Sulfur Dynamics in an Experimentally Acidified Mire in northwestern Ontario

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By

Richard S. Behr

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in partial fulfillment of the requirements for the degree of Masters of Science.....

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SULPHUR DYNAMICS IN AN EXPERIMENTAL ACIDIFIED MIRE IN NORTHWESTERN ONTARIO

BY

RICHARD S. BEHR

A thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

MASTER OF SCIENCE

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inviting me to his laboratory in Woods Hole, so I could learn the technique used for pyrite analysis - a trip that saved me an unthinkable number of hours.

Most importantly, I thank my wife, Julie, for everything.

Preface

Research conducted for my master's thesis is presented in the form of two manuscripts: the first manuscript reports on the biogeochemistry of sulfur in a small basin mire in the Experimental Lakes Area of northwestern Ontario (Chapter 2); and the second reports on an investigation of the effects of experimental acidification on the sulfur dynamics of the same mire (Chapter 3).

Results from these investigations were written as self contained units, Chapter 2 and Chapter 3, which will eventually be submitted to a professional scientific journal for publication. The manuscript style thesis was chosen to provide maximum experience in writing a publishable scientific paper and also to facilitate the publishing process.

Chapter 1 is a review of the relevant sulfur literature and an introduction to the two manuscripts.

Chapter 2 investigates the process of microbial sulfate reduction in an acidic Sphagnum mire. The short term end products of sulfate reduction in the mire are identified and compared to the long term distribution of sulfur forms in the peat. The spatial and/or temporal characteristics of sulfate reduction and its related sulfur forms within the mire are also examined.

Chapter 3 examines the effect of experimental acidification with sulfuric and nitric acid on the sulfur dynamics of a small basin mire. The major questions are: 1)

what is the fate of the added SO_4^{2-}? 2) is sulfate reduction stimulated by the additional SO_4^{2-} input? 3) are there any differences in the way added SO_4^{2-} is processed in relation to season and/or location in the mire? and 4) what are the overall effects of additional SO_4^{2-} loading on the sulfur budget of the mire?

Chapter 4 includes a discussion of the major results from the two investigations and the importance of these findings to the understanding of sulfur dynamics in wetlands. In conclusion, I suggest future work which is necessary to increase our understanding of the sulfur transformations that are important in wetland ecosystems.

Abstract

The occurrence and distribution of end products of sulfate reduction were measured in a small (3.67 ha) Sphagnum dominated mire (Experimental Lakes Area, northwestern Ontario). In situ incubations with $^{35}SO_4^{2-}$ were also performed. An experimental area (2.66 ha) was acidified with lake water plus H_2SO_4 and HNO_3, while a control area (0.88 ha) received only lake water. Three acid additions took place in 1983 and 6 in 1984, about 1 month apart. During an addition the experimental area received 86 mg S m^{-2}, compared to 13 mg S m^{-2} for the control area.

Surface and pore water SO_4^{2-} concentrations in both the control and experimental area were high shortly after snow melt, decreased during the summer months, and increased during September and October in response to SO_4^{2-} input from autumn rains and from the resolubilization of oxidized sulfur. The margin or minerotrophic area of the mire had higher SO_4^{2-} concentrations than the central oligotrophic area at all times because of the additional SO_4^{2-} input from upland runoff it received. Hydrogen sulfide occurred only in the minerotrophic pore water profiles. The minerotrophic area was lower in H^+ concentration than the central oligotrophic area (30 vs. 100 μeq H^+ L^{-1}). Concentrations of SO_4^{2-} in surface water pools increased after all acidifications and usually returned to near pre-acidification concentrations within 7 days. Increases in

pore water SO_4^{2-} content occurred less consistently than in the surface water, yet acidifications always increased pore water H_2S in the minerotrophic site, demonstrating that sulfate reduction was stimulated by the additions.

Organic sulfur accounted for about 95% of the total sulfur present (30-155 μmol S g^{-1}), with pyrite accounting for most of the remainder; both decreased significantly below 20 cm. Addition of $^{35}SO_4^{2-}$ showed that pyrite formed rapidly and accounted for 90% of the short term inorganic sulfur formation. $AV^{35}S$ and $^{35}S^{o}$ also formed. More $Fe^{35}S_2$, $AV^{35}S$, and $^{35}S^{o}$ formed in the minerotrophic area than in the oligotrophic area. During acidifications, large amounts of SO_4^{2-} were "sorbed" by Sphagnum spp. before reaching the water table. The top 20 cm appeared to be dynamic in terms of S accumulation, with increases in total S over winter and spring and decreases during summer drawdown. Below this zone the total S accumulation rate was 0.49 g S m^{-2} yr^{-1} slightly less than the average value (0.90 g S m^{-2} yr^{-1}) obtained from 4 years of mass balance data (1981-1984).

Table of Contents

List of Appendices

List of Tables

List of Figures

Chapter 2. The Biogeochemistry of Sulfur in an Experimentally Acidified Mire in Northwestern Ontario.

Chapter 3. The Effects of Acidification on the Sulfur Dynamics of an Experimentally Acidified Mire in northwestern Ontario

Chapter 1

Review of Relevant Sulfur Literature

and

General Introduction

The cycling of sulfur has been investigated in many ecosystems, including deciduous and coniferous watersheds (Eaton et al 1978; Johnson and Henderson 1979; Johnson 1984), agricultural soils (Tabatabai 1984), coastal marine sediments (Jorgensen 1977; Howarth and Jorgensen 1984), saltwater marshes (Howarth and Teal 1979; Howarth and Giblin 1983; Howes et al 1984), and freshwater lakes (Nriagu 1968; King and Klug 1982; Cook and Schindler 1983; Kelly and Rudd 1984). However, sulfur cycling in wetlands has received much less attention (Casagrande et al 1977; Casagrande et al 1979; Rippon et al 1980; Brown 1980; Brown and Macqueen 1982; Wieder 1982; Wieder and Lang 1984) and only a few investigators have examined sulfur cycling in Sphagnum dominated wetlands (Brown 1980; Brown and Macqueen 1982; Wieder 1982; Wieder and Lang 1984). The paucity of data is of special concern since many Sphagnum dominated wetlands are located in areas of North America known to be sensitive to acidic deposition (Gorham et al 1984). Presently little is known about biogeochemical cycling in peatlands, much less the effect acidification may have on them. Since wetland environments are intermediate in the continuum between limnetic and terrestrial ecosystems it seems reasonable that sulfur transformations within wetlands would have characteristics common to both. This similarity might be helpful in determining the fate of SO_4^{2-} in wetlands since sulfur cycling in limnetic and terrestrial ecosystems is better understood. Gorham et al (1984) suggested that a

variety of approaches could be utilized to determine the possible effects acidic deposition may have on peatlands, including geographical surveys, experimental studies: short term and long term, and paleoecological investigations.

Sulfate is the dominant inorganic sulfur form in most environments and consequently reactions involving SO_4^{2-} have been studied in the greatest detail. The microbial reduction of SO_4^{2-} occurs primarily in anoxic habitats containing organic matter and SO_4^{2-}, and has received much more attention than other processes (see later).

The process of microbial sulfate reduction has been examined in coastal marine sediments (Jorgenson 1977; Howarth and Jorgenson 1984), saltwater marshes (Howarth and Teal 1979; Howarth and Giblin 1983; Howes et al 1984), and freshwater lakes (Stuiver 1964; Nriagu 1968; King and Klug 1983; Kelly and Rudd 1984). These investigations focused on: 1) the determination of rates of sulfate reduction and its importance in carbon mineralization; 2) identification of the end products; and 3) the potential importance of the acid neutralizing ability of the sulfate reducing bacteria for lakes undergoing acidification with sulfuric acid.

Based on SO_4^{2-} budgets for watersheds containing freshwater wetlands, many investigators have demonstrated that wetlands are sinks for atmospherically delivered SO_4^{2-}-S (Hemond 1980; Rippon et al 1980; Braekke 1980; Wieder and Lang 1984) and some have suggested the retention was partly due to the microbial reduction of SO_4^{2-} (Hemond

1980; Braekke 1980). However, reported measurements of the end products of sulfate reduction are limited (Casagrande et al 1977; Brown 1980; Altschuler et al 1983).

Casagrande et al (1977) and Altschuler et al (1983) examined the distribution of sulfur in 2 different areas of the peat-forming Florida Everglades: Casagrande et al (1977) site was representative of a marine derived peat, while Altschuler et al (1983) was representative of a freshwater derived peat. The average total sulfur content of the marine mangrove swamp peat was 1.61 mmol S g^{-1} dry wt., about 6 times the total sulfur content of the freshwater derived peat examined by Altschuler et al (1983). Casagrande et al (1977) also examined sulfur distribution in the Okefenokee Swamp of Georgia, a freshwater peat-forming system. They found the total sulfur content to be about 57 µmol S g^{-1} dry wt. and was relatively constant with depth. The freshwater Everglade peat examined by Altschuler et al (1983) contained about 4.5 times the total sulfur of the Okefenokee swamp peat (261 vs. 57 µmol S g^{-1} dry wt.).

Regardless of total sulfur concentrations, organic sulfur, defined as carbon bonded sulfur and carbon oxygen sulfur (esters), accounted for over 70% of the total sulfur in both studies of the Everglades (Casagrande et al 1977; Altschuler et al 1983). Later, Casagrande et al (1979) determined that 25% of the total sulfur occurred as carbon oxygen sulfur. Sulfate esters are a potential source of SO_4^{2-} for sulfate reducing bacteria in deep peat (Altschuler

et al 1983) and in lake sediments (King and Klug 1980), where SO_4^{2-} concentrations are extremely low.

Working in a bog in southern England, Brown (1980) is the only investigator known to the author to incubate a peat core with $^{35}SO_4^{2-}$ to determine the end products of sulfate reduction. After an 8 day incubation, Brown (1980) found that H_2S was the major end product of sulfate reduction in the anaerobic zone, with lesser amounts of FeS, FeS_2, and organic sulfur forming. More recently, Brown and Macqueen (1982) determined that 78% of $^{35}SO_4^{2-}$ added to waterlogged peat cores remained in the top 5 cm of peat and was recovered primarily as organic sulfur after a 3 week incubation.

Brown (1980) also measured the concentration and distribution of acid volatile sulfide (AVS= H_2S + FeS), elemental sulfur (S^o), pyrite (FeS_2), organic sulfur, and total sulfur, in short peat cores (30 cm). Total sulfur concentration increased with depth from about 150 to 297 μmol S g^{-1} dry wt. at 7.5 cm, to 359 to 375 μmol S g^{-1} dry wt. at 22.5 cm (Brown 1980). Organic sulfur accounted for about 60% of the total sulfur, somewhat less than that for the Florida Everglades (Casagrande et al 1977). The remaining 40% was represented by SO_4^{2-}, AVS, FeS_2, and S^o (more than 80% of this fraction was AVS).

The concentration of SO_4^{2-} in the surface water of Brown's bog (208 μmol L^{-1}) was significantly higher than any of the bog water samples collected by Gorham et al (1985)

(0.7-21 μmol SO_4^{2-} L^{-1}) during their transect of North American bogs. Brown's (1980) high SO_4^{2-} concentrations are at least partly a result of 200 years of high SO_2 emissions in Britain.

Increased sulfur loading to wetland ecosystems has presumably resulted in the elimination of certain Sphagnum spp. from bogs where they were once dominant peat formers, changes in the ionic composition of wetland water (most notably, significant increases in SO_4^{2-} and H^+ concentration), and increased sulfur accumulation within watersheds containing wetlands and within Sphagnum spp. themselves.

In an analysis of peat profiles from blanket bogs in the southern Pennines, Tallis (1964) determined that Sphagnum spp. once formed a greater percentage of the vegetation than they presently do, and suggested the loss was due to 200 years of high sulfur deposition. Later, Ferguson et al (1978) determined from laboratory experiments that some of the same Sphagnum spp. now absent were among the most sensitive to various sulfur pollutants, thus supporting Tallis's earlier observation. More recently, Ferguson and Lee (1983) reintroduced 5 Sphagnum spp. to the southern Pennines, and found that only one of the 5 continued to grow after 1 year, even though bulk sulfur deposition has presumably decreased in recent years.

Eighteen months after transplanting 5 Sphagnum spp. to two locations in the United Kingdom, Ferguson et al (1984)

found that the 5 Sphagnum spp. transplanted at a polluted site in the southern Pennines of England contained more sulfur than any of the Sphagnum spp. which had been transplanted in North Wales, a relatively unpolluted site. Likewise, Sphagnum mosses and Cladonia lichens collected from ombrotrophic bogs in southern Finland all contained more sulfur than those collected from similar systems in northern Finland, which received far less bulk sulfur depostion than those of the southern bogs (Pakarinen 1980). In addition, sulfur concentration in Sphagnum and Cladonia was positively correlated with atmospheric deposition rates of SO_4^{2-} along the south-north gradient (Pakarinen 1980).

In the 1950's, Gorham (1958) found a positive correlation between H^+ and SO_4^{2-} concentration for bogs in the English Lake District. Similary, low pH (3.82), high ionic conductivity (130 µmho cm^{-2}), and high SO_4^{2-} concentrations (364 µmol SO_4^{2-} L^{-1}) of 24 moorland pools in Belgain were thought to result from industrial acidification (Vangenechten and Vanderborght 1980).

Sulfate reduction rates in freshwater ecosystems are often limited by the concentration of SO_4^{2-}, this is in contrast to marine systems, which are limited by the supply of oxidizable organic matter (Berner 1984). Therefore, the observed increases in rates of sulfate reduction following addition of SO_4^{2-} from acid mine drainage and experimental acidification are not surprising.

Increased rates of sulfate reduction in lakes receiving SO_4^{2-} from acid mine drainage or from experimental acidification have been responsible for neutralization of significant amounts of sulfuric acid (Herlihy and Mills 1985; Kelly et al 1982; Cook and Schindler 1983; Cook et al submitted). In fact, alkalinity generated from sulfate reduction helped offset the potential acidification of Thoreau's bog in Mass., an area receiving acid deposition (Hemond 1980). Similarly, acid mine drainage entering a bog in West Virginia had no effect on the outflow chemistry; presumably sulfate reducing bacteria consumed the additional SO_4^{2-} and H^+ from acid drainage (Wieder and Lang 1984).

In light of the lack of information regarding the occurrence and distribution of sulfur in Sphagnum dominated wetlands and their potential acidification, an investigation was necessary that would: 1) determine the occurrence and distribution of the various sulfur forms present in a relatively undisturbed Sphagnum wetland; and 2) examine the possible effects acidification with sulfuric acid may have on the various sulfur transformations within the wetland.

Chapter 2

The Biogeochemistry of Sulfur in an Experimentally Acidified Mire in Northwestern Ontario

Abstract

During the ice free season of 1983 and 1984, SO_4^{2-} and H^+ were measured weekly in surface water while SO_4^{2-}, H_2S, and H^+ were measured monthly in pore water in a small (3.67 ha) Sphagnum dominated mire in northwestern Ontario (Experimental Lakes Area). Surface and pore water SO_4^{2-} concentration were high shortly after snow melt, decreased during the summer months, and increased during September and October in response to SO_4^{2-} input from autumn rains. The margin or minerotrophic area of the mire had higher SO_4^{2-} concentrations than the central oligotrophic area at all times because of the additional SO_4^{2-} input from upland runoff the minerotrophic area receives. Hydrogen sulfide occurred in pore water only in the minerotrophic area. The minerotrophic area was lower in H^+ concentration than the central oligotrophic area (30 vs. 100 μeq H^+ L^{-1}).

Organic sulfur accounted for about 95% of the total sulfur present (30-155 μmol S g^{-1}), with pyrite accounting for most of remainder. Both decreased significantly below 20 cm. Pyrite formed rapidly from $^{35}SO_4^{2-}$ and accounted for >55% of the inorganic ^{35}S formed in 72 hour in situ incubations. $AV^{35}S$ and $^{35}S^o$ also formed. More $Fe^{35}S_2$, $AV^{35}S$, and $^{35}S^o$ formed in the minerotrophic area than in the oligotrophic area, probably because of the greater supply of SO_4^{2-} and the lower H^+ concentration in the minerotrophic area. Organic ^{35}S accounted for about 80% of the total

recovered ^{35}S after more than 2 months of *in situ* incubation. A 30% reduction in recovered inorganic sulfur for spring vs. autumn cores occurred in the central oligotrophic area compared to a 37% reduction in the minerotrophic area. This resulted from the exposure of previously anoxic environments to O_2 during the annual summer drawdown period.

Introduction

The process of microbial sulfate reduction has been examined in coastal marine sediments (Jorgensen 1977; Howarth and Jorgensen 1984), saltwater marshes (Howarth and Teal 1979; Howarth and Giblin 1983; Howes et al 1984), and freshwater lakes (Stuiver 1967; Nriagu 1968; King and Klug 1982; Kelly and Rudd 1984). In comparison to saltwater and freshwater lake ecosystems, little has been done to investigate the sulfur dynamics of wetlands. Gorham et al (1984) have mentioned the paucity of data related to the occurrence of sulfur in wetland ecosystems.

Based on SO_4^{2-} budgets for watersheds containing freshwater wetlands, many investigators have determined that wetlands are sinks for atmospherically delivered SO_4^{2-}-S (Hemond 1980; Rippon et al 1980; Braekke 1980; Wieder 1982; Wieder and Lang 1984) and some have suggested the retention was partly due to the microbial reduction of SO_4^{2-} (Hemond 1980; Braekke 1980; Wieder 1982; Wieder and Lang 1984). However, there have been few reported measurements of the end products of sulfate reduction in freshwater wetlands (Altschuler et al 1983; Casagrande et al 1977; Casagrande et al 1979; Brown 1980). Working in a bog in southern England, Brown (1980) was the only investigator known to the author to incubate a core with $^{35}SO_4^{2-}$ to determine the end products of sulfate reduction. After an 8 day incubation, Brown (1980) found that $H_2{}^{35}S$ was the major end product of sulfate reduction in the anaerobic zone, with lesser amounts

of $Fe^{35}S$, $Fe^{35}S_2$, and organic ^{35}sulfur forming.

Concentrations of SO_4^{2-} and H_2S in Brown's system were high, 200 µmol SO_4^{2-} L^{-1} and 30 µmol H_2S L^{-1}, respectively, probably the result of 200 years of high SO_2 emissions in Britain. In contrast, in a transect of bogs across North America, Gorham et al (1985) never observed SO_4^{2-} concentrations as high as those reported by Brown (1980). Brown's bog received a significant amount of its water input (ie. mineral input) from groundwater and therefore one might expect the occurrence and distribution of sulfur forms to be considerably different than for a bog which receives most of the mineral input from direct precipitation and upland runoff. In addition, the occurrence and distribution of sulfur forms in a wetland that has received little anthropogenic input of sulfur may also be different from a system that has received large amounts of anthropogenic sulfur.

The purpose of the present study was to determine if sulfate reduction was occurring in an acidic Sphagnum mire receiving experimental acid inputs, and to identify the end products of the reduction. Also, I examined spatial and/or temporal characteristics of sulfate reduction and the various forms of reduced sulfur within the mire. The experimental inputs were applied monthly during the ice free season to mimic acid precipitation events. In this paper I deal primarily with general seasonal trends and differences in the 2 major areas of the mire: the nutrient poor

oligotrophic area and the richer minerotrophic lagg area. Detailed comparisons of the effects of acidification on the minerotrophic and oligotrophic areas are treated elsewhere (Chapter 3).

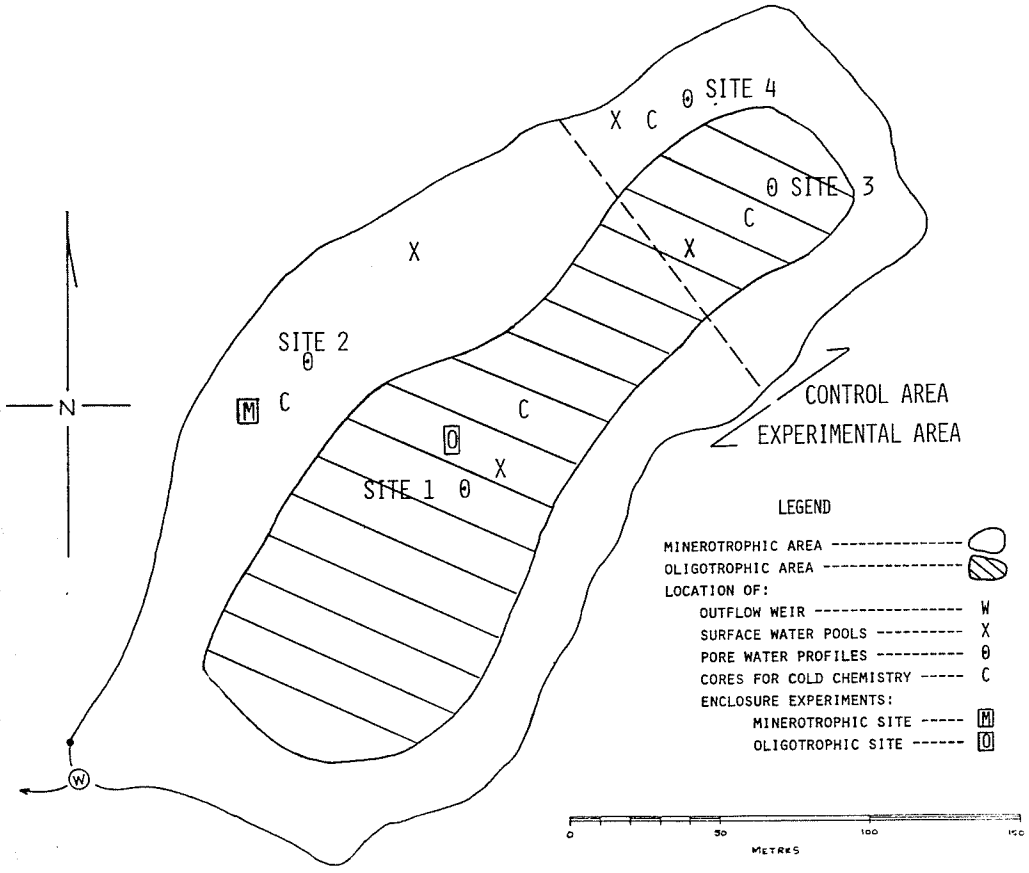
During this study, surface and pore waters collected throughout the mire were analyzed for SO_4^{2-} and H_2S concentrations during the ice free season of 1983 and 1984. Short peat cores were also obtained from various regions throughout the mire and were analyzed to determine the concentration and distribution of the various sulfur forms. The inorganic forms measured were: acid volatile sulfide (AVS); elemental sulfur (S^o); and pyrite (FeS_2). Organic sulfur was assumed to be the difference between the sum of these inorganic forms and total sulfur.

A radionuclide, $^{35}SO_4^{2-}$, was added to the mire in two experiments to measure the immediate end products of sulfate reduction, and to help explain the occurrence and distribution of the various sulfur forms accumulating on a long term basis.

Description of study area

The experimental mire is located at the Experimental Lakes Area (ELA) in northwestern Ontario, on the Canadian Shield, about 56 km southeast of Kenora. The small oval mire is centrally located within the northeast drainage sub-basin of Rawson lake ($49^o40'N$, $93^o43'$), and occupies 3.67 ha of this 10.8 ha sub-basin (Figure 1). The surrounding upland

Figure 1. Location of the experimental mire in the northeast drainage sub-basin of Rawson lake.


SITE 4
SITE 3
SITE 2
SITE 1
CONTROL AREA
EXPERIMENTAL AREA
N
W
LEGEND
MINEROTROPHIC AREA
OLIGOTROPHIC AREA
LOCATION OF:
OUTFLOW WEIR W
SURFACE WATER POOLS X
PORE WATER PROFILES θ
CORES FOR COLD CHEMISTRY C
ENCLOSURE EXPERIMENTS:
MINEROTROPHIC SITE M
OLIGOTROPHIC SITE O
0
50
100
150
METRES

and the southwestern half of the mire burned in 1974. Except for the trees, Vitt and Bayley (1984) determined that there was no difference in vegetation in the burned and unburned portions of the mire. The unburned half of the mire is dominated by Picea mariana (Mill.) BSP. while the burned half is dominated by juvenile Pinus banksiana Lamb.. Sphagnum angustifolium (Russ.) C. Jens. and S. magellanicum Brid. form the ground cover throughout the mire with the exception of a small pool near the center of the mire which is dominated by S. fallax (Klinggr.) Klinggr.. The characteristic understory plants (eg. Smilacina trifolia (L.) Desf., Ledum groendandium Oeder, and Carex trisperma Dew.) are abundant throughout the mire. For more detail see Vitt and Bayley (1984). All water from the watershed passes through the mire before being discharged via a boulder zone to Rawson lake. Thus the margin or lagg of the mire receives more water and mineral input than the interior of the mire. Consequently the chemistry and vegetation of the lagg is significantly different than the central region of the mire. In their analysis of the vegetational and chemical characteristics of this mire, Vitt and Bayley (1984) were able to divide the mire into two distinct areas: 1) a lagg area (called the minerotrophic area); and 2) a central area (called the oligotrophic area), characterized by nutrient poor conditons relative to the minerotrophic lagg area (Figure 1).

Part of the mire was experimentally acidified with sulfuric and nitric acid (Figure 1)(Chapter 3) in 1983 and 1984 accounting for 28% and 47% of the annual SO_4^{2-}-S loading, respectively. The control area received only lake water, while the experimental area received acidified lake water. Surface water, pore water, and peat cores were collected from both experimental and control areas of the mire. The effects of addition of sulfuric acid have been ephemeral and have not yet appeared to alter the water chemistry of the experimental area of the mire (Chapter 3).

Methods and Materials

Pore water and surface water

Pore waters were measured at four sampling sites within the mire. Two of the four sites (sites 1 and 2) are located in the experimental area of the mire, and the other two (sites 3 and 4) are in the control area (Figure 1). Sites 1 and 3 are characteristic of the nutrient poor, oligotrophic area of the mire, while sites 2 and 4 are characteristic of the more nutrient rich, minerotrophic lagg area (Figure 1). All of these sites are located in hollows.

Pore water profiles were obtained on a monthly basis from May through October. Pore water samples were obtained at 5 cm intervals from the surface of the water table to a depth of about 35 cm and were analyzed for SO_4^{2-}, H_2S, and H^+ concentration.

Pore water samples from the various depths were obtained by suction using a hollow stainless steel tube (6

mm outside diameter) about 1 m in length, lined with small-diameter tygon tubing. One end of the stainless steel tube had slots in 1.5 cm of its length to permit entry of pore water, and a nylon screen inserted to filter out large particulate matter. A plastic syringe (50 mL) was attached to the other end with a 3 way valve. Pore water profiles were obtained by inserting the stainless steel tube into the peat below the water table, and withdrawing a sample with gentle suction. The first portion of the pore water obtained was expelled through the 3 way valve, taking care not to let air enter the syringe. Samples for H^+ and H_2S analyses were collected in 5 mL glass syringes fitted with 3 way valves which had been previously filled with deoxygenated (boiled) water. Sulfate samples were collected in 5 mL plastic mini vials that had been rinsed 3 times with distilled-deionized water.

Surface water samples were collected weekly during the ice free season. In 1983 surface water samples were collected from the experimental area in the oligotrophic central pool and in a small tree hollow near the edge of the mire (called the mineral pool) (Figure 1). In 1984 two additional surface water stations were added in the control region of the mire (oligotrophic control and minerotrophic control) (Figure 1). Surface waters were analyzed for SO_4^{2-} and H^+.

Hydrogen ion concentration was determined within 3 h of collection using an Orion research meter and a Fisher glass

combination electrode. Hydrogen sulfide samples were analyzed by the method of Stainton et al (1977). The H_2S analysis was always completed within 3 h of collection. Sulfate samples were filtered with a Swinnex filtration device equipped with a distilled-deionized rinsed 0.22 um nucleopore filter and were refrigerated until analyzed with a Dionex ion chromatograph.

Core Sampling and Sulfur Analysis

Short peat cores (40 cm) were collected to determine the concentration of AVS, S^o, FeS_2, organic sulfur, and total sulfur.

Sixteen cores were analyzed for AVS, S^o, and FeS_2; 8 from the minerotrophic lagg area (Figure 1) and 8 from the central oligotrophic area (Figure 1). All but 2 cores were from the experimental area. The first 6 cores, 3 from each area were used to determine the cold sulfur species and were all collected in the spring, while the water table was near the moss surface. The remaining 10 cores from the 2 areas were obtained from enclosures used for the sulfur-35 (see below) experiments and were analyzed for both the cold sulfur forms and for the incorporation of $^{35}SO_4^{2-}$. The last 4 cores, 2 from each area, were collected in October and are called autumn cores.

The short peat cores (40 cm) were obtained with a piston type coring device (5 cm diameter) to retain the peat within the tube and to minimize compaction. Each core was placed in a freezer within 30 min of collection until

analysis the following day. Frozen peat cores were extruded, and sectioned into 5 cm segments. One half of each section was used for determination of dry weight and total sulfur. The second half was halved again, with one portion used for determination of AVS and (FeS_2 + S^o), and the other for S^o.

