, LaZerte (1993) calculated a total S-SO_4 input of 1020 kg S per hectare of swamp surface over the

7-year period, compared to a total export of 1045 kg S/ha (~2% net export). Therefore, cumulative net export from PC1 appears to be from the upland part of the catchment (see also Chapter 4), although the particularly large negative export values observed in certain years (*e.g.* 1987/88) are undoubtedly due to enhanced SO_4 export from the swamp.

Table 9-4. Estimates of annual net S retention (+) or release (-) at 8 representative catchments in the Muskoka-Haliburton region. Sulphur retention or release (kg S/ha/yr) was calculated as [input (bulk*1.22+0.6) – stream export].

	RC-1	*BC-1*	*PC1-08*	*HP-6*	*HP6-A*	*DE-6*	*DE-5*	*CB-1*
1980-81	0.6	1.7		-5.4	-1.3	6.7	6.0	3.6
1981-82	0.9	4.7		-9.2	0.9	7.6	11.9	4.2
1982-83	-4.2	-4.6		-8.0	-4.7	2.7	7.9	-1.5
1983-84	-2.4	-3.3		-8.2	-7.3	-5.6	6.4	-2.8
1984-85	-2.9	-2.0	-6.2	-7.3	-4.2	0.0	5.5	-0.8
1985-86	2.4	0.9	-1.4	-5.6	-0.1	7.5	8.0	3.7
1986-87	1.8	1.7	-1.1	0.1	3.2	6.2	7.3	4.3
1987-88	-0.3	1.5	-3.2	-5.6	-3.5	-0.6	7.4	-0.5
1988-89	-3.0	-0.6	-4.6	-6.5	-5.5	0.4	5.4	-0.6
1989-90	-4.3	-0.5	-4.9	-6.5	-2.5	1.3	4.0	-2.1
1990-91	-4.7	-1.5	-6.7	-7.2	-4.5	-6.1	3.1	-3.2
1991-92	-1.9	3.6	-1.9	-3.6	-1.4	2.6	6.9	0.6
1992-93	-6.4	-3.9		-6.8	-1.1	4.8	6.4	-0.5
1993-94	-1.6			-5.6	-1.2	6.0	6.3	0.7
1994-95	-1.9			-4.8	-0.2	6.3	7.0	-0.5
1995-96	-2.9			-6.0	-1.0	6.6	7.3	-1.6
1996-97	-3.2			-6.4	-2.0	3.9	5.8	-2.4
1997-98	-0.3			-2.7	-2.4	3.9	3.7	1.2
SUM	**-34**	**-2**	**-30**	**-105**	**-39**	**54**	**116**	**2**

Clearly, negative S budgets in the Muskoka-Haliburton region cannot be entirely explained by additional inputs from dry deposition or weathering (see Tables 9-3 and 9-4). Data presented in

Chapter 2 illustrate that net SO_4 export is a common feature of catchments in the Muskoka-Haliburton region, and even if inputs are increased by ~25% to account for additional dry deposition and weathering, net export still occurs in most years (Table 9-4). The Dickie Lake catchments are a notable exception, and retain S over the long term. Possible explanations for net SO_4 retention in the wetland-dominated Dickie Lake catchment were outlined in Chapter 2, however, further work would be required to determine the unique hydrology of the Dickie catchment, which tends to favour S retention during both wet and dry years.

The generally negative SO_4 mass budgets for catchments in the Muskoka-Haliburton region imply that S is being exported from an internal source. Internal pools of S in upland and wetland-draining catchments, as well as the factors driving net export are discussed further in Chapter 10.

CHAPTER 10: SUMMARY & CONCLUSIONS

This project was designed to address the following 2 observations and related hypotheses:

1. Trends in annual SO_4 concentration and export are similar among a number of distinct catchments in the Muskoka-Haliburton region. What factor(s) is (are) responsible for synchronous patterns of SO_4 chemistry among streams?
2. Sulphate export from catchments exceeds input in bulk deposition in many years of record. What are the sources and controls of this apparent net export? Do they differ between upland, and wetland-draining catchments? What are the implications of (a) net SO_4 export, and (b) changing climate on the recovery of downstream water bodies and forest soils from historic acid deposition?

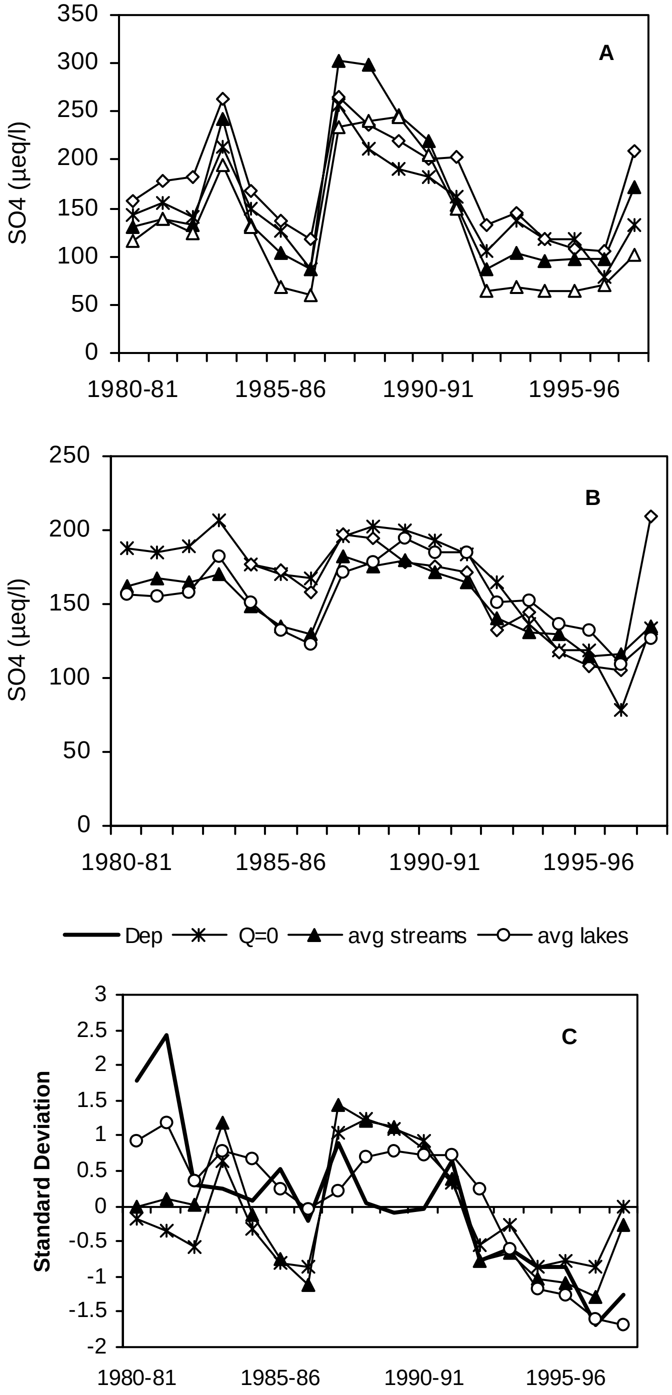
In order to address these questions, 3 approaches were taken, including (i) the analysis of existing long-term monitoring data (chemical, meteorological & hydrologic data), (ii) collection of additional monitoring data (including stable isotope data) and (iii) implementation of several laboratory experiments and a field experiment. Using these methods, the following conclusions were obtained:

1. SYNCHRONOUS PATTERNS OF SO_4 CHEMISTRY

Analysis of existing long-term monitoring data from a number of catchments in the Muskoka-Haliburton region revealed that temporal patterns of annual stream SO_4 concentrations were highly coherent among streams (Chapter 2). Synchronous patterns in SO_4 chemistry among a range of catchments which vary greatly in their physiography (till depth, soil depth & type, slope, wetland coverage), forest covers (coniferous, deciduous) and management (cottage development, forest harvesting) indicates the involvement of large-scale, or regional factors. Two factors that act on a broad-scale and could therefore be responsible for synchronous patterns in stream SO_4 concentrations are deposition and climate. Deposition is the primary source of S to catchments on the Canadian Shield, which have negligible mineral S deposits and low weathering rates; however, temporal changes in SO_4 deposition are not as strongly correlated to changes in stream SO_4 chemistry as expected (Figure 10-1). Instead, inter-annual variations in climate, particularly summer precipitation and temperature, appear to be related to changes in SO_4 concentrations and export in drainage streams, which ultimately influence SO_4 concentrations in downstream lakes (Chapter 3). Catchment dryness, or the number of days with zero stream flow (*i.e*. Q=0) was a particularly good predictor of annual average SO_4 concentrations in many streams (Chapters 2 & 3; Figure 10-1).

Stream flow was less and streams were dry for longer in years which had summers (June-August) that were both warmer (>18°C) and drier (<230 mm precipitation) than average. In wetland-draining streams the relationship with summer climate is particularly evident – SO_4 concentrations and export increase considerably following summer droughts, and this was previously ascribed to changes in wetland water table level (Dillon and LaZerte, 1992; Devito *et al*., 1999; LaZerte 1993). However, SO_4 concentrations in entirely upland-draining catchments also increase following particularly dry summers, although the magnitude of change between wet and dry years in upland streams is much less compared to wetland-draining streams. Nevertheless, long-term monitoring data suggest that climate may also affect SO_4 generation and export in upland catchments, because temporal patterns of SO_4 concentrations are synchronous in both upland and wetland-draining systems (Figure 10-1). Furthermore, climate variations ultimately affect SO_4 concentrations in lakes through changes in SO_4 export or retention in the terrestrial catchment.

Figure 10-1. Sulphate concentrations in wetland-draining (A) and upland streams (B). Lower graph (C) presents temporal patterns of annual average SO_4 concentration in streams (average 8 streams), lakes (average 8 lakes), deposition, and # days with zero-stream flow (average 8 streams).



In order to investigate the relationship between climate and SO_4 generation in upland systems, existing soil percolate and tensiometer data from the PC1-08 catchment were explored (Chapter 4). It was found that SO_4 concentrations in percolate from the surface organic horizon (LFH) were highest immediately following periods with low soil moisture. Increases in SO_4 concentration following dry periods were not entirely due to evapoconcentration or dry deposition, and therefore must be a result of SO_4 release from surface soil. Patterns of annual average SO_4 concentrations in LFH and B-horizon percolate, respectively, were correlated ($r=0.80$, $p<0.05$). However, increases in SO_4 concentration following dry periods were not as large in mineral soil percolate, likely due to adsorption/desorption reactions in the B-horizon which tend to dampen the SO_4 signal from LFH percolate (*i.e.* decrease the amplitude of peaks). Consequently, these observations led to the design of 2 laboratory experiments.

The first experiment was designed to test directly the effects of changing moisture conditions (and temperature) on SO_4 generation in forest soils. The second experiment determined the potential for adsorption and desorption reactions to buffer SO_4 concentrations in infiltrating LFH percolate and account for the relatively steady SO_4 concentrations measured in percolate draining the B-horizon. A further and more important goal of the second experiment was to assess the response of the adsorbed pool to changes in SO_4 deposition and to evaluate the potential contribution of desorption to net SO_4 export from upland catchments.

