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THE UNIVERSITY OF ALBERTA

BIOLOGICAL EFFECTS OF WET ACID DEPOSITION ON PEATLAND BRYOPHYTES

BY

LINE ROCHEFORT

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

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THE UNIVERSITY OF ALBERTA

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled BIOLOGICAL EFFECTS OF WET ACID DEPOSITION ON PEATLAND BRYOPHYTES submitted by Line Rochefort in partial fulfillment of the requirements for the degree of Master of Science in Peatland Ecology.

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et

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ABSTRACT

The impact of acid deposition of five peatland bryophytes (*Sphagnum angustifolium, S. magellanicum, S. fuscum, Tomenthypnum nitens, and Scorpidium scorpioides*) was investigated. Growth, production, decomposition, chlorophyll content, and species community structure were parameters measured to document the effect of simulated acid rain. Additionally, nitrate reductase activity was measured in *S. angustifolium* to determine the role of the *Sphagnum* mat in the retention of nitrogen by an experimentally acidified peatland at the Experimental Lakes Area, northwestern Ontario (ELA).

In a rich fen in Alberta, growth and chlorophyll b content production were significantly stimulated in *T. nitens* whereas in *S. scorpioides*, they were unaffected by simulated acid applications. Growth and chlorophyll b values were 2.6 mm and 0.08 mg Chl. g^{-1} dw for *T. nitens* in the control plots compared to 6.2 mm and 0.17 mg Chl. g^{-1} dw in the experimental plots. The difference between the species response is believed to be related to their position along the hummock-hollow gradient of fens. In laboratory experiments, the nitrate component of acidic rain accounted for more growth and augment chlorophyll content.

In a poor fen in northwestern Ontario, decomposition of the three dominant *Sphagnum* species was unaffected by three years of simulated acid rain, but production was promoted. Theoretically, this suggests that experimental acidification will result in greater peat

accumulation.

Under natural conditions, in the ombrotrophic central zone of mire 239, production and growth were generally greater in hollows and mid-hummocks (157-239 g m^{-2} yr^{-1}; 25-34 mm) than hummocks (69-116 g m^{-2} yr^{-1}; 7-13 mm). A parallel relationship was found for the decomposition rates where losses in hollow, mid-[illegible] hummock-top are roughly in the ratio 13:9:7. This means that the rate of peat accumulation is more or less even in this ombrotrophic zone and the hummock-hollow reliefs are somewhat in a constant state. In the lagg zone, production was either not different between the *Sphagnum* species or hummock production (303 and 175 g m^{-2} yr^{-1}) was greater than hollow (198 and 100 g m^{-2} yr^{-1}) and mid-hummock production (103 and 59 g m^{-2} yr^{-1}) with the same ratio of decomposition rate between the species as mentioned above. Thus hummocks appear to be expanding in this minerotrophic lagg zone.

After three years of acid applications, there was still a good relationship between nitrate additions and the induced nitrate reductase activity of *Sphagnum*. *The Sphagnum* mat was identified as being one of the most important sink of nitrate ions in the experimentally acidified poor fen.

RESUME

Les effets des précipitations acides sur cinq mousses de tourbière (*Sphagnum angustifolium, S. magellanicum, S. fuscum, Tomenthypnum nitens, and Scorpidium scorpioides*) ont été étudiés. La croissance, la production, la décomposition, le contenu en chlorophylle et la composition des espèces sont les paramètres choisis pour documenter l'effet de pluies acides artificielles. De plus, l'activité enzymatique de la nitrate réductase a été mesurée pour déterminer l'importance des sphaignes dans la rétention de l'azote d'un fen acidifié expérimentalement à Experimental Lakes Area, dans le nord-ouest de l'Ontario.

Dans un fen riche en Alberta, la croissance et le contenu en chlorophylle *b* de *T. nitens* ont été stimulés par l'application de pluies acides artificielles. Ces paramètres n'ont pas varié entre les contrôles et les traitements pour *S. scorpioides*. Cette différence de comportement entre les deux espèces est estimée être reliée à leur position le long du gradient butte-dépression des fens. A partir d'expériences de laboratoire, la composante nitrate des pluies acides a été isolée comme facteur qui stimule la croissance et la production de chlorophylle.

Dans un fen pauvre en Ontario, le taux de décomposition des trois espèces de sphaignes dominantes n'a pas été affecté par trois années de pluies acides simulées, mais la production des sphaignes a été stimulée. Ceci suggèrerait que le taux d'accumulation de tourbe devrait

être plus grand en cas d'acidification expérimentale. En conditions naturelles, la production et la croissance, dans la zone ombrotrophe, sont généralement plus grandes dans les dépressions et à mi-buttes (157-239 g m^{-2} yr^{-1}; 25-34 mm) que sur les buttes (69-116 g m^{-2} yr^{-1}; 7-13 mm). Une relation parallèle est trouvée pour le taux de décomposition où les pertes dans les dépressions, mi-buttes, et sur les buttes sont approximativement 13:9:7 en terme de proportion. Ce qui signifie que le taux d'accumulation de tourbe est plus ou moins égal dans cette zone et que la topographie des buttes est dans un état stable. Dans la bordure minérotrophique de la tourbière, la production est soit semblable entre les espèces de sphaignes, soit plus grande pour les buttes (303 and 175 g m^{-2} yr^{-1}) que pour les dépressions (198 and 100 g m^{-2} yr^{-1}) ou les mi-buttes (103 and 59 g m^{-2} yr^{-1}), avec la même proportion de taux de décomposition entre les espèces tel que mentionnée précédemment. Il semble donc que les buttes dans cette bordure minérotrophique soient en pleine expansion.

Après trois années d'arrosages acidiques, il y a encore une bonne relation entre l'addition de nitrates et l'induction de l'activité de la nitrate réductase des sphaignes. La couche de sphaignes est identifiée comme la composante absorbante des ions de nitrate dans le fen pauvre acidifié expérimentalement.

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I. INTRODUCTION

In recent years, acid deposition has been the subject of considerable research. However, most of this work was directed to impacts of acid deposition on terrestrial ecosystems (see Abrahamsen 1980; Hutchinson and Havas 1980; Overein *et al.* 1980, for reviews) and aquatic systems (e.g., Schindler *et al.* 1980a, 1980b; Harvey *et al.* 1981; Schindler and Turner 1982; Schindler *et al.* 1985, 1986). Until recently little attention had been paid to the biological or ecological impact of acidic precipitation associated with peatlands (Gorham *et al.* 1984a). To remedy this situation in North America, efforts have been devoted lately to long-term or large scale projects (see notably Bayley *et al.* 1987; Gorham *et al.* 1986; Urban *et al.* 1986).

An overview of current knowledge and research of the impact of acid deposition on peatlands is discussed in Chapter II. The nature of acid deposition is first described. The natural acidification of peatlands is reviewed, as it is necessary to determine the effects of natural processes before any evaluation of anthropogenic acidification effects can be made. Processes that produce acidity in peatlands include: cation exchange in peatland vegetation, particularly *Sphagnum* species (Clymo 1963); dissociation of polygalacturonic acids produced by *Sphagnum* species (Kilham 1982); uptake of nutrients by peatland biota (Reuss 1977; Kilham 1982); oxidation and reduction of sulphur and nitrogen compounds (Hemond 1980; Clymo 1984; Reuss 1977); and, production of organic acids by decomposition of vegetation (McKnight *et al*. 1985). Peatlands through intrinsic properties can govern their own evolution from slightly alkaline or circumneutral to more acidic types (Gorham *et al*. 1986). These changes are reflected in shifts in plant communities over time as revealed, for example, by examination of plant remains in stratigraphic profiles of peatlands (Janssens 1983; Nicholson 1987).

Anthropogenic sources of acidity can influence peatlands in various ways. There is some evidence that bryophytes, the dominant vegetation of peatlands, may be more vulnerable to acid deposition than vascular plants. Spraying of simulated acid rain on various boreal mosses has shown that detrimental effects can occur at pH 3.5 or lower (Hutchinson *et al*. 1986; Raeymaekers and Glime 1986). Various European studies have linked modifications in mire vegetation over time to atmospheric pollutants (Lee *et al*. 1986). From a biogeochemical perspective, there is evidence that sulphate reduction and nitrate uptake have increased considerably in peatlands of eastern North America since the period before acid deposition (Hemond 1980). Experimental application of sulfuric and nitric acids to peatlands has shown that sulfates and nitrates are rapidly assimilated by the vegetation and microorganisms (Bayley *et al*. 1987). Thus, nutrient uptake and microbial reduction appear to mitigate acidification processes, but considerably more research is required to validate these assumptions.

Whole peatland ecosystem responses to acid deposition have mainly been considered in terms of sensitivity of different peatland types (Anderson 1986; Gorham *et al*. 1986). Poor fens are recognized as being most sensitive to acidification effects because of their very low alkalinities, pH values of about 4.0 to 5.5, and lack of buffering capacity. Rich fens have higher buffering capacities, and bogs are considered to be less sensitive as they are already highly acidic and, therefore, less likely to change in their acid-base chemistry.

In light of these findings, I report in this thesis, the results of the biological effects of acid deposition of five bryophytes (*Sphagnum angustifolium, S. magellanicum, S. fuscum, Tomenthypnum nitens, Scorpidium scorpioides*) and on the role of the *Sphagnum* mat in the retention of nitrate from artificial acid applications. These species were chosen for two reasons. First, they were the dominant species colonizing a poor fen (*Sphagnum* mosses) and a rich fen (brown mosses). Second, within a type of fen, they occupied different microhabitats along hummock-hollow gradients.

In this thesis, I present the results in three papers. The first, (Chapter III), investigates whether brown mosses (*Tomenthypnum nitens* and *Scorpidium scorpioides*) are affected by acid deposition even if rich fen ecosystems have been rated as insensitive. It is based on field and laboratory experimental manipulations done in Alberta, where mosses were sprayed with simulated acid precipitation. The results comprise quantitative data on growth and chlorophyll content.

The second paper (Chapter IV) deals with the production—decomposition dynamics of the *Sphagnum* species in a poor fen as observed in natural and experimentally acidified conditions. Quantitative measurements were made at an experimentally acidified *Sphagnum*-dominated peatland, a long-term project in the Experimental Lakes Area, Ontario. Along with this, is a study of the effect of simulated acid precipitation on the *Sphagnum* community structure.

The third paper (Chapter V) addresses the question of the ability of the *Sphagnum* mat to retain deposited inorganic nitrogen in a poor fen that is being experimentally acidified with nitric and sulfuric acids.

Lastly, a short concluding discussion (Chapter VI) integrates my results with those of other studies and discusses the possible effects of acid deposition on the vegetation of poor and rich fens.

In this regard, the objectives of this research are: 1- to investigate the effects of simulated acid rain on *Tomenthypnum nitens* and *Scorpidium scorpioides* of an extreme rich fen by monitoring growth and chlorophyll content, 2- in addition to the previous field experiment, laboratory experiments were undertaken to determine at which pH level "acid rain" is deleterious to plant growth and which component in "acid rain" is most detrimental to growth and chlorophyll content of the moss, 3- to assess the effect of acid deposition on a) the growth and production of the three dominant species of *Sphagnum*, b) the decomposition rate of Sphagna, and c) the *Sphagnum* community structures, 4- to compare production and decomposition dynamics between *Sphagnum* species (*S. angustifolium*, *S. magellanicum* and *S. fuscum*) along hummock-hollow gradients, and 5- to determine the importance of the *Sphagnum* mat to immobilize deposited inorganic nitrogen in a poor fen which is being experimentally acidified with nitric and sulfuric acids.

An extensive body of literature exists on peatlands (see Gorham *et al.* 1984b, for an excellent bibliography) and over the years a vocabulary specific to the description of peatland types has been developed. The terminology, however, is not always consistent over publications. Throughout this thesis, the terms "peatland" and "mire" are used interchangeably, and are meant to describe areas where wet organic soils are prevalent. Bog is used to designate ombrotrophic peatlands, receiving water through precipitation and being ionically poor, and nitrogen and phosphorus deficient. Finally, fens are associated with minerotrophy, that is peatlands influenced by soil water flow, these generally are more ionically rich than bogs, but have similar to slightly greater amounts of N and P. Based on water chemistry criteria, fens have been subdivided into poor fen (pH 4.0 - 5.5; Ca 0 - 5 mg L^{-1}; Mg 0 - 2 mg L^{-1}) and rich fen (pH 7.3 - 7.8; Ca 30 - 85 mg L^{-1}; Mg 2 - 34 mg L^{-1}).