The section for AVS analysis was placed in a reaction vessel containing 50 mL of 6 N HCl which was continuously flushed with oxygen-free nitrogen and samples stirred for 2 h. AVS volatilized from the sediment was trapped in a basic zinc acetate trap (Howarth and Teal 1979). The resultant ZnS precipitate was quantified by an iodine titration (Golterman 1967). This method was found to have a recovery efficiency of 95% with Na_2S standards. Correction for efficiency of recovery was not made.

After the removal of AVS, the peat sections were transferred to 350 mL round bottomed flasks for measurement of FeS_2 and S^o by the chromium (II) reduction technique (Zhabina and Volkov 1978; Howarth and Jorgensen 1984). This technique reduces FeS_2 and S^o to H_2S, which is then trapped in basic zinc acetate as previously described. The efficiency of the chromium (II) reduction procedure using FeS_2 standards was 85% and samples were corrected for this efficiency.

Elemental sulfur content was measured in the remaining section (see below) and subtracted from the total S in the chromium (II) reduction fraction to determine the amount of

FeS_2 present.

The section used for the S^o determination was also sparged with 6 N HCl to remove AVS before dried. Samples were dryed at 70°C, weighed and ground with a mortar and pestle before extraction of S^o with 80 mL of acetone. After about 10 h of stirring, the acetone and peat slurry was filtered via vacuum filtration. The filtrate, acetone, containing the extracted S^o was transferred to a 350 mL round bottomed flask. Sulfur was measured using the chromium (II) reduction procedure followed by iodine titration of the trapped sulfide. Eight S^o standards determined with this procedure resulted in an average efficiency of 60% and samples were corrected for this efficiency.

To determine the amount of radioactivity associated with each of the inorganic sulfur species, a 3 mL subsample was obtained from each titration flask and mixed with 17 mL of Instagel fluor (Packard Instruments Inc.). All sample radioactivity was determined by liquid scintillation counting and was quench corrected by the internal standard method.

Total sulfur content was determined on one core from each area with a LECO sulfur analyzer, model SC-132. After dry combustion of 0.1-0.15 g of dry sample, the SO_2 evolved was measured by infrared spectroscopy.

Sulfate Reduction Experiments

The radiotracer enclosure experiments started 11 July 84 in the minerotrophic area and 6 August 84 in the oligotrophic area. After installation of the enclosure, peat and pore water were allowed to equilibrate for 3 days before addition of $^{35}SO_4^{2-}$.

Radioactive sulfur-35, as $^{35}SO_4^{2-}$, was added to enclosures at two sites: one in the minerotrophic area and the other in the oligotrophic area. Both were located in the experimental area (Figure 1). The radioactive solution was sprayed onto the surface of the mire vegetation which was enclosed in a plexiglas frame (44 x 46 x 50 cm deep).

The 3000 mL $^{35}SO_4^{2-}$ solution used lake water and contained 0.4 mCi $^{35}SO_4^{2-}$, 300 µmol SO_4^{2-} L^{-1}, 600 µmol NO_3^{1-} L^{-1}, and 630 µeq H^+ L^{-1}. The loading of H^+, SO_4^{2-} and NO_3^{1-} (µeq m^{-2}. $event^{-1}$) was about the same as the loading for an acidification experiment (Chapter 3), but the total volume of water applied was increased (equivalent to 3 cm of precipitation). After the 3000 mL $^{35}SO_4^{2-}$ solution was applied, an additional 3480 mL of lake water was applied to ensure that a significant amount of the label reached the water table. The $^{35}SO_4^{2-}$ and rinse solution was applied to the moss surface just before sunset to minimize evapotranspiration.

During both experiments, 5 short peat cores were obtained at specific time intervals after the $^{35}SO_4^{2-}$ had been applied. The first 3 cores from each experiment (1, 3,

and 15 days) were analyzed for the incorporation of ^{35}S into $AV^{35}S$, $^{35}S^{o}$, and $Fe^{35}S_2$. For the last 2 cores from each experiment (82 and 83 days or 62 and 63 days), $^{35}S^{o}$ + $Fe^{35}S_2$ were measured as one fraction (Cr-reducible) rather than separately. In addition, to estimate the amount of labelled organic sulfur, a quarter section from each interval was digested with 20 mL of Aqua Regia for 12-16 h. Before digestion, each section was first sparged with 6N HCl (as described for AVS) and then washed four times with tap water to remove any unreduced $^{35}SO_4^{2-}$. In laboratory tests with Sphagnum angustifolium peat 95% of the unreduced $^{35}SO_4^{2-}$ was removed with this washing technique. The final digest was made up to 100 mL and a 2 mL subsample was mixed with 18 mL of Instagel for radioactive assay. Organic ^{35}sulfur was estimated by the difference between the Aqua Regia fraction (all reduced S except $AV^{35}S$) and the chromium reducible fraction ($Fe^{35}S_2$ + $^{35}S^{o}$).

Cores from the minerotrophic enclosure site were obtained 1, 3, 15, 82, and 83 days after the spike application. Cores from the oligotrophic enclosure site were obtained 1, 3, 15, 62, and 63 days after the $^{35}SO_4^{2-}$ application.

Before application of $^{35}SO_4^{2-}$, 6 pore water samplers (at 10, 15, 20, 25, 30, and 35 cm depths) were installed in the enclosure. Pore water samples were collected for SO_4^{2-} and H^{+} analysis and analyzed as previously described. In addition, a 500 µL subsample from each SO_4^{2-} sample obtained

after the $^{35}SO_4^{2-}$ addition was mixed with 20 mL of ACS fluor (Amersham) and the radioactivity associated with dissolved ^{35}S determined. The majority of this activity was assumed to be associated with $^{35}SO_4^{2-}$.

RESULTS

Sulfur Chemistry of pore water and surface water

Sulfate concentrations varied significantly within the mire both spatially and temporally. The surface and pore water of the minerotrophic area were characterized by high SO_4^{2-} concentrations relative to the oligotrophic central area (Figures 2 and 3). The average surface water SO_4^{2-} concentration for the experimental minerotrophic pool during 1984 was 71.7 μmol L^{-1} compared to 12.5 μmol L^{-1} for the oligotrophic central pool. After spring runoff the concentration of SO_4^{2-} in the surface and pore water of the experimental minerotrophic area decreased substantially and remained low until there was a substantial input of SO_4^{2-} from direct precipitation and runoff (Figures 2 and 4) in September '84. There were short periods of elevated SO_4^{2-} due to experimental acidification (Chapter 3). It is important to note, that overall the general seasonal trends at the experimental sites were the same as those observed at the control sites during 1983 and 1984. In both minerotrophic sites, SO_4^{2-} concentrations decreased with depth (Figures 3 and 4), a result of the bacterial reduction of SO_4^{2-}.

Figure 2. Seasonal SO_4^{2-} concentrations in the experimental oligotrophic and minerotrophic surface water pools during the 1984 ice free season.

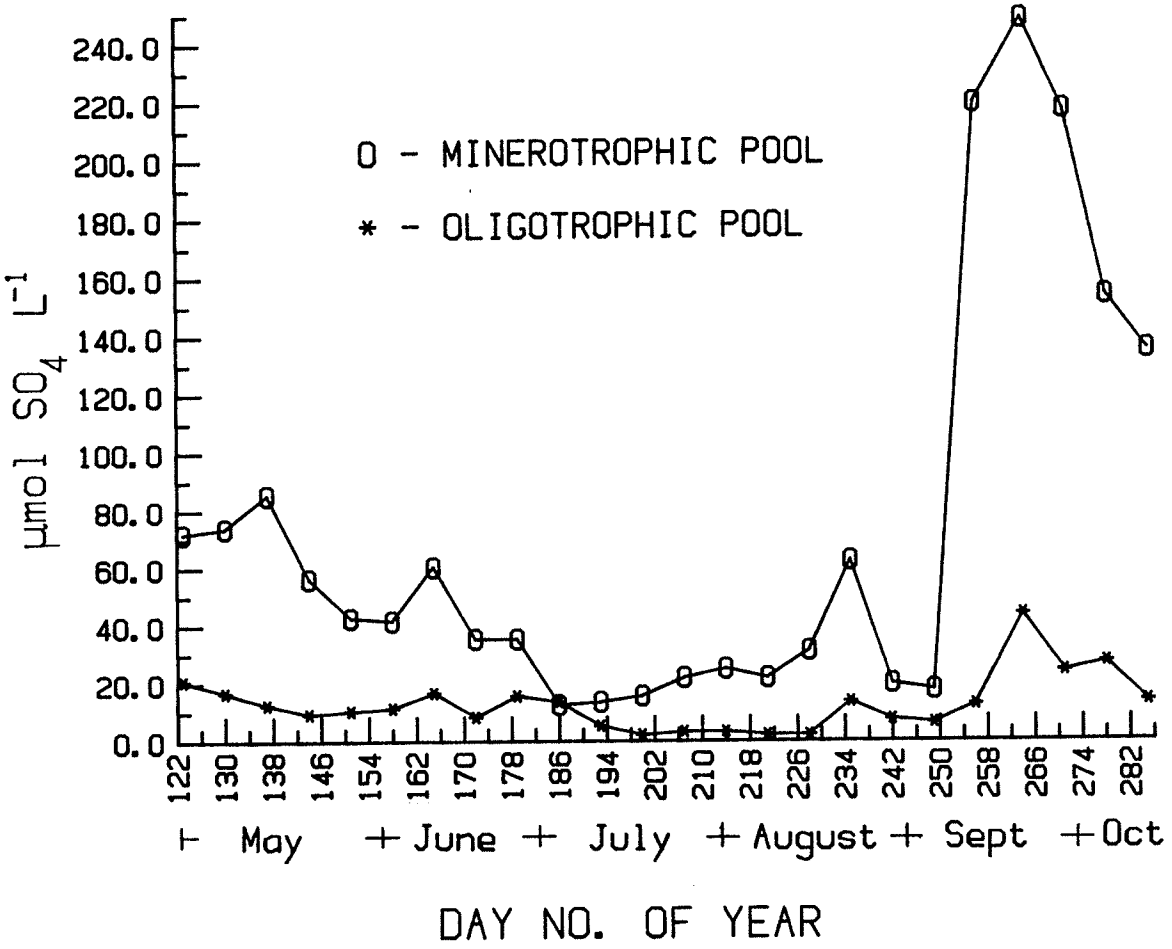

O - MINEROTROPHIC POOL
* - OLIGOTROPHIC POOL
µmol SO_4 L^{-1}
240.0
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
122
130
138
146
154
162
170
178
186
194
202
210
218
226
234
242
250
258
266
274
282
May
June
July
August
Sept
Oct
DAY NO. OF YEAR

Figure 3. Sulfate concentrations as a function of depth in the experimental oligotrophic and minerotrophic sites for 20-June-84.

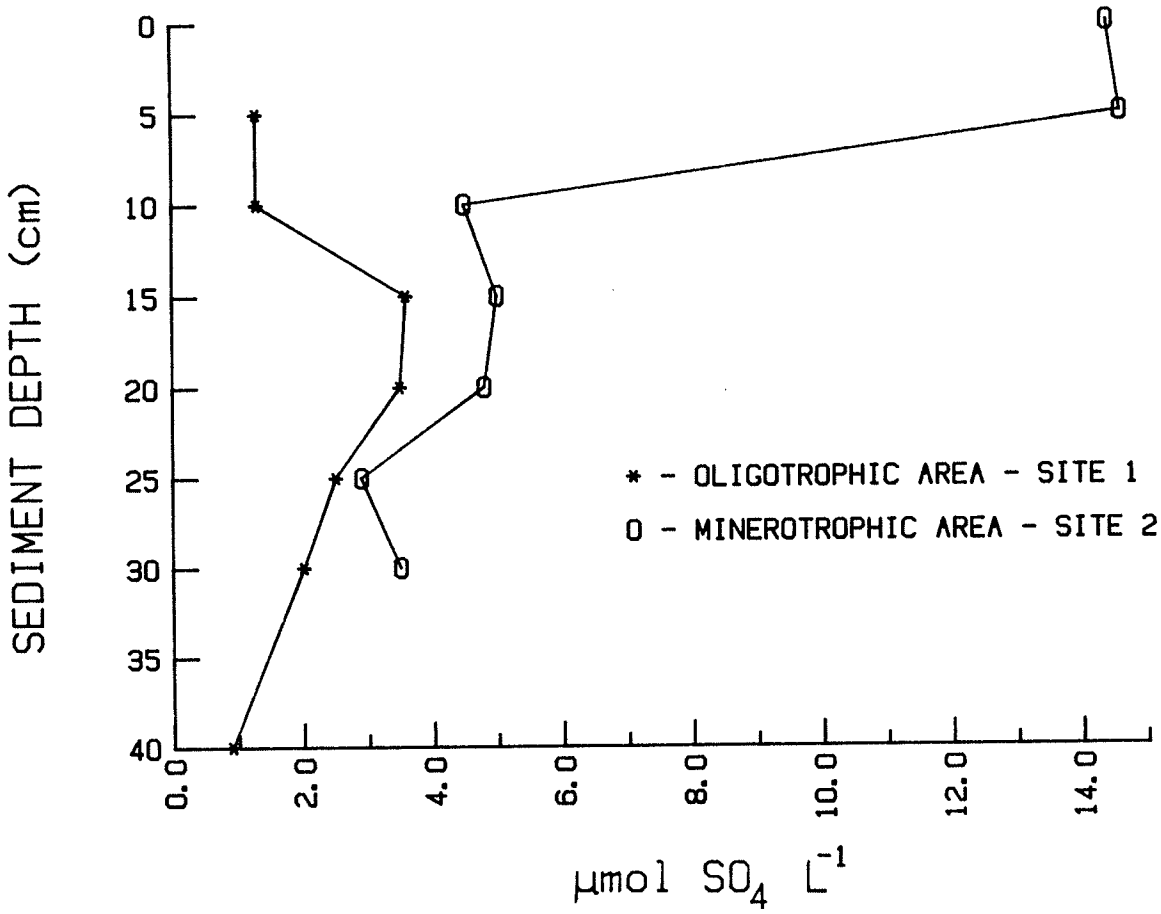
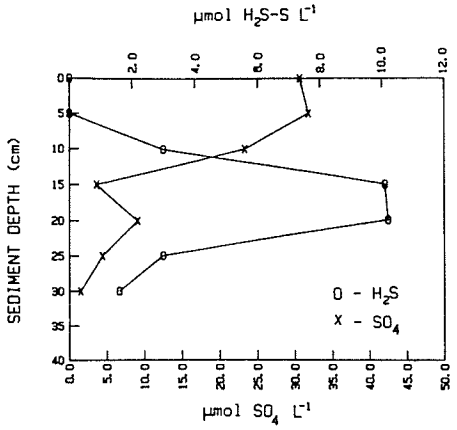
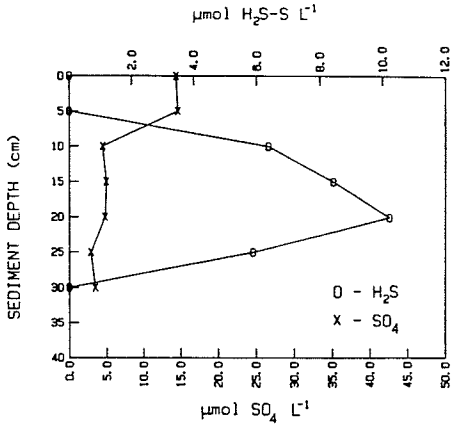

SEDIMENT DEPTH (cm)
0
5
10
15
20
25
30
35
40
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
μmol SO_4 L^{-1}
* - OLIGOTROPHIC AREA - SITE 1
O - MINEROTROPHIC AREA - SITE 2

Figure 4. May - October-84 monthly SO_4^{2-} and H_2S concentration profiles for the experimental minerotrophic area (site 2).

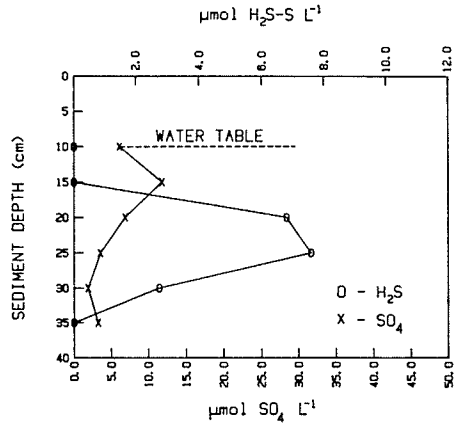
23-MAY-84



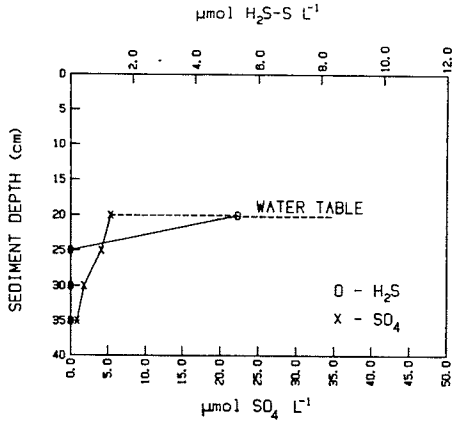
20-JUNE-84



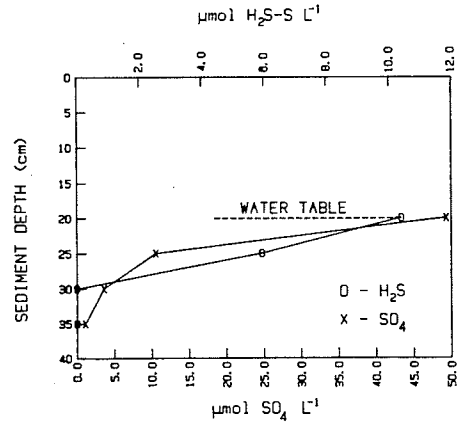
18-JULY-84



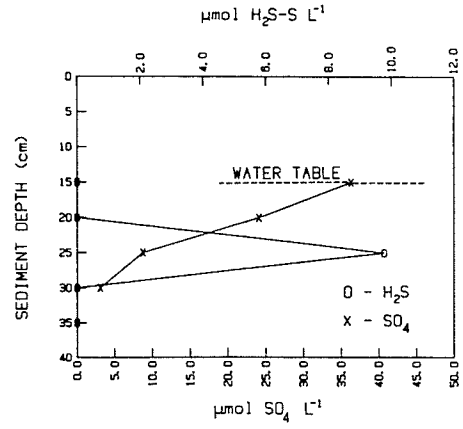
15-AUGUST-84



12-SEPTEMBER-84



10-OCTOBER-84



Surface water concentrations of SO_4^{2-} at the central oligotrophic pools (Figure 1), were consistently lower (< 15 μmol L^{-1}) than concentrations in the experimental minerotrophic pool (Figure 2). The pore water samples were slightly lower in SO_4^{2-} concentrations than the respective surface water pool.

The occurrence of H_2S in the pore water of the mire was primarily confined to the minerotrophic sites. Hydrogen sulfide was detected in all but one of the monthly profiles obtained from the two minerotrophic sites in 1984. When H_2S was present in the minerotrophic profiles, concentrations usually increased with depth (Figure 4), with maximum concentrations occurring between 15-25 cm. Hydrogen sulfide concentrations never exceeded 20 μmol S L^{-1} in either minerotrophic site. Generally there was more pore water H_2S present during the May, June, and July profiles for both minerotrophic sites than in the August, September, or October profiles (Figure 4). In contrast, oligotrophic sites contained measurable amounts of H_2S in their pore water only occasionally in 1984 and in 1983.

The concentration of H^+ (as measured by pH) with depth also showed a distinct pattern. The central oligotrophic sites were characterized by significantly higher H^+ concentrations than the minerotrophic lagg sites. The H^+ concentration ranged from 90-200 μeq L^{-1} (pH 4.04-3.70) in the central oligotrophic sites with a rather constant concentration with depth. This was in contrast to the

minerotrophic sites which were less acidic (30-60 μeq L^{-1}) (pH 4.52-4.22) with decreasing H^+ concentrations with depth (ie. increase in pH). Surface water H^+ concentrations in the minerotrophic and oligotrophic pools were similar to their respective pore water profiles.

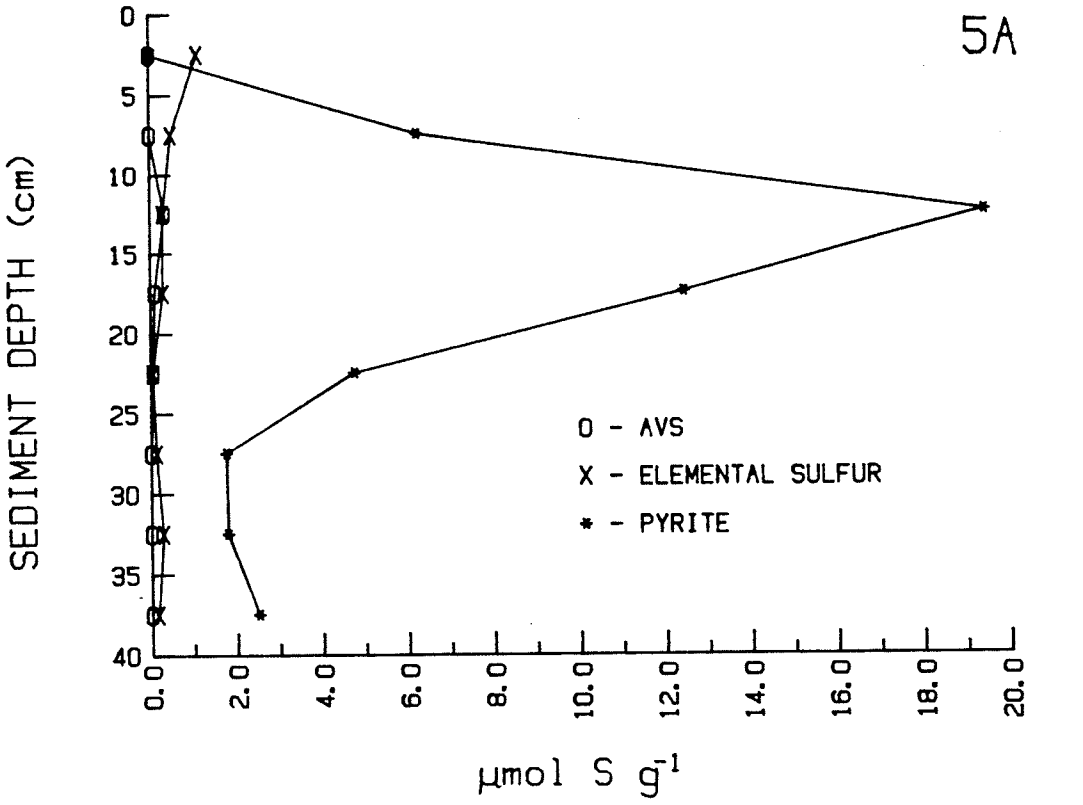
Sulfur Constituents of Short Peat Cores

The 8 cores from the minerotrophic lagg area contained significantly more AVS, S^o, and FeS_2 in the top 35 cm of peat than did the 8 cores from the central oligotrophic area (Figures 5a and 6a). The total sulfur content was also higher in the minerotrophic area (Figures 5b and 6b). The total inorganic sulfur content was higher for cores collected before the water table dropped (spring cores) than in the October cores (autumn cores) which were collected after the drawdown period had occurred. Differences between minerotrophic and oligotrophic area cores were significant, however, there were no significant differences between experimental and control, minerotrophic and oligotrophic cores.

Minerotrophic area. Organic sulfur was the dominant form of sulfur, accounting for 93% of the total sulfur present, while inorganic S (AVS + S^o + FeS_2) made up the remaining 7%. A maximum in total sulfur content (156 μmol S g^{-1}) occurred at 10-15 cm, coincident with the inorganic sulfur maxima (Figure 5a). Inorganic sulfur represented 13% of the total sulfur in the 10-15 cm interval. Total inorganic sulfur varied seasonally, with 37% less in the

Figure 5. Concentration of acid volatile sulfide (AVS), elemental sulfur (S^o), and pyrite (FeS_2) as a function of depth in the experimental minerotrophic area (site 2) (figure 5a), and the concentration of total sulfur, organic sulfur, and inorganic sulfur (AVS + S^o + FeS_2) as a function of depth for the same core (figure 5b).

MINEROTROPHIC CORE - SITE 2 31-MAY-84



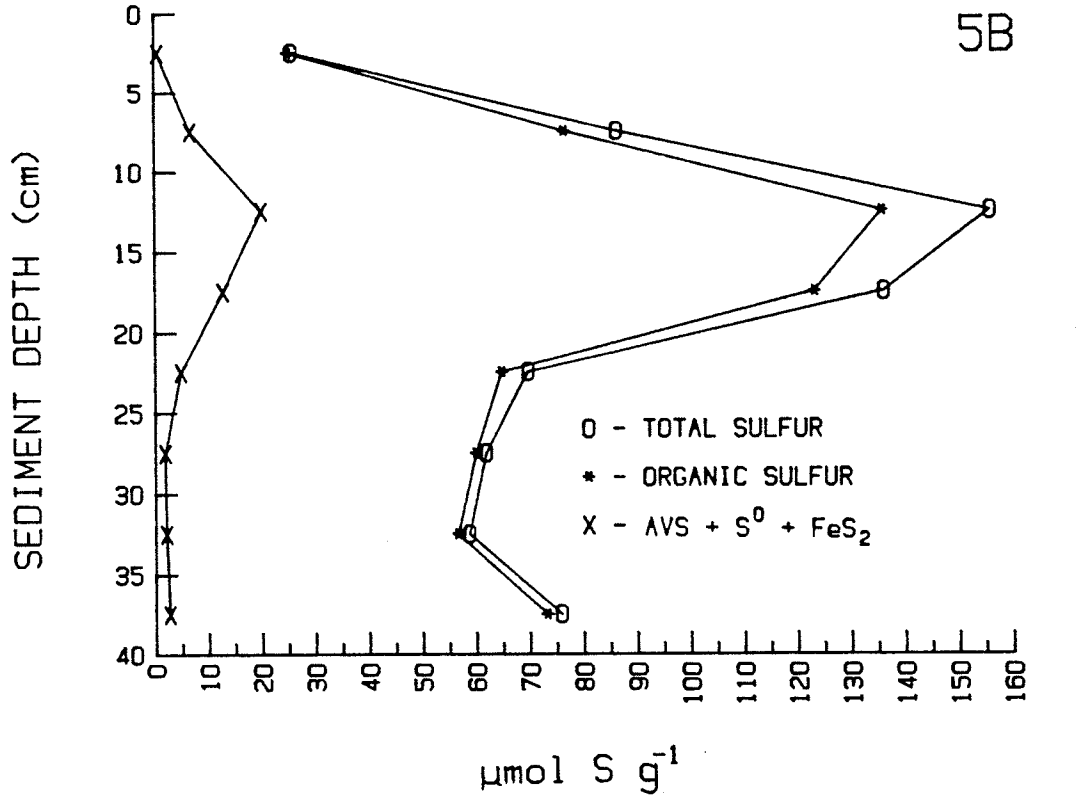
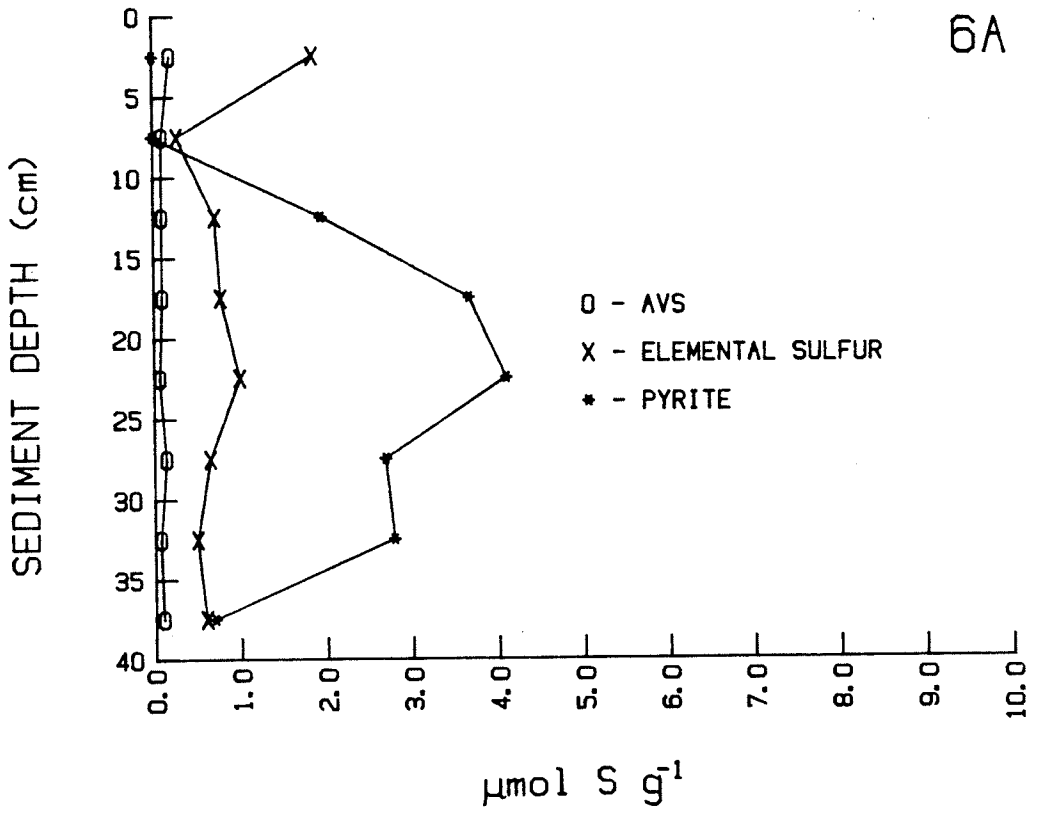
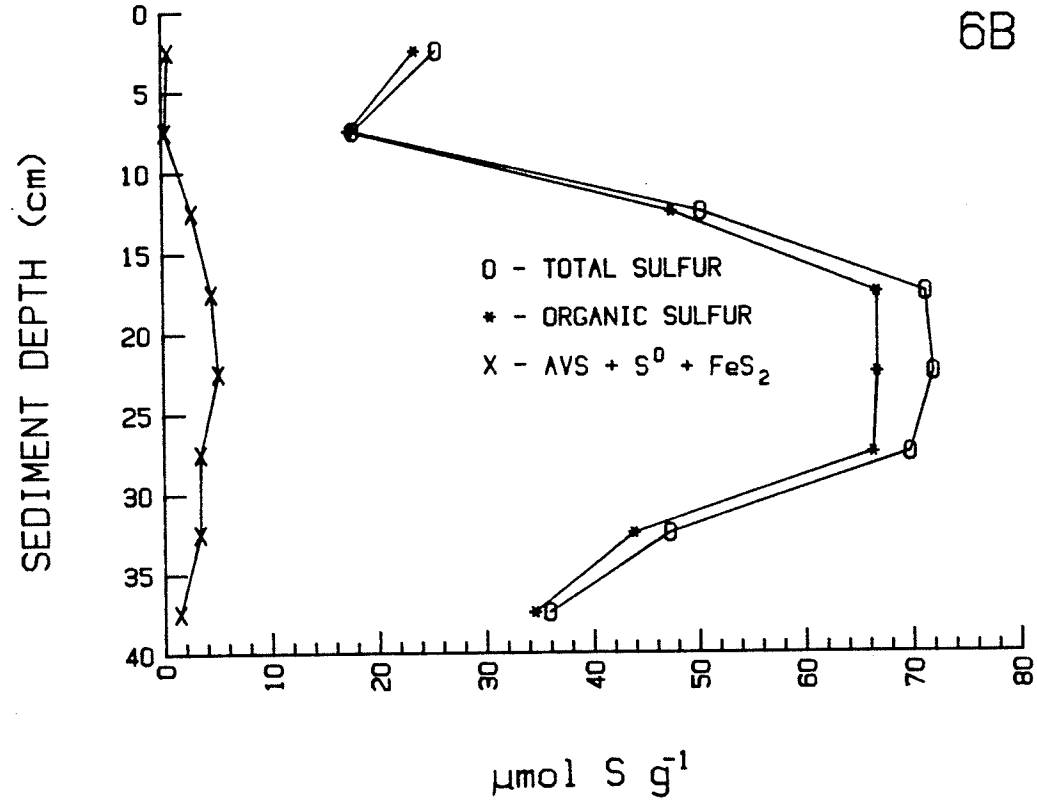


Figure 6. Concentration of acid volatile sulfide (AVS), elemental sulfur (S^o) and pyrite (FeS_2) as a function of depth in the experimental oligotrophic area (site 1) (figure 6a), and the concentration of total sulfur, and inorganic sulfur (AVS + S^o + FeS_2) as a function of depth for the same core (figure 6b).