The effect of both drying and re-wetting and temperature on SO_4 generation was tested using a number of different materials collected from the PC1 and S50 catchments including forest floor (LFH), mineral soil (B-horizon), wetland soil (peat) and *Sphagnum* moss (Chapter 5). Increased SO_4 concentrations in wetland and upland-draining streams have been observed following periods that are both dry, and warmer than average. While it was hypothesized that alternating moisture conditions were the primary cause of high SO_4 concentrations, temperature may have exerted an additional stimulatory effect, and/or contributed to dry conditions by enhancing moisture losses due to evapo-transpiration.

The results of this experiment indicated that the effect of drying and re-wetting on SO_4 release from peat was immediate (within 24 h of re-wetting), and that SO_4 concentrations in dried and subsequently rewet peat were 3- (S50) to 4-times (PC1) greater than in continuously moist peat. Changing moisture conditions did not have an immediate effect on *Sphagnum*, although SO_4 concentrations in *Sphagnum* extracts tended to increase over the 30-d incubation, suggesting that SO_4 release from *Sphagnum* could be important under prolonged dry/warm conditions. However, large and immediate increases in SO_4 export that have been reported in wetland-draining streams following dry periods are likely due primarily to enhanced release from dried and subsequently re-wet peat rather than to increased mineralization in *Sphagnum* material. The mass of S in *Sphagnum* is also small compared to S storage in peat.

Sulphate release from dried coniferous forest floor material also increased immediately following drying and re-wetting, and results of the laboratory experiment supported field measurements at PC1-08 that showed higher SO_4 concentrations in LFH percolate following decreases in soil moisture. Increased temperature enhanced SO_4 release from both peat and LFH, although changing moisture conditions were responsible for the majority of SO_4 generation. Neither temperature nor drying affected SO_4 release from upland mineral soil, but $SO_{4(NaH2PO4)}$ concentrations in B-horizon soil were high (~ 400 mg/kg), and these data indicate that the mineral soil constitutes a large pool of adsorbed SO_4 in the upland part of the PC1 catchment.

The second laboratory experiment assessed the potential for SO_4 adsorption and desorption from mineral soil to respond to changes in SO_4 input (Chapter 6). Sulphate concentrations in percolate draining the B-horizon show little temporal variation, despite large changes in input concentrations of SO_4 in LFH percolate (Chapter 4). Similar patterns in lysimeters solutions at the Lac Laflamme catchment were hypothesized to be due to adsorption and desorption reactions in the mineral soil which effectively 'buffer' SO_4 concentrations in infiltrating water (Houle and Carignan, 1995). Consequently, when SO_4 concentrations in LFH percolate are high, adsorption in the B-horizon results in lower SO_4 concentrations at the base of the profile whereas low SO_4 concentrations in LFH percolate are compensated for by increased desorption from mineral soil. Therefore, although patterns of standardized annual SO_4 concentrations in LFH and B-horizon percolate are significantly correlated (*i.e.* $r = 0.80$, $p<0.05$ at PC1-08), the amplitude of inter-annual changes in SO_4 is smaller in B-horizon percolate. The variable response of adsorption/desorption reactions in mineral soil to changes in SO_4 in infiltrating water suggests that these processes should also be responsive to changes in SO_4 input in deposition.

2. SOURCE(S) AND CONTROLS OF S EXPORT IN UPLAND AND WETLAND-DRAINING CATCHMENTS

While changes in climate appear to be responsible for inter-annual variations in SO_4 concentrations in upland and wetland-draining catchments, climate was further hypothesized to be responsible for apparent negative SO_4 budgets in Muskoka-Haliburton catchments. In wetland-draining catchments such as PC1, negative SO_4 budgets in dry years appear to be explained by changes in wetland hydrology which determine whether SO_4 is reduced (and retained) or oxidized/mineralized (*i.e.* released) in peat. While high SO_4 concentrations and export following dry periods were inferred to be due to the oxidation of reduced S species in peat (either metal sulphides or organic S compounds) upon exposure to air (*e.g.* Dillon *et al*., 1997), this has never been directly tested.

Results of a laboratory experiment conducted as part of this study (Chapter 5), confirmed that SO_4 release from peat increased in response to changes in moisture, and that *Sphagnum* mineralization was likely not a large contributor to SO_4 release from wetlands. In addition, S-isotope ratio measurements in the hydrologic inputs (*i.e.* deposition, upland PC1-08 stream) and outputs (PC1 stream) of the PC1 swamp indicated that SO_4 peaks in the PC1 stream following droughts are likely due to release from reduced S compounds in peat (Chapter 7). The original hypothesis of this study was that SO_4 concentrations in PC1 would be low, and $\delta^{34}S$ ratios in stream water would exceed those in inputs to the swamp during wet periods when the water table was at or near the peat surface. Conversely, $\delta^{34}S\text{-}SO_4$ ratios were predicted to decrease and SO_4 concentrations in PC1 were expected to increase following sustained dry periods that resulted in a decline in water table height. It should be noted that the hydrologic residence time within the swamp is key to the development of anaerobic conditions, and even during periods of low precipitation, saturated conditions that favour SO_4 reduction may persist within the wetland.

Above average rainfall during the summers of 1999 and 2000 maintained high water table levels in the PC1 swamp during the 2 years of intensive isotope monitoring (1999-2000). Sulphate concentrations in PC1 stream water were low (average 4.8 and 4.2 mg/l in 1999/00 and 2000/01, respectively) compared to the long-term (1980/81-2000/01) average of 7 mg/l. Furthermore, $\delta^{34}S$ ratios in PC1 (average +8.6 ± 2.6‰) were generally higher than in deposition (+5.1 ± 0.6‰) or upland stream flow (PC1-08; 5.8 ± 0.7‰), supporting the hypothesis that SO_4 reduction in the wetland under saturated conditions causes increased $\delta^{34}S\text{-}SO_4$ ratios in drainage water. However, pervasiveness of wet conditions over the 2-year monitoring period did not allow the 2nd part of the hypothesis to be evaluated (*i.e.* lower $\delta^{34}S$ and higher SO_4 concentrations following dry periods). Monitoring of stable isotope ratios in the PC1 catchment is continuing, however, and when isotope and SO_4 concentration data from the relatively dry summers of 2001 and 2002 become available, the importance of oxidation of reduced S compounds to post-drought peaks in SO_4 will be evaluated.

Isotope measurements were also used to test the hypothesis that streambed sediment in upland catchments function as 'mini wetlands' - storing S during wet conditions, and exporting SO_4 following dry periods. This prediction was based on the fact that patterns of SO_4 chemistry are synchronous among both upland and wetland-draining catchments, and climate apparently has a similar (but smaller) effect on SO_4 generation in upland systems. Riparian soil in the PC1-08 stream channel is relatively enriched in organic matter compared to upland soil, and total S concentrations were generally higher in subsurface soil from the PC1-08 streambed compared to upland soil in the same depth interval (Table 9-1). In addition, negative $\delta^{34}S$ ratios indicate the occurrence of SO_4 reduction in riparian soil, although samples from only 1 pit were analyzed (Table 9-1).

Nonetheless, $\delta^{34}S$ signatures in PC1-08 stream water were not significantly different from $\delta^{34}S$ values in bulk deposition, indicating that SO_4 reduction in stream soil was not sufficient to alter $\delta^{34}S$-SO_4 ratios in the stream (Chapter 7). In addition, while stream flow in PC1 was nearly continuous through the dry summers of 1999 and 2000, flow in PC1-08 ceased completely for almost 7 weeks in 2000/01. Even following extended dry periods that resulted in a water table draw down of at least 19 cm in the streambed, $\delta^{34}S$ ratios in PC1-08 did not decline and there was no evidence of re-oxidation of reduced S compounds in stream water. While these results could not discount the occurrence of SO_4 reduction in stream soil (certainly negative $\delta^{34}S$ ratios in riparian soil are indicative of reduction), they do provide evidence that increases in SO_4 concentration in PC1-08 following dry periods are not entirely due to re-oxidation of reduced S compounds in stream soil. Considered together, isotope data and results of the analysis of tensiometer and lysimeter data (Chapter 4), indicate that increased SO_4 concentrations in upland streams following dry periods are more likely due to enhanced mineralization of organic S compounds in upland soil, caused by alternating moisture conditions and/or increased temperature. Further work would be required to investigate the effects of varying soil moisture (*i.e.* SO_4 mineralization at different soil moisture contents), temperature and time of incubation on SO_4 release from upland soil. Stable isotope data are unlikely to provide additional information on processes involved in S cycling in aerobic upland systems, since the primary processes of adsorption/desorption and immobilization/mineralization do not cause significant isotope fractionation. For example, Van Stempvoort *et al*. (1990) found that there was little difference (~0.3‰) between the $\delta^{34}S$ values of adsorbed and dissolved sulphate in soil. Similarly, plant assimilation results in only slight isotopic fractionation (<2‰), and although Alewell *et al*. (1999) suggest that mineralization was responsible for a -1‰ difference in $\delta^{34}S\text{-}SO_4$ values in stream water relative to deposition at the Hubbard Brook, interpretation of such small fractionations is tenuous (Mayer *et al*., 1995).

Thus far, 2 primary pools and sources of S export have been identified in catchments, namely peat in wetlands, and soil (organic and mineral) in upland systems. Organic S in both pools may be responsive to changes in catchment dryness, and inter-annual variations in climate appear to be largely responsible for synchronous temporal patterns in SO_4 chemistry among catchments. In wetland-draining catchments climate variations that influence wetland hydrology can account for both temporal patterns of SO_4 export as well as the magnitude of net export. However, upland soils (*e.g*. PC1-08) appear to export more SO_4 than they receive in bulk deposition in every year of record.

Net export appears to be a common feature of upland catchments in regions that have received historically high acid deposition (*e.g*. Driscoll *et al*., 1998; Feger *et al*., 1995; Houle and Carignan, 1995; Löfgren *et al*., 2001; Mitchell *et al*., 1996; Table 10-1). The causes and sources of net SO_4 export, however, remain unclear. A number of explanations have been proposed in the literature including poorly estimated inputs (*i.e*. dry deposition and/or weathering), and net release from internal pools (desorption, mineralization) (*e.g*. Driscoll *et al*., 2001; Edwards *et al*., 1999; Mitchell *et al*., 1986; Wilander, 2001). An increasing number of reports, however, have suggested that SO_4 release from internal pools is responsible for negative S budgets, and that net export is related to decreasing deposition (*e.g*. Driscoll *et al*., 2001; Houle and Carignan, 1995; Mitchell *et al*., 2001).

Net SO_4 export from upland forest soil may occur from 2 potential internal sources, namely desorption from the adsorbed pool, and mineralization of organic S compounds. As shown in figure 10-2, total S input to the PC1-08 catchment over an 8-year monitoring period (1987/88-1994/95) was 83 kg S/ha whereas export in stream water was 113 kg S/ha, which corresponds to a net loss of 30 kg S/ha. The forest at PC1-08 did not increase in biomass over this time period and no harvesting occurred in the catchment (Watmough and Dillon, 2001). Net S accumulation in biomass was therefore ignored in the budget calculation, assuming that the S content of vegetation remained constant over the same time period. Sulphate uptake by vegetation and subsequent return of organic S to the forest floor in litter fall, root turnover and exudates and throughfall, however, may be large relative to inorganic SO_4 input in deposition (Figure 10-2). Net export of 30 kg S/ha in stream water represents a 10% loss from the adsorbed pool (desorption) or 5% loss from the organic-S pool (mineralization). The following sections will discuss the processes of desorption and mineralization in more detail.