Style and format of Chapters III and IV reflect the requirements of the periodicals in which they will be published.

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II. ACID DEPOSITION AND ITS EFFECTS ON PEATLANDS VEGETATION: A REVIEW OF LITERATURE.[1]

Anthropogenic acid deposition is an environmental concern in North America, Europe, and other industrialized regions of the world. Much of the total peatland area in the world also occurs in these regions. Widespread disruption of peatland ecosystems could have serious and large scale consequences for freshwater lakes and streams.

Anthropogenic acid deposition (wet and dry) is a widely acknowledged phenomenon in many industrialized regions of the world Under natural conditions, precipitation (including both rainwater and snowfall) is characterized by a pH of 5.6 (Charlson and Rodhe 1982). This pH results from an equilibrium reaction in which carbon dioxide (CO_2) dissolves in water vapor to form carbonic acid (H_2CO_3), a weak acid which dissociates slightly (Likens *et al.* 1979). Acidity of rainfall is caused by the strong mineral acids H_2SO_4 and HNO_3, and the weak inorganic base NH_4OH. Weak acids and BrØnsted acids have a minimal influence on the pH of precipitation (Galloway *et al.* (1976, 1984) and Valenta *et al.* (1986). Sulfate and nitrate are the primary anions in acidic precipitation, although chloride anions may occasionally be important (Yue *et al.* 1976). By

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[1] A version of this chapter has been published in: Turchenek, L. (Ed.). 1987. Present and potential effects of anthropogenic activities on waters associated with peatlands in Alberta. Research Management Division, Alberta Environment, Edmonton, Alberta.

definition, acidic precipitation is rain or snow with a pH < 5.0 because natural precipitations contain small amounts of both weak and strong acids (Schindler, in press).

Acid deposition arises from the emission of sulfur oxides and nitrogen oxides associated with the smelting of sulfide metal ores, the combustion of fossil fuels and other industrial processes. In Canada, two-thirds of the SO_x emissions are from several large smelting operations; most of the remaining emissions are from combustion of fossil fuels for power generation, commercial and industrial activities and home heating. Automobiles and transportation are responsible for two-thirds of NO_x emissions (Summers and Whelpdale 1976). Once emitted in the air, the pollutant may undergo several photochemical or photoxidation reactions in the gaseous and/or liquid phase.

<u>Sulfur Dioxide Chemistry</u> (Brosset 1973)

During combustion of sulfurous fuels, sulfur is primarily converted to SO_2. Approximately 2-3 percent of the SO_2 is oxidized in the stack and converted to concentrated H_2SO_4, part of which is emitted to the ambient air (first reaction below). The SO_2 that is not oxidized in the stacks is emitted in the atmosphere and reacts with very small particles covered by an aqueous film or with water drops. Sulfur dioxide is dissolved forming H_2SO_3, which is dissociated and then rapidly oxidized to H_2SO_4 (second reaction below).

$$H_2SO_4 \xrightarrow[H_2O]{} H^+ + HSO_4^- \xrightarrow[H_2O]{} 2H^+ + SO_4^-$$

concentrated
acid

emitted
from
stack

$$SO_2 \xrightarrow[H_2O]{} H_2SO_3 \xrightarrow[H_2O]{} H^+ + HSO_3^- \xrightarrow[H_2O]{} 2H^+ + SO_3^{2-}$$

catalytical
oxidation

$2H^+ + SO_4^{2-}$

diluted acid

Nitrogen Oxide Chemistry (Legge *et al*. 1980)

The conversion of NO_x to HNO_3 takes place in a series of complicated reactions during which nitrogen oxides undergo various oxidation stages to finally produce HNO_3.

combustion processes

$$N_2 + O_2 \longrightarrow 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

atmospheric reactions near the emission source

$$2NO + O_2 \longrightarrow 2NO_2$$

reactions in the ambient polluted atmosphere

$$NO_2 + h\nu \longrightarrow O(^3P) + NO$$ (P is the quantum level)

$$O(^3P) + O_2 + M \longrightarrow O_3 + M$$ (M is other molecule)

$$NO + O_3 \longrightarrow NO_2 + O_2 + \text{energy}$$

$$O_3 + NO_2 \longrightarrow NO_3 + O_2$$

$$\begin{aligned} NO_3 + h\nu &\longrightarrow NO_3 + O(^3P) \\ &\longrightarrow NO + O_2 \end{aligned}$$

$$NO_3 + NO_2 \xrightarrow[M]{} N_2O_5$$

nitric and nitrous acids formation

$$HO_2 + NO_2 \longrightarrow HONO + O_2$$

$$HONO + h\nu \xrightarrow[M]{} HO^\cdot + NO$$

$$NO + NO_2 + H_2O \longrightarrow 2HONO$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

$$NO_3 + H_2O \longrightarrow HNO_3$$ (+ other products)

$$OH^\cdot + NO_2 + M \longrightarrow HONO_2 + M$$

Atmospheric factors as temperature, air pressure, humidity, wind velocity, light intensity (UV), availability of aerosols, and water vapor control these atmospheric chemical reactions and the composition of the ultimate deposition.

Acids are removed from the atmosphere by dry and wet deposition processes. Dry deposition occurs continuously and includes absorption and adsorption of gases and gravitational settling of fine aerosol and coarse dust particles (Altshuller 1976). Wet deposition occurs intermittently; it includes the transfer of dissolved and suspended materials in raindrops, snowflakes, hail, dew, and fog (Evans 1984). Depending on the atmospheric conditions at the time of release, these gases and particles may be transported over many hundreds of kilometers (Altshuller 1976). Therefore acid precipitation may become an environmental problem in areas quite distant from industrial centers.

Scandinavia and northeastern North America are currently receiving acid precipitation with mean pH of 4.0 and acid rain events as low as pH 3.0 (Bolin 1971; Likens *et al.* 1972). Fog events have been recorded with pH < 1.5 or 2. The effects of this precipitation are a problem of increasing importance (Likens and Bormann 1974; MOI 1983; U.S. EPA 1984). In Europe, from 1955 to 1974, the pH value of rain dropped from approximately 6.5 to slightly above 4.0 (Odèn 1976). In North America, the northern Atlantic coast and lower Great Lakes basin have the highest wet-deposition rates for NO_3^- and SO_4^{2-}, and the average pH value of rainfall is 4.0. The rest of North America rarely receives precipitation having a pH value higher than 5.0, except for the northern plains and western Canada (Munger and Eisenreich 1983). Acid deposition has been recognized as having a great ecological impact in both terrestrial (e.g., Abrahamsen 1980; Bell 1986; Binns 1985; Bormann 1985; Cowling 1980; Hutchinson and Havas 1980; Overein *et al.* 1980; Ulrich and Matzner 1986) and aquatic systems (Harvey *et al.* 1981; Schindler *et al.* 1980a, 1980b; Schindler and Turner 1982; Schindler *et al.* 1985, 1986). Unfortunately little research has been conducted on the ecological effects of acid deposition upon peatlands and our understanding of their vulnerability is limited (Gorham *et al.* 1984).

Peatlands can be defined as areas where wet organic soils are prevalent, having 1) a water-table near or above the mineral soil for most of the thawed season, 2) a peat formed by the accumulation of undecomposed remains of hydrophilic vegetation (peat 40 cm or thicker), and 3) pools of open water less than 2 m deep (Zoltai and Pollet 1983). The term mire is used for potentially peat forming ecosystems and includes ecosystems such as swamp, bog, fen, moor, muskeg and peatland (Gore 1983). Peatlands are estimated to occupy 420-450 million ha worldwide (Kivinen and Pakarinen 1981), including approximately 170 million ha in Canada representing 12% of the geographic surface (Clayton *et al.* 1977). These peatlands play a significant role in energy flow, biogeochemical cycling, groundwater recharge, hydrological control of floods, lakes and rivers, and life cycles of several animal species (Longton 1984). Economic, recreational, and educational values of peatlands are discussed by CLIMP (1986), Goodwin and Niering (1974), Greeson *et al.* (1979), and Sjörs (1980).

The concept of acidification of peatlands is complex because peatlands are naturally acidic. The processes of natural and anthropogenic acidification have to be distinguished in order to assess the ecological impacts of air pollution on peatlands. The remainder of this chapter reviews literature on the effects of deposition of acid and acid-forming substances on peatland ecosystems. Part I describes natural acidification processes occurring in peatlands, including biogeochemical interactions and plant community changes along gradients of acidity. Part II summarizes the effects of anthropogenic acidification on (i) peatland vegetation, (ii) water chemistry, and (iii) wetland ecosystems.

i. NATURAL ACIDIFICATION OF PEATLANDS

Peatlands are formed by the accumulation of incompletely decomposed plants in waterlogged environments which are anoxic beneath the water surface (Clymo 1983). Peatland vegetation itself initiates deposition of peat. The composition of plant species growing on peatlands is influenced by several factors including climate, moisture regime, nutrient status, water quality, seed availability, and frequency of disturbances (Malmer 1958, 1962; Zoltai *et al*. 1973). Peat build-up, in turn, changes the physical characteristics of the peatland, and is reflected in the vegetation.

Peatlands may develop by two different processes in most northern climate. Terrestrialization (infilling) is a process where a lake or pond is gradually filled in by extension of peat-forming communities outwards from the shoreline (Gore 1983). Paludification refers to the creation of a peatland by the drowning or submerging of uplands. As peatlands develop and change, the abundance and quality of the water control their evolution. Factors such as nutrient content, acidity, and oxygen richness of the water determine the type of peatland that will arise and the vegetation that will occur.

It is these water-related factors that separate the two fundamental peatland types - fen and bog. Fens (also called minerotrophic peatlands) receive water mainly from underground and/or surfaces sources (i.e., mineral water that has received nutrients from its passage through soil and bedrock). Since moving water flushes away acids and other metabolic byproducts, minerotrophic peatlands are the least acidic, ranging from somewhat acidic to basic pH (4.2 to 8.5). Fens may be dominated by sedges (family Cyperaceae), shrubs, or trees, and are typically rich in species (Sjörs 1952). In contrast, bogs (also called ombrotrophic or rain-fed peatlands) receive water only from precipitation (rain, fog, or snow) and are poor in nutrients. With little nutrient input (oligotrophic conditions) or flushing by water, these are acidic (pH < 4.2). They are notably poor in species and peat mosses (*Sphagnum* species) are the principal peat formers.

The concepts of minerotrophy-ombrotrophy and plant indicators to distinguish minerotrophic from ombrotrophic sites are discussed in detail by Sjörs (1959, 1961a, 1961b, 1963). Limited data are available for peatlands in Alberta (see Horton *et al.* 1979; Slack *et al.* 1980; Turchenek *et al.* 1984; Vitt *et al.* 1975a). Bog and fen water characteristics for pH and numerous ions are given by Gorham and Pearsall (1956), Gorham (1967) and Sjörs (1952, 1963).

In *Sphagnum* dominated peatlands, surface water pH values typically range from 3.8 to 4.6. This acidity is produced naturally in peatlands. This section reviews the different aspects of the chemical ecology of *Sphagnum* and the biochemical processes that are sources of acidity in peatlands (Figure II-1).

A. Vegetation as sources of acidity

1. Cation-exchange

Sphagnum species are prominent wetland plants with the capability to direct succession by acidification (Andrus 1986; Andrus *et al*. 1983). *Sphagnum* mosses dominate in nutrient poor and acidic sites. They are known to play a role in creating these acid conditions. *Sphagnum* uptake experiments showed that cations from solution were taken up and exchanged with H^+ (Skene 1915; Williams and Thompson 1936; Ramaut 1954). Later Clymo (1963) indicated a strong correlation between the cation-exchange capacity (CEC) of *Sphagnum* species and their content of unesterified polyuronic acid (see also Knight *et al*. 1961; Spearing 1972; Theander 1954). Plant CEC and uronic acids are related to the dryness of the microhabitat. Species growing highest above the water level on hummock have the highest uronic (PGA) contents and the greatest cation-exchange capacity (Clymo 1986; Vitt *et al*. 1975b). Thus water in the hummocks is more acidic than hollow or pool water (Bellamy and Rieley 1967; Clymo 1984). Because polyuronic acids are found in the holocellulose fraction of the cell wall of *Sphagnum* (Craigie and Maass 1966), most of the cation exchange properties persist after death. In general, Sphagna have higher exchange capacity than other plants of oligotrophic habitats, including true mosses (Brown and Bate 1972; Clymo 1963).