OLIGOTROPHIC CORE - SITE 1 13-JUNE-84





October cores than in the spring cores.

In a typical core from the minerotrophic area (Figure 5a), 78% of the inorganic sulfur was FeS_2, with AVS and S^o representing about 2 and 20% respectively of the total inorganic sulfur present on a per core basis (0-40 cm). Maxima in FeS_2 concentration occurred near the 15 cm depth (Figure 5a), and was observed in all cores from the minerotrophic area (10-25 μmol FeS_2-S g^{-1}).

The maximum concentration of S^o occurred within the top 10 cm of the minerotrophic cores and accounted for up to 42% of the inorganic sulfur present in the top 10 cm.

Acid volatile sulfide in the minerotrophic peat cores was less than 4% of the total inorganic sulfur. Maximum AVS concentration (0.5 μmol S g^{-1}) occurred at a depth of 10-25 cm, below and above which AVS was found at extremely low levels. The absence of AVS from the surface moss was probably due to aerobic conditions.

Oligotrophic area. The maximum total sulfur content in the oligotrophic core (71 μmol S g^{-1}) was about half the maximum for the minerotrophic core (156 μmol S g^{-1}) with organic sulfur accounting for about 95% of the total sulfur. The depth interval (20-25 cm) which contained the highest total sulfur content also contained the inorganic sulfur peak (Figure 6b).

As in the minerotrophic area, pyrite was the dominant form of inorganic sulfur in the 8 cores from the oligotrophic central area, representing an average of 63% of

the total inorganic sulfur. AVS and S^o averaged about 3% and 34%, respectively of the total inorganic sulfur. The pyrite profile was similar in shape to that for the minerotrophic area, with maximum FeS_2 concentrations occurring at 20-25 cm (Figure 6a). The maximum FeS_2 concentrations above the 25 cm depth were much lower in the oligotrophic than in the minerotrophic cores (4 µmol vs. 20 µmol S g^{-1}). However, below a depth of 25 cm there was little difference in the amount of FeS_2 present between the two areas (about 1.80 µmol S g^{-1} in both areas).

Elemental sulfur accounted for a greater percentage of the total inorganic sulfur in the oligotrophic core (34%) than in the minerotrophic core (20%).

Acid volatile sulfur was a minor component of the total inorganic sulfur in the oligotrophic core, accounting for less than 4% of the total inorganic sulfur for the 8 cores analyzed and was seldom found at concentrations exceeding 0.25 µmol S g^{-1}.

The reduction in the recovered inorganic sulfur (µmol S m^{-2}) for spring vs. the autumn cores was 30% in the oligotrophic area compared to 37% in the minerotrophic area.

In situ Incubations with $^{35}SO_4^{2-}$

The concentration of the added SO_4^{2-} (300 µmol L^{-1}) overwhelmed the ambient SO_4^{2-} concentrations in both minerotrophic and oligotrophic experiments. In addition, since the specific activity of the two $^{35}SO_4^{2-}$ spike solutions were similar the initial specific activity in each

enclosure was also similar.

In both the minerotrophic and oligotrophic enclosure experiments significant quantities of labelled reduced inorganic sulfur formed within 24 hours of the addition of $^{35}SO_4^{2-}$ (Tables 1 and 2). The total amount of reduced inorganic ^{35}S recovered after 1, 3, and 15 days of incubation was significantly greater in the minerotrophic site than in the oligotrophic site (Tables 1 and 2). Activity associated with $^{35}S^o$ and $Fe^{35}S_2$ accounted for > 90% of the recovered inorganic reduced sulfur at all sampling times (Tables 1 and 2). Organic sulfur accounted for about 80% of the total recovered label in both experiments after 82 and 62 days of incubation, while $AV^{35}S$, $^{35}S^o$, and $Fe^{35}S_2$ acccounted for the remaining 20% in both experiments.

Minerotrophic area. The total amount of reduced inorganic ^{35}S activity in the minerotrophic experiment decreased with time (Table 1). In the 5 cores analyzed, 90% of the recovered reduced sulfur occurred in the top 15 cm of peat. Less than 1% of the pore water sulfur-35 activity occurred below 20 cm. After 1 day of incubation, 5% of the total reduced recovered label was $AV^{35}S$, 37% as $^{35}S^o$, and 58% as $Fe^{35}S_2$. Fifteen days after the spike application the percentage of recovered label represented by $AV^{35}S$, $^{35}S^o$, and $Fe^{35}S_2$ was similar to that observed for the cold chemistry: 1%, 18%, and 81% after 15 days of incubation compared to 2%, 14%, and 84% for the cold chemistry.

Table 1 - Total recovered dpm core^{-1} for $AV^{35}S$, $^{35}S^{o}$, $Fe^{35}S_2$, and organic sulfur with time for the minerotrophic enclosure experiment. The percent value (%) refers to the fraction each of the 3 inorganic ^{35}sulfur species represents of the total inorganic ^{35}sulfur recovered.

Time, day	$AV^{35}S$	(%)	$^{35}S^{o}$	(%)	$Fe^{35}S_2$	(%)	$Fe^{35}S_2 + {}^{35}S^{o}$	(%)	$AV^{35}S + Fe^{35}S_2 + {}^{35}S^{o}$	organic sulfur	total recovered sulfur
1	160,000	5	1,200,000	38	1,800,000	57	3,000,000	95	3,160,000	----	----
3	22,000	1	370,000	25	1,100,000	74	1,470,000	99	1,492,000	----	----
15	24,000	1	330,000	18	1,500,000	81	1,830,000	99	1,854,000	----	----
82	*13,000		----		----		*750,000		*762,000	*2,971,000	*3,733,000

* value based on the average of two cores, all others based on one core.

Table 2 - Total recovered dpm core^{-1} for $AV^{35}S$, $^{35}S^{o}$, $Fe^{35}S_2$, and organic sulfur with time for the oligotrophic enclosure experiment.

The percent value (%) refers to the fraction each of the 3 inorganic ^{35}sulfur species represents of the total inorganic ^{35}sulfur recovered.

Time, day	$AV^{35}S$	(%)	$^{35}S^{o}$	(%)	$Fe^{35}S_2$	(%)	$Fe^{35}S_2 + {}^{35}S^{o}$	(%)	$AV^{35}S + Fe^{35}S_2 + {}^{35}S^{o}$	organic sulfur	total recovered sulfur
1	15,000	10	46,000	30	90,000	60	136,000	90	151,000	----	----
3	22,000	9	90,000	36	140,000	55	230,000	91	252,000	----	----
15	40,000	7	190,000	32	370,000	61	560,000	93	600,000	----	----
62	*27,000		----		----		*510,000		*537,000	*2,004,000	*2,541,000

* value based on the average of two cores, all others based one core.

After 82 days of incubation, 62% of the reduced ^{35}S observed during the first 15 days of incubation was gone (Table 1). This can be compared to the decrease in total inorganic sulfur for spring vs. autumn cores (37%). Organic ^{35}sulfur accounted for 80% of the total recovered ^{35}S after 82 days of incubation (Table 1), compared to 93% for the cold sulfur. The similarity in product ratio for inorganic and organic sulfur must be interpreted with caution since the ratio of labelled end products resulted entirely from an acid application, while the cold sulfur ratio formed primarily under natural conditions.

Oligotrophic area. The total amount of reduced inorganic ^{35}S activity recovered in the oligotrophic site increased with time (Table 2). In contrast to the minerotrophic site, there was no decrease in the amount of inorganic sulfur present (μmol S m^{-2}) with time. However, the total amount of reduced inorganic ^{35}S activity recovered at all times was less in the oligotrophic site compared to the minerotrophic site. For example, after 3 days of incubation, there was about 5 times more reduced activity in the minerotrophic site than in the oligotrophic site. Yet, after 62 days of incubation, the amount of total reduced inorganic ^{35}S activity recovered in the oligotrophic site (537,000 dpm $\cdot$ core $^{-1}$) was similar to that recovered after 82 days in the minerotrophic site (762,000 dpm $\cdot$ core $^{-1}$), the amount of organic sulfur formation was also similar (Tables 1 and 2).

As in the minerotrophic experiment, more than 90% of the recovered reduced sulfur occurred above 15 cm, and again less than 1% of the pore water sulfur-35 occurred below 20 cm. The percentage of label in $AV^{35}S$, $^{35}S^{o}$, and $Fe^{35}S_2$ did not differ in the first 3 cores from the oligotrophic enclosure (Table 1). After 15 days, $AV^{35}S$ accounted for 7%, $^{35}S^{o}$ accounted for 32%, and $Fe^{35}S_2$ accounted for 61% of reduced inorganic ^{35}S. The total inorganic S fractions were 6% AVS, 16% S^{o}, and 78% FeS_2.

As with the minerotrophic enclosure experiment, FeS_2 represented a slightly larger fraction (78%) of total inorganic sulfur in the cold chemistry ratios than it did in any of the labelled cores taken during the first 15 days of incubation (Table 1). The formation of labelled organic sulfur accounted for 79% of the total recovered sulfur after 62 days of incubation (Table 2). Like the minerotrophic experiment, the percent labelled organic sulfur (79%) was less than that represented by the cold organic sulfur (95%). Even though the labelled end product distribution formed under an acid regime, the end product distribution was remarkably similar to the cold sulfur distribution.

Discussion

Sulfate reduction occurred throughout the experimental mire, even in environments with H^{+} concentrations greater than 100 $\mu eq\ L^{-1}$ ($pH < 4$) (Tables 1 and 2). Molar rates of sulfate reduction could not be determined for the minerotrophic or oligotrophic enclosure experiment. However,

because the specific activities of the SO_4^{2-} pools were fairly similar initially it was possible to safely compare the relative rates of sulfate reduction in the two experiments after 1 day of incubation.

More rapid sulfate reduction occurred in the minerotrophic site than in the oligotrophic site, as demonstrated from the in situ incubations with sulfur-35 after 1 day (Tables 1 and 2). Also there was a greater abundance of the inorganic end products of sulfate reduction (AVS, FeS_2, S^o) in the minerotrophic area than in the oligotrophic area (Figures 5a and 6a). After 3 days of incubation there appeared to be recycling of ^{35}S in the minerotrophic enclosure which makes the specific activity complicated and thus makes it difficult to compare the relative amounts of reduced ^{35}S in the two experiments. The apparent differences in sulfate reduction rates between the two areas may result from the lower surface and pore water SO_4^{2-} concentration in the oligotrophic area (Figures 2 and 3), the higher H^+ concentration in the oligotrophic area compared to the minerotrophic area, and/or differences in the availability of oxidizable organic matter between the two areas.

Sulfate reduction rates in freshwater environments are often limited by the SO_4^{2-} concentration rather than by the concentration of oxidizable organic matter, in contrast to marine sediments (Berner 1984). Sulfate reduction rates in the mire were even more SO_4^{2-} limited than freshwater lake

sediments. Sulfate concentrations in ELA lakes (35 μmol SO_4^{2-} L^{-1}; Schindler, personal communication) were similar to the mire in May and June. However, in lakes, the sediment has a reservoir of SO_4^{2-} available in the water column which constantly diffuses into the sediment and fuels sulfate reduction (Kelly and Rudd 1984). In contrast, the amount of water in the mire is small compared to sediment and therefore the SO_4^{2-} content is much more seasonally variable (Figures 2 and 4).

Sulfate reduction rates within the mire are undoubtedly quite variable because the amount of SO_4^{2-} is limited and the supply is not constant. Significant inputs of SO_4^{2-} to the mire from spring snowmelt and rain storms (including acidifications) increase the SO_4^{2-} concentrations of surface and pore water, and probably increase the rate of sulfate reduction temporarily. In fact, when SO_4^{2-} in the mire was increased due to experimental acidification, rates of SO_4^{2-} loss also increased, indicating SO_4^{2-} limitation (Chapter 3). Increased rates of sulfate reduction also occur in lakes receiving additional SO_4^{2-} from acid mine drainage (Herlihy and Mills 1985) and experimental acidification (Cook and Schindler 1983).

Sulfate reducing bacteria are known to be inhibited by H^+ concentrations greater than 1 μeq L^{-1} (pH < 6) (Postgate 1984), and laboratory experiments with mixed sediments also show inhibition of sulfate reduction at pH 4, compared to pH 6 (Kelly and Rudd 1984). Although the H^+ concentration in

the minerotrophic area (30 μeq L^{-1}) might be expected to inhibit sulfate reducing bacteria, the H^+ concentration in the oligotrophic area (>100 μeq L^{-1}) would be even more inhibitory. However, sulfate reduction was certainly occurring in both areas. The higher H^+ concentration might be responsible for the apparently slower $^{35}SO_4^{2-}$ reduction rates in the oligotrophic area (Tables 1 and 2).

Differences in the availability of organic substrates suitable for sulfate reducing bacteria might also cause the difference in rate, but this seems unlikely because both sites are dominated by the same vegetation (Vitt and Bayley 1984) and net peat accumulation is similar (Appendix VI).

Many investigators have observed that watersheds containing freshwater wetlands are net sinks for SO_4^{2-}-S in rain and in groundwater on an annual basis (Hemond 1980; Rippon et al 1980; Brown 1980; Braekke 1980,1981; Wieder and Lang 1984). The experimental mire is undoubtedly a net sink for SO_4^{2-} -S on an annual basis. This is based on the annual SO_4^{2-}-S mass balance (Chapter 3), the <u>in situ</u> enclosure experiments with sulfur-35 (Tables 1 and 2), and the disappearance of SO_4^{2-} with depth (Figure 4) and with time (Figure 2) in the minerotrophic and oligotrophic area. At certain times of the year however, wetlands are sources of SO_4^{2-}-S (Braekke 1981; Wieder and Lang 1984). Braekke (1981) suggested that observed increases in SO_4^{2-} concentration of groundwater and water discharged from such systems occurs after the interruption of extended dry

conditions with significant rainfall and that it results partly from the resolubilization and wash-out of oxidized organic and inorganic sulfur formed during the preceding dry period. Evidence for this phenomenon has usually been indirect (ie. based on SO_4^{2-} mass balance). The oxidation of sulfur forms has not been previously observed directly within a freshwater mire system, although pyrite oxidation has in a New England salt marsh (Howarth and Teal 1979). In this study, evidence for the occurrence of this phenomenon in the ELA mire includes: 1) the decrease in inorganic sulfide content of spring vs. autumn cores, for both the minerotrophic and oligotrophic areas; 2) the reduction in ^{35}S activity in the minerotrophic enclosure experiment after 82 days of incubation (Table 1); 3) significant increases in pore water SO_4^{2-} concentration following the first autumn rains in the minerotrophic area (Figure 4) and oligotrophic area (Appendix II); and 4) the decreasing sulfur content of peat (inorganic and organic sulfur) below the depth of peak concentrations in both areas suggests the existence of a removal mechanism (Figures 5b and 6b).

All of the above changes are partly or wholly caused by water table fluctuations. The water table level dropped a maximum of 15 cm in the minerotrophic area between the date of collection of spring and autumn cores (Beaty unpublished data); a similar drop also occurred in the oligotrophic area between spring and autumn cores (14 cm) (Beaty unpublished data). This drop resulted in the exposure to air of

previously anaerobic peat containing inorganic sulfide and organic sulfur. Since FeS_2 and AVS are rapidly oxidized chemically and/or biologically to S^o and SO_4^{2-} in the presence of oxygen (Berner 1984), it is likely that increased penetration of oxygen during the drawdown period caused the decrease in inorganic sulfide content. Because total sulfur determinations were made only on spring cores, I am unable to conclude that a similar decrease in organic sulfur content occurred.

Likewise, the reduction in recovered reduced ^{35}S during the minerotrophic enclosure experiment (Table 1) resulted from a similar drop in water table level (15 cm). Since > 90% of the reduced ^{35}S formed in the top 15 cm of saturated peat, a drop in water table level would result in the exposure of recently formed $AV^{35}S$, $^{35}S^o$, and $Fe^{35}S_2$ to air. Sulfide oxidation also occurs in the epilimnetic sediments of ELA lakes (Kelly personal communication), and is coincident with increased penetration of O_2 into sediments during winter. Reoxidation of organic sulfur also occurs, but to a smaller extent than the inorganic sulfides (Kelly personal communication). Howarth and Teal (1979) observed a similar seasonality in pyrite production and oxidation in a New England salt marsh, where pyrite accumulated during fall, winter, and spring was later nearly completely reoxidized during the summer months. They hypothesized that pyrite oxidation resulted from the release of O_2 by metabolizing grass roots in an otherwise anoxic environment.

The 12 September SO_4^{2-} profile showed a 10-fold increase in surface SO_4^{2-} concentration from the 15 August profile (Figure 4), partly due to SO_4^{2-} input via precipitation, but probably partly from the washing out of SO_4^{2-} formed from the reoxidation of inorganic sulfide during drawdown. A simlar increase occurred in the oligotrophic site profile in 1984 (Appendix II).

A decrease in the amount of reduced ^{35}S did not occurr during the oligotrophic enclosure experiment (Table 2) as in the minerotrophic experiment. This difference is partly because the water table level did not drop as much during the oligotrophic experiment and in fact a net rise of 2.1 cm occurred. The anoxic zone probably rose with the water table.

The decreasing inorganic and organic sulfur content with depth in both the oligotrophic and minerotrophic areas (Figures 5b and 6b) must result from a mechanism that releases and exports sulfur from the mire. It seems likely that summer drawdown, reoxidation, resolubilization, and export of SO_4^{2-}-S could prevent a large fraction of recently formed sulfur from being permanently stored in the anaerobic peat. In the examination of the distribution of various elements in an ombrotrophic bog, Damman (1978) found that many of the elements showed similar losses below the water table and were attributed to a fluctuating water table.

Total sulfur concentrations in peat in the mire are in the range reported for freshwater lakes (King and Klug 1982)

and other freshwater wetlands (Casagrande et al 1977). As with these systems organic sulfur was the dominant sulfur form in the mire (Figures 6a,b) (Tables 1 and 2). However, the decrease in total sulfur content (organic and inorganic) with depth was unlike the data of Brown (1980) or Casagrande et al (1977), where total sulfur content increased or remained relatively constant with depth rather than decrease as they do in the experimental mire. In their systems the water level is maintained at a more constant depth because of ground water discharge and therefore the drawdown-reoxidation cycle may not be as important as in the experimental mire.

Pyrite's rapid formation and dominance as an inorganic end product of sulfate reduction throughout the mire under experimental acid conditions and natural acid conditions (Tables 1 and 2) (figure 5a and 6a) is similar to that for saltwater marsh ecosystems (Howarth and Teal 1979). However, FeS_2 dominance was in contrast to Brown's (1980) results from an English bog. Brown (1980) injected a tracer quantity of $^{35}SO_4^{2-}$ into a peat core, and after an 8 day incubation, H_2S accounted for 60% of the original activity below 12.5 cm with FeS_2 and organic sulfur accounted for less than 40% of the original activity at all depth. Howarth (1979) has explained FeS_2 dominance over FeS in terms of their solubility products, and the effect of H^+ concentration on S^{2-} activity. The solubility product for FeS_2 (2.4×10^{-28}) is much less than that for FeS ($2.75 \times$

10^{-18}), and both FeS_2 and FeS are dependent on S^{2-} and Fe^{2+} activity. Increasing H^+ concentration causes a decrease in S^{2-} activity, resulting in a lower ion activity product. The lower K_{sp} for FeS_2 vs. FeS makes it possible for FeS_2 to be oversaturated, while FeS is undersaturated and thus FeS_2 would be the preferred iron sulfide mineral. The H^+ concentration (20-100 μeq L^{-1}) in the mire were similar to the saltwater marsh sediment where FeS_2 is the dominant inorganic sulfide (Howarth and Giblin 1982). The H^+ concentration in Brown's (1980) bog was significantly lower (usually < 32 μeq L^{-1}) than the mire and may partially account for the lack of pyrite formation.

Both organic and inorganic sulfur content decrease significantly with depth below their maximum concentrations in the zone of water table fluctuations (figure 5b and 6b). However, the inorganic sulfur, primarily FeS_2, all but disappears below 30 cm and therefore organic sulfur accounts for nearly all of the long term sulfur storage. This may be a consequence of the refractory nature of the organic sulfur present, relative to pyrite. If the organic sulfur was less easily oxidized or degraded compared to the inorganic sulfur forms, the percent organic sulfur would increase at the expense of the inorganic forms, as it apparently does. The depth profiles for organic and inorganic sulfur in both areas support this theory (figure 5b and 6b).

In addition, although a direct comparison of the percent organic sulfur formed during the in situ incubations

with $^{35}SO_4^{2-}$ with the percentage of cold organic sulfur may be inappropriate (as discussed earlier), it is interesting that the percent of organic ^{35}sulfur in the in situ experiments (79-80%) were both less than the percent cold organic sulfur present in both the minerotrophic and oligotrophic areas, 93% and 95% respectively. In light of the measured decrease in inorganic sulfur between spring and autumn cores it seems possible that the greater abundance of organic sulfur in the cold sulfur chemistry as compared to the in situ experiments may have resulted from the preferential removal of pyrite by the reoxidation cycle outlined previously.

The resistance of organic sulfur in the mire to changing redox conditions is consistent with long term ^{35}S experiments in oligotrophic lake sediments (Kelly, personal communication). This apparent resistance to redox changes may be because the organic sulfur is already in an oxidized state, for example sulfate esters. Sulfate esters account for 30-40% of the organic sulfur in eutrophic lake sediments (King and Klug 1982) and freshwater wetlands (Casagrande and Siefert 1977). The biological incorporation of SO_4^{2-}-S into organic compounds such as sulfate esters occurs in the oxic layers of soils and is very important in terrestrial sulfur cycling (Swank et al 1983). In light of the organic sulfur content of freshwater wetland sediments, future work should focus on its mode of formation and chemical reactivity in wetland ecosystems.

Chapter 3

The Effects of Acidification on the Sulfur Dynamics of an Experimentally Acidified Mire in Northwestern Ontario

Abstract

A small Sphagnum dominated mire (Experimental Lakes Area, northwestern Ontario) was divided into an experimental and control area. The experimental area (2.66 ha) was acidified with sulfuric and nitric acid during half of the 1983 ice free season and the entire 1984 season. Three monthly acidifications were applied in 1983 and 6 in 1984. The control area (0.88 ha) received lake water during the experiments. During an acidification the experimental area received about 86 mg S m^{-2}, compared to 13 mg S m^{-2} for the control area. Sampling sites were located in the experimental and control areas of the mire.

The concentration of SO_4^{2-} in surface water pools increased in response to all acidifications and usually returned to near pre-acidification concentrations within 7 days. Smaller increases in SO_4^{2-} concentrations occurred in the control pools. Increases in pore water SO_4^{2-} content in both the experimental and control areas were smaller and less consistent than those of the surface water. Hydrogen sulfide occurred only in the minerotrophic pore water profiles and always increased after acidification. A large amount of the added SO_4^{2-} was "sorbed" by the surface Sphagnum spp. before reaching the water table. Annual SO_4^{2-}-S mass balance budgets for 1981- 1984 demonstrated that the mire was a sink for SO_4^{2-}-S and showed that more SO_4^{2-} was retained during the 2 acidification years (73%)

than during the two previous years (55%). Some of the sulfur reactions resulting in sulfur retention were enhanced by the additional SO_4^{2-}-S loading.

Introduction

Acid deposition, in the form of sulfuric and nitric acids, has resulted in the perturbation of many ecosystems and has hence stimulated a considerable amount of research. Much of the research has focused on understanding the effects of acid deposition on lakes, including aquatic sulfur cycling (Drablos and Tollan 1980; Schindler 1980; Schindler et al. 1980; Schindler and Turner, 1982; Kelly et al 1982). Sulfur cycling and the effects of acidification on terrestrial ecosystems has also been investigated in deciduous and coniferous watersheds (Eaton et al 1978; Johnson and Henderson 1979; Johnson 1984) and in agricultural soils (Tabatabai 1984).

Investigations of the possible effects of acidic deposition on North American wetlands are rare, yet many of these wetlands are adjacent to the oligotrophic lakes that are located in highly acid vulnerable areas. Gorham et al (1984) mentioned the paucity of data related to the ecological effects of acid deposition on peatlands in their review of the subject. This is especially important since much of the 210 million ha of peatland in North America is located in areas thought to be sensitive to acidic deposition.

There has been more research in Britain on the possible effects of acid deposition on peatlands. In an analysis of peat profiles from blanket bogs in the southern Pennines,

Tallis (1964) determined that Sphagnum spp. once formed a greater percentage of the vegetation than they presently do, and suggested the loss was due to 200 years of high SO_2 deposition. Later, Ferguson et al (1978) determined from laboratory experiments, that some of the Sphagnum spp. now absent from the blanket bogs were among the most sensitive to various sulfur pollutants, thus supporting Tallis's earlier observations. More recently, Ferguson and Lee (1983) reintroduced 5 Sphagnum spp. to the southern Pennines, and found that only one of the 5 spp. continued to grow after 1 year, even though bulk sulfur deposition has presumably decreased in recent years.