Table 10-1. Sulphur pools (kg S/ha) and net stream export in several long-term monitored catchments in North America and Europe.

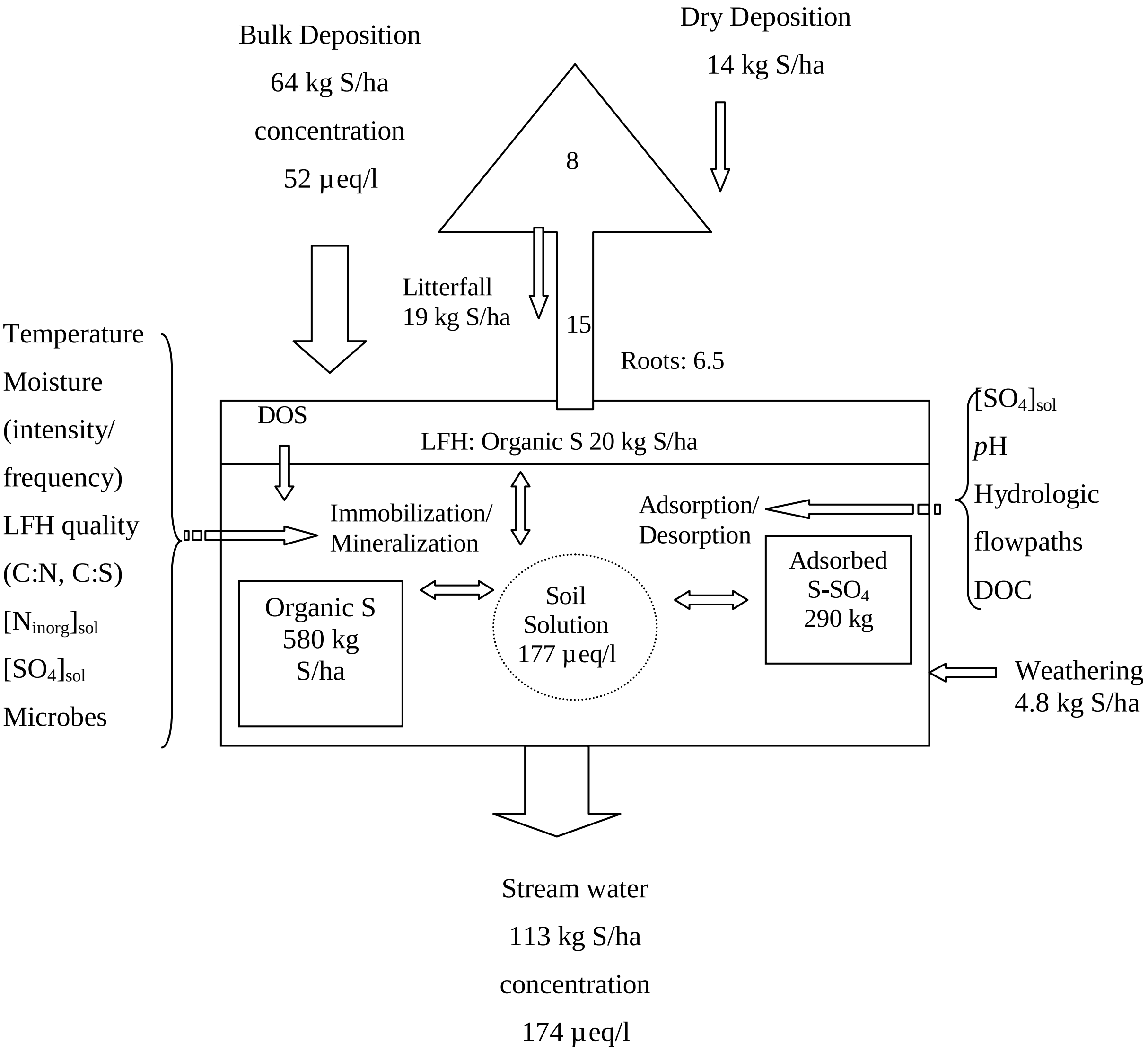
Site	*Organic-S (kg S/ha)*	*Adsorbed S-SO_4 (kg S/ha)*	*Net Export* (kg S/ha)*
Huntington Forest, NY (mixed hardwood) (Mitchell *et al*., 1996)	1200	100	~ -2.5 (TF+SF-stream)
Hubbard Brook, NH W6 (mixed hardwood) (Alewell *et al*., 1999; Hornbeck *et al*., 1997	1576	124	-6 (bulk-stream)
Lac Laflamme, QC (balsam fir) (Houle and Caringnan, 1995)	1230	113	-5 (wet-stream)
Sweden (Norway spruce) (Lofgren *et al*., 2001; Wilander, 2001)	670-800	67-833	-4 ('total'-stream)
Villingen, Germany (Feger, 1995)	1200	680	-10

Note: TF = throughfall, SF = stemflow, 'total' = estimated total (wet+dry) non-sea salt deposition + weathering; wet = wet-only deposition, bulk = bulk deposition; stream = stream export.

Desorption

The degree to which SO_4 adsorption is reversible is an important question, which will affect the recovery of acid impacted surface waters and soils in response to decreases in deposition. Sulphate adsorption increases with SO_4 concentration in soil solution (Chao *et al*., 1962), but it is not clear how catchments with SO_4-adsorbing soils will respond to decreased inputs.

Figure 10-2. Sum of S fluxes (kg S/ha) over an 8-year period (1987/88 through 1994/95) and pools (kg S/ha) in the PC1-08 catchment. Factors affecting SO_4 retention or release in the organic-S and adsorbed SO_4 pool are also indicated. Concentrations (µeq./l) are the average for the 8-year period. Explanation of potential fluxes in dry deposition and weathering are given in Chapter 9.



If SO_4 adsorption is reversible, then soils may gradually release SO_4 in response to decreasing deposition. When SO_4 inputs stabilize, soil solution SO_4 and adsorbed SO_4 should reach a new equilibrium, at which point inputs equal outputs with no net adsorption or desorption (Reuss and Johnson, 1986).

Sulphate adsorption isotherms are often used to describe the partitioning of SO_4 between dissolved and sorbed phases. According to Cosby *et al*. (1986), if SO_4 adsorption is completely reversible, then desorption should follow the same curve as adsorption (*i.e*. curves are symmetric). In this case, total desorption after cessation of deposition requires a much longer time than total adsorption following deposition increases (Cosby *et al*., 1986; Houle and Carignan, 1995). In contrast, if part or all of the adsorbed SO_4 is permanently sorbed, then there is hysteresis in the isotherm, and the desorption/recovery time will be shorter.

Most studies have reported that the majority of adsorbed SO_4 is readily liberated in water extractions, indicating that SO_4 adsorption is largely reversible (*e.g*. Alewell and Matzner, 1993; Harrison *et al*., 1989). Others have pointed out that since sorption reactions are kinetic, then desorption should be almost completely reversible given sufficient reaction time (Mitchell *et al*., 1992b; Sharpley, 1990). The residence time of water in the solum and the dominant hydrologic flow paths will therefore influence adsorption/desorption reactions (Figure 10-2), and under high flow conditions SO_4 partitioning will not be as predicted by adsorption isotherms.

Results of this study showed that SO_4 adsorption/desorption in soil from PC1 and HP6 responded linearly to changes in SO_4 input (Chapter 6). Therefore changes in SO_4 inputs to soil – ultimately *via* deposition are expected to bring about changes in the partitioning of SO_4 between solution and soil at these catchments (Figure 10-2). The adsorbed S pool at PC1 is particularly large, and further measurements of soil depth, bulk density and adsorbed SO_4 (and total S) concentrations would be required to adequately quantify the adsorbed S (and total S) pools at other catchments in Muskoka-Haliburton. However, if we assume that the magnitude of S storage at other catchments falls within the range of values estimated at HP6 (43 kg S-SO_4/ha) and PC1 (290 kg S-SO_4/ha), then the adsorbed pool would be equivalent to 5 - 36 years bulk deposition (20-year average 8 kg S-SO_4/ha/yr). Catchments such as PC1-08, with large pools of reversibly sorbed SO_4 will de-sorb more SO_4 in response to decreased deposition, compared to HP6 or S50 which have smaller pools of adsorbed SO_4 (Alewell and Matzner, 1993). Therefore, soils with small pools of adsorbed SO_4 should appear to respond more rapidly to changes in deposition than catchments with large stores of adsorbed SO_4, which may de-sorb more SO_4 per unit change in deposition. This was demonstrated recently in a comparison of S-dynamics among European catchments. Prechtel *et al.* (2001) reported that catchments in Scandinavia and the Czech Republic/Slovakia, which have thin soils and relatively small SO_4 storage responded more rapidly to decreased deposition than catchments in Germany with deeply weathered soils and high storage capacity (see also Table 10-1).

Results presented in this study demonstrated the processes of adsorption/desorption, and allowed the size of the adsorbed SO_4 pool in soil to be approximated, however, they could not ascertain whether desorption is the sole contributor to net SO_4 export. Current models do not permit the evaluation of desorption as a long-term source of net SO_4 export, since they assume that the adsorbed pool is independent of other pools in soil (*i.e*. organic S pool) and that deposition is the sole input (*e.g*. Driscoll *et al*., 1995; Houle and Carignan, 1995). Such simulations that consider the adsorbed pool to be a progressively shrinking source will likely under-estimate the potential contribution of desorption to negative S budgets. In reality, SO_4 in soil solution is a function of both physico-chemical (adsorption/desorption) and biological reactions (immobilization/ mineralization reactions) (Figure 10-2), and the adsorbed pool may be relatively stable over time if it is continuously replenished by mineralization (Bohn *et al*., 1986). The balance between SO_4 leaching losses and SO_4 inputs through deposition and mineralization will therefore determine the long-term status of the adsorbed pool.

Mineralization

Mineralization of organic S in mineral soil and the forest floor is another potential source of SO_4 to surface waters (Figure 10-2). Oxygen and S isotope data from a number of catchments indicate that stream SO_4 has been biologically cycled prior to export and differences in isotopic signatures between deposition and stream water are apparently consistent with a mineralization source (Alewell *et al*., 1999; Gelineau *et al*., 1989; Mayer *et al*., 1995). Slight changes in S isotope signatures among bulk deposition, soil percolate and upland stream water that were measured in this study could also be interpreted as evidence of biological processing (Chapter 7).