If neutral water is sprayed over a *Sphagnum* plant (dead or alive) the water becomes more acid because cations from the environment (Ca^{2+}, Mg^{2+}, K^+, Na^+, etc.) replace the H^+ ions from carbonyl ligand of uronic acids in the cell wall (Clymo 1967). These H^+ ions produce a decrease of water pH as they are slowly leached away by rain and flowing water. Indeed, Clymo hypothesized that the ability of *Sphagnum* to produce acidity depends on growth rate and the production of new -COOH groups. With realistic values of rainfall, concentration of cations in rain, and *Sphagnum* growth rates, Clymo (1967) found that a mean water pH of about 4.2 could be maintained in an unpolluted atmosphere. Clymo (1984) also presented an acidity budget for Moor House peatland and found that *Sphagnum* cation exchange contributed to about half of the measured acidity.

Brown mosses (e.g. *Drepanocladus*) have also been found to influence successional patterns toward more acidic type of habitats. In a marsh of Lawrence Lake, Michigan, Glime *et al.* (1982) described a direction of succession from alkaline marsh to *Sphagnum* bog, where they found that non-*Sphagnum* mosses were the agent for lowering the pH of their immediate environment.

2. Polygalacturonic acid

The reduction of environmental pH by Sphagna is considered to be an adaptive metabolic (internal) process rather than a passive chemical process (cation-exchange) over which the moss has little control (Kilham 1982). Kilham suggested that the dissociation of polygalacturonic acid (PGA), not the production of hydrogen ions by cation-exchange, is of primary importance in determining ambient pH. Further, environmental acidity may be regulated by the amount of PGA actively produced by plants. This hypothesis has been challenged and discussed by Andrus (1986).

3. Net biological uptake of nutrient ions

Nutrient uptake (Ca^{2+}, K^+, NH_4^+, NO_3^-, etc.) can affect the acidification processes of a bog ecosystem (Kilham 1982). Because charge balance must be maintained between plants and their environment (Reuss, 1977), when a plant takes up cations in excess of anions, other cations (usually H^+) are released into the environment. Nilsson *et al.* (1982) call this process "cation excess", which they define as the excess of cation uptake over anion uptake.

In general, oxidation reactions are net consumers of alkalinity, while reduction is an alkalinity producer. Acidity-generation, associated with net biological uptake (NBU after Kilham 1982), results from peat accumulation i.e. the difference between uptake and decomposition. Although NBU is an important and often the largest source of acidity within a system (Urban *et al.* 1986), this mineral acidity is usually not exported from the peatland because it is offset by alkalinity produced by atmospheric deposition, denitrification, dissimilatory sulfate reduction, weathering of Fe and Al inputs and run-off from the upland. In a transect of North American bogs (from Manitoba to Newfoundland), mineral acidity never exceeded organic acidity (i.e. hydrogen ions in excess of organic anions) in any of the sites (Urban *et al.* 1986).

B. Biogeochemical interactions

1. Carbonic acid

Villeret (1951) claimed that high concentrations of CO_2 found in bog waters (i.e., carbonic acid) was the principal chemical factor responsible for mire acidity. But experimental evidence (Clymo 1986; Gorham 1956) has discounted this theory. Clymo (1986) showed that CO_2 in water was a secondary, not a primary, source of acidity. There were also detailed physico-chemical objections that high CO_2 concentration in water and carbonic acid cannot maintain pH below 5.6.

2. Oxidation and reduction of sulfur and nitrogen compounds

Another possible source of acidity is the supply and interconversion (redox processes) of sulphur compounds. At and below the water table in peat bogs, H_2S is produced (Clymo 1984; Hemond 1980, 1983; Behr 1985). A generalized equation for sulfate reduction by bacteria is as follows (Nriagu and Hem 1978):

$$SO_4^{2-} + 2(CH_2O) \longrightarrow H_2S + 2HCO_3^-$$

By this reduction process, alkalinity is generated but this H_2S may be reoxidized to SO_4^{2-} with companion release of $2H^+$, after upward diffusion or a drawdown of the water-table (Gorham 1956, 1967; Behr 1985; Bayley *et al* 1986).

Kilham (1982) also described the bacterial oxidation of pyrite and elemental sulfur in bog ecosystems. Production of sulfuric acids would occur according to the following generalized reactions (Wetzel 1975):

$$FeS_2 + 3.5\ O_2 + H_2O \longrightarrow FeSO_4 + H_2SO_4$$

$$2S^o + 3O_2 + 2H_2O \longrightarrow 2H_2SO_4$$

Soil nitrogen (N) transformations involve production and consumption of H^+ ions (Reuss 1977). The oxidation of ammonium to nitrate by aerobic chemautotrophic bacteria results in the production of acid:

(a) $NH_4^+ + 1.5\ O_2 \longrightarrow 2H^+ + NO_2^- + H_2O$

nitrosammonas

(b) $NO_2^- + 0.5\ O_2 \longrightarrow NO_3^-$

nitrobacter

Assuming subsequent plant uptake of NO_3^-, part of the acidity produced would be neutralized (cf to the section on net biological uptake of nutrient ions). Therefore ammonium contained in rainfall is another component to consider when studying the effects of acidification on peatlands. The importance of nitrification in peatlands is poorly known (Hemond 1983)

3. Organic acids

Two processes of organic acid production may be distinguished: the release of organic acids by excretion from living plants (Ramaut 1955a, 1955b), and the production of humic and fulvic acids by decomposition of vegetation (McKnight *et al.* 1985; Perdue and Lytle 1983). Relatively little acid is excreted by growing *Sphagnum* (Clymo 1967) but large amounts may be produced during decomposition (Clymo 1984). Organic acids are generated by incomplete oxidation of decomposing organic matter as illustrated below:

$$(CH_2O)_n + O_2 + H_2O \longrightarrow RCOOH$$

$$RCOOH \longleftrightarrow H^+ + RCOO^-$$

Organic acids can make significant contributions to water acidity in swamps and bogs with pH as low as 3.0 to 3.4 (Moore and Bellamy 1974; Oliver *et al.* 1983; Veery 1975). Recent works showed that the production of organic acids was the dominant source of acidity for a large array of bogs inventoried in North America, Ireland and England (Gorham *et al.* 1984; Gorham and Detenbeck 1986; Hemond 1980; Urban *et al.* 1986). Hemond (1980) indicated that production of weak organic acids is within subsurface interstitial waters, where anaerobic conditions are prevalent.

The chemistry of organic acids in surface waters is different from that of mineral acids (Jones *et al*. 1986). Two important differences are that 1) organic acids can be an important pH buffer for waters in the pH 4.5-5.5 range; and 2) organic ligands chelate such metals as aluminum. The property of chelation of these organic ligands can protect peatland ecosystems by substantially reducing the toxicity of such metals as aluminum. On the other hand, very little is known about the direct effect of organic acids on biota.

C. Succession

In humid climates where precipitation exceeds evaporation, and where decomposition is slower than production, production of peat allows development of raised bogs. Slowly the peat surface is isolated from groundwater influences, and changes in water chemistry and vegetation occur. As a consequence, all the natural acidification processes described above are manifested, and they increase the acidity of the peatland. Gorham *et al*. (1986) enumerated these changes as follows:

> "As fens are converted into bogs pH declines sharply because of alteration in local hydrology. Removal of hydrologic inputs to a peatland from adjacent or underlying mineral soils cuts off the supply of bases that neutralize polyuronic acids produced by *Sphagnum* (Clymo 1986) and the complex, yellow-brown organic acids produced by decomposition of plant remains (Urban *et al*. (1986). Moreover, retardation of flow consequent upon removal of such hydrologic inputs allows

> organic acids to reach higher concentrations before being flushed from the peatland; surface waters of acid bogs are often distinctly more tea-coloured and higher in dissolved organic carbon (DOC) than waters of circumneutral fens (Glaser *et al.* 1981)."

Once initiated, the transformation of poor fen to acid bog is believed to be rapid as indicated by a bimodal pH frequency distribution for the vast peatlands of northern Minnesota, northern Swedish peatlands (see Figure II-2) and central Alberta peatlands (Turchenek *et al.* 1984). To explain this bimodal distribution, Gorham *et al.* (1986) suggested:

> As declining minerotrophic inputs of alkalinity are titrated away by organic acids from the decay process, acidity shifts quickly from a pH around 6 to a pH around 4, so that sites with intermediate pH values are relatively scarce. (see also Figure II-3; Gorham *et al.* 1984)

To date, there are no records of the actual change in pH as a fen is transformed into a bog. Although the complete transformation of one square meter of extreme rich fen to bog has been proven possible (Bellamy and Rieley 1967). Gorham *et al.* (1984) considered poor fens as one of the most sensitive peatland ecosystems to acid deposition because of their very low alkalinities, pH values of about 4.0 to 5.5, and lack of buffering capacity. Rich fens have higher buffering capacities, and bogs were also considered to be less sensitive as they are already highly acidic and, therefore, less likely to change in their acid-base chemistry.

D. Plant community succession along acidification gradients

Spatial analysis of peatland flora in northern and western Alberta (Horton *et al.* 1979; Slack *et al.* 1980; Vitt *et al.* 1975a), revealed marked changes in the nature of plant communities along natural gradients of acidity in peatlands. In that region, indicators of typical rich fen species includes *Tomenthypnum nitens, Scorpidium scorpioides, Drepanocladus revolvens, Sphagnum warnstorfii, Campylium stellatum, Utricularia intermedia, Calliergon trifarium, Tofieldia glutinosa, Drosera anglica,* and *Muhlenbergia glomerata*. In transitional fens, the mires are more likely to be dominated by species characteristic of intermediate conditions of pH a[illegible]lcium concentrations (e.g. *Drepanocladus vernicosus, D.* [illegible]*cus, D. polycarpus, Brachythecium mildeanum,* [illegible]*tentilla palustris, Carex diandra* and *C. lasiocarpa*). In poor fen conditions, many of these plants disappear and are replaced by such species as *Tomenthypnum falcifolium, Drepanocladus exannulatus, Sphagnum jensenii, S. angustifolium,* and *Rubus chamaemorus*. Finally in truly ombrotrophic conditions, species as *Sphagnum fuscum, S. magellanicum,* and *S. nemoreum,* dominate the peatland. Gorham *et al.* (1986) have also described similar species community shifts that would occur along gradient from minerotrophy to ombrotrophy for peatlands of northern Minnesota.

Changes in plant communities through time are also observed in peat cores. New developments in quantitative analyses of bryophyte stratigraphy in peat deposits (Janssens 1983; Gorham *et al*. 1986; Janssens and Glaser 1986) permit reconstruction in some detail of the transformation of circumneutral fens into acid bogs. In all these studies, one point is common; as fens are transformed into bogs species richness declines.

ii. ANTHROPOGENIC ACIDIFICATION

Acid precipitation, has not been mentioned in this chapter as a source of acidity in bog water. Sulfuric mineral acids were determined as the primary acid form in wetlands in New Jersey (Johnson 1979), Sudbury, Ontario (Gloooschenko and Stevens 1986), and in Belgium (Vangenechten 1981). Gorham *et al*. (1985) showed that the acidity of bog waters in northern England was dominated by strong mineral acids and the concentration of sulfuric acid deposited from the atmosphere was higher than the coloured organic acids. Earlier, Gorham (1958) had noticed that acidity of bog surface waters increased as one approached industrial centers in Britain. This raises the question what is the effect of acid precipitation (a relatively new acid component) on the dynamics of peatlands?

The purpose of this section is to review the literature dealing with possible effects of anthropogenic acidic substances on peatlands. The first part will focus on the effects of acidic deposition on vegetation - especially the bryophytes. The second part deals with chemical dynamics - particularly sulfur and nitrogen, as affected by acid rain. The third section will examine acid deposition effects at the ecosystem level.