In the 1950's, Gorham (1958) found a positive correlation between H^+ and SO_4^{2-} concentration for bogs in the English Lake District. Similary, low pH (3.82), high ionic conductivity (130 µmho cm^{-2}), and high SO_4^{2-} concentration (364 µmol L^{-1}) of 24 moorland pools in Belgain were suggested to be the result of industrial acidification (Vangenechten and Vanderborght 1980).

Increased rates of sulfate reduction in lakes receiving SO_4^{2-} from acid mine drainage and experimental acidification has been responsible for the reduction in the efficiency of acidification (Herligy and Mills 1985; Kelly et al 1982; Cook and Schindler 1983; Cook et al in press). Alkalinity generated from sulfate reduction helped offset the potential acidification of Thoreau's bog in Mass., an area receiving acid deposition (Hemond 1980). Similarly, acid mine

drainage entering a bog in West Virginia had no effect on the outflow chemistry, apparently because sulfate reducing bacteria consumed the additional SO_4^{2-} and H^+ (Wieder and Lang 1984).

Presently little is known about the biogeochemical cycling of sulfur in peatlands, or about the effect acidification may have on the sulfur cycle. To investigate the effects of acidification on an undisturbed wetland, a small mire located in the Experimental Lakes Area (ELA) of northwestern Ontario was experimentally acidified with sulfuric and nitric acid. An irrigation system was constructed on the mire's surface to apply acidified (pH 3) and unacidified lake water (pH 6-7) to an experimental and control area. The control area received only lake water, while the experimental area received acidified lake water during irrigation experiments.

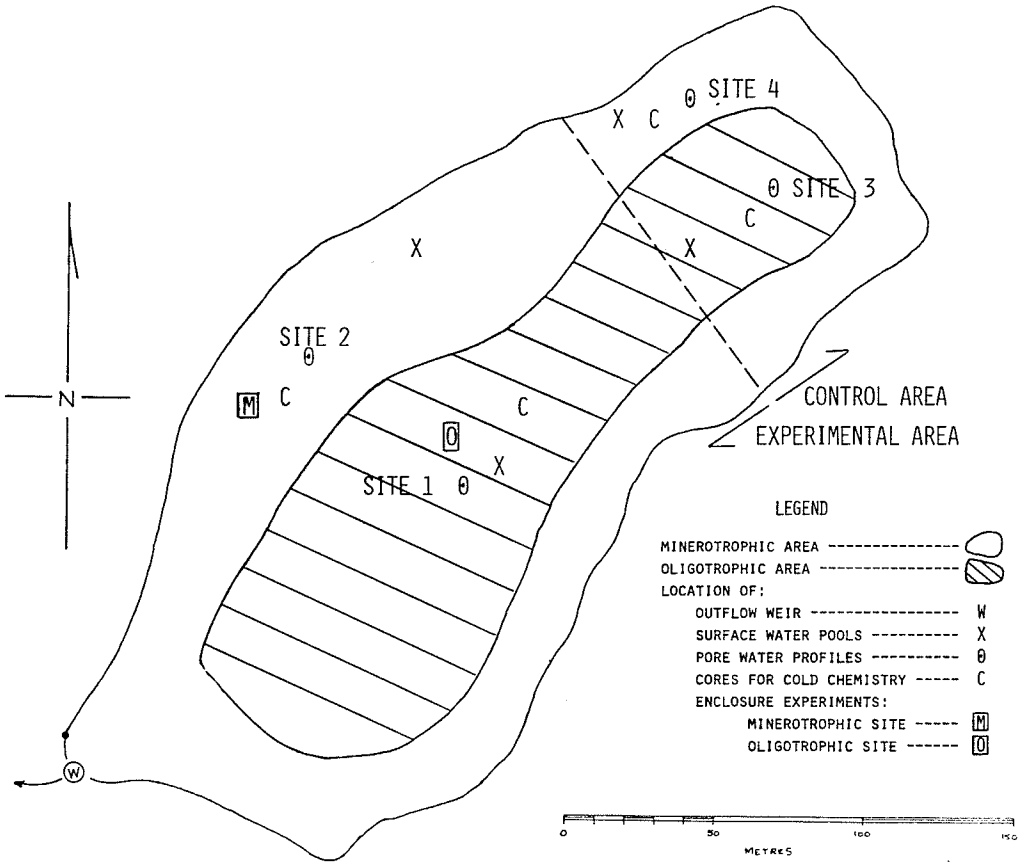
This study investigated the effects of experimental acidification with sulfuric acid on the sulfur dynamics of a small basin mire. The major questions addressed were: 1) what was the fate of the added SO_4^{2-}? 2) was sulfate reduction stimulated by the additional SO_4^{2-} input? 3) were there any differences in the way the added SO_4^{2-} was processed in relation to season and/or location in the mire? and 4) what was the overall effect of additional SO_4^{2-} loading on the sulfur budget of the mire?

Description of study area

The experimental mire is located at the Experimental Lakes Area (ELA) in northwestern Ontario, on the Canadian Shield, about 56 km southeast of Kenora. The small oval mire is centrally located within the northeast drainage sub-basin of Rawson Lake (49^{o} $40^{'}$ N, 93^{o} $43^{'}$), and occupies 3.67 ha of this 10.8 ha sub-basin (Figure 1). The surrounding upland and the southwestern half of the mire burned in 1974. The upland burned again in 1980. Except for the trees, Vitt and Bayley (1984) determined that there was no difference in vegetation in the burned and unburned portions of the mire. The unburned half of the mire is dominated by Picea mariana (Mill.) BSP. while the burned half is dominated by juvenile Pinus banksiana Lamb.. Sphagnum angustifolium (Russ.) C. Jens. and S. magellanicum Brid. form the ground cover throughout the mire with the exception of a small pool near the center of the mire which is dominated by S. fallax (Klinggr.) Klinggr.. The characteristic understory plants (eg. Smilacina trifolia (L.) Desf., Ledum groendandium Oeder, and Carex trisperma Dew.) are abundant throughout the mire. For more detail see Vitt and Bayley (1984).

All water from the watershed passes through the mire and out a weir before being discharged via a boulder zone to Rawson Lake. Thus the margin or lagg of the mire receives more water and mineral input than the interior of the mire. Consequently the chemistry and vegetation of the lagg is significantly different than the central region of the mire.

Figure 1. Location of the experimental mire in the northeast drainage sub-basin of Rawson lake.


SITE 4
SITE 3
SITE 2
SITE 1
CONTROL AREA
EXPERIMENTAL AREA
N
W
LEGEND
MINEROTROPHIC AREA
OLIGOTROPHIC AREA
LOCATION OF:
OUTFLOW WEIR W
SURFACE WATER POOLS X
PORE WATER PROFILES θ
CORES FOR COLD CHEMISTRY C
ENCLOSURE EXPERIMENTS:
MINEROTROPHIC SITE M
OLIGOTROPHIC SITE O
0
50
100
150
METRES

In their analysis of the vegetational and chemical characteristics of this mire, Vitt and Bayley (1984) were able to divide the mire into two distinct areas: 1) a lagg area (called the minerotrophic area); and 2) a central area (called the oligotrophic area), characterized by nutrient poor conditons relative to the minerotrophic lagg area (Figure 1).

Experimental Design

The mire was divided into an experimental and control area. The control area received only lake water, while the experimental area received acidified lake water during the irrigation events (Figure 1). Irrigation water was pumped from a nearby lake and delivered to the mire surface via 160 sprinkler heads located on laterals spaced at 14 m intervals along a 300 m mainline. The control area (0.88 ha) located in the northeast end of the mire received only lake water. Sulfuric and nitric acid were injected into the mainline irrigation pipe just below the control area with a chemical metering pump, and was applied to 2.66 ha of mire surface. Only a small area of the mire (4 %) adjacent to the outflow weir was excluded from the irrigation. For more details on design and operation of the irrigation system see Bayley et al submitted.

To date there have been 9 acidifications: 3 in 1983 (3 August, 31 August, 11 October) and 6 in 1984 one each month, May - October. Each acidification lasted 4-5 h, followed by 20-30 min rinse with lake water, to mimic a natural rain

storm. The SO_4^{2-}-S loading during an irrigation event in the experimental area was about 86 mg S m^{-2}, compared to 13 mg S m^{-2} for the control area which received only lake water.

Methods and Materials

Sampling and Chemical methods

Surface water samples were collected weekly during the ice free season. Surface water samples were collected in 1983 in the oligotrophic central pool and in a small tree hollow near the edge of the mire characteristic of more mineral conditions (called the minerotrophic pool) (Figure 1). Both stations received acidified water during the experiments. In 1984 two additional surface water stations were added in the control area of the mire (oligotrophic control and minerotrophic control) (Figure 1). Surface water samples were analyzed for SO_4^{2-} and H^+ concentration.

Pore waters were measured monthly at four sampling sites within the mire. Two of the four sites (sites 1 and 2) are located in the experimental area of the mire, and the other two (sites 3 and 4) are in the control area of mire (Figure 1). Sites 1 and 3 are characteristic of the nutrient poor, oligotrophic area of the mire, while sites 2 and 4 are characteristic of the more nutrient rich, minerotrophic lagg area (Figure 1). All of these sites were located in hollows and were sampled for pore water on a monthly basis in 1983 and 1984. Pore water samples were obtained at 5 cm intervals from the top of the water table

to a depth of about 35 cm and were analyzed for SO_4^{2-}, H_2S, and H^+ concentrations.

Pore water samples from the various depths were obtained by suction using a hollow stainless steel tube (6 mm outside diameter) about 1 m in length, lined with small-diameter tygon tubing. One end of the tube had slots in 1.5 cm of its length to permit entry of the pore water, and a nylon screen inserted to filter out large particulate matter. A plastic syringe (50 mL) was attached to the other end with a 3 way valve. Pore water was thus obtained by inserting the stainless steel tube to a known depth below the water table, and withdrawing a sample with gentle suction. Only pore water from the saturated zone could be sampled with this device. The first portion of the pore water obtained was expelled through the 3 way valve, taking care not to let air enter the syringe. Samples for H^+ and H_2S analyses were collected in 5 mL glass syringes fitted with 3 way valves which had been previously filled with deoxygenated (boiled) water. Three mL samples were collected for each analysis. Sulfate samples were collected in 5 mL plastic mini vials which had been rinsed 3 times with distilled-deionized water.

Hydrogen ion concentration was determined within 3 h of collection using an Orion research meter and a Fisher glass combination electrode. Hydrogen sulfide samples were analyzed by the method of Stainton et al (1977). Due to the small sample size, appropriate changes were made to

accommodate the 3 mL sample. Reagents were injected through the 3 way valve to prevent contamination by atmospheric oxygen. The H_2S analysis was always completed within 3 h of collection. Sulfate samples were filtered with a Swinnex filtration device equipped with a distilled-deionized rinsed 0.22 um nucleopore filter and were refrigerated until analyzed with a Dionex ion chromatograph.

Acidification Sampling

Pore water samples were collected before, immediately after, and 12-18 h after each acidification experiment. Surface water samples were obtained from pools located in each of the 4 areas: before, during, directly after, 12 h after, 24 h after, and 7 days after the acidification experiment.

Laboratory Experiments

Two laboratory experiments were conducted to investigate absorption of SO_4^{2-} by the three dominant Sphagnum spp.: S. fuscum; S. magellanicum; and S. angustifolium. In one experiment I determined the loss of SO_4^{2-} from the water with time for whole plants. In the second experiment, whole plants of each spp. were divided into 3 parts: capitulum (0-1 cm), green (2-5 cm), and brown (5-10 cm), and loss of SO_4^{2-} was determined for the 3 parts for each species. Duplicates were run on all treatments.

In both experiments the moss samples were placed in jars containing 50 mL of irrigation water containing 136 µmol SO_4^{2-} L^{-1}, 272 µmol NO_3^{1-} L^{-1}, and 125 µeq H^+ L^{-1}.

Five mL subsamples from each jar were obtained after 1, 12, and 20 h. Sulfate samples were filtered and analyzed as described previously. The dry weight of the samples were measured after drying at 70°C. Results were expressed as percent SO_4^{2-} absorption per gram dry weight of Sphagnum.

Sulfate-S budget

An input/output approach was used to calculate the annual accumulation rate of SO_4^{2-}-S m^{-2} in the mire. Sulfate entered the mire by direct precipitation on the mire surface, runoff from the upland, and from acidification in 1983 and 1984. The major loss of SO_4^{2-}-S was via the bedrock controlled outflow. Loss of SO_4^{2-} due to escape of H_2S to the atmosphere was not measured but believed to be small (Chapter 2).

Bulk precipitation samples were collected after every storm to calculate SO_4^{2-} input from direct precipitation. Direct runoff into the mire was calculated from the measured concentration of SO_4^{2-} in runoff times the volume of runoff from either the northwest or east sub-basin of L239. Acidification SO_4^{2-}-S was equivalent to the annual SO_4^{2-}-S loading plus lake water SO_4^{2-}-S. The outflow was gauged with a recording concrete plume and was sampled weekly during the ice free season to determine SO_4^{2-} exported via outflow. All SO_4^{2-} samples were analyzed as described earlier.

Results

Background Chemistry

Sulfate concentrations within the mire varied significantly in both time and space. The surface waters of the minerotrophic lagg area had higher SO_4^{2-} concentrations than the central area of the mire throughout the ice free season (Figure 2). In addition, SO_4^{2-} concentration in the surface pools was usually higher than the corresponding pore water profile for that area of the mire.

Typical SO_4^{2-} pore water profiles from the experimental oligotrophic and minerotrophic areas of the mire are shown in figure 3. Generally, highest concentrations of SO_4^{2-} at the minerotrophic sites were at or near the surface, decreasing with depth, due to sulfate reduction. Surface concentrations of SO_4^{2-} were as high as 50-100 µmol SO_4^{2-} L^{-1} shortly after spring snow melt or after a significant amount of precipitation. Later in the season or after extended dry periods, SO_4^{2-} concentrations fell below 5 µmol SO_4^{2-} L^{-1}.

Increasing concentrations of H_2S with depth were observed only in the minerotrophic lagg sites. Sulfide concentrations in the minerotrophic sites ranged from undetectable to 10-15 µmol S L^{-1}. In general, the highest concentrations occurred after significant SO_4^{2-} inputs to the system (see later). In 1984, measurable amounts of H_2S were found in the two central oligotrophic sites only on two occasions (ie. > 1 µmol S L^{-1}).

Figure 2. Seasonal SO_4^{2-} concentration in the experimental oligotrophic and minerotrophic surface water pools during the 1984 ice free season.

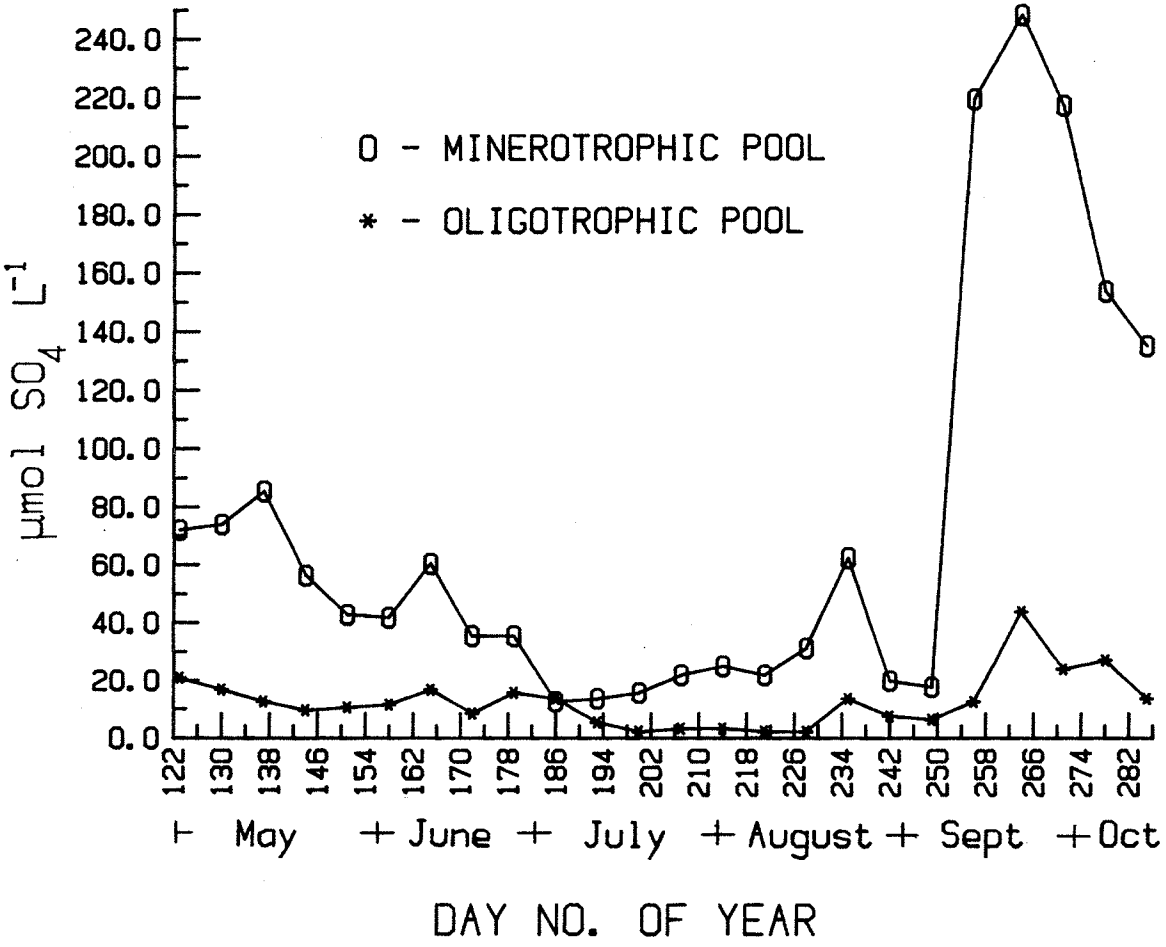
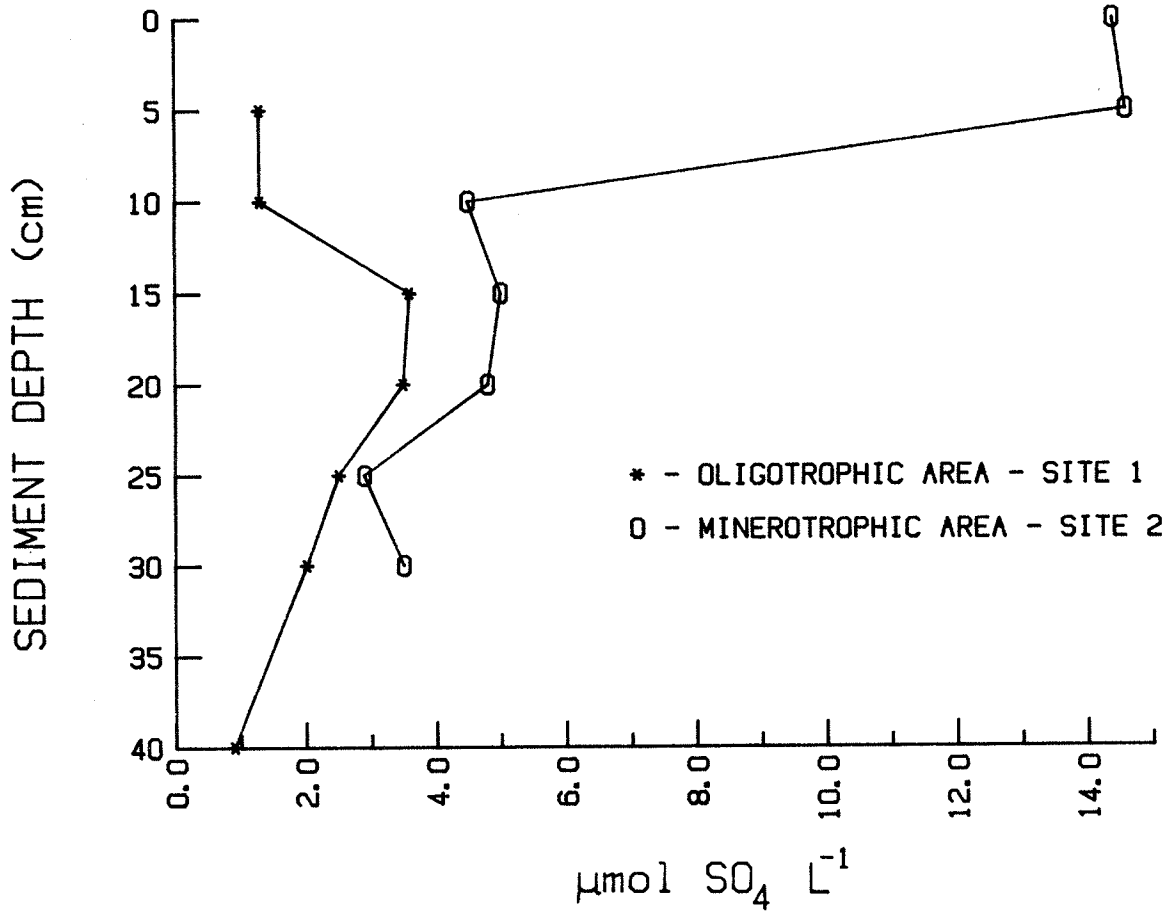

O - MINEROTROPHIC POOL
* - OLIGOTROPHIC POOL
µmol SO_4 L^{-1}
240.0
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
122
130
138
146
154
162
170
178
186
194
202
210
218
226
234
242
250
258
266
274
282
May
June
July
August
Sept
Oct
DAY NO. OF YEAR

Figure 3. Sulfate concentration as a function of depth in the experimental oligotrophic and minerotrophic sites for 20-June-84.


SEDIMENT DEPTH (cm)
0
5
10
15
20
25
30
35
40
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
μmol SO_4 L^{-1}
* - OLIGOTROPHIC AREA - SITE 1
0 - MINEROTROPHIC AREA - SITE 2

The H^+ concentration of the oligotrophic center pool, which characterizes the oligotrophic area, averaged 92.3 μeq H^+ L^{-1} (pH 4.03) in 1983 and 126.6 μeq H^+ L^{-1} (pH 3.9) in 1984. The H^+ concentration of the experimental minerotrophic pool was 14.4 μeq H^+ L^{-1} (pH 4.84) in 1984.

There was also a considerable difference in the H^+ concentration in pore water of the oligotrophic and minerotrophic sites. The oligotrophic sites had significantly higher H^+ concentrations than the minerotrophic lagg sites. The H^+ concentration was usually in the range of 90-200 μeq L^{-1} (pH 4.04-3.70) in the central oligotrophic sites with a rather constant concentration with depth. The minerotrophic lagg sites had H^+ concentrations ranging from 30-60 μeq H^+ L^{-1} (pH 4.52-4.22) at the surface of the water table, decreasing to 10-30 μeq L^{-1} (pH 5.00-4.52) with depth.

Effects of Acidification on Mire Water Chemistry

Typical increases in SO_4^{2-} concentration for the oligotrophic and minerotrophic pools in response to acidifications are shown in figures 4a and 4b. Sulfate concentrations in surface pools increased rapidly after addition of sulfuric acid during the 9 acidifications (Figures 4a,b). The increase in SO_4^{2-} concentrations were greatest for the oligotrophic and minerotrophic pools during the July and August acidifications (Figures 4a,b). On 20 June 1984, SO_4^{2-} concentration increased about 5X in the oligotrophic pool directly after the acidification (Figure

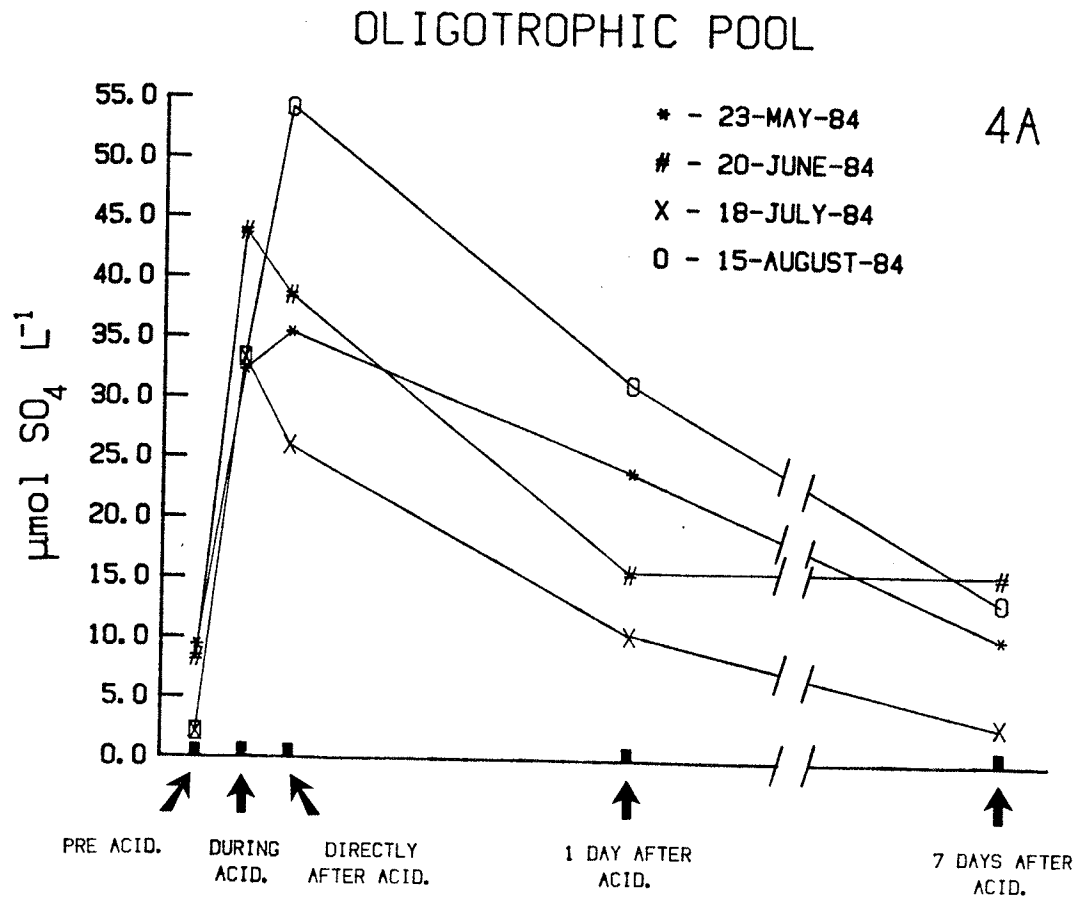
4a). Sulfate concentrations decreased throughout the mire during the summer months (Chapter 2), and therefore the August acidification resulted in significantly greater increases in SO_4^{2-} concentration (20X) in the oligotrophic pool (Figure 4a), although peak concentrations were similar.

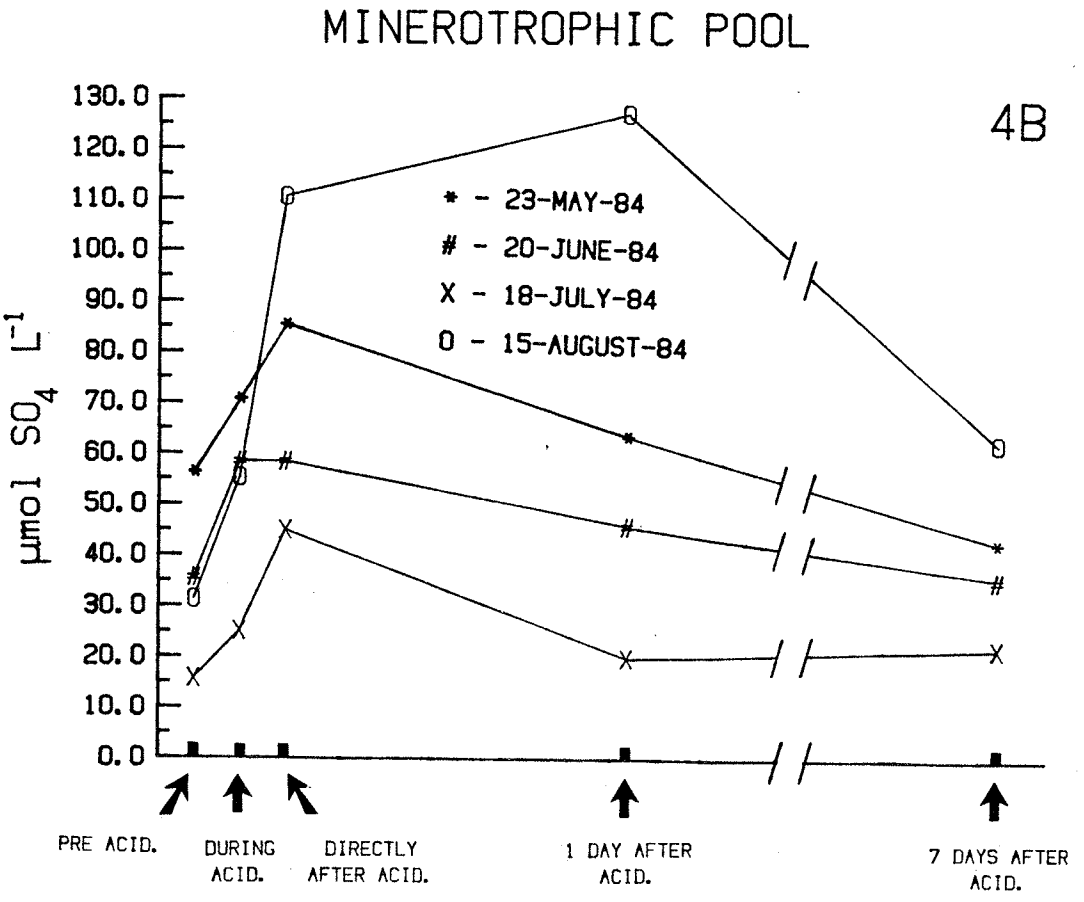
The minerotrophic pool also increased in SO_4^{2-} concentration, but since the initial concentrations were higher, the percent increase was significantly less. Like the oligotrophic pool, SO_4^{2-} increases were much greater for the midsummer acidifications, when pre-acidification concentrations were lower (Figure 4b). Overall, SO_4^{2-} concentrations decreased rapidily after acidification in the minerotrophic and oligotrophic pools. Generally, SO_4^{2-} concentration were near pre-acidification levels within 7 days of the acidification in both the oligotrophic and minerotrophic pools.