While mineralization appears to be occurring in upland forest soils, could net mineralization be large enough to explain discrepancies in S budgets? Mineralization rates that exceed S inputs in atmospheric deposition have been measured in some studies. For example, Houle *et al*., (2001) extrapolated laboratory incubation results and calculated that ~12 kg S/ha/yr could be released *via* mineralization of LFH material at 20°C. Similarly, using data presented in David *et al*. (1983) it was estimated that as much as 28 kg S/ha/yr could be mobilized in the forest floor annually at Huntington Forest. In this study, it was calculated that as much as 0.9 kg S-SO_4 could be released from dried coniferous LFH material at 25°C within 24-h of re-wetting (see Chapter 5). If this newly released SO_4 were subsequently leached from the soil to the stream channel, mineralization could be an important contributor to stream export. For example, only 3-5 drying and re-wetting cycles in LFH material under these conditions would be sufficient to supply the magnitude of annual net S export that is measured in the PC1-08 stream (3-9 kg S/ha/yr). Given the relatively small S pool in the forest floor at PC1-08 (20 kg S/ha) compared to net export estimates, it is unlikely that mineralization in surface organic material is solely responsible for net S export from catchments. However, it may not be accurate to consider the forest floor S pool as an independent and finite source of S, since roots which extend beneath the forest floor and in to the mineral soil can redistribute SO_4 from subsurface soil to the forest floor *via* litter fall. In addition, at predominantly deciduous catchments such as S50 or HP6, the S pool in the forest floor and the relatively organic-rich A horizon (LaZerte and Scott, 1996) may be much larger compared to PC1-08. Therefore, mineralization in surface organic horizons may be a more important contributor to net export in deciduous catchments. Certainly, the results of the drying and re-wetting experiment (Chapter 5) indicated that SO_4 release in sugar maple LFH was at least 2-times greater than in coniferous LFH. More work would be required to evaluate S pool sizes in predominantly deciduous catchments such as HP6 in the Muskoka-Haliburton region.

In both deciduous and coniferous catchments, however, the bulk of S storage is present in subsurface mineral soil (Figure 10-2). In most forest soils, the majority of total soil S is organic, consisting of C-bonded S compounds and ester sulphates (Mitchell *et al.*, 1992c). While we do not have direct measurements of C-S and ester-SO_4 concentrations in mineral soil at PC1, reduced inorganic S compounds are negligible in most well-drained upland soils, and so subtraction of adsorbed S-SO_4 (290 kg S/ha) from total S numbers (870 kg S/ha) yields a reasonable estimate of organic S storage (*i.e*. ~580 kg S/ha) in mineral soil.

While the pool of organic S in mineral soil is certainly large, results presented in Chapter 5 indicated that SO_4 was not released from mineral soil in response to changing moisture or temperature. Similarly, changes in N availability did not influence net SO_4 concentrations in mineral soil in short-term (24h) incubations (Chapter 8). One could conclude from these tests that biological processes are not important for S turnover in mineral soil, and that the organic S pool is relatively recalcitrant. However, SO_4 release through mineralization of organic S compounds in mineral soil may have been difficult to detect with the experimental design. As was indicated in Chapters 4 & 6, adsorption/desorption reactions are clearly important for buffering SO_4 concentrations in infiltrating LFH percolate and respond to changes in SO_4 input. Therefore any SO_4 that was released in response to changes in temperature and moisture (Chapter 5), or N-additions (Chapter 8) may have been subsequently adsorbed by mineral soil surfaces. The time frame of biological S-cycling should also be considered when designing mineralization studies, since the net effect of immobilization/mineralization reactions may only be manifested over longer time periods than are typically covered in laboratory incubations (*e.g*. Houle et al., 2001). In order to assess directly the potential for mineralization in mineral soil, longer-term incubations or field incubations may be required, optimally using isotope tracers to label the organic S compounds.

While results of this study could not demonstrate the process of mineralization in B-horizon soil, possibly due to methodological difficulties outlined above, the large organic S pool in mineral soil represents an important source of mineralization. Therefore the question remains as to whether mineralization could contribute to net S export from catchments. If mineralization is supplying net SO_4 export, it follows that at some point in the past organic S was instead accumulated in soil. This would imply that immobilization and tree uptake previously exceeded mineralization and stream export, however at some point the balance shifted from net retention to net mineralization. Why would such a shift occur? There is no evidence that such a shift would occur naturally over such a short time scale (*i.e*. decades) in the absence of changes in deposition, climate or management. Negative budgets have been reported over a wide geographic area, from eastern North America to Scandinavia and Central Europe. These regions have all received high S deposition in the past, but in all cases S deposition has more recently declined (last 10-30 years). Could net mineralization be a response to decreased deposition (a)? Or, alternatively, could climate changes in part explain negative S budgets (b)?

(a) Deposition effects

Sulphur deposition could affect mineralization through changes in the exogeneous supply of SO_4 (*i.e.* availability in soil solution), and/or by longer-term effects on substrate quality (*i.e.* endogeneous S concentration) (Figure 10-2). Sulphate immobilization increases in response to greater SO_4 availability (Fitzgerald *et al.*, 1983), and there is also evidence that S enzyme activity is inhibited at higher SO_4 concentrations (Freney *et al.*, 1986). If the opposing reactions of decreased immobilization and enhanced enzyme activity under conditions of lower SO_4 availability also hold, then net SO_4 mineralization could in theory increase in response to decreased deposition. Indeed, data presented in Chapter 8 indicated that net SO_4 concentrations were higher in LFH material that was incubated with low SO_4 (<42 µeq/l) compared to high SO_4 (>208 µeq/l). A different method, possibly using isotope tracers would be required to test the effect of variable SO_4 additions on net SO_4 release from mineral soil, given the potential masking effect of the adsorbed pool noted in Chapters 5 and 8.

Sulphur release through mineralization may also be affected by the supply of N (Figure 10-2). While S deposition has declined markedly in many regions over the past few decades, N deposition has stayed constant or increased slightly, and is now almost equal to S deposition. In the Muskoka-Haliburton region, N deposition is currently around 8 kg N/ha/year (57 meq/m^2/yr), made up of ~60% N-NO_3 and 40% N-NH_4. Nitrogen is normally the limiting nutrient in terrestrial systems, and some studies have suggested that N-availability may influence rates of litter decomposition (Berg and Matzner, 1996; Fog, 1988). In a survey of litter decomposition rates across a geographical gradient of N deposition, Kuperman (1999) found that S mineralization was greater at sites with increased exogeneous N availability. In contrast, N additions did not appear to affect net SO_4 concentrations in either LFH or mineral soil from PC1 (Chapter 8). However, longer-term changes in substrate quality (*i.e*. endogeneous N content) due to the gradual accumulation of N in vegetation and soil could also affect mineralization rates (*e.g*. Aber *et al*., 1989; Berg and Matzner, 1996). Further work would be required to elucidate the interactions between N availability and S cycling in soil.

Similar to N, long-term SO_4 deposition may also result in gradual changes in substrate quality by altering the S content of vegetation and soil. Several studies have shown that the S content of foliage and the forest floor increases along a spatial deposition gradient (Driscoll *et al*., 2001; Pregitzer *et al*. 1992), or an historical gradient of deposition (Zhao *et al*., 1994). While net S accumulation in trees is a small part of the overall catchment S balance, Johnson (1984) reported that trees are able to accumulate and cycle *excess* S. This apparent contradiction implies that any excess S is not stored in wood, but is rather concentrated in foliage (or roots) and returns to the forest floor in litter fall (or root turnover/exudates). Indeed, the S distribution in forest biomass (Table 9-2) indicates that even if the total S content of foliage (crown) were to double over a 20-year period of elevated deposition, this would only result in an accumulation rate of 7/20, or 0.35 kg S/ha/yr, which would be undetectable in catchment S budgets. Mitchell *et al*. (1989) postulated that the large organic S pool in mineral soil could be the result of centuries of accumulation of dissolved organic S compounds (DOS) in the subsurface. Root turnover and root exudates are also likely an important source of organic-S to soil (Figure 10-2). Leaching of organic acids from the forest floor is an integral component of pedogenesis, and translocation of DOS compounds *via* percolating solution to the B-horizon could easily account for the magnitude of organic S accumulation in mineral soil since forests were established after the last glaciation (~8,000 yrs b.p.) (Houle *et al*., 2001; Mitchell *et al*., 1989). In theory, if increased S deposition resulted in a proportional increase in S cycling through the biomass, then organic S inputs to the forest floor in litterfall and root turnover might have also increased, resulting in potentially greater DOS transfer (and presumably accumulation) to the B-horizon.

On a related note, if the S content of litter inputs to soil have increased over time, this should result in a shift in the C:S ratio of surface soil toward lower values. Agricultural studies commonly cite the C:S ratio as an indicator of the S nutritional status of soil (*e.g*. Chapman, 1997; Eriksen, 1997a). A C:S ratio of 400 or greater is indicative of S limitation and immobilization, whereas a C:S ratio of less than 200 indicates S present in excess of microbial demands and tends to favour mineralization (Scherer, 2001). Apparently either process can dominate at ratios between 200 and 400. The C:S ratio of forest floor material at PC1 (250) is close to the limit where S mineralization might be favoured to occur (Chapter 8).

Organic S storage in soil is clearly large enough to sustain the magnitude of net S export that is currently measured in Muskoka-Haliburton catchments for decades. While the above discussion indicates that deposition may have a direct (*i.e*. exogeneous SO_4 availability) or indirect effect (substrate S content) on S mineralization, it is unclear whether the shift from net S accumulation to net export, which most certainly has occurred, was a direct response to changing deposition.

Possible clues as to the cause(s) of shifts in S budgets can be gained by reviewing the few studies that have estimated historical changes in soil S storage. For example, reconstructed S budgets for the Bohemian Forest (BF, Germany) and Tatra Mountains (TM, Slovakia) were in balance until the 1930s, became positive during the 1950s through 1980s but then switched to negative values in the late 1980s (TM) or mid 1990s (BF) (Kopacek *et al.*, 2001). Deposition over the same time period was relatively stable through the 1930s, increased rapidly between 1950 and 1980, reached a maximum in the early 1980s, but has since declined to current levels that are similar to those in the 1930s (BF) to 1950s (TM). Both desorption and mineralization, respectively were suggested to contribute to net export in these catchments. Adsorption/desorption processes have clear links to changes in deposition, however no explanation was given as to why S mineralization might have become a source of SO_4 coincident with the period of declining deposition (Kopacek *et al*., 2001).

Bailey *et al*. (2001) similarly estimated S accumulation in soil in Northern Ireland over the period 1940 to 1990. Sulphur budgets were apparently positive between 1940 and 1965, but became negative from the 1970s onwards at the same time that SO_4 deposition began to decline. The authors suggested that decreases in S inputs in deposition and fertilizer may have stimulated S mineralization, and noted that variations in rainfall S concentration were inversely coherent with S concentrations in stream water. The latter observation may indicate that changes in exogeneous SO_4 supply affected net mineralization (Bailey *et al*., 2001).

While mineralization rates may have increased in response to lower SO_4 in soil solution, it is also possible that immobilization and plant uptake of S have declined in recent decades proportional to the decrease in deposition; particularly if previous microbial immobilization and plant uptake were greater than biological demand. Therefore, even if gross mineralization rates have remained constant over time, a decrease in total immobilization could result in greater net mineralization.