A. Bryophyte sensitivity to air pollution

The dominant vegetation of peatlands (bryophytes) may be more vulnerable to acid precipitation than vascular plants. The leaves of bryophytes are one cell thick, have a thin or no cuticle and no stomates (Proctor 1979). Because of this direct contact with the atmosphere, they absorb required nutrients (Flint and Gregory 1969) and moisture from the atmosphere. Thus most terrestrial bryophytes are classified as being poikilohydric. Spearing (1972), Brown and Buck (1978a, 1978b,1979) and Buck and Brown (1978) have shown that mosses have a high cation exchange capacity in all parts of the plant. Since most mosses have poorly developed internal conducting tissue, external ectohydric capillary movements of liquid occurs along the stems and leaves. Whorled and overlapping leaf arrangements, as well as thick cell walls, are morphological adaptations for precipitation interception and moisture conservation. These morphological characteristics, evolved for direct response to the atmosphere, result in organisms susceptible to acid precipitation injury (Glime *et al.* 1984).

Lichens were first recognized and used as bio-indicators of atmospheric pollution in France and Britain (Grindon 1859; Macmillan 1861; Nylander 1866). During the late 1960's a strong correlation between the distribution of lichens and levels of air pollution was established (for a review see LeBlanc and Rao 1974). As the concept of bio-indicator species evolved, mosses were used successfully as indicators of air quality. Subsequently, bryophytes have been used more frequently for environmental studies (Gilbert 1970a, 1970b; Kauppi and Mikkonen 1980; Stefan and Rudolph 1979; Sundström and Hällgren 1973). With time, the techniques of bio-monitoring have become more refined. Examples include; using moss bags (see e.g., Temple *et al.* 1981); live tissue analyses to détermine metallic and non-metallic elements (Pakarinen 1978, 1981; Pakarinen and Tolonen 1976, 1977) and; *in situ* sampling of ombrotrophic mosses and lichens to avoid soil contamination (Glooschenko and Capobianco 1978; Glooschenko *et al.* 1981; Schell 1986). For review of the use of mosses and lichens as bio-indicators see LeBlanc and Rao (1974), Nash (1976a) and Richardson and Nieboer (1981).

In Canada, bio-monitoring studies using bryophytes have been conducted by LeBlanc and DeSloover (1970); LeBlanc *et al.* (1972a, 1972b) and LeBlanc *et al.* (1974). In Alberta, studies of bryophytes and lichens as bio-indicators were conducted by Addison and Puckett (1980), Case (1980, 1984), Kennedy *et al.* (1985), Nash (1973, 1976b) and Skorepa and Vitt (1976). Recently direct evidence of acid rain effect on lichens has appeared in the literature (Fritz-Sheridan 1985; Gilbert 1986; Lechowicz 1982). The physiological responses of bryophytes sensitive to SO_2 and other air pollutants have been studied (Winner and Bewley 1978a, 1978b; Winner and Koch 1982), but similar responses to acid precipitation are poorly decounted. The next sections will review what it is known about wet acid deposition effects on peatland vegetation.

1. Acid deposition on boreal mosses

Hutchinson *et al.* (1985) sprayed simulated acid rain (2:1 molar ratio of sulfuric to nitric acid) on the feather moss (*Pleurozium schreberi*) and lichens (*Cladina* spp.) of the boreal forest over a period of 5 growing seasons. The feather moss community was deleteriously affected (moss coverage, growth, chlorophyll content) by sprays of pH 2.5 and 3.0, and to a lesser extent by sprays of pH 3.5. Lichens were less sensitive. In laboratory experiments sprays containing sulfuric acid were more detrimental than nitric acid alone, or water sprays (pH 5.6). While ambient rains of pH 4.0-4.5 may not be harmful to the boreal mosses, it is apparent that occasional extreme acid rain events may be deleterious.

Glime *et al.* (1984, 1985, 1986) investigated laboratory and field responses of five boreal bryophyte species (*Dicranum polysetum, Hylocomium splendens, Pleurozium schreberi, Ptilium crista-castrensis* and *Rhytidiadelphus triquetrus*) to simulated acidic rain. Total chlorophyll concentrations, growth, and formation of side branches decreased in relation to increase in H^+ concentration of acid solution. At pH 2.5, moss chlorophyll was reduced in the two minutes following moist conditions. However, the authors give no indication of the ability of the moss to recover from these short episodes. In long term experiments, plants sprayed at pH 2.5 to 3.5 showed signs of chlorosis and the lower stem parts became necrotic, while pH 2.5 caused cessation of growth. Once again sulfuric acid treatments were more toxic than nitric acid treatments. Further additions of HNO_3 increased chlorophyll if the pH was not extremely low. These results were not too surprising as nitrogen is a limiting nutrient.

2. Experimental acidification of a peatland

Experimental acidification of a *Sphagnum*-dominated poor fen at the Experimental Lakes Area (ELA), Ontario indicated significant effects of acidification at the population and ecosystem level (Bayley *et al.* in press). As discussed earlier the poor fen was considered the most sensitive type of peatland in regard to acid precipitation by Gorham *et al.* (1984).

Acidification was carried out by irrigating the fen with simulated rain (pH 3) composed of 50% nitric acid - 50% sulfuric acid once a month. The acid-loading to the site was equivalent to reducing the mean annual pH of precipitation from 5.0 to about 4.0, a value typical of northeastern American rainfall. An unacidified portion of the site served as a control and received an equal volume of water without acid (Bayley *et al.* in press).

Three dominant *Sphagnum* species (*S. angustifolium, S. fuscum* and *S. magellanicum*) were monitored for growth. Initial years of acidification resulted in an increase of stem length for the species growing in the oligotrophic part of the mire. In the minerotrophic area, only the hummock-top species, which are isolated from ground water influences, showed an increase in growth due to acidification (Bayley *et al.* in press).

3. European investigations

In natural peatlands of Britain, *Sphagnum* species are now largely absent from the blanket bog vegetation of the southern Pennines, where in the past they were the dominant peat-formers (Moss

1913; Pearsall 1950; Tallis 1964). The disappearance of *Sphagnum* plants in that area is correlated with atmospheric pollution caused by the Industrial Revolution of the last 200 years. Today only *S. recurvum*, which has a wide ecological amplitude, is widespread and abundant. *Sphagnum imbricatum* occurs in abundance as sub-fossil remains in peat mires throughout the British Isles, but it is rare today (Green 1968). The exact conditions under which it thrived in the past remain an enigma.

Ferguson et *al*. (1978) and Ferguson and Lee (1979, 1980) showed that the same *Sphagnum* species studied by Tallis (1964) were susceptible to both acid rain and sulphur pollutants. These workers measured a range of concentrations of HSO_3^-, SO_2, SO_4^{2-} (within the ranges detected in British precipitation) which caused a diminution in chlorophyll content, inhibition of photosynthetic carbon fixation, inhibition of growth, and in some cases death of the mosses. Low concentrations of these chemicals stimulated growth. They suggested that past fallouts of SO_2 and its derivatives could explain the disappearance of *Sphagnum* species from the mires.

Transplant experiments have verified that *Sphagnum* still cannot survive naturally in polluted British sites. Transplants of *Sphagnum* from an uncontaminated site to the polluted sites in the southern Pennines barely thrived or died (Ferguson and Lee 1983a). Since the mean annual concentrations of sulphur dioxide in the southern Pennines have fallen in the past decades (Ferguson and Lee 1983b), SO_2 toxicity alone is unlikely to account for the paucity of *Sphagnum* or for the failure of transplants. It has been suggested that detrimental effects were probably the result of an interaction between present atmospheric nitrogen and sulphur pollutants (components of acid rain) with the legacies (soot particles) of previous pollution episodes which are accumulated in the surface peats (Ferguson and Lee 1983a).

In a review of the responses of ombrotrophic mires to acidic deposition, Lee *et al.* (1986) pointed out the increasing importance of the present-day nitrogen supply from the atmosphere. Increases of the concentrations of nitrate in both air and rain have been observed in recent decades in UK and North America (Brimblecombe and Stedman 1982; Salmon *et al.* 1978). The effects of these new inputs of nitrogen on peatlands could be important because ombrotrophic mires are nitrogen deficient habitats (Damman 1986). *Sphagnum* species are adapted to nitrate-nitrogen and there is evidence that ammonium inhibits nitrate uptake (Press and Lee 1982; Woodin *et al.* 1985). However low concentrations of both ions (NH_4^+ and NO_3^-) are not detrimental (Rudolph and Voigt 1985). Woodin, Press and Lee (1985) demonstrated that natural atmospheric nitrogen deposition in Sweden induced the nitrate reductase activity in *Sphagnum fuscum* plants, but repeated additions of nitrate caused a gradual inhibition of the induction the enzyme. Ferguson *et al.* (1984) transplanted five *Sphagnum* species from an unpolluted site in North Wales to a polluted site in the southern Pennines. Tissue analysis showed changes in element concentrations, particularly increases in total nitrogen, within a few months. In another project, concentrations of nitrate and ammonium within the range measured in southern Pennine bulk deposition failed to stimulate and even reduce the growth of *Sphagnum cuspidatum* in laboratory experiments (Press *et al.* 1986; Lee *et al.* 1986).

In summary, transplants of *Sphagnum* mosses in a nitrogen-rich atmosphere of the southern Pennines, showed poor growth, rapid and massive accumulation of nitrogen in their tissue, and marked change in nitrogen enzyme activity. These results suggest that other or some factor associated with NOx pollution as well as sulphur pollutants can affect the growth and metabolism of ombrotrophic *Sphagnum* species and, hence, the ecology of mires. In conclusion, Lee *et al.* (1986) emphasized that for further studies it will be important to consider interactions between sulphate, nitrate and ammonium ions on the growth of *Sphagnum* species and the ecology of ombrotrophic mires.

In some lakes of Sweden, acidification has led to progressive, oligotrophication (Cowling 1982; Cowling and Linthurst 1981; Haines 1981), where macrophyte communities dominated by *Lobelia* and *Isoetes* have regressed and been replaced by *Sphagnum*-dominated communities during the last decades (Grahn 1986; Grahn *et al.* 1974). Grahn (1977) showed a correlation between pH and *Sphagnum* occurrence. He stated that the *Sphagnum* appearance in lakes was correlated with the deposition of airborne acid substances. It is possible that *Sphagnum* may alter the lake water chemistry due to its acidifying properties and may lead to reduced nutrient cycling and lowered aquatic productivity. According to Grahn *et al.* (1974), several important ions are bound to the CEC sites in the *Sphagnum* mat and thereby unavailable to other organisms. Because *Sphagnum* mosses are very poor substratum for aquatic organisms, the life conditions for many members of the lake-bottom fauna deteriorated. Takeover by *Sphagnum* has been reported once in North America, at Lake Golden in New York State by Hendrey and Vertucci (1980).

Similarly, *Drepanocladus fluitans* and *Leptodictyum riparium* (acidophilic bryophytes) have been observed to cover lake bottoms (Gorham and Gordon 1963).

In the Netherlands, some macrophyte communities belonging to heathland vegetation and oligotrophic soft waters have declined during the last 30 years (Roelofs 1983; Shuurkes *et al.* 1986). The observed changes in macrophytes appeared to be caused by airborne sulphur and nitrogen (ammonium) deposition (Roelofs *et al.* 1984). Roelofs (1986) concluded that: 1) acidification of oligotrophic, poorly buffered heathland soils as a result of acid precipitation leads to a reduction in species richness; 2) acidification of water above a carbonate-free sediment leads to disappearance of all submerged macrophytes due to lack of carbon dioxide, and; 3) acidification of a water body above a sediment containing little carbonate, as a result of ammonium-containing precipitation, leads to suppression of the isoetid plant community by luxuriant growth of *Juncus bulbosus* and/or *Sphagnum* species as a result of increased carbon dioxide and ammonium levels (see also Schuurkes *et al.* 1986) in the water layer.

A study of old (ca 1920) and recent (1978) diatom assemblages from 16 Dutch moorland pools showed that acidification of humic poor moorland pools reduce diatom diversity (van Dam [illegible] *al.* 1981). In Belgian boglakes, acid sulphur-rich precipitation (wet and dry) lowered the pH and increased sulphate concentrations (Vangenechten and Vandergorght 1980; Vangenechten *et al.* 1984). Present water conditions of these moorland pools were unfavorable for most freshwater fish and algal communities were impoverished.