Irrigation with lake water (36 μmol SO_4^{2-} L^{-1}) in the control area resulted in much smaller increases in SO_4^{2-} concentration in the minerotrophic and oligotrophic control pools, and were much closer to pre-irrigation SO_4^{2-} levels after 1 day, than were the experimental pools (see Appendix IV).

In contrast to the surface pools, pore water concentrations of SO_4^{2-} did not always increase following acidification in the oligotrophic area. The 3 acidifications in 1983 (3 August; 31 August; 11 October) increased pore water SO_4^{2-} concentration in the

Figure 4. Sulfate concentration in the experimental oligotrophic and minerotrophic surface water pools in response to 4 1984 acidifications (figure 4a and 4b respectively).


OLIGOTROPHIC POOL
4A
* - 23-MAY-84
# - 20-JUNE-84
X - 18-JULY-84
0 - 15-AUGUST-84
µmol SO_4 L^{-1}
55.0
50.0
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
PRE ACID.
DURING ACID.
DIRECTLY AFTER ACID.
1 DAY AFTER ACID.
7 DAYS AFTER ACID.


MINEROTROPHIC POOL
4B
* - 23-MAY-84
# - 20-JUNE-84
X - 18-JULY-84
0 - 15-AUGUST-84
µmol SO_4 L^{-1}
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
PRE ACID.
DURING ACID.
DIRECTLY AFTER ACID.
1 DAY AFTER ACID.
7 DAYS AFTER ACID.

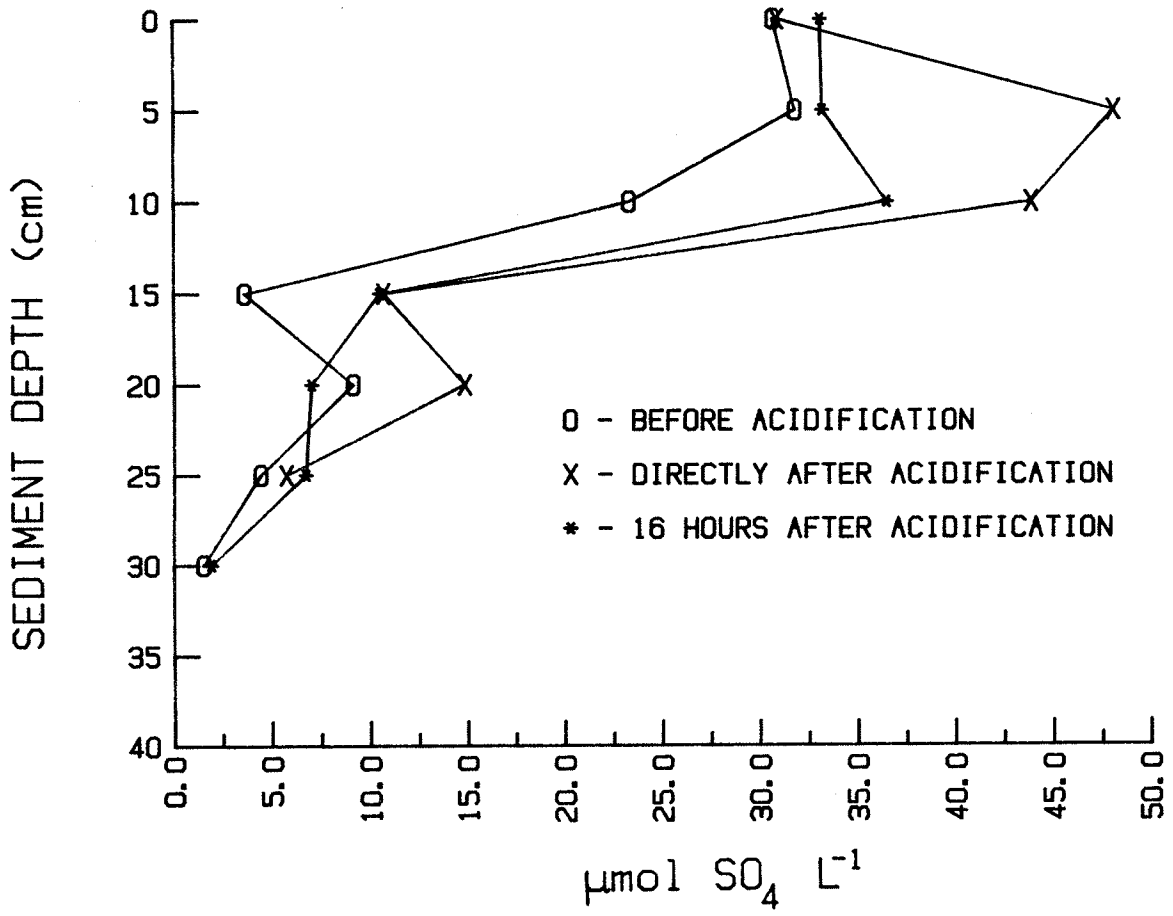
minerotrophic site only. In 1984, 4 of the 6 acidifications resulted in increases in pore water SO_4^{2-} concentration in the oligotrophic site, while all 6 acidifications caused increases in the minerotrophic site. In the minerotrophic site, pore water samples collected 15-20 h after acidification were usually lower in SO_4^{2-} than samples collected directly after acidification (Figure 5). The autumn acidifications of 1983 and 1984 (September and October) were notable exceptions: SO_4^{2-} disappearances after the autumn acidifications were slower than those for the spring and summer acidifications of 1984.

Increases in SO_4^{2-} concentration in the oligotrophic control pore water profile were very small, when they occurred, and the same was generally true for the minerotrophic control pore water profile, when increases did occur they were usually greatest in the minerotrophic control profile.

The addition of sulfuric acid resulted in increased concentrations of H_2S in the minerotrophic site directly after each of the 9 acidifications. This was in contrast to the oligotrophic site, where H_2S was rarely present before acidification and only twice after acidification.

The highest natural concentrations of H_2S in the experimental and control minerotrophic site occurred in May, June, and July (Chapter 2). The 20 June 1984 acidification resulted in an increase in H_2S directly after acidification (Figure 6). Usually H_2S concentrations 15-20 h after

Figure 5. Sulfate concentration as a function of depth in the experimental minerotrophic area (site 2) in response to the 23-May-84 acidification.


SEDIMENT DEPTH (cm)
0
5
10
15
20
25
30
35
40
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
µmol SO_4 L^{-1}
O - BEFORE ACIDIFICATION
X - DIRECTLY AFTER ACIDIFICATION
* - 16 HOURS AFTER ACIDIFICATION

acidification remained higher than the pre-acidification levels (Figure 6), and in some cases the 15-20 h profile contained more H_2S than the profile obtained directly after acidification (Figure 7). The pre-acidification H_2S profiles for August, September, and October of 1984 only contained H_2S in 1 or 2 of the depth intervals sampled, probably because of the low SO_4^{2-} concentration during this time (Chapter 2). After the addition of sulfuric acid during the August, September, and October acidifications, usually at least 1 or 2 additional depth intervals contained H_2S. The concentration of H_2S in the pore water of the minerotrophic control site also increased after each irrigation with lake water (Figure 8). No increase was detected in the oligotrophic site. The increase in H_2S from pre to post irrigation was similar for the control and experimental minerotrophic sites, even though the increase in SO_4^{2-} concentration in the control site was much less than for the experimental site.

The H^+ increases shown in figures 9a and 9b for the oligotrophic and minerotrophic pools were typical for the 9 acidifications. Increases in H^+ concentration were usually greater in the oligotrophic pool than in the minerotrophic pool (Figures 9a,b). Frequently, within 1 to 7 days after the acidification, H^+ concentrations decreased to pre-acidification levels (Figures 9a,b), however, this was not always the case. Minimal changes in the H^+ concentration in the control pools occurred following irrigation with lake

Figure 6. Hydrogen sulfide concentration as a function of depth in the experimental minerotrophic area (site 2) in response to the 20-June-84 acidification.

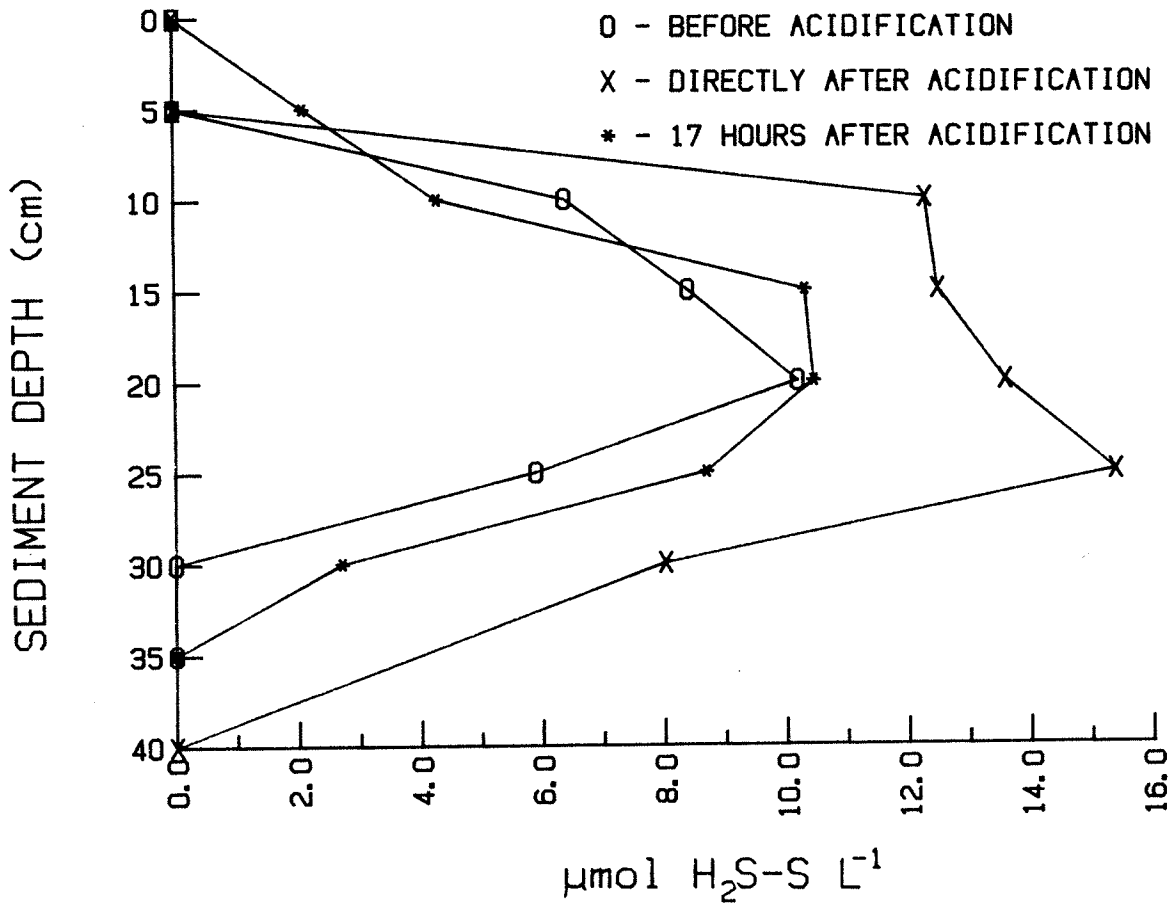

O - BEFORE ACIDIFICATION
X - DIRECTLY AFTER ACIDIFICATION
* - 17 HOURS AFTER ACIDIFICATION
SEDIMENT DEPTH (cm)
0
5
10
15
20
25
30
35
40
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
µmol H2S-S L-1

Figure 7. Hydrogen sulfide concentation as a function of depth in the experimental minerotrophic area (site 2) in response to the 23-May-84 acidification.

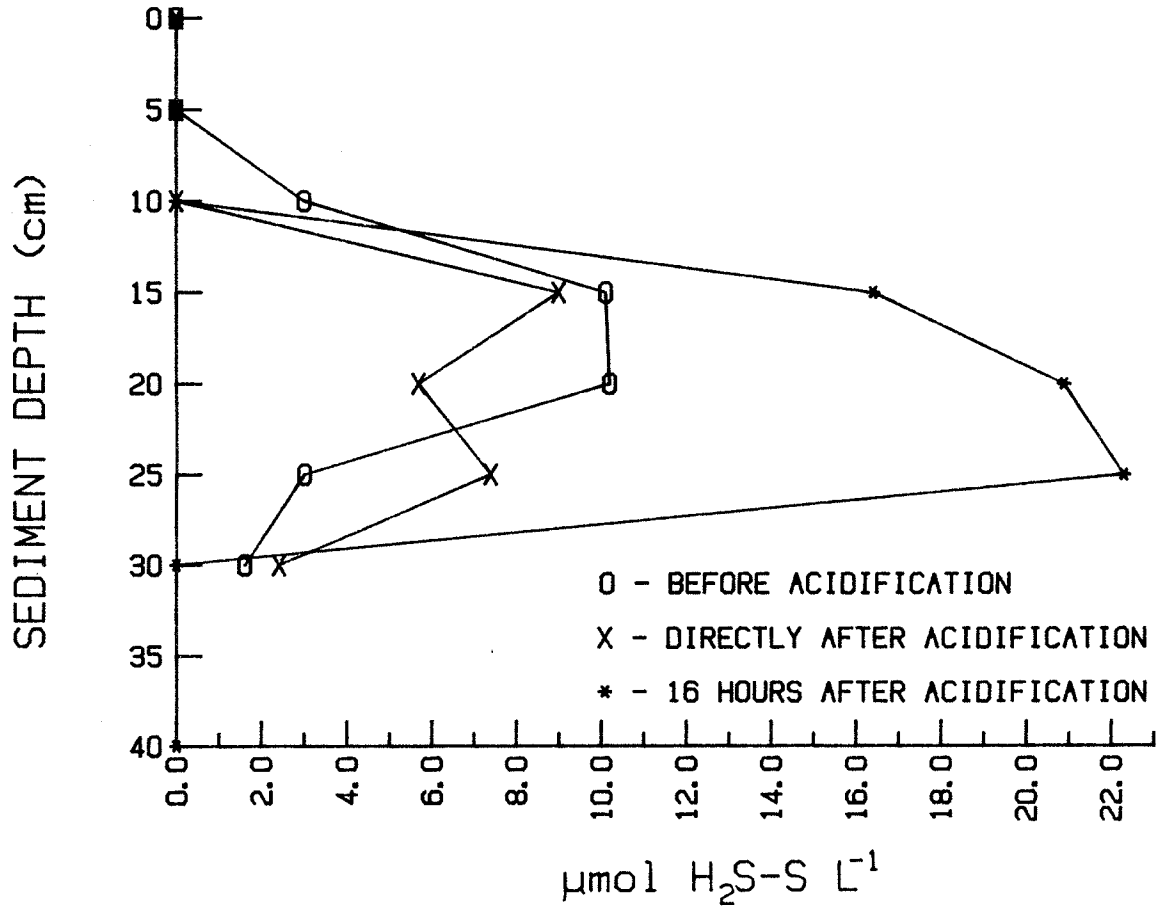
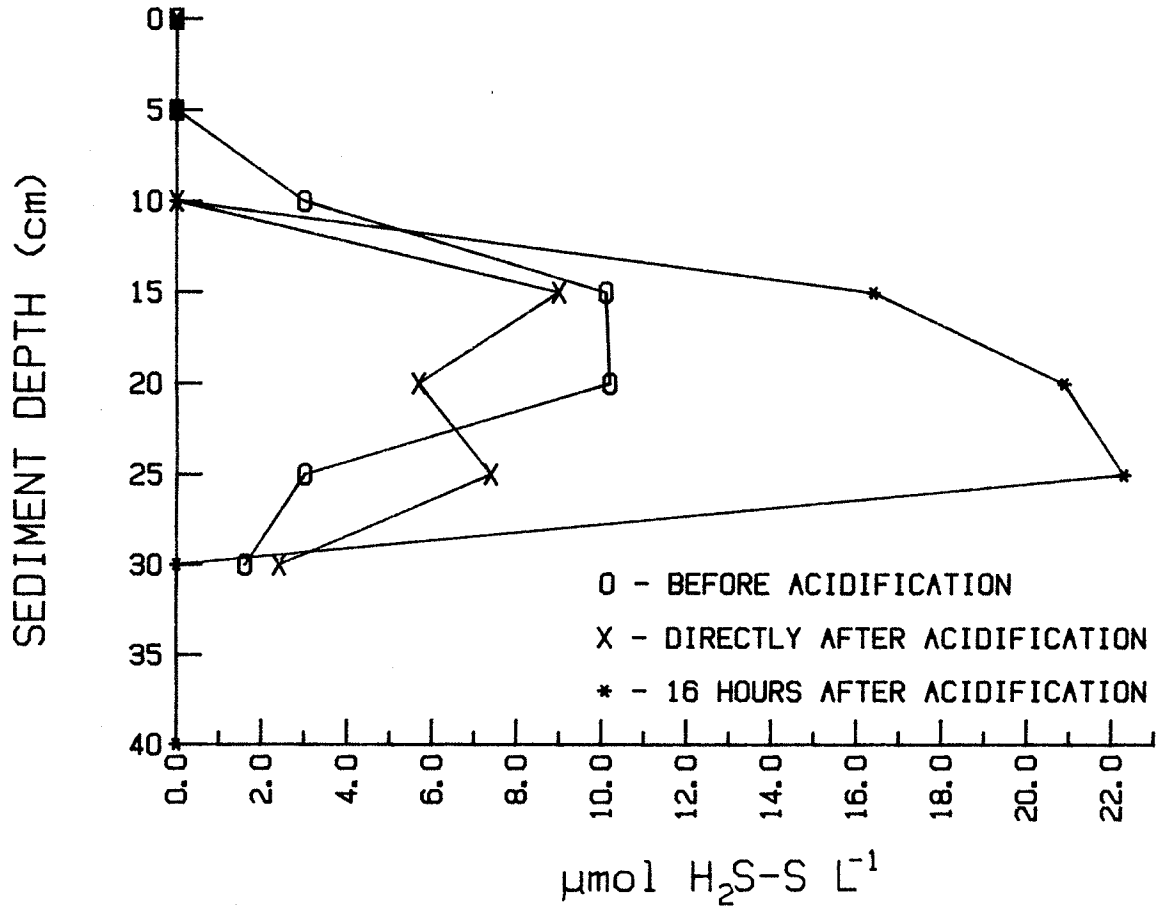

SEDIMENT DEPTH (cm)
0
5
10
15
20
25
30
35
40
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
µmol H_2S-S L^{-1}
0 - BEFORE ACIDIFICATION
X - DIRECTLY AFTER ACIDIFICATION
* - 16 HOURS AFTER ACIDIFICATION

Figure 8. Hydrogen sulfide concentration as a function of depth in the control minerotrophic area (site 4) in response to the 23-May-84 acidification.


SEDIMENT DEPTH (cm)
0
5
10
15
20
25
30
35
40
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
µmol H2S-S L-1
O - BEFORE ACIDIFICATION
X - DIRECTLY AFTER ACIDIFICATION
* - 16 HOURS AFTER ACIDIFICATION

water.

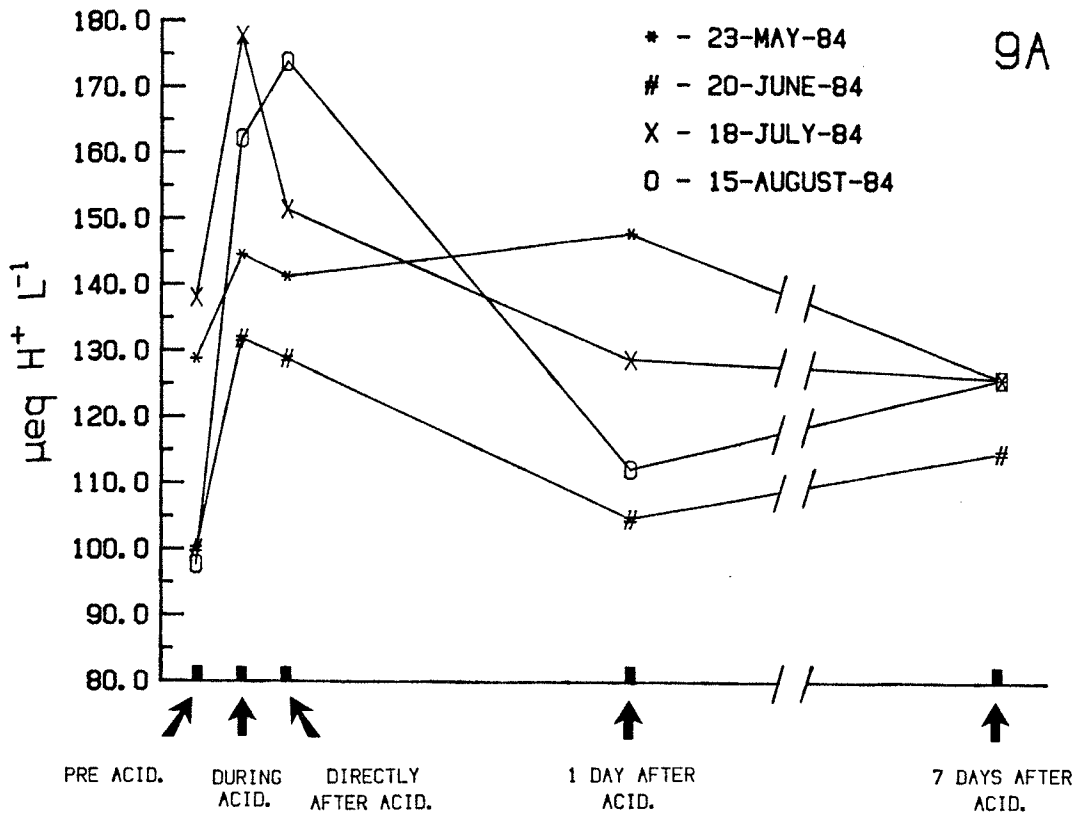
Contrary to the surface pools, the effect of acidification on H^+ in the pore water of the minerotrophic and oligotrophic sites was not consistent. Some acidifications resulted in increases in pore water H^+ concentration, and only in the top 10 cm of saturated peat, while others resulted in decreases in H^+ concentration immediately following the acidification event. No significant or consistent change in H^+ occurred in the control surface or pore water sites (see Appendix IV and V).

Laboratory Experiments

Whole plants and plant parts of the 3 Sphagnum spp. all absorbed significant amounts of SO_4^{2-} within 1 h (Table 1). The percent absorption, for whole plants, was highest for S. angustifolium, followed by S. fuscum and S. magellanicum (Figure 10). In addition, the whole plants caused a greater percent loss of SO_4^{2-} than any of the 3 individual plant parts for each of the respective species. There was little difference in percent loss between plant parts for a given species (Table 1). In general, there was at least a 50 % loss of SO_4^{2-} within 1 h, for whole plants and plant parts for the 3 species (Table 1). It was not known whether the reduction in SO_4^{2-} concentration was a result of passive or active uptake by the plants, although one would expect the rapid removal of SO_4^{2-} (50% loss in 1 h) was primarily through passive uptake and/or adsorption to plant surfaces.

Figure 9. Hydrogen ion concentration in the experimental oligotrophic and the experimental minerotrophic surface water pools in response to 4 1984 acidifications (figure 9a and 9b respectively).

OLIGOTROPHIC POOL



MINEROTROPHIC POOL

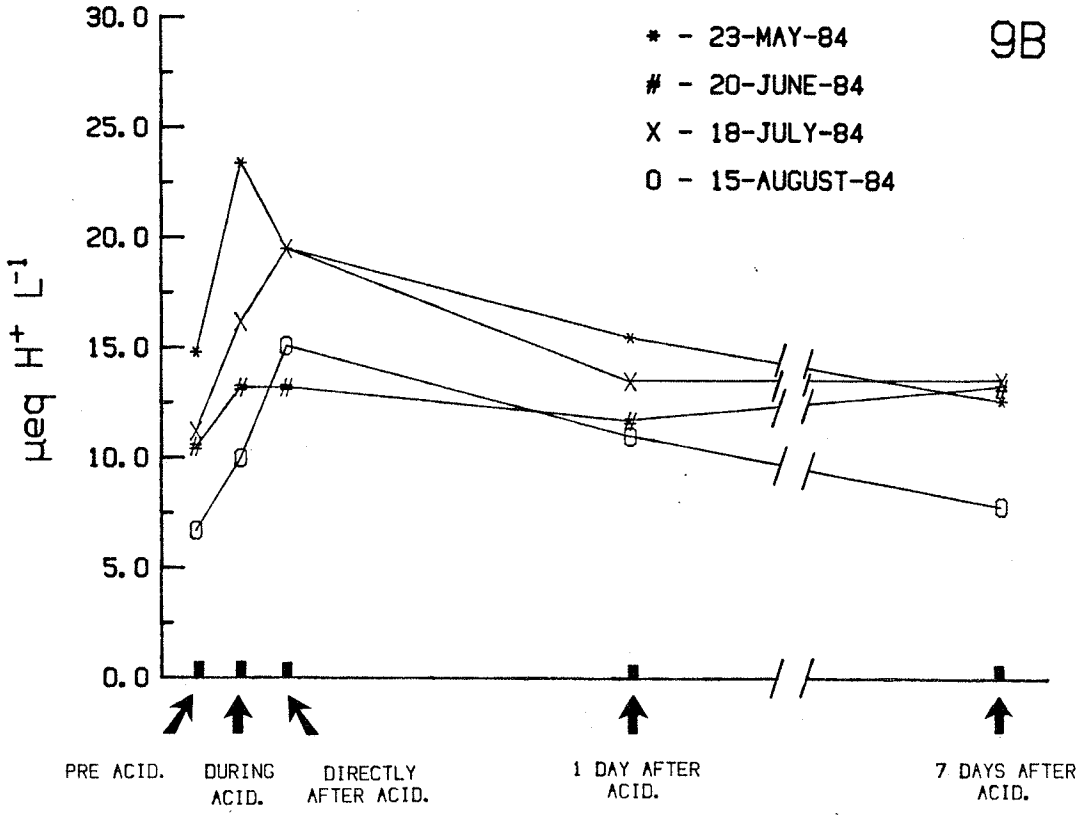


Figure 10. Percent loss of SO_4^{2-} from water containing three Sphagnum spp. as a function of time.