(b) Climate effects

Climate exerts a strong control on organic matter decomposition, and may also affect the release of inorganic nutrients through mineralization (Figure 10-2). The average global temperature has increased by approximately 0.5°C over the past century, and is expected to increase further due to the continuing input of greenhouse gases into the atmosphere (Kirschbaum, 1999). Higher temperatures have been shown to increase N-mineralization and nitrification (Foster, 1989; Parker and Larson, 1962), and C respiration (Cao and Woodward, 1998; Davidson *et al*., 1998;

Leiros *et al*., 1999; Waksman and Gerretsen, 1931). Storage of N and C in soil was found to be inversely correlated with temperature (Post *et al*., 1982; 1985). Several studies have also documented a stimulatory effect of temperature on S mineralization (Foster 1989; Jaggi *et al*., 1999; Kieft *et al*., 1987; Williams, 1967). Sulphate mineralization is in part mediated by extra-cellular enzymes, which apparently have different temperature activity optima (Strickland *et al*., 1984). Temperature enhanced SO_4 release from dried peat in this study, and appeared to increase SO_4 release from coniferous LFH material (Chapter 5).

Extreme climatic events have also become more common in recent decades. Hurricanes, floods and droughts were more frequent during the 1980s and 1990s than in any other decade on record, and there has been a tendency towards heavier precipitation over the past 40 years (Francis and Hengeveld, 1998). An increase in weather intensity might be manifested in a greater frequency and duration of dry periods that are subsequently broken by more intense precipitation events. Associated fluctuations in soil moisture (*i.e*. drying and re-wetting) can have large effects on nutrient mineralization (Grierson *et al*., 1998; Pulleman and Tietema, 1999). Results of this study showed that drying and re-wetting events could have a substantial effect on SO_4 release from organic material (Chapter 5).

The El Niño phenomenon is an example of an extreme climate event that has increased in both frequency and persistence over the past 30 years (Francis and Hengeveld, 1998). In an El Niño year, the normally strong easterly trade winds slacken, and warm water gradually returns to the eastern Pacific, preventing upwelling of cooler bottom waters. The consequent rise in sea surface temperature changes the pattern of rising and falling air masses over the equatorial Pacific Ocean, ultimately altering atmospheric circulation around the globe. In south-central Ontario, El Niño years are associated with dry, warm summer conditions, which markedly affect stream hydrology. In El Niño years, flow in many streams ceases for up to months at a time, and soil moisture becomes limiting in upland soils (Chapter 4). Chemical export is also affected, particularly in wetland-draining catchments. Prolonged dry conditions cause wetlands to switch from net retainers to net sources of SO_4, which can have large effects on downstream lakes (Chapter 3).

Climate may have other indirect effects on SO_4 cycling. For example, changes in the seasonal distribution of runoff, which have been reported at the Turkey Lakes Watershed (Beall *et al*., 2001) could have important implications for hydrological and chemical fluxes. For example, if summers become drier but fall precipitation increases there could be a greater proportion of flow through organic-rich surface soil, which would increase the export of many chemicals such as DOC and SO_4. Similarly, if rain events become more ‘flashy’, such that dry periods are interspersed with sudden storm events, there could be more surface runoff (thatched roof effect) and less flow through the soil profile. Changes in climate that influence hydrologic flow paths could have important implications for chemicals such as SO_4 and DOC, which are found in relatively high soluble concentrations in the forest floor, but passage through the underlying mineral soil greatly reduces their concentrations in runoff mainly through adsorption reactions. Prolonged dry conditions could also result in greater macropore flow if drying and re-wetting result in soil cracking and root death. Flow *via* macropores would similarly allow SO_4 (and DOC) in soil percolate to effectively bypass adsorption sites in mineral soil.

The period of data collection in Muskoka-Haliburton catchments (1980-present) happens to coincide with a period of extreme climate. While climate is certainly responsible for inter-annual variations in SO_4 concentrations and export, it is uncertain whether climate is entirely responsible for negative catchment S budgets. In wetlands such as the PC1 swamp, net retention *vs*. net export appears to be entirely a function of climate, as it affects the hydrologic balance within the wetland. In upland streams such as PC1-08, SO_4 concentrations are also related to changes in catchment dryness, however net export occurs in both wet and dry years. Shifts from positive to negative SO_4 retention in European catchments coincided with the timing of large declines in atmospheric S deposition and fertilizer inputs (Bailey *et al*., 2001; Eriksen, 1997b; Kopacek *et al*., 2001). These studies indicate a relationship between S inputs and catchment retention that could not be evaluated in the data record for catchments in south-central Ontario. However, given the timing of the 3 largest peaks in SO_2 emissions in the eastern US (1943, 1977, 1979) and eastern Canada (1974, 1979, 1981), it is likely that S deposition in Muskoka-Haliburton was highest in the 1970s (Dillon *et al*., 1988). Similar to the European situation, a subsequent decline in deposition through the early 1980s may have precipitated the 'bleeding' of stored S from catchment soil, and thereby explain generally negative catchment budgets observed from the 1980s onwards (Tables 9-3, 9-4). Results from this study cannot confirm the linkage between changes in deposition and net SO_4 export in the field, however the adsorbed SO_4 pool at PC1 is certainly large enough to account for net export for decades. Lower adsorbed S-SO_4 storage at HP6 suggests that desorption is not as important for net S-export at this catchment. The relative importance of desorption *vs*. mineralization; however, is likely to vary depending on soil type, litter quality, hydrology, *etc*. It is possible, that mineralization might be a more important contributor to net S export at deciduous catchments such as HP6 and S50 which have relatively deep, organic rich A horizons (LaZerte and Scott, 1996; Lozano *et al*., 1987), and where SO_4 mineralization rates in the forest floor are apparently greater (Chapter 5; see also Foster, 1989). Further work, however, would be required to accurately quantify S pools at other Muskoka-Haliburton catchments.

In summary, a number of sources could account for the generally negative S budgets calculated for Muskoka-Haliburton catchments. While dry deposition and mineral weathering likely account for part of the net export, budget calculations indicate excess S losses even when conservative estimates of these inputs are included and therefore other explanations must be invoked. Desorption and mineralization likely both contribute to net export, but results presented in this study do not allow the relative importance of either source to be assessed. Rather, it is suggested that the physico-chemical processes of adsorption desorption and biological processes of immobilization and mineralization should be considered together, as the inorganic and organic S pools in soil are not independent. Sulphate partitioning to mineral soil will be directly related to changes in SO_4 in soil solution, which may be brought about by variations in SO_4 deposition, and/or biological transformations (Figure 10-2). Biological transformations may in turn be affected by variations in climate that bring about changes in soil moisture and temperature. Adsorption/desorption reactions are likely the primary short-term (immediate) controls on SO_4 concentrations in soil, whereas mineralization and immobilization may be more important in the long-term (*i.e.* years). Fluctuating moisture conditions and changes in temperature, however, may increase mineralization rates and result in a greater contribution of mineralization to SO_4 export than would be expected. If catchments are currently a net source of S it follows that at some point in the past S was instead accumulated. The shift between net retention and net export must have occurred prior to the onset of monitoring, and was possibly precipitated by large declines in S deposition that likely occurred between the 1970s and early 1980s. The duration of net export will be determined by the magnitude of S storage in catchment soil, and the time until deposition inputs become stable (assuming no climate variations). Catchments with large S accumulations will release more S-SO_4 per unit change in deposition, and therefore will exhibit 'delayed recovery'. Ultimately, models that couple the physico-chemical processes of adsorption/desorption with the biological processes of immobilization/mineralization are required to adequately interpret and predict catchment responses to deposition. Annual variations in climate are superimposed on the long-term trend of decreasing deposition, and therefore may mask predicted trajectories of recovery.

REFERENCES

Aber, J.D., Nadelhoffer, K.J., Steudler, P.A., Melillo, J.M., 1989. Nitrogen saturation in Northern forest ecosystems. Bioscience 39, 378-386.

Adams, R., Rawajfih, Z., 1977. Basaluminite and alunite: A possible cause of sulfate retention in acid soils. Soil Science Society of America Journal 41, 686-692.

Agriculture Canada Expert Committee on Soil Survey, 1998. Canadian System of Soil Classification. Publ. 1646. 187 pp.

Ahrens, C.D., 1991. Meteorology Today: An Introduction to Weather, Climate and the Environment. West Publishing Co., St. Paul, MN.

Alewell, C., Mitchell, M.J., Likens, G.E., Krouse, H.R., 1999. Sources of stream sulfate at the Hubbard Brook Experimental Forest: Long-term analyses using stable isotopes. Biogeochemistry 44, 281-299.

Alewell, C., Matzner, E. 1993. Reversibility of soil solution acidity and of sulfate retention in acid forest soils. Water, Air, and Soil Pollution 71, 155-165.

Andreae, M.O., Jaeschke, W.A., 1992. Exchange of sulphur between biosphere and atmosphere over temperate and tropical regions. *In*: Howarth, R.W., J.W.B. Stewart, Ivanov, M.V. (Eds.) Sulphur cycling on the continents. Scope 48. John Wiley and Sons Ltd., Chichester.

Atlas, R.M., Bartha, R., 1993. Microbial Ecology Fundamentals and Applications. The Benjamin Cummings Publishing Co., Inc. Redwood City, CA.

Bailey, J.S., Deng, Y., Smith, R.V., 2001. Changes in soil organic carbon storage under grassland as evidenced by changes in sulphur input-output budgets. Chemosphere 42, 141-151.

Baron, J.S., Allstott, E.J., Newkirk, B.K., 1995. Analysis of long term sulfate and nitrate budgets in a Rocky Mountain basin. *In*: Tonnessen, K., Williams, M.W., Tranter, M. (Eds.) Biogeochemistry of seasonally snow-covered catchments. IAHS Pub. No.228. pp. 255-261.

Baumgardner, R.E., Lavery, T.F., Rogers, C.M., Isil, S.S., 2002. Estimates of the atmospheric deposition of sulfur and nitrogen species: Clean Air Status and Trends Network, 1990-2000. Environmental Science and Technology 36, 2614-2629.

Bayley, S.E., Behr, R.S., Kelly, C.A., 1986. Retention and release of S from a freshwater wetland. Water, Air, and Soil Pollution 31, 101-114.

Beall, F.D., Semkin, R.G., Jeffries, D.S., 2001. Trends in the output of first-order basins at the Turkey Lakes Watershed, 1982-1996. Ecosystems 4, 514-526.

Benson, B.J., Lenters, J.D., Magnuson, J.J., Stubbs, M., Kratz, T.K., Dillon, P.J., Hecky, R.E., Lathrop, R.C., 2000. Regional coherence of climatic and lake thermal variables of four lake districts in the Upper Great Lakes Region of North America. Freshwater Biology 43, 517-527.

Berg, B., Matzner, E., 1996. Effect of N deposition on decomposition of plant LFH and soil organic matter in forest systems. Environmental Reviews 5, 1-25.

Biron, P.M., Roy, A.G., Courchesne, F., Hendershot, W.H., Cote, B., Fyles, J., 1999. The effects of antecedent moisture conditions on the relationship of hydrology to hydrochemistry in a small forested watershed. Hydrological Processes 13, 1541-1555.