B. Acid deposition effect on the biogeochemistry of peatlands

Surface bog waters from Manitoba to Newfoundland have lower concentrations of nitrate and sulphate than precipitation despite the concentrating effect of evapotranspiration (Urban *et al.* 1986). Urban *et al.* (1986) also noticed a subtle shift in organic versus mineral acidity produced, with the importance of mineral acidity increasing eastward along the transect. These findings suggest that acid rain components are interacting with peatland ecosystems. In this section, nitrate and sulfate relationships within peatlands are documented, followed by a discussion of peatlands as potential sources of acidity for aquatic ecosystems.

1. Nitrogen dynamics

Nitrogen has been characterized as playing a dual role in the ecology of *Sphagnum* bogs (Urban and Bayley 1986). Nitrogen is often considered as a limiting nutrient in many North American bogs (Moizuk and Livingstone 1966; Tilton 1978; Watt and Heinselman 1965). On the other hand, supply of nitrogen from British precipitation is known to damage *Sphagnum* and probably prevents many bryophyte species from recolonizing the mires of southern England (Lee *et al.* 1986). Nitrate is efficiently retained within peatlands (Hemond 1983; Moore 1978), except for polluted British sites (Lee *et al.* 1986) as noted previously. The data of Bayley *et al.* (in press) also show that peatlands are an efficient sink for nitrate in an experimentally acidified peatland. Nitrate throughout the year was undetectable in surface water and outputs of nitrate were only 0.4% of inputs (Figure II-4). The major mechanism of uptake is not known.

Urban and Bayley (1986) proposed three possible mechanisms of nitrogen transformation in peatlands: denitrification, assimilation by plants, and dissimilatory reduction to ammonium. Bayley *et al.* (in press) observed little increase in ammonium in their water chemistry, indicating that the process of dissimilatory NO_3^- reduction is probably negligible. In contrast, Hemond (1983) suggested that dissimilatory reduction to ammonium may be important in a Massachussetts bog. No direct measurement of this process has yet been made in peatlands. Background rates of denitrification were very low at Marcell bog (Minnesota) and ELA site (Urban *et al.* in reivew) and no denitrification response to the acid application at ELA was detected. These later results suggest that plant uptake is probably the major sink for NO_3^- deposited by rainfall.

Vascular plants in acidic habitats, chiefly Ericaceae, have a restricted ability to utilize nitrate (Havill *et al.* 1974). *Sphagnum* species, however, have been shown to utilize nitrogen in the NO_3^- form. In a field experiment, Bayley *et al.* (in press) demonstrated that the nitrate in an acid spray was removed during the time the water flowed from the top of the *Sphagnum* mat to a funnel beneath the mat, i.e., within 10 cm. These field results were confirmed by laboratory experiments. Three *Sphagnum* species were soaked in acid spray medium (668 ueq) in glass jars (Bayley *et al.* in press). Within 20 hours, 100% of the nitrate from the water was removed (see Figure II-5). Similar results were obtained with non-living plant material, therefore passive ion exchange was hypothesized as an important mechanism controlling this uptake.

The uptake of NO_3^- by vascular plants results in the release or exchange of OH^- ion (Reuss 1977), suggesting that H^+ from nitric acid in rainfall would be neutralized by the subsequent uptake of NO_3^-. Studies of NO_3^- uptake with *Sphagnum* are needed to evaluate if the later process also occurs in peat. At present, the above studies suggest that the deposition of anthropogenic nitrate ($H^+NO_3^-$) is fertilizing North American peat bogs. This is in direct contrast to the situation in England where nitric acid fallout is detrimental to the British mires. More investigations are needed to determine the threshold of toxicity at which nitrate changes from being beneficial to detrimental in peatland ecosystems.

Ammonium is also an important pollutant in Canada (Barrie and Sirois 1982). Ammonium deposition seems to be largely retained by most catchments (Jones *et al.* 1986) including wetlands, but the effects of ammonium on the chemistry of peatlands are poorly understood.

2. Sulfur dynamics

Sulfate retention within North American bogs ranges from 22% to 90% on an annual basis (Bayley *et al.* 1986; Urban *et al.* 1986). Experimental acidification of the ELA peatland with H_2SO_4 increased the annual retention of SO_4^{2-} (Bayley *et al.* 1986). A decrease in SO_4^{2-} concentrations as water passes through a wetland has been noticed in other studies (Braekke 1981a; Kerekes *et al.* 1986a; Rippon 1980; Vitt and Bayley 1984; Wieder and Lang 1982, 1984). For example, Vitt and Bayley (1984) indicated that concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^--N and alkalinity were significantly lower upon leaving an oligotrophic fen than when entering it, while hydrogen ion concentration was significantly higher (and pH lower) when leaving the fen. Sulfate is more mobile than nitrate and penetrates more deeply into the peat. This greater mobility of sulfuric acid may, by different processes, result in changes or damage to peatlands.

Sulfuric acid toxicity to vegetation has been recognized by Ferguson *et al.* (1978), Glime *et al.* (1984), and Hutchinson *et al.* (1985). However, alkalinity may also be generated through sulfate reduction. The anaerobic reduction of sulfate to sulfide (H_2S) requires low oxygen levels and a fixed carbon energy source, as it is carried out by heterotrophic anaerobic organisms (Reuss 1977). Such conditions are encountered in peatlands. Consequently, high concentrations of sulfide compounds may accumulate, and produce alkalinity, as H^+ ions are consumed. An increase in sulfate reduction rate can significantly increase the rate of peat oxidation (Hemond 1980). However sulfate reduction might not be sustained indefinitely as an accumulation of hydrogen sulfide in the water could reach toxic levels. Accumulation of sulfide may also produce an acid pulse either after periods of drought (Bayley *et al.* 1986; Bayley and Schindler 1986) or seasonal drawdowns (Gorham 1956). Aeration of anoxic soils may result in rapid acidification, as H^+ are released during the oxidation of sulfide to sulfate (Braekke 1981b, c). If heavy rain follows, some sulfuric acid is exported. During periods of sulfate flushing, concurrent stripping of other cations may occur (Braekke 1981b, c). Bayley *et al.* (1986) demonstrated that the sulfate released in an autumn sulfate pulse was accompanied by the release of Ca^{2+} and Mg^{2+}, but was not accompanied by H^+ release in this unpolluted northwestern Ontario site.

Sulfate retention is dependent on seasonal changes in hydrology. Therefore one may question to what extent sulfate retention process is actually a permanent sink of acidity. Jones *et al.* (1986) suggested that it was at least a partial permanent role since all peat deposits contain sulfur.

3. Peatlands as potential sources of acidity in lakes

Many peatlands in North America produce and export organic acids, causing streams and lakes to become tea-coloured (DOC > 10 mg L^{-1}; Gorham *et al.* 1986). Such streams and lakes often lie on noncalcareous substrata (markedly igneous and metamorphic rocks of the Precambrian Shield) with little buffering capacity (calcium about 50 ueq L^{-1}). Gorham *et al.* (1985) have called attention to the fact that "brown" acidic water can affect streams and lakes:

> Even in cases where their bicarbonate buffering capacity can accommodate a natural acid input from bog drainage, such lake waters may be especially susceptible to acid deposition from urban/industrial sources of air pollution, because further acid input can readily drive the pH down to levels toxic to the biota.

In Halifax County, Nova Scotia, lake acidification is due not only to acid deposition from the atmosphere but also to inputs of coloured organic acids from bogs or peaty catchments (Gorham *et al.* in prep.; Kerekes *et al.* 1986a). Even if the organic acids are natural contributors to the acidity of these coloured waters, anthropogenic sulfur may further increase the acidity of these waters, particularly at times of high discharge and snowmelt (Kerekes *et al.* 1986b; LaZerte and Dillon, 1984). These increases in acidity of streams and rivers can prove detrimental to fish (Brown 1980; Sjörs 1980). Kerekes *et al.* (1986a) believed that the additional anthropogenic acidity in coloured, organic waters probably contributed to the reported decline of Atlantic salmon in rivers in southwestern Nova Scotia (Farmer *et al.* 1980). However, it is unknown if wetland acidity pulses have increased in number or magnitude with increased acid rain. No accompanying release of heavy metals or trace metals (Al, Cu, Fe, Mn, Zn) from these acid pulses has been reported.

C. Peatland ecosystem responses to acidification

The sensitivity of peatlands to acid deposition remains a subject of controversy. Acidic deposition could accelerate the acidification process of natural peatlands. Gorham *et al.* (1986) presented a conceptual model showing the possible effects of anthropogenic acid deposition on a poor-fen (see Figure II-6).

> Even in peatlands where uptake and reduction lower nitrate and sulphate concentrations well below those in atmospheric precipitation, acid deposition can perhaps leach surface peats above the water-table (in fens vulnerable to acidification) to the point that *Sphagnum* invasion is either initiated or accelerated. If that happens it is likely to cause further autogenic acidification as *Sphagnum* generates polyuronic acids, peat rises above the groundwater-table, minerotrophic inputs to the

> peat surface are cut off, and the slowing of water flow allows the build-up of soluble, coloured organic acids produced during decomposition.

Peat plateaus and palsa bogs influenced by permafrost are components of northern America that may be affected more rapidly by acidification as the frozen ground restricts the volume of peat accessible to acid deposition. Consequently microbial reduction and sources of minerotrophy are reduced, and the neutralizing capacity of the system is diminished (Gorham *et al.* 1984).

Hemond (1980) pointed out that sulfate reduction and nitrate uptake have increased considerably in North American peatlands since the period before acid rain. These processes may have prevented mineral acidification of bogs which would otherwise have occurred. But he recognized that there is no mechanism for the protection of above ground biota against acid precipitation, and there is also a limit to the extent to which the system can be theoretically protected.

Increased atmospheric deposition of strong acids may have an affect on nutrient availability in peatlands. Oligotrophic peat has a low degree of base-saturation, and such cations as Ca, Mg, K and NH_4 are available from the adsorbed phase rather than the water solution (Gorham 1967; Clymo 1983). An increase in H^+ ions caused by mineral acids could displace the nutrients on the peat exchange complex and nutrients will be more difficult to obtain for plant growth.

CONCLUSION

At present, there is uncertainty concerning the sensitivity of peatlands to acid deposition. Evidence suggests that nitrate and sulfate deposition are neutralized by plant uptake and microbial reduction, but this neutralization may be limited. More investigations are needed to establish the degree to which nutrient uptake and microbial reduction can mitigate acidification processes (Gorham *et al*. 1984). Laboratory investigations by British workers revealed that *Sphagnum* is affected by ambient levels of acid precipitation. To date, no data on the effect of acid deposition on wetland vegetation in North America are available.

The acid precipitation problem in recent years has stimulated research in peatland hydrochemistry although our understanding remains primarily descriptive. The processes that play the most prominent roles in controlling alkalinity and acidity in peatlands are (1) sulfate, nitrate, and ammonium retention, (2) production of organic acids via decomposition and, (3) assimilation (biological uptake). Careful examination of the acidity/alkalinity budgets of peatlands is needed to identify sources and sinks of acidity and to enable the relative rating of the importance of acid deposition in peatland acidification.

More specifically the biogeochemical cycles of sulfate and nitrate within peatland ecosystem need to be examined carefully. Nitric and sulfuric acids are the main mineral acids forming our acidic precipitation in North America, and nitrate and sulfate are known to undergo significant transformations within peatlands. ✓

Sulfate is dynamic in the first 30 cm of the peat (including at least 10 cm below the water table). Sulfate within a peatland system can be reduced, reoxidized, assimilated by the vegetation, and markedly influenced the ionic flux in the peat. All these transformations are dependent on the hydrological state of the system. We need to develop a model to understand the dynamic of sulfur for the first 20-40 cm of a peat system where 1- sinks and sources of sulfur will be quantified, 2- different chemical forms will be identified, 3- exchange rate or flux between water, vegetation and peat will be measured, and 4- hydrological data will be included. Some aspects of sulfur dynamics in peatland have been treated by Behr (1985), but our knowledge of sulfur biogeochemistry is still insufficient to formulate a model.

Nitrate is an anion less mobile than sulfate. As an important nutrient, nitrogen cycling is closely coupled with the peatland vegetation. The various nitrogen-plant interactions (mainly nitrate with mosses) needs more investigations to determine 1- nitrate uptake rate by *Sphagnum* mosses, 2- physiologically where nitrate is used or stored, and 3- the concentrations when nitrate or ammonium become toxic to plants.