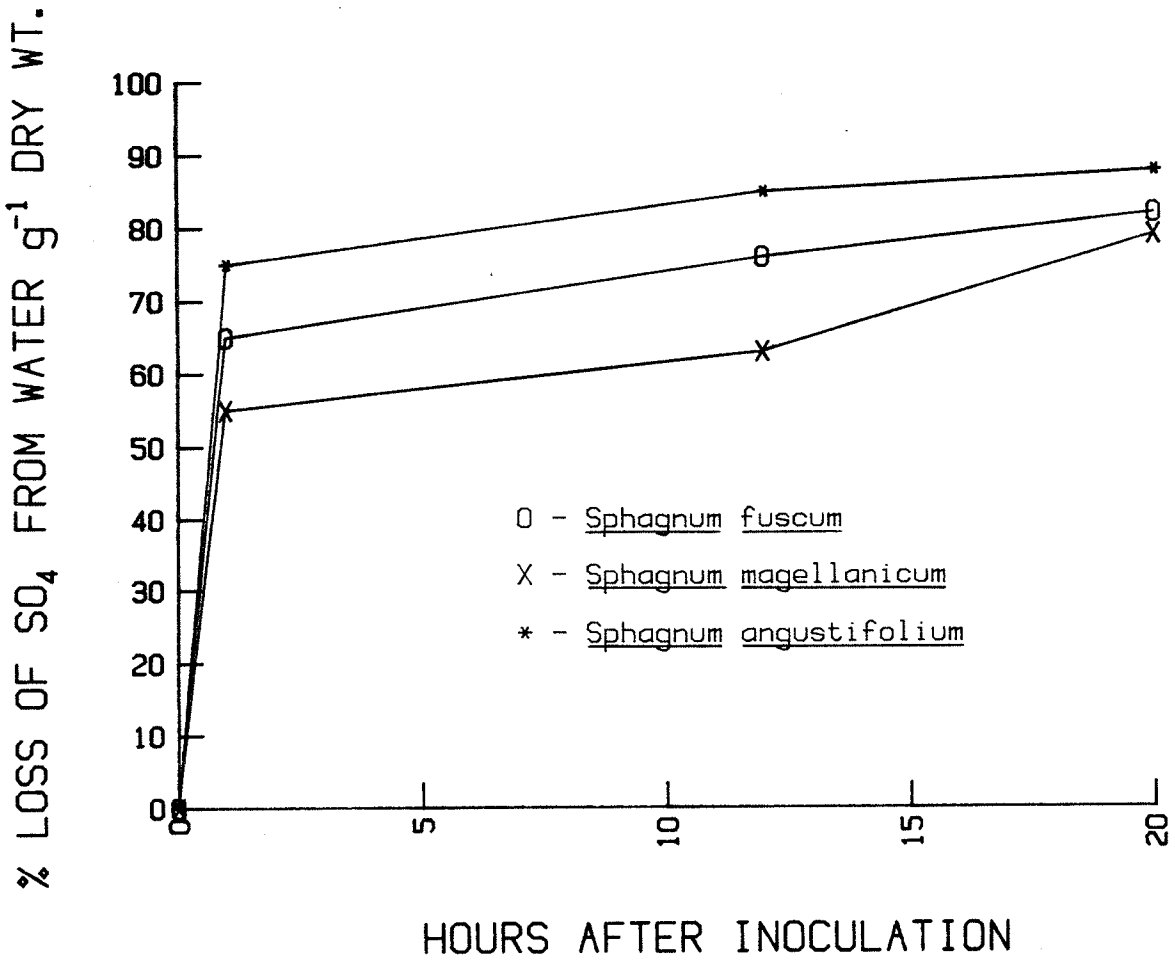

% LOSS OF SO_4 FROM WATER g^{-1} DRY WT.
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
O - Sphagnum fuscum
X - Sphagnum magellanicum
* - Sphagnum angustifolium
HOURS AFTER INOCULATION

Table 1 - Percent loss of SO_4^{2-} from water containing whole plants and plant parts for *Sphagnum angustifolium*, *S. magellanicum*, and *S. fuscum*., as a function of time.

Whole Plants

time, h	*S. angustifolium*	*S. magellanicum*	*S. fuscum*
1	75	55	65
12	85	63	76
20	90	79	82

Capitulum (0-1 cm)

time, h	*S. angustifolium*	*S. magellanicum*	*S. fuscum*
1	66	56	57
12	75	62	70
20	87	73	56

Green part (2-5 cm)

time, h	*S. angustifolium*	*S. magellanicum*	*S. fuscum*
1	78	67	47
12	83	68	64
20	96	73	69

Brown part (5-10 cm)

time, h	*S. angustifolium*	*S. magellanicum*	*S. fuscum*
1	72	56	48
12	81	63	49
20	90	66	59

Sulfate Mass Balance

The annual SO_4^{2-} mass balance budget for 1981-1984 demonstrated the mire was a sink for SO_4^{2-}-S (Table 2). The additional SO_4^{2-}-S input from acidification in 1983 and 1984 accounted for 28 and 47% of the total annual SO_4^{2-}-S input to the mire. In addition, the mire retained more SO_4^{2-}-S (g m^{-2} yr^{-1}) during the two acidification years than in 1981 or 1982, even though the total SO_4^{2-}-S input during the two acidification years was similar to the two pre-acidification years (Table 2). In addition, the long term sulfur accumulation rate (g S m^{-2} yr^{-1}) within the mire was calculated by multiplying an estimate of the total sulfur content of the peat (g S g^{-1}), by the annual net rate of peat accumulation (g m^{-2} yr^{-1}). The total sulfur value used for this calculation (1.96×10^{-3} g S g^{-1}) was obtained from the average total sulfur content of peat between 20 and 40 cm in two peat cores analyzed for total sulfur concentration (Chapter 2). The average net rate of peat accumulation for 3 cores (251 g m^{-2} yr^{-1}) was estimated by the ^{210}Pb dating method (Methods and Results in Appendix VI). The long term sulfur accumulation rate was 0.49 g S m^{-2} yr^{-1}, somewhat less than sulfur accumulation rate based on the 4 years of SO_4^{2-}-S mass balance data, (0.64-1.28 g m^{-2} yr^{-1}, Table 2).

Discussion

This work revealed a number of routes that added SO_4^{2-} may follow: 1) SO_4^{2-} may be immediately absorbed or adsorbed by living and dead Sphagnum spp. before reaching the water

Table 2. 1981-1984 SO_4^{2-} - S budgets for the 239 Mire. Acid was added to the mire during half of 1983 and during the entire 1984 ice-free season.

	1981			1982			1983			1984		
	g mire^{-1} yr^{-1}	g m^{-2} yr^{-1}	% of input	g mire^{-1} yr^{-1}	g m^{-2} yr^{-1}	% of input	g mire^{-1} yr^{-1}	g m^{-2} yr^{-1}	% of input	g mire^{-1} yr^{-1}	g m^{-2} yr^{-1}	% of input
Natural precipitation	13,579	0.37	37	25,690	0.70	45	14,680	0.40	36	15,414	0.42	24
Acid precipitation (incl. Roddy Lake water)	-	-	-	-	-	-	11,377	0.31	28	30,094	0.82	47
Runoff into mire*	23,488	0.64	63	31,195	0.85	55	14,680	0.40	36	18,350	0.50	29
Total	37,067	1.01	100	56,885	1.55	100	40,737	1.11	100	63,858	1.74	100
Outflow	13,355	0.36	36	30,995	0.84	54	10,887	0.30	27	16,520	0.45	26
Retention	23,712	0.65	64	25,890	0.71	46	29,850	0.81	73	47,338	1.29	74

*Runoff proportional to: northwest sub-basin - 1981; east sub-basin - 1982; east sub-basin - 1983; east sub-basin - 1984.

table (partly active uptake by the living plants, but probably mostly passive uptake) (Figure 10); 2) SO_4^{2-} may be reduced by sulfate reducing bacteria in the anaerobic zone (Figures 6,7, and 8), resultant sulfur may be stored in various sulfur forms or reoxidized later (Chapter 2); 3) SO_4^{2-} may remain in the surface water or pore water without being sorbed or reduced; and/or 4) it may be exported via the outflow (Table 2).

The relatively small and ephemeral increases in surface and pore water SO_4^{2-} concentration following acidification (500 µmol SO_4^{2-} L^{-1}) in conjunction with the significant uptake of SO_4^{2-} by Sphagnum spp. in laboratory experiments (Figure 10)(Table 1) indicate that a significant amount of the applied SO_4^{2-} was sorbed by the Sphagnum spp. before reaching the water table. This is consistent with findings of Brown and Macqueen (1982), where 78% of $^{35}SO_4^{2-}$ (in distilled water), added to peat cores was found in the top 4 cm of peat after 3 weeks of incubation; organic ^{35}sulfur was the main product. This is also similar to the ground layer of terrestrial watersheds, where large amounts of SO_4^{2-} present in precipitation are adsorbed (Johnson and Henderson 1979) and/or rapidly transformed to non-salt extractable sulfur, largely organic sulfate esters (Fitzgerald et al 1983; Swank et al 1984).

Based on the ability of Sphagnum spp. to take up SO_4^{2-} in laboratory experiments (Table 1), the in situ formation of organic sulfur (Chapter 2), and the dominance of organic

sulfur in surface peat (20 - 150 μmol S g^{-1} dry wt.) (Chapter 2), it is likely that a portion of the added SO_4^{2-} is transformed to organic sulfur in the aerobic zone of the peat profile.

Ferguson et al (1984) observed a similar phenomenon when five Sphagnum spp. collected from an unpolluted area were transplanted to two blanket bogs: one located in the southern Pennines, an area with high bulk sulfur deposition (9.78 g S m^{-2} yr^{-1}); and the second bog was a relatively unpolluted site in North Wales (5.82 g S m^{-2} yr^{-1}). After 18 months they found the total sulfur content of the apical shoots for all 5 spp. transplanted in the southern Pennine site were higher than those for the North Wales site. Although the mechanism of sulfur incorporation and form of sulfur were unknown these results are consistent with my observations on increased SO_4^{2-} leading to increased loss of SO_4^{2-} from the water to the plants (Tables 1 and 2).

Addition of SO_4^{2-} to freshwater ecosystems has increased the rate of sulfate reduction (Hemond 1980; Wieder 1982; Herling and Mills 1985; Cook and Schindler 1983). This occurred in the minerotrophic area of the mire as demonstrated by increases in pore water H_2S following acidification (Figures 6 and 7). Although the increases in pore water H_2S in both experimental and control minerotrophic sites were similar, the higher SO_4^{2-} levels in the experimental minerotrophic site may have maintained the post-acidification H_2S levels longer, unfortunately because

no additional pore water samples were collected after the 12-17 h samples I am unable to conclude that this occurred. Because sulfate reduction in the minerotrophic area is SO_4^{2-} limited, especially in midsummer (Chapter 2), even small increases in pore water SO_4^{2-} content may be expected to increase sulfate reduction rates (Figure 8). Sulfate reduction measurements in the mire have demonstrated that sulfate reduction does occur in the oligotrophic area even though H_2S was not detected in the pore water (Chapter 2); therefore it is possible that sulfate reduction rates in the oligotrophic area also increased after acidification.

In situ incubation with $^{35}SO_4^{2-}$ in the minerotrophic and oligotrophic areas have shown that AV^{35}S Fe$^{35}S_2$, and $^{35}S^o$ form rapidly (Chapter 2), and probably the rates of formation increased due to acidification at least in the minerotrophic area where H_2S concentrations increased (Figures 6 and 7). The precipitation of S^{2-} as FeS, FeS_2, or S^o results in alkalinity production and may help offset acidification of the mire, as long as the reduced sulfur is not reoxidized to SO_4^{2-}.

In an oligotrophic lake experimentally acidified with sulfuric acid, epilimnetic and hypolimnetic sulfate reduction accounted for 85% of the internal alkalinity production which decreased the efficiency of acidification by 66-81% (Cook et al submitted). Sulfate reduction rates within the mire could not be determined (Chapter 2) and therefore I am unable to quantify alkalinity production via

sulfate reduction. However, after a year and a half of acidification there has been no increase in H^+ concentration (Bayley personal communication) and probably increased sulfate reduction rates are partly responsible.

Although sulfate reduction rates could not be determined, both the long term sulfur accumulation rate (0.49 g S m^{-2} yr^{-1}) and the recent sulfur accumulation rates (0.64-1.28 g S m^{-2} yr^{-1}) indicate that the mire is an efficient sink for SO_4^{2-}-S. Theses independent estimates of sulfur accumulation are reasonably similar. However, the somewhat higher rates of sulfur accumulation based on the 1981-1984 SO_4^{2-}-S mass balance data may be interpreted as evidence that the recent increase in atmospheric SO_4^{2-}-S deposition in the ELA (Schindler personal communication) has resulted in greater rates of sulfur accumulation, even before the acidification years.

Many investigators have observed autumn peaks in SO_4^{2-} concentration of ground water and water discharged from watersheds with and without wetlands (Wieder and Lange 1984; Braekke 1980; Brown 1980). Braekke (1980) attributed the increase in ground water SO_4^{2-} content to accumulation of dry and wet sulfur deposition and the oxidation of organic sulfur and inorganic sulfide during the preceding dry months.

The sudden release of large amounts of acidified water from watersheds containing wetlands may be detrimental to aquatic ecosystems downstream. Norwegian literature cited

by Brown (1980) suggested autumn acidification of rivers and subsequent fish kills were the result of the autumn flushing of sulfuric acid formed from the oxidation of reduced sulfur during the preceding dry months. Brown (1980) calculated that the exposure of 2.76 cm of anaerobic peat could release 40 kg S ha^{-1} of stored sulfide from a small British bog, this was equivalent to the annual sulfur loading for the region. In the experimental mire, a comparison of the inorganic sulfide content of spring vs. autumn cores (collected after the summer dry period) revealed about a 33% decrease in the amount of reduced inorganic sulfide present (Chapter 2). The resolubilization of the oxidized sulfides would help explain the September and October increases in pore water SO_4^{2-} concentration (Chapter 2), and the autumn peak in SO_4^{2-} concentration discharged from the watershed for 1981-1984 (unpublished data). The apparent increase in sulfur accumulation in recent years may be of concern in regards to the sulfur reoxidation cycle. As more and more sulfur is stored (in recent peat), the amount of sulfur that may potentially be released due to a given drop in water level will also increase. This phenomenon may be especially important in areas where wetlands contribute significantly to the hydrologic input of downstream aquatic ecosystems.

In summary, acidification with sulfuric acid resulted in temporary increases in SO_4^{2-} concentration in surface and pore water. Much of the SO_4^{2-} added to the mire was "sorbed" by the surface Sphagnum spp. before reaching the water

saturated zone. Sulfate that reached the water table increased the rate of sulfate reduction in the minerotrophic area and probably also increased the rate of formation of iron sulfides and elemental sulfur. A similar increase in the rate of sulfate reduction in the oligotrophic area probably also occurred following acidification. The mire retained more sulfur per unit area during the two acidification years than during the 2 preceding years, and for all 4 years the net accumulation rates were higher than long-term sulfur accumulation in older peat as determined by Pb-210 dating. The potential for increase in sulfur accumulation as absorbed and adsorbed sulfur, organic sulfur: reduced and oxidized, and reduced inorganic sulfides is unknown. Prolonged acidification may eventually result in the elimination of sensitive Sphagnum spp. as observed in Britain (Ferguson and Lee 1983). If this results in decreased sulfur retention by one or more of the mechanisms listed above, the result would be increased sulfur export with resultant stream acidification.

Chapter 4

Overall Summary and Conclusions

The two papers contained in this thesis have investigated two interrelated topics: the first, sulfur cycling in a Sphagnum dominated wetland, and the second, the effects of acidification on the sulfur dynamics of this wetland. Until this study was undertaken there had been no experimental North American investigations on the effects of acidic deposition on Sphagnum dominated wetlands, although there have been investigations in Britain (Ferguson et al 1978), as previously discussed. The occurrence and distribution of sulfur compounds have been reported for the Everglades and similar wetland ecosytems (Casagrande et al 1977; Altschuler et al 1983); however, Brown (1980) has been the only person to report on the distribution of sulfur compounds in a Sphagnum dominated wetland. This investigation has increased the present understanding of sulfur cycling and how acidic deposition in the form of sulfuric acid can affect the natural sulfur dynamics of Sphagnum dominated wetlands.

A large amount of SO_4^{2-} entered the mire during spring snowmelt with sporadic inputs occurring from rain events during the remainder of the year. Because a significant amount of the SO_4^{2-} input resulted from upland runoff, the margin or minerotrophic area of the mire received more mineral input than the central oligotrophic area which is physically isolated from much of the upland runoff and thus depends primarily on atmospheric input for its mineral input. Sulfate concentrations in surface and pore water

reflected this difference in SO_4^{2-} supply. In this mire, the minerotrophic area (lagg) is quite extensive. The ratio of upland area to mire surface and the slope of upland area are important factors which determine how much of the mire is affected by the mineral water runoff.

Because so little was known about the sulfur biogeochemistry of wetlands, I concentrated on the examination of the sulfur chemistry of the two major areas: the minerotrophic and oligotrophic areas.

Weekly and monthly SO_4^{2-} samples from both surface pools and pore water profiles not only demonstrated the large difference in SO_4^{2-} concentrations between the two areas, with concentrations much lower in the oligotrophic areas. There was also a pronounced seasonal variability in SO_4^{2-} concentrations at one location. It was obvious that SO_4^{2-} supply to the system was very important, especially since the process of sulfate reduction must have a source of SO_4^{2-} to fuel the reaction. In fact, many of the observed differences between the minerotrophic and oligotrophic area might be the result of SO_4^{2-} supply. Although sulfate reduction occurred throughout the mire, the enclosure experiments with $^{35}SO_4^{2-}$ apparently showed higher sulfate reduction rates in the minerotrophic area than in the oligotrophic area. The inorganic end products of sulfate reduction in peat cores (AVS, S^o, FeS_2) were also more abundant in the minerotrophic area. As discussed in Chapter 2, this difference may partly result from the difference in

H^+ concentration between the two areas. However, one may argue that the higher SO_4^{2-} supply in the minerotrophic area supports higher sulfate reduction rates which inturn consume more H^+ ions, thus enabling the sediment to maintain a lower H^+ concentration. The higher H^+ concentrations of the oligotrophic area may be a consequence, rather than a cause of, lower sulfate reduction rates resulting from a lower SO_4^{2-} supply.

The 9 acidifications were a significant source of SO_4^{2-} to the mire, accounting for 28% and 47% of the total SO_4^{2-}-S input to the mire during 1983 and 1984. This was especially true during the July and August acidifications, when SO_4^{2-} concentrations in pools and pore water were extremely low due to the lack of precipitation. The increase in H_2S concentration in the pore water of the minerotrophic area following each acidification demonstrated that sulfate reduction rates were SO_4^{2-} limited. Even in May, when SO_4^{2-} concentrations in the minerotrophic area were relatively high, pore water H_2S concentrations increased. Although H_2S was not detected in the oligotrophic area before or after the acidifications, it is likely that sulfate reduction rates did increase following acidifications, since the added SO_4^{2-}disappeared rapidly.

Although AVS, FeS_2, S^o, and organic sulfur were forming throughout the mire, organic sulfur accounted for the majority (94%) of total sulfur present in 40 cm peat cores. The dominance of organic sulfur in the enclosure experiments

also indicated the importance of organic sulfur. Organic sulfur accounted for about 80% of the total sulfur recovered in both the minerotrophic and oligotrophic experiments after 82 and 62 days of incubation.

Organic sulfur forms from the assimilatory reduction of SO_4^{2-} by plants and microorganisms, and may also form from the reaction of H_2S with various organic compounds (Nissenbaum and Kaplan 1976; Casagrande et al 1979). Lake sediment sulfur is often dominated by organic sulfur which has generally been thought to be derived primarily from seston (King and Klug 1983). Recently, Nriagu and Soon (1985) demonstrated that the sulfur isotope signal of organic sulfur in oligotrophic lake sediments was most compatible with a microbial sulfate reduction origin. The formation of large amounts of sulfur-35 labelled organic matter along with the dominance of organic sulfur in the peat profile suggest that a portion of the organic sulfur present may have formed from the reaction of H_2S with organic matter. A portion of the organic sulfur present is derived from the remains of dead plants, primarily Sphagnum spp., this sulfur probably consists mostly of carbon bonded sulfur (ie. amino acids and proteins).

The recent and long term sulfur accumulation rates based on the 1981-1984 SO_4^{2-}-S mass balance data (0.64-1.28 g S m^{-2} yr^{-1}) and the ^{210}Pb dated cores (0.49 g S m^{-2} yr^{-1}) both indicate that a significant amount of the incoming SO_4^{2-} is retained by the mire. Sulfate-S deposition in the

ELA has increased in recent years (Schindler personal communication) and may be reflected by the slightly greater S accumulation rates during 1981-1984 compared to the S accumulation rate based on sediment accumulation rate and total sulfur content of peat deposited more than 50 years ago. In contrast, sulfur acccumulation rates in 2 ombrotrophic bogs located in northern Finland (Pakarinen and Tolonen 1980) were about 10 fold less than than my estimates (0.49-1.28 g S m^{-2} yr^{-1}). The atmospheric deposition of SO_4^{2-} is similar for the two areas but unlike their system the ELA mire is not an ombrotrophic system, because it receives upland runoff in addition to direct atmospheric precipitation which helps explain the difference in sulfur accumulation rate.

When SO_4^{2-} is microbially reduced, H^+ ions are consumed, and this is very important in the regulation of lake acidification (Kelly et al 1982). Alkalinity generated by sulfate reduction may only be temporary if the reduced sulfur is later reoxidized, so even though inorganic sulfides are forming quite rapidly from SO_4^{2-}, the summer drawdown of the water table resulted in the oxidation of up to 37% of the inorganic sulfide present in the top 20 cm of peat. Therefore much of the H^+ originally consumed may be returned to the pore water and acidity increases upon reoxidation of the reduced sulfur.

The process whereby reduced sulfur compounds are reoxidized and released to the pore water during the summer

drawdown may become a serious problem as the amount of stored sulfur compounds within the peat profile continues to increase due to the increased sulfur loading. The release of large amounts of sulfuric acid from wetlands following such a reoxidation cycle has reportedly caused the acidification of rivers (In Brown 1980). The formation of organic sulfur, specifically sulfate esters, from microbially produced H_2S may be very important in this regard, due to its more resistant nature (Casagrande et al 1979), and its greater abundance. For example, the formation of SO_4^{2-} esters from H_2S results in the production of only 1 µeq $\square SO_4^{2-}\square^{-1}$ of alkalinity compared to 2 µeq $\square SO_4^{2-}\square^{-1}$ when FeS_2, AVS, or carbon bonded sulfur are formed, Ester sulfates are considered a geochemical stable form of sulfur (Casagrande et al 1980) and therefore alkalinity generated via sulfate ester formation may be considered more resistant. However, more study is needed in peat-forming environments before their importance can be assesed.

Only recently have scientists become aware of the potential importance of organic sulfur formation in aquatic ecosystems. In light of my findings and others, I believe that future sulfur work in wetlands should focus on the identification of the various organic sulfur forms present, their distribution, and their mode of formation: specifically, are they primarily the result of bacterial SO_4^{2-} reduction or the accumulation of plant material, and

how will changes in bog ecology affect each of these sulfur retaining processes?

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Appendix I

1983 and 1984 weekly SO_4^{2-} and H^+ concentration for surface water pools in the mire.

1983 weekly SO_4^{2-} concentration in surface water pools
SO_4^{2-} - umol SO_4^{2-} L^{-1}

Date	Oligotrophic experimental
5-May	7.5
12-May	7.5
19-May	6.5
26-May	5.0
1-June	3.0
8-June	3.0
15-June	4.0
22-June	3.0
29-June	2.0
6-July	
11-July	
13-July	4.0
20-July	2.0
27-July	
3-August	
10-August	
17-August	3.0
24-August	4.0
31-August	
7-September	
14-September	
21-September	16.5
29-September	8.0
5-October	15.5
12-October	8.5
19-October	

1984 weekly SO_4^{2-} concentration in surface water pools
SO_4^{2-} - umol SO_4^{2-} L^{-1}

Date	Minerotrophic experimental	Minerotrophic control	Oligotrophic experimental	Oligotrophic control
2-May	71.9		20.8	
9-May	73.9		16.7	
16-May	85.4		12.5	
23-May	56.2	37.5	9.4	12.5
30-May	42.7	18.7	10.4	7.3
6-June	41.7	29.2	11.4	6.2
13-June	60.4	43.7	16.7	8.3
20-June	35.4	13.5	8.3	5.2
27-June	35.4	17.7	15.6	5.2
4-July	12.5	8.3	13.5	6.2
11-July	13.5	14.6	5.2	1.0
18-July	15.6	10.4	2.1	1.0
25-July	21.9	11.4	3.1	2.1
1-August	25.0	20.8	3.1	1.0
8-August	21.9	44.8	2.1	1.0
15-August	31.3	37.5	2.1	4.2
22-August	62.5	96.9	13.5	5.2
29-August	19.8	21.9	7.3	3.1
5-September	17.7	29.2	6.2	4.2
12-September	220.0	168.8	12.5	12.5
19-September	249.0	365.7	43.8	21.9
26-September	217.8	286.5	24.0	17.7
3-October	154.2	158.4	27.1	26.0
10-October	135.5	255.3	13.5	24.0
17-October				
24-October				

1983 weekly H^+ concentration in surface water pools
H^+ - ueq L^{-1}

Date	Oligotrophic experimental
5-May	54.9
12-May	87.1
19-May	57.5
26-May	70.8
1-June	67.6
8-June	102.3
15-June	79.4
22-June	100.0
29-June	107.1
6-July	123.0
11-July	93.3
20-July	107.1
27-July	104.7
3-August	91.2
10-August	93.3
17-August	93.3
24-August	87.1
31-August	83.2
7-September	89.1
14-September	93.3
21-September	107.1
29-September	100.0
5-October	109.6
11-October	97.7
19-October	138.0

1984 weekly H^+ concentration in surface water pools
H^+ - ueq H^+ L^{-1}

Date	Minerotrophic experimental	Minerotrophic control	Oligotrophic experimental	Oligotrophic control
2-May				
9-May	4.1		128.8	
16-May	4.4		117.5	
23-May	14.8	13.5	128.8	97.7
30-May	12.6	13.5	125.9	109.6
6-June	16.2	16.6	117.5	104.7
13-June	17.4	13.5	144.5	123.0
20-June	10.5	8.5	100.0	87.1
27-June	13.2	9.9	114.8	104.7
4-July	16.2	11.7	138.0	125.9
11-July	11.7	10.5	131.8	128.8
18-July	11.2	8.7	138.0	131.8
25-July	13.5	8.1	125.9	131.8
1-August	9.3	6.4	109.6	107.1
8-August	7.6	3.2	102.3	93.3
15-August	6.8	6.4	91.2	125.9
22-August	7.8	9.1	125.9	117.5
29-August	5.1	5.0	100.0	117.5
5-September	5.4	6.3	104.7	138.0
12-September	10.2	10.5	117.5	147.9
19-September	12.0	15.1	120.2	107.1
26-September	16.2	18.6	128.8	138.0
3-October	14.1	22.9	141.2	151.3
10-October	13.2	17.4	134.9	173.8
17-October	38.0	31.6	177.8	173.8
24-October	29.5	21.9	186.2	165.9

Appendix II

1983 and 1984 monthly SO_4^{2-}, H^+, and H_2S concentration for the 4 pore water profiles in the mire

Sulfate profiles for 1983
SO_4^{2-} - umol SO_4^{2-}

Site 1

Detph, cm	25-May-83	29-June-83	20-July-83	31-August-83	28-September-83	11-October-83
0	0.3					
5	1.7	1.6	0.6			5.8
10	2.1	1.8	1.4	1.4	2.1	1.2
15	0.5	1.9	2.1	1.1	2.9	1.0
20	0.9	1.6	2.6	1.7	1.5	1.8
25	0.4	1.4	1.4	0.5	1.5	
30	0.3	1.1	1.1			1.8
35	0.2	1.4	0.8	0.4		
40	0.1	4.5			0.8	

Site 2

Detph, cm	25-May-83	29-June-83	20-July-83	31-August-83	28-September-83	11-October-83
0	51.2			8.3		47.6
5	40.9		6.3		20.6	29.7
10	39.9	6.7	7.0	2.7	4.9	5.1
15	33.1	5.0	8.1	2.3	5.6	6.3
20	15.9	7.8	8.7	2.4	7.7	4.3
25	6.6	6.7	4.7	1.3		
30		8.1	2.1		1.3	1.8
35		3.0	1.4			
40		2.0	1.4			

Site 3

Detph, cm	25-May-83	29-June-83	20-July-83	31-August-83	28-September-83	11-October-83
0						
5			1.4			
10		1.4	1.0			21.0
15		1.2	0.6		3.0	1.8
20		1.0	0.6		1.6	1.3
25		0.7	1.3	1.0		
30		0.6	0.8	0.9	1.9	1.2
35		0.5	0.6	0.5		
40		1.0	0.9	0.3	1.3	1.4

Site 4

Detph, cm	25-May-83	29-June-83	20-July-83	31-August-83	28-September-83	11-October-83
0						
5			1.2			52.4
10		9.2	1.4		15.0	47.5
15		9.3	0.8	3.7	3.6	11.0
20		5.8	1.2	1.2	3.8	3.9
25		4.4	1.0	1.0		
30		5.4	0.6	0.6	2.0	1.7
35			1.5			
40			0.8		1.3	

Sulfate profiles for 1984
SO_4^{2-} - umol SO_4^{2-} L^{-1}

Site 1

Detph, cm	23-May-83	20-June-83	18-July-83	15-August-83	12-September-83	10-October-83
0	4.8					
5	1.2	1.3	1.5			
10	1.6	1.3	2.0	2.7		93.2
15	0.9	3.6	0.5	2.0	5.3	87.3
20	0.8	3.5	1.1	1.4	1.5	69.0
25		2.5	1.0	1.2	0.8	31.1
30	0.7	2.0	0.5	1.1	0.9	3.1
35			1.3	1.6	0.8	1.6
40	0.3	0.9				