Bohn, H.L., Barrow, N.J., Rajan, S.S.S., Parfitt, R.L., 1986. Reactions of inorganic sulfur in soils. *In*: Sulfur in Agriculture. American Society of Agronomy, Madison, WI.

Bollmann, A., and Conrad, R., 1998. Influence of O_2 availability on NO and N_2O release by nitrification and denitrification in soils. Global Change Biology 4, 387-396.

Brady, N., 1990. The nature and properties of soils. 10th edition. Macmillan Publishing Co., NY.

Brown, K.A., MacQueen, J.F., 1985. Sulphate uptake from surface water by peat. Soil Biology and Biochemistry 17, 411-420.

Cabrera, M.L., 1993. Modeling the flush of nitrogen mineralization caused by drying and rewetting soils. Soil Science of America Journal 57, 63-66.

Carvalho, L, Moss, B., 1999. Climate sensitivity of Oak Mere: A low altitude acid lake. Freshwater Biology 42, 585-591.
Chapman, S.J., 1997. Barley straw decomposition and S immobilization. Soil Biology and Biochemistry 29, 109-114.

Christophersen, N., Wright, R.F., 1981. Sulfate budget and a model for sulfate concentrations in stream water at Birkenes, a small forested catchment in southernmost Norway. Water Resources Research 17, 377-389.

Clair, T.A., Dillon, P.J., Ion, J., Jeffries, D.S., Papineau, M., Vet, R., 1995. Regional precipitation and surface water chemistry trends in southeastern Canada (1983-1991). Canadian Journal of Fisheries and Aquatic Science 52, 197-212.

Cooper, 1972. Arylsulphatase activity in northern Nigerian soils. Soil Biology and Biochemistry 4, 333-337.

Cosby, B.J., Hornberger, G.M., Wright, R.F., Galloway, J.N., 1986. Modeling the effects of acid deposition: Control of long-term sulfate dynamics by soil sulfate adsorption. Water Resources Research 22, 1283-1291.

Courchesne, F., Landry, R., 1994. Sulfate retention by spodosols in the presence of organic ligands. Soil Science 158, 329-336.

Dail, D.B., Fitzgerald, J.W., 1999. S cycling in soil and stream sediment: influence of season and in situ concentrations of carbon, nitrogen and sulfur. Soil Biology and Biochemistry 31, 1395-1404.

Dann, M.S., Lynch, J.A., Corbett, 1986. Comparison of methods for estimating sulfate export from a forested watershed. Journal of Environmental Quality 15, 140-145.

David, M.B., Mitchell, M.J., Scott, T.J., 1987. Importance of biological processes in the sulfur budget of a northern hardwood ecosystem. Biology and Fertility of Soils 5: 258-264.

David, M.B., Schindler, S.C., Mitchell, M.J., Strick, J.E., 1983. Importance of organic and inorganic sulfur to mineralization processes in a forest soil. Soil Biology and Biochemistry 15, 671-677.

David, M.B., Mitchell, M.J., Nakas, J.P., 1982. Organic and inorganic sulfur of a forest soil and their relationship to microbial activity. Soil Science Society of America Journal 46, 847-852.

Davidson, E.A., Verchot, L.V., Cattanio, J.H, Ackerman, I.L., Carvalho, J.E.M, 2000. Effects of soil water content on soil respiration in forests and cattle pastures of eastern Amazonia. Biogeochemistry 48, 53-69.

Davidson, E.A., Belk, E., Boone, R.D., 1998. Soil water content and temperature as independent or confounded factors controlling soil respiration in a temperate mixed hardwood forest. Global Change Biology 4, 217-227.

Devito, K.J., Westbrook, C.J., Schiff, S.L., 1999. Nitrogen mineralization and nitrification in upland and peatland forest soils in two Canadian Shield catchments. Canadian Journal of Forest Research 29, 1793-1804.

Devito, K.D., Hill, A.R., Dillon, P.J., 1999. Episodic sulphate export from wetlands in acidified headwater catchments: prediction at the landscape scale, Biogeochemistry 44, 187-203.

Devito, K.D., Hill, A.R., 1999. Sulphate mobilization and pore water chemistry in relation to groundwater hydrology and summer drought in two conifer swamps on the Canadian Shield. Water, Air, and Soil Pollution 113, 97-114.

Devito, K.D., Hill, A.R., 1997. Sulphate dynamics in relation to groundwater-surface water interactions in headwater wetlands of the southern Canadian Shield. Hydrological Processes 11, 485-500.

Devito, K.J., 1995. Sulphate mass balances of Precambrian Shield wetlands: the influence of catchment hydrology. Canadian Journal of Fisheries and Aquatic Science 52, 1750-1760.

Dillon, P.J., Evans, H.E., 2002. Long-term changes in the chemistry of a soft-water lake under changing acid deposition rates and climate fluctuations. Verh. Internat. Verein. Limnol. (in press).

Dillon, P.J., Molot, L.A., Futter, M., 1997. The effect of El Niño-related drought on the recovery of acidified lakes. Environmental Monitoring and Assessment 46, 105-111.

Dillon, P.J., LaZerte, B.D., 1992. Response of the Plastic Lake catchment, Ontario, to reduced sulphur deposition. Environmental Pollution 77, 211-217.

Dillon, P.J., Molot, L.A., Scheider, W.A., 1991. Phosphorus and nitrogen export from forested stream catchments in central Ontario. Journal of Environmental Quality 20, 857-864.

Dillon, P.J., Molot, L.A., 1990. The role of ammonium and nitrate retention in the acidification of lakes and forested catchments. Biogeochemistry 11, 23-43

Dillon, P.J., Lusis, M., Reid, R.A., Yap, D., 1988. Ten-year trends in sulphate, nitrate and hydrogen deposition in central Ontario. Atmospheric Environment 22, 901-905.

Dillon, P.J., Reid, R.A., de Grosbois, E., 1987. The rate of acidification of aquatic ecosystems in Ontario, Canada. Nature 329, 45-48.

Dillon, P.J., Jeffries, D.S., Scheider, W.A., 1982. The use of calibrated lakes and watersheds for estimating atmospheric deposition near a large point source. Water, Air, and Soil Pollution 18, 241-258.

Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L, Weathers, K.C., 2001. Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies. Bioscience 51, 180-198.

Driscoll, C.T., Likens, G.E., Church, M.R., 1998a. Recovery of surface waters in the northeastern U.S. from decreases in atmospheric deposition of sulfur. Water, Air, and Soil Pollution 105, 319-329.

Driscoll, C.T., Postek, K.M., Mateti, D., Sequeira, K., Aber, J.D., Kretser, W.J., Mitchell, M.J., Raynal, D.J., 1998b. The response of lake water in the Adirondack region of New York to changes in acidic deposition. Environmental Science and Policy 1, 185-198.

Driscoll, C.T., Postek, K.M., Kretser, W., Raynal. D.J., 1995. Long-term trends in the chemistry of precipitation and lake water in the Adirondack region of New York, USA. Water, Air, and Soil Pollution 85, 583-588.

Edwards, P.J., Gregory, J.D., Allen, H.L., 1999. Seasonal sulfate deposition and export patterns for a small Appalachian watershed. Water, Air, and Soil Pollution 110, 137-155.

Eimers, M.C., Dillon, P.J., 2002. Climate effects on sulphate flux from forested catchments in south-central Ontario. Biogeochemistry 61, 337-355.

Eriksen, J., 1997a. Sulphur cycling in Danish agricultural soils: inorganic sulphate dynamics and plant uptake. Soil Biology and Biochemistry 29, 1379-1385.

Eriksen, J., 1997b. Animal manures as S fertilizer. Sulphur Agriculture 20, 27-30.

Feger, K.H., 1995. Solute fluxes and sulfur cycling in forested catchments in SW Germany as influenced by experimental $(NH_4)_2SO_4$ treatments. Water, Air, and Soil Pollution 79, 109-130.

Findeis, J., LaZerte, B., Scott, L., 1993. Dorset Research Centre Biogeochemistry Study: Lysimeters and tensiometers. Ontario Ministry of Environment and Energy DR 93/2.

Fitzhugh, R.D., Furman, T., Korsak, A.K., 2001. Sources of stream sulphate in headwater catchments in Otter Creek Wilderness, West Virginia, USA. Hydrological Processes 15, 541-556.

Fog, K., 1988.The effect of added nitrogen on the rate of decomposition of organic matter. Biological Reviews 63, 433-462.

Foster, N.W., 1989. Influences of seasonal temperature on nitrogen and sulfur mineralization/immobilization in a maple-birch forest floor in central Ontario. Canadian Journal of Soil Science 69, 501-514.

Francis, D., Hengeveld, H., 1998. Extreme weather and climate change. Environment Canada.

Freney, J.R., 1986. Forms and reactions of organic sulfur compounds in soil. *In*: Sulfur in Agriculture. American Society of Agronomy, Madison, WI.

Fuller, R.D., David, M.B., Driscoll, C.T., 1985. Sulfate relationships in some forested spodosols of the northeastern U.S. Soil Science Society of America Journal 49, 1034-1040.

Ghani, A., McLaren, R.G., Swift, R.S., 1992. Sulphur mineralization and transformations in soils as influenced by additions of carbon, nitrogen and sulphur. Soil Biology and Chemistry 24, 331-341.

Gobran, G.R., Selim, H.M., Hultberg, H., Andersson, I., 1998. Sulfate adsorption-desorption in a Swedish forest soil. Water, Air, and Soil Pollution 108, 411-424.

Gobran, G.R., Nilsson, S.I., 1988. Effects of forest floor leachate on sulfate retention in a spodosol soil. Journal of Environmental Quality 17, 235-239.

Grierson, P.F., Comerford, N.B., Jokela, E.J., 1998. Phosphorus mineralization kinetics and response of microbial phosphorus to drying and rewetting in a Florida spodosol. Soil Biology and Biochemistry 10/11, 1323-1331.

Groscheova, H., Novak, M., Alewell, C., 2000. Changes in the δ^{34}S ratio of pore-water sulfate in incubated *Sphagnum* peat. Wetlands 20, 62-69.

Hansen, A. 1996. A Pinatubo climate modelling investigation. *In*: Fiocco, G., Fua, D., Visconti, G. (*eds*). The Mount Pinatubo Eruption: Effects on the Atmosphere and Climate. Springer-Verlag, Heidelberg Germany.

Harrison, R.B., Johnson, D.E., Todd, D.E., 1989. Sulfate adsorption and desorption reversibility in a variety of forest soils. Journal of Environmental Quality 18, 419-426.

Henricksen, A., 1970. Determination of total nitrogen, phosphorus and iron in freshwater by photo-oxidation with ultraviolet radiation. Analyst London 95, 601-608.

Hern, J.A., 1990. Influence of soil sulphate adsorption on lake acidification. Verh. Internat. Verein. Limnol. 24, 150-151.

Hesslein, R.H., Capel, M.J., Fox, D.E., 1988. Stable isotopes in sulfate in the inputs and outputs of a Canadian Shield watershed. Biogeochemistry 5, 263-273.

Hinton, M.J., Schiff, S.L., English, M.C., 1998. Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield. Biogeochemistry 41, 175-197.