Our understanding of the effects of acid precipitations will be closely related to our knowledge of sulfur and nitrogen behaviour in peatland ecosystems. I believe that elaboration of basic models of biogeochemical cycling of sulfur and nitrogen will help us to predict the effects of new inputs of nitrates and sulfates coming acid precipitations.

Along with developing models of nitrogen and sulfur cycling, the concept of indicator species should be developed to assist in determining the degree of natural or anthropogenic acidification of a given peatland.

Figure II-1 has been removed because of the unavailability of copyright permission. Figure II-1 represented the Ecosystem processes and the pathways of chemical inputs and outputs in an idealized peatland. From Gorham, E., S. E. Bayley, and D. W. Schindler, 1984. Can. J. Fish. Aquat. Sci. 41:1256-1268.

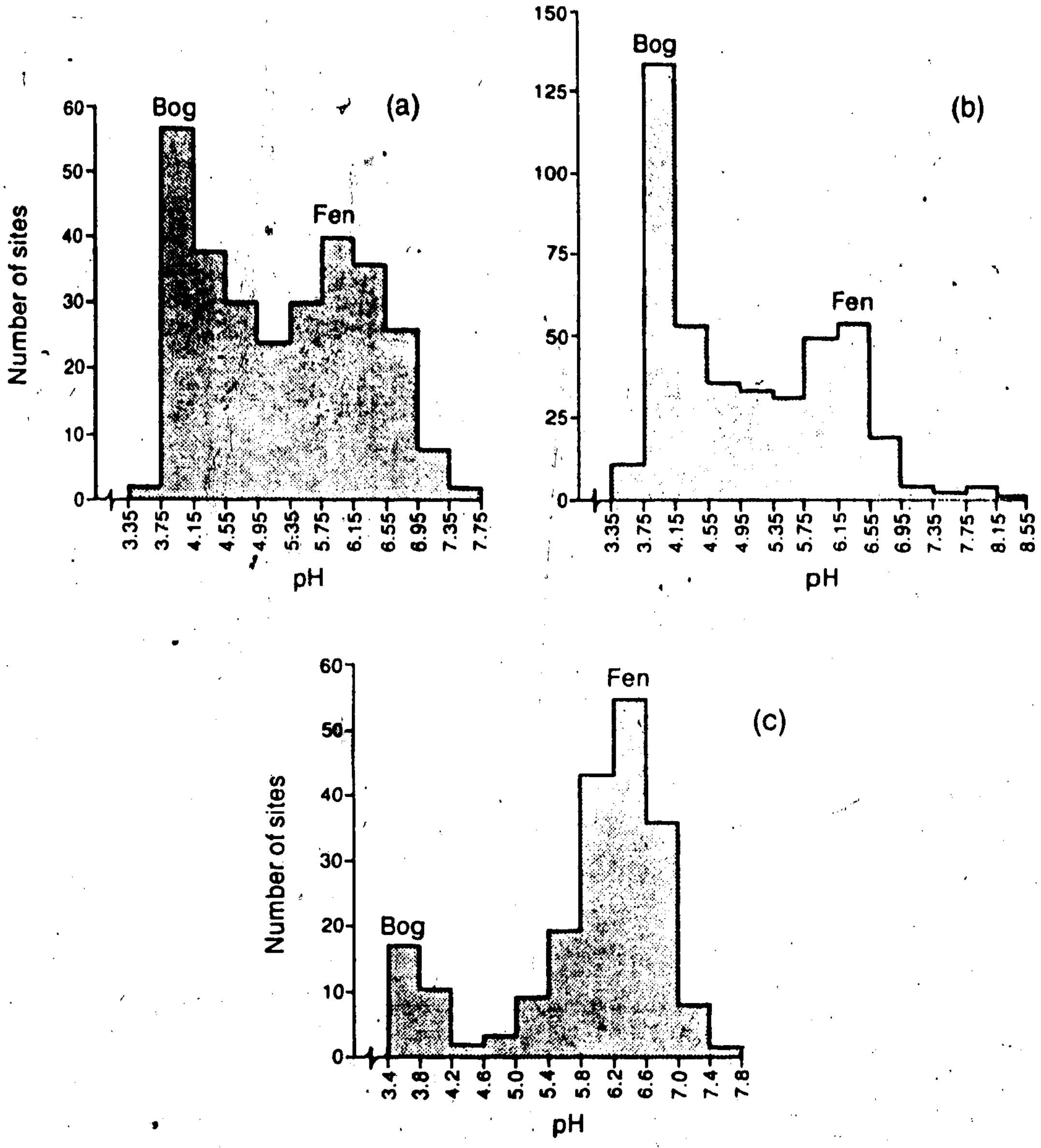

Figure II-2. Frequency distribution of pH in surface waters collected from the different plant communities of peatlands in (a) northern Minnesota (b) northern Sweden and (c) central Alberta. Minnesota data from Gorham *et al.* 1984; Swedish data from Sjörs (1952); Alberta data from Turchenek (1984).

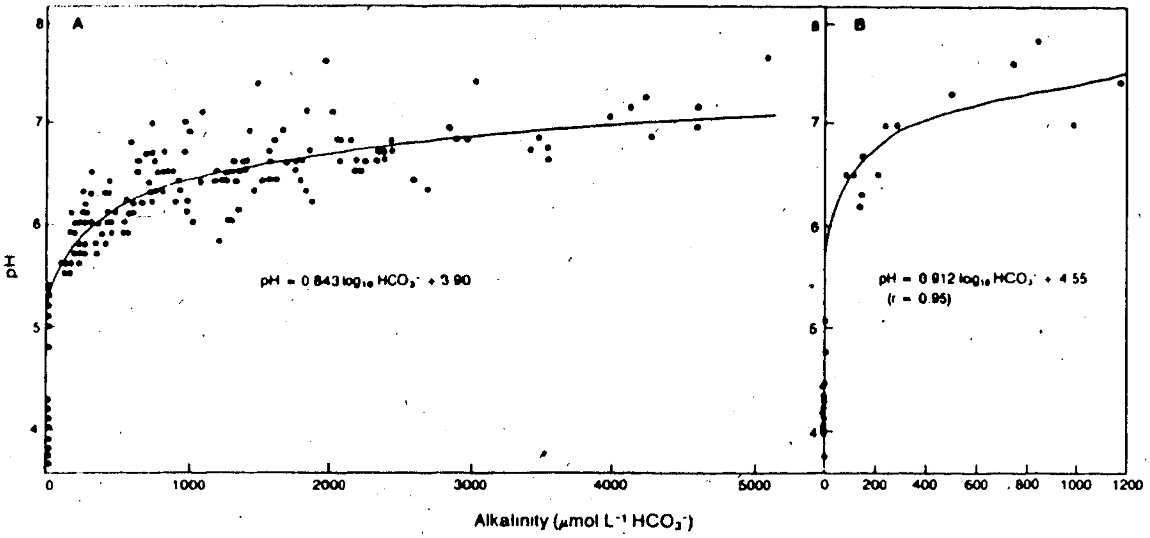

Figure II-3. Relationship between pH and alkalinity in surface waters from fen and bog sites A) in Athabasca area, central Alberta and B) in the English Lake District (regression for 15 waters with some bicarbonate present). Data from Turchenek (1984) and Gorham *et al.* (1984).

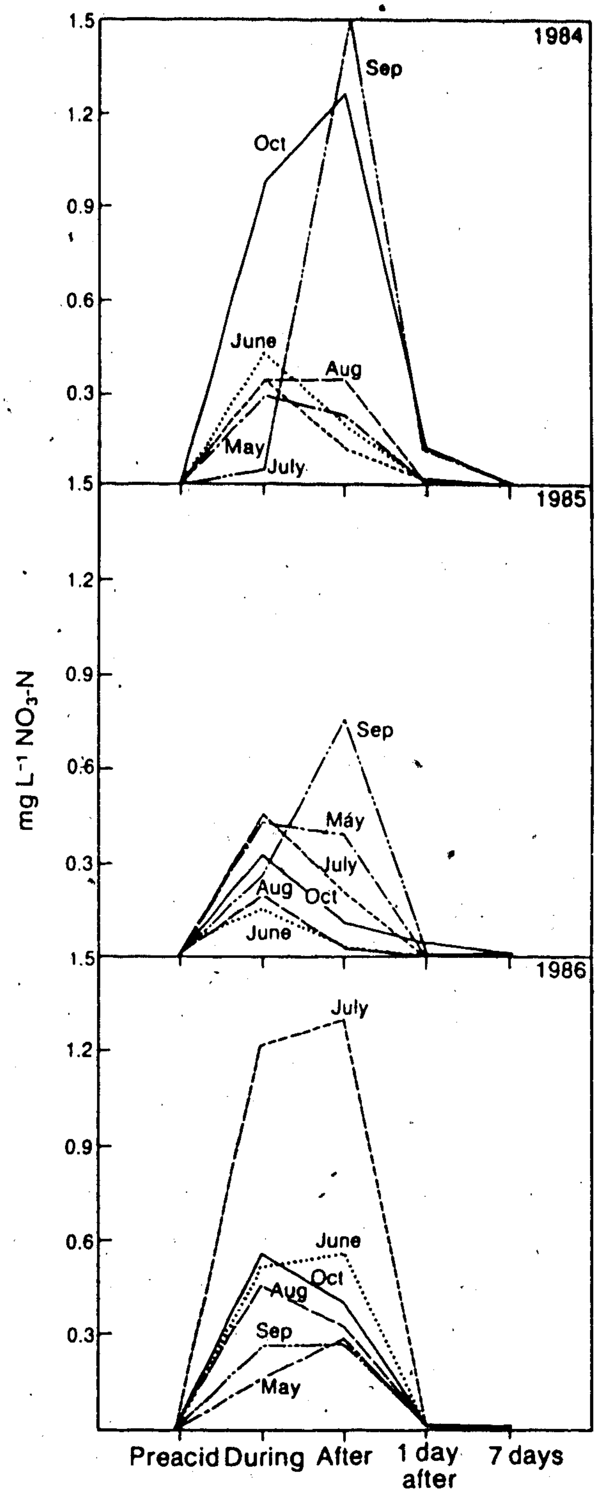

Figure II-4. A) Concentration of NO_3-N in the oligotrophic central pool before and after acidification experiments. Samples collected prior to acidification, two hours after the start of acidification (during), just after, 1 day after and 7 days after acidification. Data from Bayley *et al.*, in press.

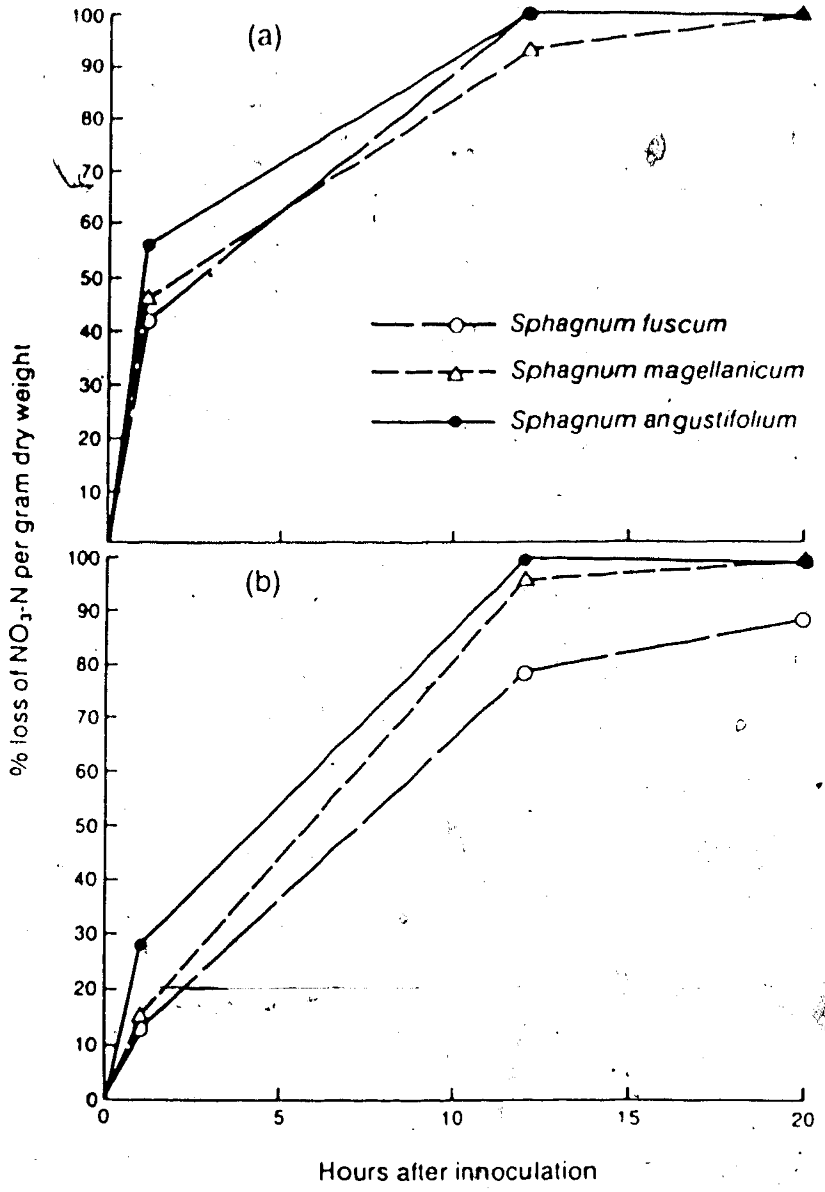

Figure II-5. A) Removal of NO$_3$ from water containing live green *Sphagnum*. B) Removal of NO$_3$ from water containing brown stems of *Sphagnum*. (Data from Bayley *et al.*, in press).