Site 2

Detph, cm	23-May-83	20-June-83	18-July-83	15-August-83	12-September-83	10-October-83
0	30.7	14.4				
5	31.8	14.6				
10	23.3	4.5	6.2			
15	3.6	5.0	11.8			36.3
20	9.1	4.8	6.9	5.3	49.3	24.1
25	4.4	2.9	3.6	4.1	10.5	8.8
30	1.5	3.5	1.9	1.8	3.6	3.1
35			3.2	0.8	1.1	
40						

Site 4

Detph, cm	25-May-83	29-June-83	20-July-83	31-August-83	28-September-83	11-October-83
0						
5			1.2			52.4
10		9.2	1.4		15.0	47.5
15		9.3	0.8	3.7	3.6	11.0
20		5.8	1.2	1.2	3.8	3.9
25		4.4	1.0	1.0		
30		5.4	0.6	0.6	2.0	1.7
35			1.5			
40			0.8		1.3	

Sulfate profiles for 1984
SO_4^{2-} - umol SO_4^{2-} L^{-1}

Site 1

Detph, cm	23-May-83	20-June-83	18-July-83	15-August-83	12-September-83	10-October-83
0	4.8					
5	1.2	1.3	1.5			
10	1.6	1.3	2.0	2.7		93.2
15	0.9	3.6	0.5	2.0	5.3	87.3
20	0.8	3.5	1.1	1.4	1.5	69.0
25		2.5	1.0	1.2	0.8	31.1
30	0.7	2.0	0.5	1.1	0.9	3.1
35			1.3	1.6	0.8	1.6
40	0.3	0.9				

Site 2

Detph, cm	23-May-83	20-June-83	18-July-83	15-August-83	12-September-83	10-October-83
0	30.7	14.4				
5	31.8	14.6				
10	23.3	4.5	6.2			
15	3.6	5.0	11.8			36.3
20	9.1	4.8	6.9	5.3	49.3	24.1
25	4.4	2.9	3.6	4.1	10.5	8.8
30	1.5	3.5	1.9	1.8	3.6	3.1
35			3.2	0.8	1.1	
40						

Site 3

Detph, cm	23-May-83	20-June-83	18-July-83	16-August-83	12-September-83	10-October-83
0	3.9					
5	0.8					
10		0.6	1.1			
15	0.3	1.1	0.8			
20	0.5	1.1	1.3	2.1	29.6	9.6
25		0.7	2.0	0.7	18.2	6.1
30	0.6	1.1	0.7	0.8	12.0	3.7
35			0.9	1.7	4.3	3.1
40	0.8					

Site 4

Detph, cm	23-May-83	20-June-83	18-July-83	16-August-83	12-September-83	10-October-83
0	25.5	8.1				
5	22.3	5.6				
10	20.7	1.8	1.3			
15	20.0	4.1	1.9	39.8		90.6
20	6.7	4.8	1.9			6.4
25	15.9	2.5	1.5	4.8	251.6	4.4
30	10.9	2.7	1.5	1.6	18.1	3.2
35			0.8	1.3	4.1	3.7
40					35.4	

1983 H^+ profiles for 1983
H^+ - ueq H^+ L^{-1}

Site 1

Detph, cm	25-May-83	29-June-83	4-August-83	31-August-83	28-September-83	11-October-83
0						
5			81.3			114.8
10			85.1	83.2	131.8	102.3
15			100.0	89.1	131.8	125.9
20			97.7	93.3	125.9	117.5
25			93.3			
30			114.8	104.7	114.8	81.3
35			114.8			
40			125.9	112.2	141.2	95.5

Site 2

Detph, cm	25-May-83	29-June-83	4-August-83	31-August-83	28-September-83	11-October-83
0				27.5		45.7
5			30.9		24.5	22.4
10			19.5	22.4	17.0	20.9
15			15.5	15.5	17.0	24.0
20			15.8	16.6	16.2	20.4
25			23.4			
30			17.0	19.5	12.9	16.6
35			15.8			
40						

Site 3

Detph, cm	25-May-83	29-June-83	3-August-83	31-August-83	28-September-83	11-October-83
0						
5						
10						158.5
15						70.8
20					89.1	75.8
25				64.6	85.1	
30				72.4		97.7
35				69.2	85.1	
40				95.5	74.1	72.4

Site 4

Detph, cm	25-May-83	29-June-83	4-August-83	31-August-83	28-September-83	11-October-83
0						
5						31.6
10					27.5	27.5
15				10.7	13.5	12.0
20				4.8	13.2	14.1
25				5.4		
30				3.9	15.1	17.4
35				5.0		
40					9.1	11.7

1984 H^+ profiles
H^+ - ueq L^{-1}

Site 1

Detph, cm	23-May-83	20-June-83	18-July-83	15-August-83	12-September-83	10-October-83
0	195.0					
5	177.8	154.9	109.6			
10	147.9	154.9	102.3	162.2	295.1	467.7
15	154.9	151.3	97.7	158.5	131.8	354.8
20	158.5	165.9	97.7	147.9	169.8	251.2
25		162.2	79.4	144.5	151.3	195.0
30	151.3	162.2	104.7	144.5	158.5	141.2
35			85.0	138.0	131.8	128.8
40	195.0	177.8				

Site 2

Detph, cm	23-May-83	20-June-83	18-July-83	15-August-83	12-September-83	10-October-83
0	56.2	52.5				
5	56.2	53.7				
10	43.6	39.8	30.9			
15	25.4	24.0	24.0			54.9
20	23.4	21.9	21.4	30.2	27.5	36.3
25	27.5	28.8	21.4	27.5	23.4	21.9
30	21.9	27.5	24.0	19.0	27.5	30.2
35		24.5	17.0	13.8	18.6	23.4
40						

Site 3

Detph, cm	23-May-83	20-June-83	18-July-83	15-August-83	12-September-83	10-October-83
0						
5	123.0					
10	104.7	125.9	100.0			
15	104.7	117.5	85.1			
20	104.7	83.2	77.6	102.3	95.5	102.3
25		100.0	67.6	89.1	75.8	93.3
30	102.3	104.7	109.6	85.1	93.3	87.1
35			77.6	77.6	97.7	79.4
40	104.7	112.2				

Site 4

Detph, cm	23-May-83	20-June-83	18-July-83	15-August-83	12-September-83	10-October-83
0	43.6	38.0				
5	33.9	32.3	28.2			
10	34.7	24.0	20.0			
15	35.5	16.2	14.1	19.0		28.8
20	22.9	14.4	15.5	15.8	38.9	20.9
25	17.8	15.8	22.4	19.0	24.5	20.4
30	34.7	22.9	13.5	20.9	22.9	21.9
35				20.4	12.0	14.1
40						

1984 H_2S profiles
H_2S - umol H_2S-S L^{-1}

Site 1

Detph, cm	23-May-83	20-June-83	18-July-83	15-August-83	12-September-83	10-October-83
0	0.0					
5	0.7	0.0	0.0			
10	0.0	0.0	0.0	0.0	0.0	0.0
15	0.0	0.0	0.0	0.0	0.0	0.0
20	0.0	0.0	0.0	0.0	0.0	0.0
25		0.0	0.0	0.0	0.0	0.0
30	0.0	0.0	0.0	0.0	0.0	0.0
35			0.0		0.0	0.0
40	0.0	0.0				

Site 2

Detph, cm	23-May-83	20-June-83	18-July-83	15-August-83	12-September-83	10-October-83
0	0.0	0.0				
5	0.0	0.0				
10	3.0	6.4	0.0			
15	10.1	8.4	0.0			0.0
20	10.2	10.2	6.8	5.3	10.4	0.0
25	3.0	5.9	7.6	0.0	5.9	9.8
30	1.6	0.0	2.7	0.0	0.0	0.0
35		0.0	0.0	0.0	0.0	0.0
40						

Site 3

Detph, cm	23-May-83	20-June-83	18-July-83	15-August-83	12-September-83	10-October-83
0	0.0					
5	1.2					
10	0.0	0.0	0.0			
15	0.0	0.0	0.0			
20	0.0	0.0	0.0	0.0	0.0	
25		0.0	0.0	0.0	0.0	
30	0.0	0.0	0.0	0.0	0.0	
35			0.0	0.0	0.0	
40	0.0					

Site 4

Detph, cm	23-May-83	20-June-83	18-July-83	15-August-83	12-September-83	10-October-83
0	0.0	0.5				
5	0.0	0.0				
10	0.0	4.5	0.0			
15	0.6	9.2	2.9	3.5		0.0
20	1.6	5.7	5.5	6.1	0.0	4.7
25	0.6	7.6	7.0	7.0	0.0	0.0
30	1.6	6.2	6.9	5.0	0.0	0.0
35			0.0	0.0	0.0	0.0
40						

Appendix III

Concentration of AVS, S^0, and FeS_2 as a function of depth for 16 cores from the mire.

umol AVS, S^0, and FeS_2 - S g^{-1} dry weight

Core #1
Date: 31-May-84
Site 2

Detph,cm	AVS	S^0	FeS_2
0-5	0.0	1.1	0.0
5-10	0.0	0.5	6.2
10-15	0.3	0.3	19.4
15-20	0.1	0.3	12.4
20-25	0.1	0.1	4.7
25-30	0.0	0.1	1.8
30-35	0.0	0.3	1.8
35-40	0.0	0.1	2.5

Core #2
Date: 2-June-84
Site 2

Detph,cm	AVS	S^0	FeS_2
0-5	0.0	0.7	0.3
5-10	0.0	2.0	1.2
10-15	0.2	1.0	16.2
15-20	0.3	0.9	6.4
20-25	0.4	0.4	1.6
25-30	0.1	0.4	0.8
30-35	0.1	0.2	2.4
35-40	0.0	0.2	1.9

Core #3
Date: 12-June-84
Site 1

Detph,cm	AVS	S^0	FeS_2
0-5	0.0	1.1	0.0
5-10	0.0	0.5	0.2
10-15	0.1	0.6	1.7
15-20	0.0	0.8	3.0
20-25	0.0	0.7	3.9
25-30	0.0	1.0	2.4
30-35	0.0	1.0	1.4
35-40	0.0	0.6	1.0

Core #4
Date: 13-June-84
Site 1

Detph,cm	AVS	S^0	FeS_2
0-5	0.2	1.9	0.0
5-10	0.1	0.3	0.0
10-15	0.1	0.7	1.9
15-20	0.1	0.8	3.7
20-25	0.1	1.0	4.1
25-30	0.1	0.7	2.7
30-35	0.1	0.5	2.8
35-40	0.1	0.6	0.7

Core #5
Date: 25-June-84
Site 4

Detph,cm	AVS	S^0	FeS_2
0-5	0.0	0.4	3.2
5-10	0.2	4.3	23.0
10-15	0.2	1.3	12.6
15-20	0.4	0.8	16.5
20-25	0.3	0.5	12.9
25-30	0.2	1.0	5.8
30-35	0.0	0.4	2.6
35-40	0.1	0.3	3.1

Core #6
Date: 28-June-84
Site 3

Detph,cm	AVS	S^0	FeS_2
0-5	0.0	1.6	0.0
5-10	0.0	1.0	0.1
10-15	0.1	0.7	1.4
15-20	0.1	0.3	2.3
20-25	0.0	0.3	1.5
25-30	0.0	0.3	0.7
30-35	0.1		
35-40	0.0		

Core #7
Date: 12-July-84
Site 2

Detph,cm	AVS	S^0	FeS_2
0-5	0.1	1.8	3.3
5-10	0.3	3.5	12.3
10-15	0.5	1.4	27.0
15-20	0.2	1.1	3.9
20-25	0.1	0.2	2.9
25-30	0.1	0.4	2.6
30-35			
35-40			

Core #8
Date: 15-July-84
Site 2

Detph,cm	AVS	S^0	FeS_2
0-5	0.0	0.9	0.7
5-10	0.3	2.3	16.9
10-15	0.3	0.9	16.3
15-20	0.2	1.1	10.4
20-25	0.1	1.0	1.9
25-30	0.1	0.4	1.4
30-35			
35-40			

Core #9
Date: 26-July-84
Site 2

Detph,cm	AVS	S^0	FeS_2
0-5	0.2	4.0	0.0
5-10	0.2	3.4	15.2
10-15	0.3	1.7	10.4
15-20	0.2	1.3	13.0
20-25	0.1	0.3	1.4
25-30	0.1	0.3	2.1
30-35			
35-40			

Core #10
Date: 9-August-84
Site 1

Detph,cm	AVS	S^0	FeS_2
0-5	0.3	1.4	0.0
5-10	0.1	0.3	0.8
10-15	0.1	0.6	3.2
15-20	0.1	0.2	0.4
20-25	0.0	0.2	1.2
25-30	0.1	0.2	1.4
30-35			
35-40			

Core #11
Date: 12-August-84
Site 1

Detph,cm	AVS	S^0	FeS_2
0-5	0.0	1.4	0.0
5-10	0.2	1.5	0.9
10-15	0.2	0.4	3.0
15-20	0.2	0.3	2.5
20-25	0.1	0.3	2.2
25-30	0.2	0.3	1.4
30-35			
35-40			

Core #12
Date: 23-August-84
Site 1

Detph,cm	AVS	S^0	FeS_2
0-5	0.1	0.2	1.2
5-10	0.1	0.0	1.0
10-15	0.2	0.4	2.9
15-20	0.0	0.2	0.0
20-25	0.1	0.2	2.9
25-30	0.1	0.4	0.4
30-35			
35-40			

Core #13
Date: 1-October-84
Site 2

Detph,cm	AVS	S^0 + FeS_2
0-5	0.0	1.0
5-10	0.0	4.9
10-15	0.3	14.2
15-20	0.2	5.9
20-25	0.0	2.2
25-30	0.0	1.1
30-35		
35-40		

Core #14
Date: 2-October-84
Site 2

Detph,cm	AVS	S^0 + FeS_2
0-5	0.0	1.3
5-10	0.1	8.1
10-15	0.3	9.4
15-20	0.3	5.1
20-25	0.1	2.6
25-30	0.1	1.0
30-35		
35-40		

Core #15
Date: 8-October-84
Site 1

Detph,cm	AVS	S^0 + FeS_2
0-5	0.1	1.1
5-10	0.0	1.7
10-15	0.1	3.4
15-20	0.1	1.7
20-25	0.1	3.4
25-30	0.0	1.1
30-35		
35-40		

Core #16
Date: 11-October-84
Site 1

Detph,cm	AVS	S^0 + FeS_2
0-5	0.0	1.0
5-10	0.1	1.5
10-15	0.2	1.9
15-20	0.1	0.6
20-25	0.2	2.3
25-30	0.0	2.0
30-35		
35-40		

Appendix IV

Concentration of SO_4^{2-} and H^+ in the surface water pools for the 9 acidifications of 1983 and 1984.

Acidification #1
Date: 3-August-83

SO_4^{2-} - umol SO_4^{2-} L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	22.5	1.9		
During	72.9	22.4		
Directly after	57.2	38.8		
1 day after	32.2	23.3		
7 days after		3.2		

H^+ - ueq L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	8.5	91.2		
During	12.3	158.5		
Directly after	13.5	166.0		
1 day after	11.2	102.3		
7 days after		93.3		

Acidification #2
Date: 31-August-83

SO_4^{2-} - umol SO_4^{2-} L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	20.4	2.8		
During				
Directly after	68.8	66.2		
1 day after	78.1	39.6		
7 days after		21.4		

H^+ - ueq L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	2.3	83.2		
During	2.9	158.5		
Directly after	3.6	190.5		
1 day after	3.6	97.7		
7 days after		89.1		

Acidification #3
Date: 11-October-83

SO_4^{2-} - umol SO_4^{2-} L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	159.4	17.1		
During	173.0	56.8		
Directly after	185.0	66.2		
1 day after	185.0	19.8		
7 days after		19.8		

H^+ - ueq L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	3.9	109.6		
During	5.2	151.3		
Directly after	6.7	144.5		
1 day after	4.5	97.7		
7 days after		138.0		

Acidification #1
Date: 23-May-84

SO_4^{2-} - umol SO_4^{2-} L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	56.3	9.4	37.5	12.5
During	70.8	32.3	41.7	12.5
Directly after	85.4	35.4	43.8	13.5
1 day after	63.6	24.0	40.6	10.4
7 days after	42.7	10.4	18.8	7.3

H^+ - ueq L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	14.8	128.8	13.5	97.7
During	23.4	144.5	12.6	100.0
Directly after	19.5	141.2	14.1	109.6
1 day after	15.5	147.9	14.4	112.2
7 days after	12.6	125.9	13.5	125.9

Acidification #2
Date: 20-June-84

SO_4^{2-} - umol SO_4^{2-} L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	35.4	8.3	13.5	5.2
During	58.3	43.8	22.9	6.2
Directly after	58.3	38.5	22.9	7.3
1 day after	45.8	15.6	19.8	6.2
7 days after	35.4	15.6	17.7	5.2

H^+ - ueq L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	10.5	100.0	8.5	87.1
During	13.2	131.8	6.4	77.6
Directly after	13.2	128.8	8.5	89.1
1 day after	11.7	104.7	7.4	93.3
7 days after	13.2	114.8	9.5	104.7

Acidification #3
Date: 18-July-84

SO_4^{2-} - umol SO_4^{2-} L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	15.6	2.1	10.4	1.0
During	25.0	33.3	15.6	5.2
Directly after	44.8	26.0	15.6	4.2
1 day after	19.8	10.4	11.4	3.1
7 days after	21.9	3.1	11.5	2.1

H^+ - ueq L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	11.2	138.0	8.7	131.8
During	16.2	177.8	10.0	123.0
Directly after	19.5	151.3	10.2	114.8
1 day after	13.5	128.8	10.7	125.9
7 days after	13.5	125.9	8.1	131.8

Acidification #4
Date: 15-August-84

SO_4^{2-} - umol SO_4^{2-} L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	31.3	2.1	32.3	4.2
During	55.2	33.3	44.8	5.2
Directly after	110.4	54.2	72.9	6.2
1 day after	127.1	31.3	136.5	5.2
7 days after	62.5	13.5	96.9	5.2

H^+ - ueq L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	6.7	97.7	6.4	125.9
During	10.0	162.2	7.1	125.9
Directly after	15.1	173.8	8.1	123.0
1 day after	11.0	112.2	8.3	123.0
7 days after	7.8	125.9	9.1	117.5

Acidification #5
Date: 12-September-84

SO_4^{2-} - umol SO_4^{2-} L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	220.0	12.5	168.8	12.5
During	264.7	69.8	225.1	18.7
Directly after	286.5	88.6	314.7	22.9
1 day after	353.2	82.3	416.8	27.1
7 days after	249.0	43.8	365.7	21.9

H^+ - ueq L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	10.2	117.5	10.5	147.9
During	15.8	165.9	8.7	138.8
Directly after	20.9	186.2	15.5	134.9
1 day after	20.9	100.0	17.0	134.9
7 days after	12.0	120.2	15.1	107.1

Acidification #6
Date: 10-October-84

SO_4^{2-} - umol SO_4^{2-} L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	135.5	13.5	255.3	24.0
During				
Directly after				
1 day after	49.0	48.0	44.8	46.9
7 days after				

H^+ - ueq L^{-1}

	Experimental		Control	
	Minerotrophic pool	Oligotrophic pool	Minerotrophic pool	Oligotrophic pool
Before acid.	13.2	134.9	17.4	173.8
During				
Directly after	15.8	165.9	30.2	263.0
1 day after				
7 days after	38.0	177.8	31.6	173.8

Appendix V

Acidification #1
Date: 3-August-83

SO_4^{2-} profiles - umol SO_4^{2-} L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	17 hours after
0			
5	1.3	1.5	10.5
10	2.2	1.7	1.3
15	1.5	0.9	1.7
20	0.6	1.5	1.5
25	0.5		1.2
30	0.6	0.8	1.5
35			
40	0.7	0.5	1.7

Site 2

Depth, cm	Before	Directly after	17 hours after
0		68.6	
5	8.0	25.3	9.0
10	4.1	32.3	5.7
15	4.9	5.5	4.8
20	4.7	4.9	7.2
25	5.0	2.2	3.2
30	3.2	1.5	0.7
35	2.7		0.0
40	0.6	1.6	

Acidification #2
Date: 31-August-83

SO_4^{2-} profiles - umol SO_4^{2-} L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	18 hours after
0			
5		1.6	2.9
10	1.4	1.2	2.6
15	1.1		2.6
20	1.7	1.1	2.2
25			
30	0.5	2.1	
35			
40	0.4	4.5	

Site 2

Depth, cm	Before	Directly after	18 hours after
0	8.3		
5		17.4	20.0
10	2.7	2.8	3.8
15	2.3	4.1	3.6
20	2.4	3.2	3.8
25			
30	1.3		
35			
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	18 hours after
0			
5			
10			
15			
20			8.0
25	1.0	0.9	1.4
30	0.9	0.8	1.0
35	0.5	0.3	
40	0.3		0.6

Site 4

Depth, cm	Before	Directly after	18 hours after
0			
5			
10		40.4	77.3
15	3.7	6.2	7.9
20	1.2		4.4
25	1.0		
30	0.6		2.2
35			
40			0.0

Acidification #3
Date: 11-October-83

SO_4^{2-} profiles - umol SO_4^{2-} L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	18 hours after
0			
5	5.8	2.5	
10	1.2	1.6	2.0
15	1.0	0.9	1.7
20	1.8	3.9	1.4
25			
30	1.8	0.7	1.9
35			
40		3.3	

Site 2

Depth, cm	Before	Directly after	18 hours after
0	47.6	55.0	48.8
5	29.7	45.7	36.9
10	5.1	7.3	6.5
15	6.3	31.3	5.1
20	4.3	5.0	4.5
25			
30	1.8		1.6
35			
40			1.3

Control Sites

Site 3

Depth, cm	Before	Directly after	18 hours after
0			
5			
10	21.0	20.6	15.3
15	1.8	2.4	2.6
20	1.3	1.7	1.1
25			
30	1.2	1.6	0.9
35			
40	1.4	2.1	1.8

Site 4

Depth, cm	Before	Directly after	18 hours after
0		56.2	54.0
5	52.4	52.9	58.1
10	47.5	46.9	52.9
15	11.0	13.2	31.7
20	3.9	5.3	5.5
25			
30	1.7	1.9	1.4
35			
40		0.5	1.2

Acidification #1
Date: 23-May-84

SO_4^{2-} profiles - umol SO_4^{2-} L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	16 hours after
0	4.8	52.9	32.3
5	1.2	43.9	80.5
10	1.6	9.2	8.0
15	0.9	1.1	0.9
20	0.8	0.8	0.7
25			
30	0.7	0.5	0.8
35			
40	0.3	0.6	

Site 2

Depth, cm	Before	Directly after	16 hours after
0	30.7	30.9	33.1
5	31.8	48.1	33.2
10	23.3	43.9	36.2
15	3.6	10.7	10.5
20	9.1	14.9	7.0
25	4.4	5.7	6.7
30	1.5		1.9
35			
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	16 hours after
0	3.9	4.7	2.5
5	0.8	0.9	0.9
10		0.9	0.7
15	0.3	0.6	0.6
20	0.5	0.8	0.4
25		0.4	
30	0.6	0.8	0.6
35			
40	0.8		

Site 4

Depth, cm	Before	Directly after	16 hours after
0	25.5	25.2	21.9
5	22.3	21.6	22.3
10	20.7	18.3	13.9
15	20.0	4.7	6.0
20	6.7	2.2	4.7
25	15.9	1.8	4.1
30	10.9		2.0
35			
40			

Acidification #2
Date: 20-June-84

SO_4^{2-} profiles - umol SO_4^{2-} L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	17 hours after
0	1.3	2.8	6.8
5	1.3	2.2	2.4
10	3.6	1.7	1.2
15	3.5	1.5	2.5
20	2.5	0.9	2.5
25	2.0	2.3	
30			
35	0.9	0.7	
40			

Site 2

Depth, cm	Before	Directly after	17 hours after
0	14.4	15.9	13.2
5	14.6	22.1	10.2
10	4.5	11.6	10.7
15	5.0	6.5	10.0
20	4.8	6.4	9.0
25	2.9	6.1	7.2
30	3.5	2.1	1.9
35			
40		5.0	

Control Sites

Site 3

Depth, cm	Before	Directly after	17 hours after
0			
5			
10	0.6	1.6	1.9
15	1.1	1.7	1.6
20	1.1	12.3	1.0
25	0.7	3.0	0.8
30	1.1	2.1	2.1
35			
40			

Site 4

Depth, cm	Before	Directly after	17 hours after
0	8.1		6.5
5	5.6	17.4	8.0
10	1.8	5.0	4.0
15	4.1	2.8	3.7
20	4.8	3.8	4.0
25	2.5	3.1	2.8
30	2.7	5.6	2.8
35		2.4	
40			1.8

Acidification #3
Date: 18-July-84

SO_4^{2-} profiles - umol SO_4^{2-} L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	15 hours after
0			
5	1.5	82.9	64.9
10	2.0	2.8	4.3
15	0.5	1.2	1.8
20	1.1	1.3	2.2
25	1.0	2.5	1.6
30	0.5	1.1	1.2
35	1.3		
40			

Site 2

Depth, cm	Before	Directly after	15 hours after
0		23.8	
5		23.6	34.0
10	6.2	12.1	18.5
15	11.8	2.4	13.4
20	6.9	2.0	5.3
25	3.6	3.1	6.4
30	1.9	2.7	8.3
35	3.2		
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	15 hours after
0			
5			
10	1.1	1.8	3.8
15	0.8	1.4	1.2
20	1.3	0.3	2.0
25	2.0	0.9	1.9
30	0.7	0.8	1.6
35	0.9		
40			

Site 4

Depth, cm	Before	Directly after	15 hours after
0			
5			7.9
10	1.3	7.9	3.3
15	1.9	2.2	2.3
20	1.9	1.8	2.9
25	1.5	0.8	2.8
30	1.5	0.7	3.1
35	0.8	2.0	2.0
40			

Acidification #4
Date: 15-August-84

SO_4^{2-} profiles - umol SO_4^{2-} L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	15 hours after
0			
5		114.8	
10	2.7	15.2	285.8
15	2.0	1.8	11.5
20	1.4	1.0	0.7
25	1.2	0.9	0.6
30	1.1	0.9	0.3
35	1.6		0.3
40			

Site 2

Depth, cm	Before	Directly after	15 hours after
0			
5			
10		176.1	36.0
15		35.8	13.1
20	5.3	5.4	6.6
25	4.1	5.2	3.2
30	1.8	4.1	2.1
35	0.8	1.8	
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15			
20	14.1	3.0	2.1
25	1.5		0.7
30		1.1	0.8
35			1.7
40			

Site 4

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15	39.8	79.9	13.9
20		5.2	4.9
25	4.8	2.1	3.4
30	1.6	1.8	1.5
35	1.3		0.8
40			

Acidification #5
Date: 12-September-84

SO_4^{2-} profiles - umol SO_4^{2-} L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	15 hours after
0			
5		8.7	
10		95.7	122.0
15	5.3	191.4	27.1
20	1.5	15.8	6.1
25	0.8	2.9	1.2
30	0.9	1.2	0.9
35	0.8		
40			

Site 2

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15		249.9	139.3
20	49.3	93.2	90.0
25	10.5	12.5	7.7
30	3.6	3.9	2.6
35	1.1	1.1	3.5
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15			
20	29.6	33.1	27.9
25	18.2	26.3	29.3
30	12.0	9.5	7.1
35	4.3	2.8	1.3
40			

Site 4

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15		377.6	350.7
20	251.6	227.5	244.0
25	18.1	8.4	42.8
30	4.1	4.1	5.0
35	35.4	2.6	3.0
40			

Acidification #6
Date: 10-October-84

SO_4^{2-} profiles - umol SO_4^{2-} L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	18 hours after
0			
5			
10	93.1	83.0	114.0
15	87.3	49.6	99.0
20	69.0	12.9	49.5
25	31.2	4.4	13.8
30	3.1	1.5	3.5
35	1.6	1.3	
40			

Site 2

Depth, cm	Before	Directly after	18 hours after
0			
5			
10		56.0	
15	36.3	46.4	65.3
20	24.1	11.0	13.3
25	8.8	3.5	5.8
30	3.1	3.0	4.4
35		2.6	1.8
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	18 hours after
0			
5			
10			
15			43.4
20	9.6	22.7	13.5
25	6.0	5.1	3.1
30	3.7	2.9	1.4
35	3.1	1.2	1.4
40			

Site 4

Depth, cm	Before	Directly after	18 hours after
0			
5			
10		132.0	
15	90.7	117.2	74.3
20	6.4	9.8	7.2
25	4.4	3.6	3.3
30	3.2	1.8	0.7
35	3.7		1.5
40			

Acidification #2
Date: 31-August-83

H^+ profiles - ueq H^+ L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	18 hours after
0			
5		83.2	128.8
10	83.2	97.7	123.0
15	89.1	91.2	109.6
20	93.3	89.1	93.3
25			
30	104.7	85.1	128.8
35			
40	112.2	61.6	165.9