Hinton, M.J., Schiff, S.L., English, M.C., 1993. Physical properties governing groundwater flow in a glacial till catchment. Journal of Hydrology 142, 229-249.

Hodson, M.E., Langan, S.J., 1999. A long-term soil leaching column experiment investigating the effect of variable sulphate loads on soil solution and soil drainage chemistry. Environmental Pollution 104, 11-19.

Hornbeck, J.W., Bailey, S.W., Buso, D.C., Shanley, J.B., 1997. Streamwater chemistry and nutrient budgets for forested watersheds in New England: variability and management implications. Forest Ecology and Management 93, 73-89.

Houle, D., Carignan, R., Ouimet, R., 2001. Soil organic sulfur dynamics in a coniferous forest. Biogeochemistry 53, 105-124.

Houle

Houle, D., Paquin, R., Camire, C., Ouimet, R. and Duchesne, L., 1997. Response of the Lac Clair Watershed to changes in precipitation chemistry (1988-1994). Canadian Journal of Forest Research 27, 1813-1821.

Houle, D. and Carignan, R., 1995. Role of SO_4 adsorption and desorption in the long-term S budget of a coniferous catchment on the Canadian Shield. Biogeochemistry 28, 162-182.

Houle, D., Carignan, R., Lachance, M., 1995. Dissolved organic carbon and sulfur in southwestern Quebec lakes: Relationships with catchment and lake properties. Limnology and Oceanography 40, 710-717.

Hultberg, H., Moldan, F., Andersson, B.I, Skeffington, R., 1998. Recovery from acidification in the forested covered catchment experiment at Gardsjon: Effects on biogeochemical output fluxes and concentrations. *In*: Hultberg, H., Skeffington, R. (Eds.) Experimental Reversal of Acid Rain Effects. John Wiley & Sons Ltd.

Huntington, T.G., 1996. Predicting watershed acidification under alternate rainfall conditions. Water, Air, and Soil Pollution 90, 429-450.

Jaggi, R.C., Aulakh, M.S., Sharma, R., 1999. Temperature effects on soil organic sulphur mineralization and elemental sulphur oxidation in subtropical soils of varying pH. Nutrient Cycling in Agroecosystems 54, 175-182.

Jeffries, D.S., 1997. Canadian Acid Rain Assessment Volume 3: Effects on Canada’s Lakes, Rivers and Wetlands. Environment Canada.

Jeffries, D.S., Clair, T.A., Dillon, P.J., Papineau, M., Stainton, M.P., 1995. Trends in surface water acidification at ecological monitoring sites in southeastern Canada (1981-1993). Water, Air, Soil Pollution 85, 577-582.

Jeffries, D.S., Snyder, W.R., 1983. Geology and geochemistry of the Muskoka-Haliburton study area. Ontario Ministry of the Environment. DR 83/2.

Johnson, D.W., 1984. Sulfur cycling in forests. Biogeochemistry 1, 29-43.

Johnson, D.W, Todd, D.E., 1983. Relationships among iron, aluminum, carbon, and sulfate in a variety of forest soils. Soil Science Society of America Journal 47, 792-800.

Johnson, D.W., Henderson, G.S., Huff, D.D., Lindberg, S.E., Richter, D.D., Shriner, D.S., Todd, D.E., Turner, J., 1982. Cycling of organic and inorganic sulphur in a chestnut oak forest. Oecologia 54, 141-148.

Kaiser, K., Kaupenjohann, M., 1998. Influence of the soil solution composition on retention and release of sulfate in acid forest soils. Water, Air, and Soil Pollution 101, 363-376.

Keller, W., Pitbaldo, J.R., Carbone, J., 1992. Chemical response of acidic lakes in the Sudbury, Ontario area to reduced sulfur emissions, 1981-1989. Canadian Journal of Fisheries and Aquatic Science 49, 25-32.

Khanna, P.K, Prenzel, J., Meiwes, K.J., Ulrich, B., Matzner, E., 1987. Dynamics of sulfate retention by acid forest soils in an acidic deposition environment. Soil Science Society of America Journal 51, 446-452.

Kirkwood, D.E., Nesbitt, H.W., 1991. Formation and evolution of soils from an acidified watershed: Plastic Lake, Ontario, Canada. Geochimica Cosmochimica Acta 55, 1295-1308.

Kirkwood, D.E., 1990. Weathering rates within the soils of Plastic Lake. MSc. Thesis, University of Western Ontario. London, Ontario Canada.

Kirschbaum, M.U.F., 1995. The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. Soil Biology and Biochemistry 27, 753-760.

Kopacek, J., Vesely, J., Stuchlik, E., 2001. Sulphur and nitrogen fluxes and budgets in the Bohemian Forest and Tatra Mountains during the Industrial Revolution (1850-2000). Hydrology and Earth System Sciences 5, 391-405.

Krauskopf, K.B., 1967. Introduction to geochemistry. McGraw-Hill, 721pp.

Kuperman, R.G., 1999. LFH decomposition and nutrient dynamics in oak-hickory forests along an historic gradient of nitrogen and sulfur deposition. Soil Biology and Biochemistry 31, 237-244.

LaZerte, B.D., Scott, L., 1996. Soil water leachate from two forested catchments on the Precambrian Shield, Ontario. Canadian Journal of Forest Research 26, 1353-1365.

LaZerte, B.D., 1993. The impact of drought and acidification on the chemical exports from a minerotrophic conifer swamp. Biogeochemistry 18, 153-175.

Leiros, M.C., Trasar-Cepeda, C., Seoane, S., Gil-Sotres, F., 1999. Dependence of mineralization of soil organic matter on temperature and moisture. Soil Biology and Biochemistry 31, 327-335.

Likens, G.E., Driscoll, C.T., Buso, D.C., Sicamma, T.G., Johnson, C.E., Lovett, G.M., 1998. The biogeochemistry of calcium at the Hubbard Brook. Biogeochemistry 41, 89-173.

Likens, G.E., Bormann, F.H., Hedin, L.O., Driscoll, C.T., Eaton, J.S., 1990. Dry deposition of sulfur: a 23-year record for the Hubbard Brook Forest Ecosystem. Tellus 42B, 319-329.

Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S., Johnson, N.M., 1977. Biogeochemistry of a forested ecosystems. Springer-Verlag, NY. 146pp.

Lindberg, S.E., Lovett, G.M., Richter, D.D., Johnson, D.W., 1986. Atmospheric deposition and canopy interactions of major ions in a forest. Science 231: 41-145.

Löfgren, S., Bringmark, L., Aastrup, M., Hultberg, H., Kindbom, K., Kvarnas, H., 2001. Sulphur balances and dynamics in three forested catchments in Sweden. Water, Air, and Soil Pollution 130, 631-636.

Lovett, G.M., Bowser, J.J., Edgerton, E.S., 1997. Atmospheric deposition to watersheds in complex terrain. Hydrological Processes 11, 645-654.

Lozano, F.C., Parton, W.J., Lau J.K.H., Vanderstar L., 1987. Physical and chemical properties of the soils at the Southern Biogeochemical Study Site. Ontario Ministry of Environment Consultant's Report – APIOS.

Lozano, F.C., Parton, W.J., 1986. Forest cover characteristics of the Harp #4 and Plastic #1 sub-catchments of the southern biogeochemical study site. Ontario Ministry of Environment Consultant's Report – APIOS.

Magid, J., Kjaergaard, C., Gorissen, A., Kuikman, P.J., 1999. Drying and rewetting of a loamy sand did not increase the turnover of native organic matter, but retarded the decomposition of added ^{14}C-labelled plant material. Soil Biology and Biochemistry 31, 595-602.

Magill, A.H., Aber, J.D., 2000. Variation in soil net mineralization rates with dissolved organic carbon additions. Soil Biology and Biochemistry 32, 597-601.

Mandernack, K.W., Lynch, L., Krouse, H.R., Morgan, M.D., 2000. Sulfur cycling in wetland peat of the New Jersey Pinelands and its effect on stream water chemistry. Geochimica Cosmochimica Acta 64, 3949-3964.

Mast, M.A., Drever, J.I., Baron, J., 1990. Chemical weathering in the Loch Vale Watershed, Rocky Mountain National Park, Colorado. Water Resources Research 26, 2971-2978.

McGill, W.B., Cole, C.V., 1981. Comparative aspects of cycling of organic C, N, S and P through soil organic matter. Geoderma 26: 267-286.

McNicoll, D.K., Mallory, M.L., Laberge, C., Cluis, D.A., 1998. Recent temporal patterns in the chemistry of small, acid-sensitive lakes in central Ontario, Canada. Water, Air, and Soil Pollution 105, 343-351.

Miller, E.K., Friedland, A.J., 1999. Atmospheric deposition to a subalpine forest in the Adirondack Mountains, New York, USA: 1986-1996. Journal of Environmental Quality 28, 270-277.

Mitchell, M.J., Mayer, B., Bailey, S.W., Hornbeck, J.W., Alewell, C., Driscoll, C.T., Likens, G.E., 2001. Use of stable isotope ratios for evaluating sulfur sources and losses at the Hubbard Brook Experimental Forest. Water, Air, and Soil Pollution 130, 75-86.

Mitchell, M.J., Raynal, D.J., Driscoll, C.T., 1996. Biogeochemistry of a forested watershed in the central Adirondack Mountains: temporal changes and mass balances. Water, Air, and Soil Pollution 88, 355-369.

Mitchell, M.J., David, M.B., Harrison, R.B., 1992a. Sulphur dynamics of forest ecosystems. *In*: Howarth, R.W., Stewart, J.W.B. and M.V. Ivanov (Eds.). Sulphur cycling on the continents. John Wiley & Sons Ltd., Chichester.

Mitchell, M.J., Burke, M.K., Shepard, J.P., 1992b. Seasonal and spatial patterns of S, Ca and N dynamics of a northern hardwood forest ecosystem. Biogeochemistry 17, 165-189.

Mitchell, M.J., Harrison, R.B., Fitzgerald, J.W., Johnson, D.W., Lindberg, S.E., Zhang, Y., Autry, A., 1992c. Sulfur distribution and cycling in forest ecosystems. *In*: Johnson, D.W., Lindberg, S.E. (Eds.) Atmospheric deposition and forest nutrient cycling. Springer-Verlag, New York, NY.

Mitchell, M.J., Foster, N.W., Shepard, J.P, Morrison, I.K., 1992d. Nutrient cycling in Huntington Forest and Turkey Lakes deciduous stands: nitrogen and sulfur. Canadian Journal of Forest Research 22, 457-464.

Mitchell, M.J., Raynal, D.J., Driscoll, C.T., 1996a. Biogeochemistry of a forested watershed in the Adirondack Mountains: Temporal changes and mass balances. Water, Air, and Soil Pollution 88, 355-369.

Mitchell, M.J., Driscoll, C.T., Kahl, J.S., Likens, G.E., Murdoch, P.S., Pardo, L.H., 1996b. Climatic control of nitrate loss from forested watersheds in the northeastern United States. Environmental Science and Technology 30, 2609-2612.