Figure II-6 has been removed because of the unavailability of copyright permission. Figure II-6 represented A conceptual model of the chemical and biological effects of acid deposition upon a fen vulnerable to acidification. From Gorham, E., J. A. Janssens, G. A. Wheeler, and P. H. Glaser. 1986. *In*: Hutchinson T. C. and Meema K. M. (eds). Effects of acid deposition on forests, wetlands, and agricultural ecosystems. J. Wiley and Sons, NY.

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III. EFFECTS OF SIMULATED ACID RAIN ON TOMENTHYPNUM NITENS AND SCORPIDIUM SCORPIOIDES IN A RICH FEN[1]

Introduction

The phenomenon of acid deposition is an environmental issue of high priority in Canada. Considerable attention has focused on the recognition and assessment of the effects of acid deposition on terrestrial and aquatic ecosystems. In contrast, little research has been done regarding the sensitivity of peatlands to acid deposition (Gorham *et al.* 1984) or on the bryophytes inhabiting these ecosystems. In Alberta, acid deposition is not as se[illegible] in eastern North America, but can be regionally important in west-central Alberta where sour gas plants are located and in the north with the exploitation of oil sands (Addison *et al.* 1984; Legge *et al.* 1980; Sandhu *et al.* 1980; Summers and Whelpdale 1976). In these areas, extensive peatland ecosystems occur, hence a preliminary evaluation of the sensitivity of their vegetation to acid deposition is warranted.

In Alberta, fens are the most common type of peatland largely due to the calcareous nature of the bedrock and the continental climate.

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[1] A version of this chapter has been submitted for publication. Rochefort, L. and D. H. Vitt. The Bryologist.

Many of these fens in the foothills and northern Alberta are transitional and extreme rich fens (Slack *et al.* 1980; Vitt *et al.* 1975). Rich fens are peatlands influenced by groundwater with a high cation content (Gorham 1967), and species richness is relatively high (Sjörs 1950, 1961, 1963). Eutrophic systems (including rich fens) are usually rated as insensitive to acidification, because the relatively high base cation content of surface waters sustains a high buffering capacity in the system (Anderson 1986, Gorham *et al.* 1984).

In this study, I investigated the effects of simulated acid rain on the vegetation of an extreme rich fen, as I believed that surface vegetation could be affected by acid deposition even if the organic soil and the overall ecosystem was well buffered.

Brown mosses (largely members of the family Amblystegiaceae) form a large part of the dominant vegetation of rich fens. Bryophytes are ideal organisms to assess potential effects of atmospheric pollutants (Raeymaekers and Glime 1986; Rao 1982), because they possess structural characteristics that make them vulnerable. For example 1) their leaves are generally one cell thick and have a thin or no cuticle and no stomata (Proctor 1979); 2) many species are poikilohydric (their water content directly reflects environmental conditions); 3) they generally have poorly developed internal conducting tissue; and 4) many species are dependent on atmospheric deposition for nutrient uptake (Anderson and Bourdeau 1955). In this study, the brown mosses, *Tomenthypnum nitens* (Brachytheciaceae) and *Scorpidium scorpioides* (Amblystegiaceae), were selected to investigate effects of simulated acid rain on rich fens.

In addition to acidification experiments in the field, two growth chamber experiments were undertaken to determine at which pH level "acid rain" is deleterious to plant growth and which component in "acid rain" is most detrimental to growth and chlorophyll content of the moss.

Study area

The experimental field site is located 50 km northwest of Edmonton, Alberta (Canada) at 53° 42′ N latitude and 113° 57′ W longitude (Figure III-1). The climate of the area is boreal cold temperate (Climate type VIII, Walter and Lieth 1960) with cold winters and cool summers receiving a mean annual precipitation of 538 mm (means of three meteorological stations: Edmonton-Stony Plain, Glenevis, and Sion; Alberta Environment, 1951-1980). The mean summer temperature is 12.0° C with a range of 10.5° C to 14.0° C, and the mean December to February temperature is -15.5° C, with a range of -11.5° C to -23.5° C. The mean frost free period is 85 days. The site is in the Boreal Mixedwood ecoregion as defined by Strong and Leggat (1981).

Approximately 43% of the province of Alberta is composed of the Boreal Mixedwood. This ecoregion is dominated by *Populus tremuloides* and to a lesser extent *Populus balsamifera*, both of which occur on medium textured, moderately to well drained soils. The ecoregion represents a transitional zone between the Aspen Parkland and Mixed Conifer-Deciduous ecoregions to the north and west.

Methods

Water chemistry

Surface waters from 3 flarks were sampled every two weeks during the 1986 ice-free season. Conductivity and pH were measured in the field using an Aqua-Digitester (Extech). Ammonium and NO_3-N were analyzed within 24 hours using a Technicon Autoanalyser as described in Stainton *et al.* (1977). Sulfate was measured by a turbidimetric method with corrections made for color (American Public Health Association 1980). Elements were analyzed by inductively coupled argon plasma spectrophotometry.

Vegetation sampling

A systematic sampling technique was used to characterize the experimental site. A transect of 20 1 m x 1 m quadrats positioned every 5 m was oriented perpendicular to the long axis of strings. Additionally, two transects each with 5 quadrats, oriented parallel to a string and a flark were sampled. Cover was estimated to the nearest 5% (beginning with 1%) by the canopy method (Daubenmire 1959; Vitt *et al.* 1975). Vegetation data were analyzed using the program TWINSPAN (Hill 1979). Voucher specimens were collected and deposited in the University of Alberta Herbarium (ALTA). Authority names and nomenclature follows Packer (1983) for vascular plants; Vitt and Andrus (1977) for *Sphagnum*; and Ireland *et al.* (1980) for mosses.

Experimental design

The experimental design consisted of three treatments, a simulated acid rain addition, a rainwater addition, and a control (no water addition) applied to two dominant brown mosses *Tomenthypnum nitens* and *Scorpidium scorpioides*. Each treatment was replicated nine times and organized in a randomized block design (Hurlbert 1984). A boardwalk of wood was constructed to reduce disturbance to the vegetation and hydrology.

'Rainwater' treatments were made by adding Ca, Cl, NH_4, NO_3, Mg, SO_4, and K to deionized water to reproduce natural rainfall occurring in Alberta (Table III-3), with a mean pH of 6.0. The purpose of the field experiment was to treat the two brown mosses with rain simulating summer precipitation from eastern Canada and United States (pH 3.5 and composed of 50% nitric acid - 50% sulfuric acid; Likens *et al.*, 1979; Brimblecombe and Stedman, 1982). , hence, the mosses received a total loading of H^+ equivalent to what they should received in one year under rain of pH 3.5. Based on a mean annual precipitation of 530 mm (Alberta Environment, 1980-83) and on mean natural pH of 6 (from Edson and Fort McMurray; AES, 1980-83), 10.4 meq of HNO_3:H_2SO_4 were added annually to each quadrat (25 cm x 25 cm) which represents a loading rate of 1.[illegible]6 g m^{-2} yr^{-1} of NO_3-N and 4.00 g m^{-2} yr^{-1} of SO_4. The simulated acid rain treatment was prepared by adding HNO_3:H_2SO_4 to the rainwater solution as prepared above. The plots were irrigated every 5 days with 1 L of solution through a 'shower plexiglass device'. Natural precipitations were not prevented to reach the sampling plots.

Growth measurements

Strips of velcro were attached near the stem apices of seven randomly selected moss plants per field plot. Length increments of the moss relative to the apical portions of the velcro were recorded in April, July, and October 1986. For *Scorpidium scorpioides*, stem length, the number of branches, and the total length of branches above the velcro were recorded. For *Tomenthypnum nitens* only stem length was recorded.

Chlorophyll analysis

Stems of *Tomenthypnum nitens* and *Scorpidium scorpioides* were collected before, during, and after the experimental acidification. Three stem tips were randomly sampled in each plot, cut two cm from the tip, placed in paper packets, air dried for 24 hours and stored in the dark until analysis of chlorophyll content. Dry mosses were weighed and chlorophyll was extracted in sealed tubes with 5 ml of dimethyl sulphoxide (DMSO) (Burnison 1980; Hiscox and Israelstam 1979; Raeymaekers and Longwith in press; and Shoaf and Lium 1976), for 16 hours at 65 °C without grinding. Spectrophotometric readings were taken with a SP6-550 UV/VIS PYE UNICAN model spectrophotometer at 750 (turbidity), 665 (Chl. a), and 645 (Chl. b) nm against a DMSO blank. The extract was then acidified with 4 ul concentrated HCl for 4-5 min., and the absorbances reread at 750 and 665 nm. This addition of HCl resulted in a final concentration of 0.012 N HCl as recommended by Marker (1972).

The equations of Lorenzen (1967) were used to calculate the concentration of chlorophyll a and pheophytin a using the Jeffrey and Humphrey (1975) extinction coefficient. Calculations for chlorophyll b were done according to Arnon's equation (Arnon 1949).

Growth chamber experiments

Tomenthypnum nitens and *Scorpidium scorpioides* mosses were collected in the fall of 1985 and 1986, placed in plastic bags and stored in the dark at 5 °C. Both species were grown in natural fen water. After two weeks of acclimation, velcro strips were tied to fifteen individual plants per treatment and the length from the top of the velcro strip to the tip of the moss was recorded with calipers. For two months, growth of the mosses was monitored in four treatments 1) control (natural fen water at pH 8.0), 2) pH 3.5, 3) pH 3.0, and 4) pH 2.5. For this first experiment, treatments were not replicated. Treatments were prepared with a ratio of 50% H_2SO_4 – 50% HNO_3 on an equivalent basis. Plants were grown in a growth room with 12 hours light-darkness, a temperature of 16 to 18 °C and a relative humidity of 65% to 75% during the light period, 8 to 10 °C and 85% to 95% relative humidity during darkness, and a light intensity of 240 umol m^{-2} sec^{-1} using High Pressure Discharge (H.I.D.) lamps with a proportion of 40% high pressure sodium (400 W) and 60% high pressure mercury vapour (metal halide – 400 W).

Based upon the results of the first experiment, a second experiment with replication was conducted with *Tomenthypnum nitens*. The growth chamber conditions were the same as in the first experiment, but clusters of *T. nitens* were planted at natural density in opaque plastic pots (11.2 cm in diameter) in order to control algal growth. The plastic pots had holes at the bottom to drain the spray treatment into an outer container. This also maintained a higher relative humidity around the mosses. Five acidic treatments adjusted to pH 3.3 were applied in 3 replicates: 1) control (natural rainwater, pH 6.0),

2) H_2SO_4, 3) HNO_3, 4) $H_2SO_4 + HNO_3$, and 5) HCl. The spray media were prepared as in the field acidification. Two hundred ml of solution were sprayed twice a week for 13 weeks to reproduce the loading of one year of precipitation of field conditions. Twice a week the plastic pots were randomly moved. For growth measurements, 7 threads were tied per pot around randomly chosen individuals.