Site 2

Depth, cm	Before	Directly after	18 hours after
0	27.5		
5		14.8	93.3
10	22.4	12.9	17.0
15	15.5	15.1	10.2
20	16.6	18.6	17.8
25		20.0	10.0
30			
35	19.5		
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	18 hours after
0			
5			
10			
15			
20			89.1
25	64.6	67.6	87.1
30	72.4	69.2	87.1
35	69.2	66.1	
40	95.5		89.1

Site 4

Depth, cm	Before	Directly after	18 hours after
0			
5			
10		25.1	30.2
15	10.7	12.6	14.1
20	4.8	8.5	14.8
25	5.4	8.5	
30	3.9		14.1
35	5.0		
40			13.8

Acidification #3
Date: 11-October-83

H^+ profiles - ueq H^+ L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	18 hours after
0			
5	114.8	125.9	
10	102.3	120.2	141.2
15	125.9	123.0	162.2
20	117.5	120.2	147.9
25			
30	81.3	190.6	144.5
35			
40	95.5	114.8	109.6

Site 2

Depth, cm	Before	Directly after	18 hours after
0	45.7	104.7	75.8
5	22.4	52.5	46.8
10	20.9	28.2	23.4
15	24.0	21.9	23.4
20	20.4	22.9	24.0
25			
30	16.6		23.4
35			
40			20.4

Control Sites

Site 3

Depth, cm	Before	Directly after	18 hours after
0			
5			
10	158.5	151.3	147.9
15	70.8	79.4	100.0
20	75.8	70.8	81.3
25			
30	97.7	79.4	95.5
35			
40	72.4	64.6	75.8

Site 4

Depth, cm	Before	Directly after	18 hours after
0		37.1	33.1
5	31.6	38.0	33.9
10	27.5	38.0	40.7
15	12.0	17.4	17.4
20	14.1	15.1	13.8
25			
30	17.4	12.9	14.8
35			
40	11.7	12.0	12.0

Acidification #1
Date: 23-May-84

H^+ profiles - ueq H^+ L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	16 hours after
0	195.0	263.0	251.2
5	177.8	177.8	208.9
10	147.9	158.5	151.3
15	154.9	144.5	151.3
20	158.5	141.2	147.9
25			
30	151.3	131.8	125.9
35			
40	195.0	144.5	

Site 2

Depth, cm	Before	Directly after	16 hours after
0	56.2	57.5	57.5
5	56.2	58.9	58.9
10	43.6	42.6	60.2
15	24.5	21.4	37.1
20	23.4	13.8	24.0
25	27.5	14.1	24.5
30	21.9	21.9	36.3
35			
40			20.4

Control Sites

Site 3

Depth, cm	Before	Directly after	16 hours after
0			
5	123.7	100.0	114.8
10	104.7	117.5	114.8
15	104.7	109.6	125.9
20	104.7	112.2	131.8
25		120.2	
30	102.3	120.2	123.0
35			
40	104.7		

Site 4

Depth, cm	Before	Directly after	16 hours after
0	43.6	33.9	47.9
5	33.9	43.6	40.7
10	34.7	33.9	30.2
15	35.5	15.8	17.4
20	22.9	15.5	18.6
25	17.8	13.5	20.9
30	34.7		21.4
35			
40			

Acidification #2
Date: 20-June-84

H^+ profiles - ueq H^+ L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	17 hours after
0			134.9
5	154.9	128.8	154.9
10	154.9	173.8	141.2
15	151.3	158.5	154.9
20	165.9	154.9	151.3
25	162.2	169.8	138.0
30	162.2	169.8	151.3
35			
40	177.8	165.9	

Site 2

Depth, cm	Before	Directly after	17 hours after
0	52.5	63.1	52.5
5	53.7	54.9	51.3
10	39.8	33.9	42.6
15	24.0	19.9	31.6
20	21.9	21.4	25.7
25	28.8	24.0	28.2
30	27.5		30.9
35	24.5		24.0
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	17 hours after
0			
5			
10	125.9	107.1	109.6
15	117.5	95.5	104.7
20	83.2	117.5	104.7
25	100.0	123.0	117.5
30	104.7	114.8	
35			
40	112.2		

Site 4

Depth, cm	Before	Directly after	17 hours after
0	38.0	41.7	40.7
5	32.3	28.2	33.1
10	24.0	25.1	20.9
15	16.2	17.0	16.2
20	14.4	18.2	17.0
25	15.8	22.4	20.0
30	22.9	25.1	27.5
35		24.0	
40			22.4

Acidification #3
Date: 18-July-84

H^+ profiles - ueq H^+ L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	15 hours after
0			
5	109.6	123.0	79.4
10	102.3	114.8	87.1
15	97.7	114.8	112.2
20	97.7	131.8	114.8
25	79.4	145.5	117.5
30	104.7	134.9	107.1
35	85.1		
40			

Site 2

Depth, cm	Before	Directly after	15 hours after
0		53.7	
5		53.7	56.2
10	30.9	35.5	42.7
15	24.0	24.0	28.2
20	21.4	22.9	25.1
25	21.0	23.4	23.4
30	24.0	24.0	25.1
35	17.0	11.0	
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	15 hours after
0			
5			
10	100.0	138.0	117.5
15	85.1	107.1	102.3
20	77.6	104.7	107.1
25	67.6	102.3	107.1
30	109.6	107.1	95.5
35	77.6	91.2	
40			

Site 4

Depth, cm	Before	Directly after	15 hours after
0			
5			22.9
10	28.2	24.5	17.8
15	20.0	20.0	15.1
20	14.1	14.8	14.4
25	15.5	17.8	19.5
30	22.4	24.0	20.4
35	13.5	19.9	22.9
40			

Acidification #4
Date: 15-August-84

H^+ profiles - ueq H^+ L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	15 hours after
0			
5		208.9	
10	162.2	138.9	295.1
15	158.5	114.8	158.1
20	147.9		141.3
25	144.5	125.9	134.9
30	144.5	117.5	141.3
35	138.0		117.5
40			

Site 2

Depth, cm	Before	Directly after	15 hours after
0			
5			
10		79.4	53.7
15		30.9	22.9
20	30.2	25.1	16.6
25	27.5	25.7	27.5
30	19.0	30.2	27.5
35	13.8	14.8	13.8
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15			
20	120.2	95.5	93.3
25	89.1	97.7	97.7
30	85.1	104.7	95.5
35	77.6	100.0	75.9
40			

Site 4

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15	19.0	35.5	14.1
20	15.8	17.8	16.6
25	19.0	20.0	18.6
30	20.9	22.9	22.9
35	20.4	21.9	18.2
40			

Acidification #5
Date: 12-September-84

H^+ profiles - ueq H^+ L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	15 hours after
0			
5		182.0	
10	295.1	154.9	436.0
15	131.8	195.0	309.0
20	169.8	162.2	195.0
25	151.3	138.0	155.0
30	158.5	288.4	151.0
35	131.8		151.0
40			

Site 2

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15		61.6	58.9
20	27.5	28.8	30.9
25	23.4	27.5	16.2
30	27.5	15.5	11.7
35	18.6	13.2	138.0
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15			
20	95.5	91.2	117.0
25	75.8	125.9	115.0
30	93.3	120.2	105.0
35	97.7		102.0
40			

Site 4

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15		43.6	64.6
20	38.9	35.5	35.5
25	24.5	19.0	25.7
30	22.9	25.7	18.2
35	12.0	16.2	23.4
40			

Acidification #6
Date: 10-October-84

H^+ profiles - ueq H^+ L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	18 hours after
0			
5			
10	467.7	239.9	316.2
15	354.8	186.2	245.5
20	251.2	158.5	195.0
25	195.0	154.9	141.2
30	141.2	154.9	104.7
35	128.8	141.2	
40			

Site 2

Depth, cm	Before	Directly after	18 hours after
0			
5			
10		70.8	
15	54.9	43.6	70.8
20	36.3	27.5	25.7
25	21.9	28.8	24.5
30	30.2	35.5	25.7
35	23.4	33.1	38.0
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	18 hours after
0			
5			
10			
15			131.8
20	102.3	117.5	95.5
25	93.3	114.8	100.0
30	87.1	112.2	102.3
35	79.4	109.6	104.7
40			

Site 4

Depth, cm	Before	Directly after	18 hours after
0			
5			
10		56.2	
15	28.8	31.6	38.0
20	20.9	22.4	19.9
25	20.4	24.5	24.0
30	21.9	27.5	22.4
35	14.1	20.4	24.0
40			

Acidification #1
Date: 23-May-84

H_2S profiles - umol H_2S-S L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	16 hours after
0		0.0	0.0
5	0.7	1.6	0.0
10	0.0	1.7	0.0
15	0.0	1.9	0.7
20	0.0	1.0	0.0
25			
30	0.0	0.0	0.0
35			
40	0.0		

Site 2

Depth, cm	Before	Directly after	16 hours after
0	0.0	0.0	0.0
5	0.0	0.0	0.0
10	3.0	0.0	0.0
15	10.1	9.0	16.4
20	10.2	5.7	20.9
25	3.0	7.4	22.3
30	1.6	2.4	0.0
35			
40			0.0

Control Sites

Site 3

Depth, cm	Before	Directly after	16 hours after
0			
5	1.2	0.0	0.0
10	0.0	0.0	0.0
15	0.0	0.0	0.0
20	0.0	0.0	0.0
25		0.0	0.0
30	0.0	0.0	0.0
35			
40	0.0		

Site 4

Depth, cm	Before	Directly after	16 hours after
0	0.0	0.0	0.0
5	0.0	2.4	0.0
10	0.0	2.9	7.1
15	0.6	12.6	16.8
20	1.6	9.2	13.8
25	0.6	5.6	13.6
30	1.6		8.4
35			
40			

Acidification #2
Date: 20-June-84

H_2S profiles - umol H_2S-S L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	17 hours after
0			0.0
5	0.0	0.0	0.0
10	0.0	3.1	0.0
15	0.0	0.0	0.0
20	0.0	0.0	0.0
25	0.0	0.0	0.0
30	0.0	0.0	0.0
35			
40	0.0	0.0	

Site 2

Depth, cm	Before	Directly after	17 hours after
0	0.0	0.0	0.0
5	0.0	0.0	2.1
10	6.4	12.3	4.3
15	8.4	12.5	10.3
20	10.2	13.6	10.5
25	5.9	15.4	8.7
30	0.0	8.0	2.7
35	0.0		0.0
40		0.0	

Control Sites

Site 3

Depth, cm	Before	Directly after	17 hours after
0			
5			
10	0.0	0.0	0.0
15	0.0	0.0	0.0
20	0.0	0.0	0.0
25	0.0	0.0	0.0
30	0.0	0.0	0.0
35			
40			

Site 4

Depth, cm	Before	Directly after	17 hours after
0	0.5	0.0	0.0
5	0.0	0.0	0.0
10	4.5	5.4	6.1
15	9.2	10.0	11.5
20	5.7	11.9	11.2
25	7.6	7.7	6.8
30	6.2	8.4	5.4
35			
40			0.0

Acidification #3
Date: 18-July-84

H_2S profiles - umol H_2S-S L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	15 hours after
0			
5	0.0	0.0	5.9
10	0.0	0.0	0.0
15	0.0	0.0	0.0
20	0.0	0.0	0.0
25	0.0	0.0	0.0
30	0.0	0.0	0.0
35	0.0		
40			

Site 2

Depth, cm	Before	Directly after	15 hours after
0		0.0	
5		0.0	0.0
10	0.0	5.3	1.5
15	0.0	7.5	6.4
20	6.9	9.4	7.5
25	7.6	9.2	8.2
30	2.7	3.3	4.3
35	0.0		
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	15 hours after
0			
5			
10	0.0	0.0	0.0
15	0.0	0.0	0.0
20	0.0	0.0	0.0
25	0.0	0.0	0.0
30	0.0	0.0	0.0
35	0.0	0.0	0.0
40			

Site 4

Depth, cm	Before	Directly after	15 hours after
0			
5			0.0
10	0.0	0.0	0.0
15	2.9	0.0	4.2
20	5.5	7.8	6.8
25	7.0	8.2	6.3
30	6.9	7.3	5.9
35	0.0	7.1	
40			

Acidification #4
Date: 15-August-84

H_2S profiles - umol H_2S-S L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	15 hours after
0			
5		0.0	
10	0.0	0.0	0.0
15	0.0	0.0	0.0
20	0.0	0.0	0.0
25	0.0	0.0	0.0
30	0.0	0.0	0.0
35			0.0
40			

Site 2

Depth, cm	Before	Directly after	15 hours after
0			
5			
10		0.0	0.0
15		0.0	0.0
20	5.3	5.2	3.6
25	0.0	6.8	6.3
30	0.0	2.0	3.7
35	0.0		0.0
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15			
20	0.0	0.0	0.0
25	0.0	0.0	0.0
30	0.0	0.0	0.0
35	0.0	0.0	0.0
40			

Site 4

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15	3.6	0.0	13.0
20	6.1	5.2	11.2
25	7.0	3.6	7.4
30	5.0	5.3	7.9
35	0.0	0.0	0.0
40			

Acidification #5
Date: 12-September-84

H_2S profiles - H_2S-S L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	15 hours after
0			
5		0.0	
10	0.0	0.0	0.0
15	0.0	0.0	0.0
20	0.0	0.0	0.0
25	0.0	0.0	0.0
30	0.0	0.0	0.0
35	0.0		0.0
40			

Site 2

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15		0.0	0.0
20	10.4	8.6	3.9
25	5.9	10.0	4.3
30	0.0	3.8	0.0
35	0.0	0.0	
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15			
20	0.0	0.0	0.0
25	0.0	0.0	0.0
30	0.0	0.0	0.0
35	0.0	0.0	0.0
40			

Site 4

Depth, cm	Before	Directly after	15 hours after
0			
5			
10			
15		0.0	0.0
20	0.0	0.0	0.5
25	0.0	0.0	1.0
30	0.0	0.0	
35	0.0	0.0	
40			

Acidification #6
Date: 10-October-84

H_2S profiles - umol H_2S-S L^{-1}

Experimental Sites

Site 1

Depth, cm	Before	Directly after	18 hours after
0			
5			
10	0.0	0.0	0.0
15	0.0	0.0	0.0
20	0.0	0.0	0.0
25	0.0	0.0	0.0
30	0.0	0.0	0.0
35	0.0	0.0	
40			

Site 2

Depth, cm	Before	Directly after	18 hours after
0			
5			
10		0.0	
15	0.0	0.0	0.0
20	0.0	7.2	7.5
25	9.8	9.9	11.1
30	0.0	4.0	9.2
35	0.0	0.0	0.0
40			

Control Sites

Site 3

Depth, cm	Before	Directly after	18 hours after
0			
5			
10			
15			0.0
20	0.0	0.0	0.0
25	0.0	0.0	0.0
30	0.0	0.0	0.0
35	0.0	0.0	0.0
40			

Site 4

Depth, cm	Before	Directly after	18 hours after
0			
5			
10		0.0	
15	0.0	0.0	0.0
20	4.7	7.2	10.2
25	0.0	0.0	0.0
30	0.0	0.0	0.0
35	0.0	0.0	0.0
40			

Appendix VI

Peat cores for ^{210}Pb determination were obtained with a 14 cm diameter stainless steel core tube. Three cores were collected from hollows located within the mire. Cores 1 and 2 were collected on 22-November-83, and core 3 was collected on 23-August-84. Cores 1 and 3 were collected in the oligtrophic area and core 2 was from the minerotrophic area. All cores were extruded into plastic bags in the field and returned to the field laboratory within 2 h where they were frozen. Frozen cores were sectioned at 1 cm intervals to a depth of 20 cm with a buck saw, below 20 cm, 2 cm intervals were taken. All peat sections were dryed at 70 ^{0}C until no further weight loss occurred with further drying. ^{210}Pb was assumed to be in secular equilibrium with ^{210}Po. The radiochemical methods of Wilkinson (1985) were used for all samples. The following is a brief description of the procedures used. In general, alternate peat sections were analyzed for ^{210}Po activity. 1.0 to 6.0 g peat samples were digested with concentrated HNO_3. Soon after the digestion began 1.0 mL of ^{208}Po (2 Bq) was added to each sample as an internal yield tracer. After final digestion with $HClO_4$, 50 mL of 10 N HCl was added to each sample. The presence of Fe was indicated by the formation of a yellow colour ($FeCl_3$). Iron interferes with the migration of Po and was extracted with iso-propyl ether before plating. Iso-propyl ether remaining in the sample after extraction was removed by boiling. Polonium was plated on silver disks for 10 h at 80 ^{0}C. Samples were counted on a surface barrier alpha spectrometer until counting errors were less than 10% of sample activity. The activity of ^{210}Po was determined by comparing the activity of the spike, ^{208}Po recovered, to the known amount of ^{208}Po added and correcting the ^{210}Po activity for this radiochemical yield. Efficiency of recovery of ^{208}Pb ranged from 45-90%.

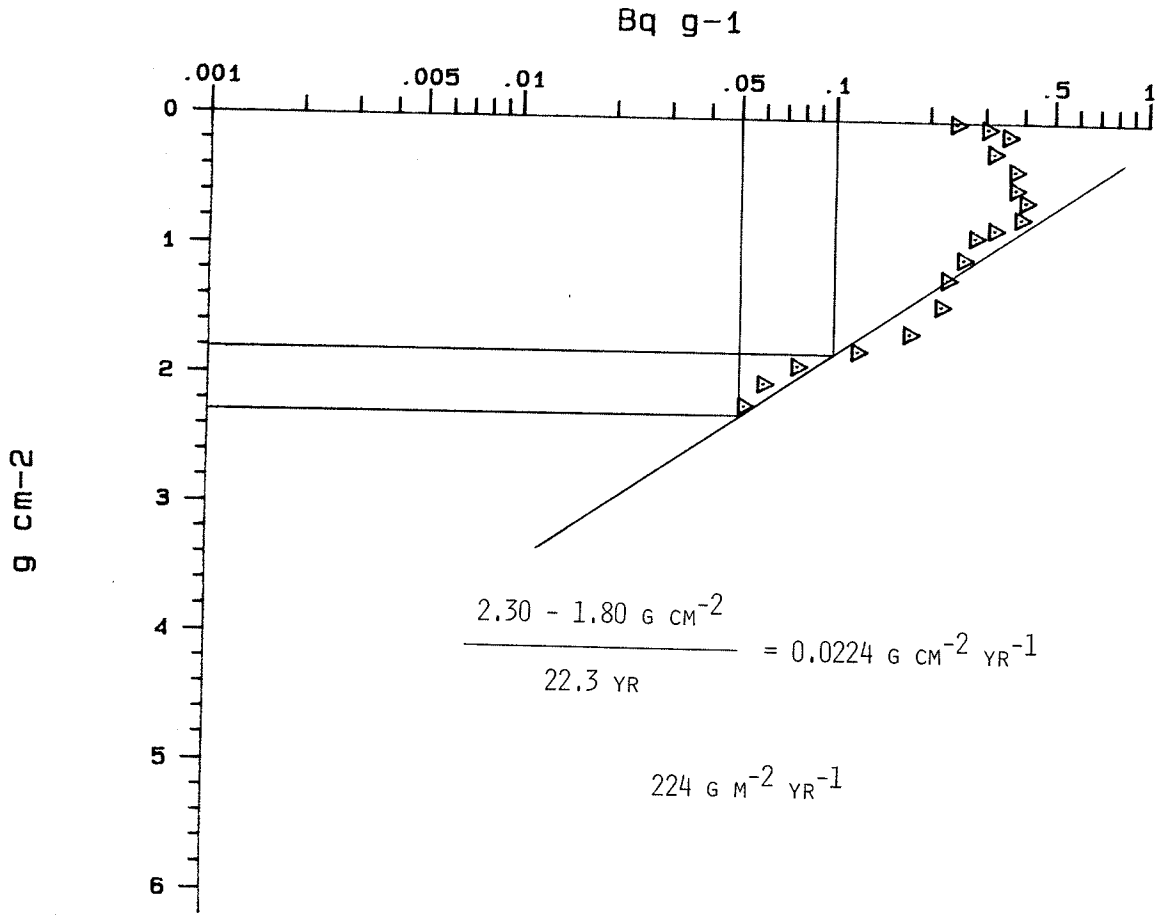
The net peat accumulation rate (g m^{-2} yr^{-1}) for each core was obtained by calculating the mass-depth accumulated (g m^{-2}) during the time it takes for the ^{210}Pb activity to decrease by one-half (22.3 yr). The mass-depth (g m^{-2}) accumulated was divided by the half-life of ^{210}Pb (22.3 yr) which yields g m^{-2} yr^{-1}. The depth interval used for these calculations was between 18 - 39 cm.

The ^{210}Pb activity (Bq g^{-1}) vs. accumulated mass-depth (g cm^{-2}) are shown below for each of the 3 cores. The calculation used to obtain the net peat accumulation is also shown for each core. The

average peat accumulation rate for the 3 peat cores was 251 g m^{-2} yr^{-1}.

The following 3 figures deomonstrate graphically how the ^{210}Pb activity vs. accumulated mass depth was used to calculate the peat accumulation rate (g m^{-2} yr^{-1}) for a particular depth interval.

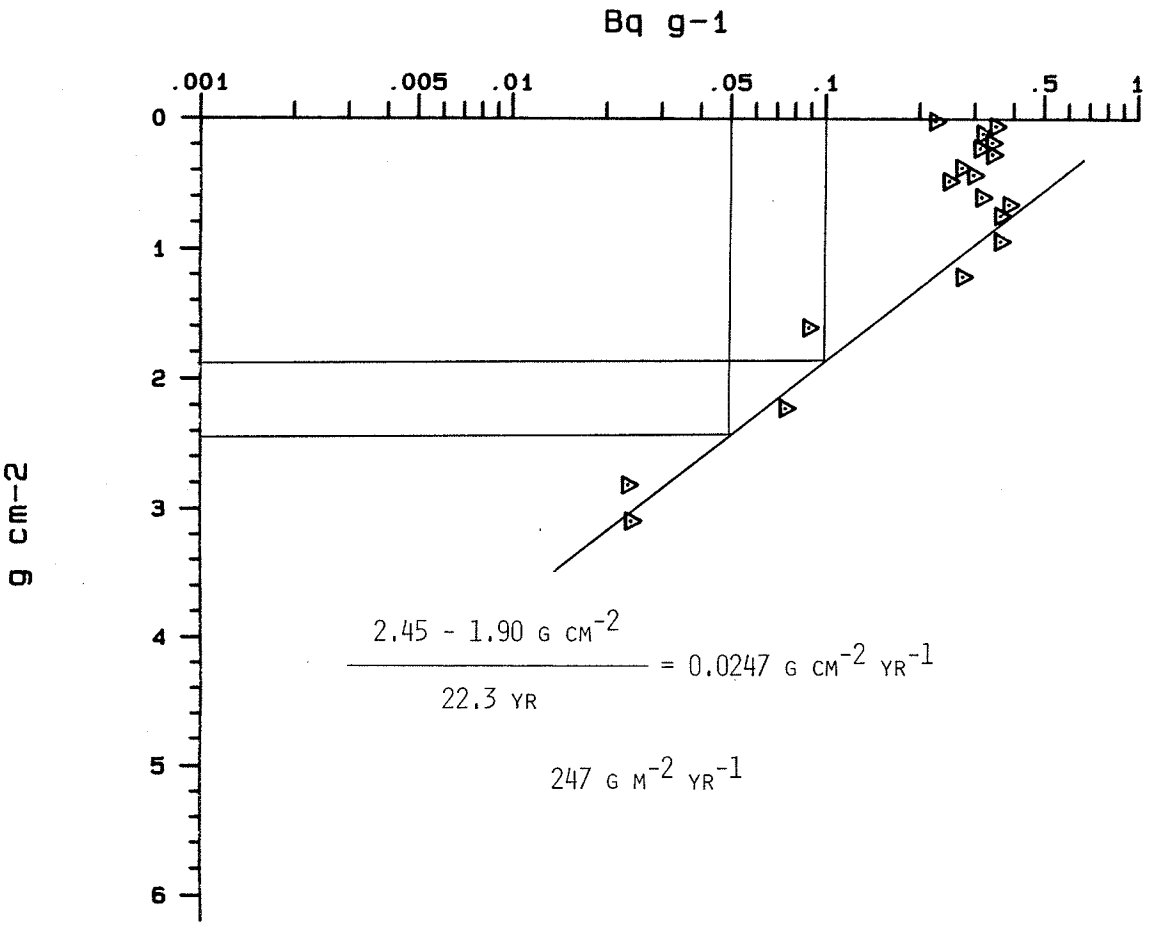
Oligotrophic site - Core #1



$$\frac{2.30 - 1.80 \text{ G CM}^{-2}}{22.3 \text{ YR}} = 0.0224 \text{ G CM}^{-2} \text{ YR}^{-1}$$

$$224 \text{ G M}^{-2} \text{ YR}^{-1}$$

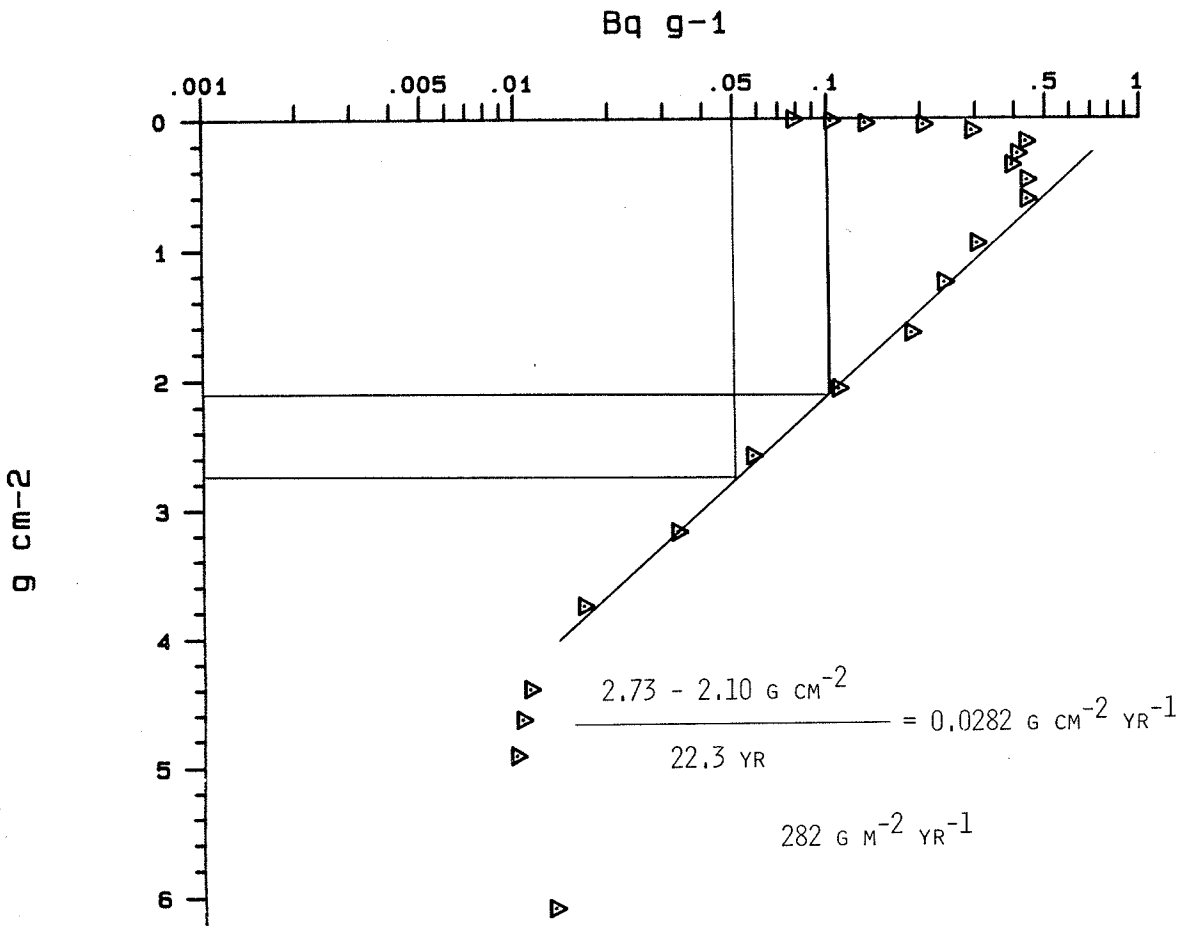
Minerotrophic site - Core #2



$$\frac{2.45 - 1.90 \text{ G CM}^{-2}}{22.3 \text{ YR}} = 0.0247 \text{ G CM}^{-2} \text{ YR}^{-1}$$

$$247 \text{ G M}^{-2} \text{ YR}^{-1}$$

Oligotrophic site - Core #3



$$\frac{2.73 - 2.10 \text{ G CM}^{-2}}{22.3 \text{ YR}} = 0.0282 \text{ G CM}^{-2} \text{ YR}^{-1}$$

$$282 \text{ G M}^{-2} \text{ YR}^{-1}$$