Mitchell, M.J., Driscoll, C.T., Fuller, R.D., David, M.B., Likens, G.E., 1989. Effect of whole-tree harvesting on the sulfur dynamics of a forest soil. Soil Science Society of America Journal 53, 933-940.

Mitchell, M.J., David, M.B., Maynard, D.G., Telang, S.A., 1986. Sulfur constituents in soils and streams of a watershed in the Rocky Mountains of Alberta. Canadian Journal of Forest Research 16, 315-320.

Morgan, M.D., 1995. Modeling excess sulfur deposition on wetland soils using stable sulfur isotopes. Water, Air, and Soil Pollution 79, 299-307.

Neary, A.J., Gizyn, W.I., 1994. Throughfall and stemflow chemistry under deciduous and coniferous forest canopies in south-central Ontario. Canadian Journal of Forest Research 24, 1089-1100.

Neary, A.J., Mistry, E., Vanderstar, L., 1987. Sulphate relationships in some central Ontario forest soils. Canadian Journal of Soil Science 67, 341-352.

Nodvin, S.C., Driscoll, C.T., Likens, G.E., 1988. Soil processes and sulfate loss at the Hubbard Brook Experimental Forest. Biogeochemistry 5, 185-199.

Nodvin, S.C., Driscoll, C.T., Likens, G.E., 1986. Simple partitioning of anions and dissolved organic carbon in a forest soil. Soil Science 142, 27-35.

Novak, M., Bottrell, S.H., Fottova, D., Buzek, F., Groscheova, H., Zak, K., 1996. Sulfur isotope signals in forest soils of central Europe along an air pollution gradient. Environmental Science Technology 30, 3473-3476.

Novak, M., Wieder, R.K., Schell, W.R., 1994. Sulfur during early diagenesis in *Sphagnum* peat: Insights from δ34S ratios in 210Pb-dated cores. Limnology and Oceanography 39, 1172-1185.

O'Brien, C., Hendershot, W.H., 1993. Separating streamflow into groundwater, solum and upwelling and its implications for hydrochemical modelling. Journal of Hydrology 146, 1-12.

Ontario Ministry of the Environment, 1994. Hydrology Data for Lakes and Catchments in Muskoka/Haliburton (1980-1992).

Ontario Ministry of Environment, 1983. Handbook of Analytical Methods for Environmental Samples. Ontario Ministry of Environment, Lab Services Branch, Toronto.

Peters, D.L., Buttle, J.M., Taylor, C.H., LaZerte, B.D., 1995. Runoff production in a forested, shallow soil, Canadian Shield basin. Water Resources Research 31, 1291-1304.

Philander, S.G., 1990. El Nino, La Nina and the Southern Oscillation. Academic Press, San Diego.

Post, W.M., Emanuel, W.R., Zinke, P.J., Stangenberger, A.G., 1985. Soil carbon pools and world life zones. Nature 298, 156-159.

Post, W.M., Pastor, J., Zinke, P.J., Stangenberger, A.G., 1985. Global patterns of soil nitrogen storage. Nature 317, 613-616.

Prechtel, A., Alewell, C.A and 13 others, 2001. Response of sulphur dynamics in European catchments to decreasing sulphate deposition. Hydrology and Earth System Sciences 5, 311-325.

Pregitzer, K.S., Burton, A.J., Mroz, G.D., Liechty, H.O, MacDonald, N.W., 1992. Foliar sulfur and nitrogen along an 800-km pollution gradient. Canadian Journal of Forest Research 22, 1761-1769.

Prietzel, J., Mayer, B., Krouse, H.R., Rehfuess, K.E., Fritz, P., 1995. Transformations of simulated wet sulfate deposition in forest soils assessed by a core experiment using stable sulfur isotopes. Water, Air, and Soil Pollution 79, 243-260.

Pulleman, M., Tietema, A., 1999. Microbial C and N transformations during drying and re-wetting of coniferous forest floor material. Soil Biology and Biochemistry 31, 275-285.

Renzetti, A.V.E., Taylor, C.H., Buttle, J.M., 1992. Subsurface flow in a shallow soil Canadian Shield watershed. Nordic Hydrology 23, 209-226.

Reuss, J.O., Johnson, D.W., 1986. Acid deposition and the acidification of soils and waters. Springer-Verlag, New York.

Rochelle, B.P, Church, M.R, 1987. Regional Patterns of Sulfur Retention in Watersheds of the Eastern U.S. Water, Air, Soil Pollution 36, 61-73.

Rose, S., 1998. Anion adsorption and desorption characteristics of a Piedmont ultisol: Some implications for the fate of sulfate deposition. Water, Air, Soil Pollution 101, 333-347.

Ryan, M., O'Toole, P., Farrell, E.P., 1998. The influence of drought and natural rewetting on nitrogen dynamics in a coniferous ecosystem in Ireland. Environmental Pollution 102, 445-451.

Scheider, W.J., Cox, C.M., Scott, L.D., 1983. Hydrological data for lakes and watersheds in the Muskoka-Haliburton study area. Ontario Ministry of Environment Data Report 83/6.

Scheider, W.J., Snyder, W.R., Clark, B., 1979. Deposition of nutrients and ions by precipitation in south-central Ontario. Water, Air, and Soil Pollution 12, 171-185.

Scherer, H.W., 2001. Sulphur in crop production – invited paper. European Journal of Agronomy 14, 81-111.

Schoenau, J.J., Bettany, J.R., 1987. Organic matter leaching as a component of carbon, nitrogen, phosphorus and sulfur cycles in a forest, grassland, and gleyed soil. Soil Science Society of America Journal 51, 646-651.

Shanley, J.B., 1992. Sulfate retention and release in soils at Panola Mountain, Georgia. Soil Science 153, 499-508.

Sharpley, A.N., 1990. Kinetics of sulfate desorption from soil. Soil Science Society of America Journal 54, 1571-1575.

Singh, B.R., 1984. Sulfate sorption by acid forest soils: 3. Desorption of sulfate from adsorbed surfaces as a function of time, desorbing ion, *p*H, and amount of adsorption. Soil Science 138, 346-352.

Sirois, A., Vet, R., MacTavish, D., 2001. Atmospheric Deposition to the Turkey Lakes Watershed: Temporal Variations and Characteristics. Ecosystems 4, 503-513.

Sirois, A., Barrie, L.A., 1988. Estimate of the Importance of Dry Deposition as a Pathway of Acidic Substances from the Atmosphere to the Biosphere in Eastern Canada. Tellus 40B, 59-80.

Sommaruga-Wögrath, S., Koinig, K.A., Schmidt, R., Sommaruga, R., Tessadri, R., Psenner, R., 1997. Temperature effects on the acidity of remote alpine lakes. Nature 387, 64-67.

Sommers, L.E., Gilmour, C.M., Wildung, R.E., Beck, S.M., 1980. The effect of water potential on decomposition processes in soils. In: Water Potential Relations in Soil Microbiology. Soil Science Society of America, Madison, WI, pp. 97-117.

Spratt, H.G., Morgan, M.D., 1990. Sulfur cycling in a cedar-dominated freshwater wetland. Limnology and Oceanography 35, 1586-1593.

Stephenson, M., Mackie, G.L., 1986. Lake acidification as a limiting factor in the distribution of the freshwater amphipod *Hyalella azteca*. Canadian Journal of Fisheries and Aquatic Science 43: 288-292.

Stoddard, J.L., Jeffries, D.S., Luekeswille, A., Clair, T.A., Dillon, P.J., Driscoll, C.T., Forsius, M., Johannessen, M., Kahl, J.S., Kellogg, J.H., Kemp, A., Mannio, J., Monteith, D.T., Wilander, A. *et al*., 1999. Regional trends in aquatic recovery from acidification in North America and Europe. Nature 401, 575-578.

Strickland, T.C., Fitzgerald, J.W., Swank, W.T., 1984. Mobilization of recently formed soil organic sulfur. Canadian Journal of Forest Research 14, 63-67.

Turk, J.T., Campbell, D.H., Spahr, N.E., 1993. Use of chemistry and stable sulfur isotopes to determine sources of trends in sulfate in Colorado lakes. Water, Air, and Soil Pollution 67, 415-431.

Urban, N.R., Eisenreich, S.J., Grigal, D.F., 1989. Sulfur cycling in a forested *Sphagnum* bog in northern Minnesota. Biogeochemistry 7, 81-109.

Van Dam, H., 1988. Acidification of three moorland pools in the Netherlands by acid precipitation and extreme drought periods over seven decades. Freshwater Biology 20, 157-176.

Waksman, S.A., Gerretsen, F.C., 1931. Influence of temperature and moisture upon the nature and extent of decomposition of plant residues by microorganisms. Ecology 12, 33-60.

Watmough, S.A., Dillon, P.J., 2002. Base cation and nitrogen budgets for seven forested catchments in central Ontario, 1983-1999. Forest Ecology and Management (*in press*).

Watmough, S.A., Dillon, P.J., 2001. Base cation losses from a coniferous catchment in central Ontario, Canada. Water, Air, Soil Pollution Focus 1, 507-524.

Watwood, M.E., Fitzgerald, J.W., Swank, W.T., Blood, E.R., 1988. Factors involved in potential sulfur accumulation in liter and soil from a coastal pine forest. Biogeochemistry 6, 3-19.

Webster, K.E., Soranno, P.A., Baines, S.B., Kratz, T.K., Bowser, C.J., Dillon, P.J., Campbell, P., Fee, E.J., Hecky, R.E., 2000. Structuring features of lake districts: landscape controls on lake chemical responses to drought. Freshwater Biology 43, 499-515.

Webster, K.E., Brezonik, P.L., 1995. Climate confounds detection of chemical trends related to acid deposition in upper midwest lakes in the USA. Water, Air, and Soil Pollution 85, 1575-1580.

Wieder, R.K, Lang, G.E., 1988. Cycling of inorganic and organic sulfur in peat from Big Run Bog in West Virginia. Biogeochemistry 5, 221-242.

Wilby, R.L., 1994. Exceptional weather in the midlands, UK, during 1988-1990 results in the rapid acidification of an upland stream. Environmental Pollution 86, 15-19.

Wilander, A., 2001. Effects of reduced S deposition on large-scale transport of sulphur in Swedish rivers. Water, Air, and Soil Pollution 130, 1421-1426.

Wilander, A., 1994. Estimation of background sulphate concentrations in natural surface waters in Sweden. Water, Air, and Soil Pollution 75, 371-.387.

Williams, C.H., 1967. Some factors affecting the mineralization of organic sulphur in soils. Plant and Soil 26, 205-223.

Wright, R.F., Jenkins, A., 2001. Climate change as a confounding factor in reversibility of acidification: RAIN and CLIMEX projects. Hydrology and Earth System Sciences 5, 477-486.

Yan, N.D., Keller, W., Scully, N.M., Lean, D.R.S., Dillon, P.J., 1996. Increased UV-B penetration in a lake owing to drought-induced acidification. Nature 381, 141-143.

Zhao, F.J., Spiro, B, Poulton, P.R., McGrath, S.P., 1998. Use of sulfur isotope ratios to determine anthropogenic sulfur signals in a grassland ecosystem. Environmental Science and Technology 32, 2288-2291.