Statistical analysis

Data for growth, chlorophyll a and b, and pheophytin a were tested for normality and homogeneity of variances by a non-parametric Kolmogorov-Smirnov and Bartlett-Box *F* tests. Differences in growth between treatment groups were examined with a one-way parametric analysis of variance (SPSSx). Multiple comparisons between treatment pairs were then analyzed with the Student-Newman-Keuls (SNK) procedure (alpha = 0.05).

Results and discussion

The surface water chemistry of the study area was strongly ionic (Table III-1). The peatland was patterned, with flarks alternating with poorly developed strings. The vegetation was dominated by brown mosses (Table III-2). Species characteristic of the flarks were *Scorpidium scorpioides, Drosera anglica, Utricularia intermedia, Tofieldia glutinosa* and *Carex paupercula*. Hummocky strings were characterized by an abundance of *Tomenthypnum nitens, Betula pumila, Picea mariana, Larix laricina* and *Oxycoccus microcarpus*. In transition between flarks and hummocks, *Campylium stellatum,* *Muhlenbergia glomerata, Scirpus caespitosus, Salix candida, Drepanocladus revolvens*, and *Triglochin maritima* were common. The surrounding forest vegetation was dominated by *Picea mariana, Larix laricina, Tomenthypnum nitens, Pleurozium schreberi, Fragaria virginiana*, and *Linnaea borealis*. On this basis, the experimental site was considered an "extreme rich fen" (Sjörs 1961, Slack *et al.* 1980).

The mean growth of *Tomenthypnum nitens* was 2.6 ± 0.9 mm for control plots, 4.0 ± 0.9 mm for plots receiving rainwater only, and 6.2 ± 1.1 mm for simulated acid rain plots (Figure III-2). Analysis of variance indicated a significant treatment effect on the growth of *T. nitens* (Table III-4). The SNK multiple range test indicated that mosses from the control and the acidic groups were significantly different ($\underline{P} < 0.05$). The growth values of *T. nitens* were within the range of published data for *T. nitens* in Alberta. C. Miller has measured mean length increment values of 2.4 mm in 1983, 8.2 mm in 1984, and 3.9 mm in 1985 (unpublished data, University of Alberta). Busby *et al.* (1978) recorded an average mean of 7.5 mm for *T. nitens* in the 1975 season.

Tomenthypnum nitens colonizes hummocks in rich fens, consequently plants may not be directly influenced by flowing mineral water. In most bryophytes, water movement is primarily via external capillary spaces between leaves and along stems (Anderson and Bourdeau 1955). Rich fen mosses like *Drepanocladus revolvens, Campylium stellatum*, and *Scorpidium scorpioides*, which are closer to the water table than *T. nitens*, are probably in a better position for trapping nutrients from the flowing water. Nutrients, mainly NO_3-N,

NH_4^+-N, and P, were scarce in the rich fen study site in 1986 (Table III-1). Thus T. *nitens* may have be limited in growth by a lack of nitrate and/or sulfate. When nitrate and sulfate were added by experimental acidification, nutrients were provided and growth of *T. nitens* was increased. In ionically poor habitats, *Sphagnum fuscum* occupies hummocks as *T. nitens*. In an another field acidification (in Ontario), we found no differences in growth of *S. fuscum* between control and acidified plots in poorly ionic conditions (hummocks developing in a lagg zone) whereas under oligotrophic conditions the growth of *S. fuscum* in the acidified plots was almost twice the growth of the control plots (Bayley *et al.* in press; see chapter IV). Thus these data suggest that in continental climate *T. nitens* and *Sphagnum* hummocks may be limited in growth under oligotrophic conditions.

For *Scorpidium scorpioides*, the mean growth (main stem length) recorded for the season was 13.0 ± 2.6 mm for control plots, 9.7 ± 2.3 mm for water sprayed plots, and 9.8 ± 2.1 mm for acidified plots (Figure III-3). Analysis of variance indicated no significant effect of treatment on the main stem length ($\underline{P} < 0.05$). The growth of *S. scorpioides* observed for this site was similar to values measured by C. Miller (unpublished data, University of Alberta; 3.5 mm for 1983, 10.6 mm for 1984, and 3.8 mm for 1985). Two other analyses of variance were performed; one on the number of branches produced ($\bar{x} = 6.2 \pm 0.8$ control; 4.8 ± 1.1 water; and 3.9 ± 0.7 acidic plots) and one on the total length of all the branches ($\bar{x} = 52.3 \pm 7.2$ mm control; 42.2 ± 10.1 mm water; and 29.7 ± 5.7 mm acidic plots). Significant effects of treatment were not detected ($\underline{P} < 0.05$). In the field site, *Scorpidium scorpioides* grew either submerged or emergent in flarks and wet hollows and would be directly and continually influenced by highly ionic groundwater. Treatment with simulated acid rain had no effect on the growth of *S. scorpioides*. It is possible that the added acidity was buffered by fen water or that nutrients provided by sulfuric and nitric acids were diluted in the groundwater. No visual damage was observed due to simulated acid rain treatment for either species.

Comparisons of growth (in mm) between bryophytes of a poor fen (Ontario; chapter IV) and a rich fen (Alberta) under similar experimental conditions indicate more growth of the poor fen Sphagna when compared to the rich fen brown mosses (Table III-7). Under similar acid rain conditions, growth was 3.5 to 4 times greater for the Sphagna when compared to the brown mosses. Under rainwater conditions, the difference in growth was more variable, from 2 to 4.5 times greater for the poor fen Sphagna. Under control conditions the difference was less, with the increase in stem length only 1.5 to 2.5 more in the poor fen species.

Prior to treatment, analyses of variance of chlorophyll *a* and chlorophyll *b* content was performed on predetermined treatment plots. Chlorophyll contents did not differ between the pre-established plots (all $P \geq 0.28$; Figure III-4a and III-5a). In the July assay, no significant differences in chlorophyll contents were observed (all $P \geq 0.40$; Figure III-4b and III-5b). At the end of the experimental season, chlorophyll *a* and chlorophyll *b* contents of *Scorpidium scorpioides* were unaffected by the experimental treatment (all $P \geq 0.62$; Figure III-5c). For *Tomenthypnum nitens*, the chlorophyll *b* content was significantly higher in the simulated acid rain plots (0.17 ± 0.02 mg Chl. g^{-1} dw) compared to the control plots (0.08 ± 0.01 mg Chl. g^{-1} dw; Figure III-4c), but chlorophyll <u>a</u> was unaffected by the treatment (Table III-5). In October, the two species were analyzed for pheophytin <u>a</u>, a degradation product of chlorophyll <u>a</u>. No increases in pheophytin <u>a</u> were observed for either species studied (all $P \geq$ [illegible]

Total chlorophyll contents varied from 0.37 to 0.72 mg g^{-1} dw for *Tomenthypnum nitens* and 0.19 to 0.43 mg g^{-1} dw for *Scorpidium scorpioides* throughout the season for the control plots. These values of total chlorophyll of *T. nitens* are within the range measured in the High Arctic by Vitt and Pakarinen (1977; < 1 mg g^{-1} dw). But in contrast to their results where they found that hydric mosses had higher chlorophyll content than xeric mosses, we found that *S. scorpioides*, a submerged species, had less chlorophyll than *T. nitens*, a hummock species.

Within each species, the content of chlorophyll varied throughout the season (see Table III-6). Chlorophyll content (<u>a</u> and <u>b</u>) was low at the beginning of the growth season, increased during the summer, and decreased again in the fall. A similar figure of variation in chlorophyll content of *Pleurozium schreberi* was reported by Raeymaekers and Glime (1986), where they observed higher chlorophyll levels (mg chl. / g dw.) during the summer than during early spring or late autumn. This pattern also followed the growth pattern that was described by Busby *et al.* (1978). Growth rates increased from May to June, then showed a steady decrease until October. Busby *et al.* (1978) reported that their seasonal variation in growth rate was correlated with total monthly precipitation ($r = 0.92$, $P < 0.01$).

Results of the chlorophyll content data agreed with those obtained for the growth of both species. One year of simulated acid rain was not harmful to *T. nitens*, but instead acted as a fertilizer providing sulfate and nitrate. This may have stimulated the production of chlorophyll a and b, and promoted growth. Hutchinson *et al.* (1986) reported reduction in growth and floor cover of the upland moss *Pleurozium schreberi* with acidic spray treatments at pH less than 4.0. Sprays of pH 3.0 and pH 2.5 were particularly damaging. Increases in growth and photosynthetic rates were not reported at any pH level. This difference in acidification effect could be explained by the fact that the acidity of the spray directly affected *P. schreberi* whereas for *T. nitens* in rich fens, the acidity was first neutralized by the buffering capacity of the system, leaving only beneficial nutrients.

To determine at which pH level "acid rain" was detrimental to the plant growth without the buffering capacity of the system, the two mosses were grown in growth chambers in solution culture. Growth decreased for *Scorpidium scorpioides* in pH treatments of 3.5 and lower (see Figure III-6a). *Tomenthypnum nitens* showed a sharp decrease in growth between pH 3.5 and pH 3.0 (see Figure III-6b). These results indicated that *T. nitens* was less sensitive to acid rain than *S. scorpioides*. *Tomenthypnum nitens* reacted similar to *Pleurozium schreberi*, where both were not affected by acidic treatment of pH above 3.5 (Hutchinson *et al.*, 1986; Raeymaekers and Glime 1986; this study). For *S. scorpioides* sensitivity to acidity was not unexpected as it is a bryophyte well adapted to high alkalinity. In the field, this moss may be protected against "acid rain" by its highly buffered aquatic habit, therefore experimentation with this plant was not pursued.

Finally, I examined the performance of *Tomenthypnum nitens* at pH 3.3 (see Figure III-6b) under five acidic treatments 1) control (simulated rain), 2) H_2SO_4, 3) HNO_3, 4) H_2SO_4 + HNO_3, and 5) HCl. Kruskal-wallis analysis of variance revealed significant differences in growth (P = 0.041) due to the diverse type of acid treatments at pH 3.3 (Figure III-7). Acid treatments containing nitric acid had a stimulative effect on growth. In contrast, hydrochloric acid had a deleterious effect. The fact that hydrochloric acid had a negative effect on *T. nitens* growth and sulfuric acid did not, was probaly due to the molecular difference between the two components which favored a faster rate of uptake of Cl inside the moss unbalancing the charge neutrality. The same conclusions were suggested by analysis of chlorophyll content (ANOVA P = 0.0062; differences between treatment means were tested by SNK multiple range test). Plants from the control and HNO_3 treatments showed higher chlorophyll a than the HCl treatment (Figure III-8), showing again the detrimental effect of the acidity. The fertilizing effect of nitrate was demonstrated by the HNO_3 spraying having significantly higher chlorophyll a content compared to the H_2SO_4 treatment and significantly higher chlorophyll b than the control or HCl treatment (Figure III-8). No differences between acid treatments in content of pheophytin a was found. In no case, did the sulfuric acid sprays reduce growth or decrease chlorophyll content as reported by Hutchinson *et al.* (1986) for the upland, terrestrial mosses *Pleurozium schreberi* and by Glime et *al.* (1986) for *Hylocomium splendens* and *Ptilium* *crista-castrensis* at low pH (<4.5).

In summary, *T. nitens*, a hummock species partially isolated from ground water influences, was affected by the simulated acid rain. Irrigation of *T. nitens* with sulfuric and nitric acids stimulated growth and the production of chlorophyll b. Growth and chlorophyll content of *Scorpidium scorpioides* were unaffected by simulated acid rain. In the long term, this differential sensitivity of moss species to simulated acid rain raises the possibility that acid precipitation could precipitate a change in species composition of rich fen plant communities and to potentially modify hummock-hollow development in these habitats.

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TABLE III-1: Ranges of cations, pH, conductivity, nitrogen, and sulfate concentrations observed at the study site throughout the field season in 1986.

Ca^{2+}	mg L^{-1}	43 - 85
Mg^{2+}	mg L^{-1}	21 - 27
Na^{+}	mg L^{-1}	23.1 -32.8
K^{+}	mg L^{-1}	2.1 -4.4
pH		7.3 - 8.3
conductivity	uS cm^{-1}	436 - 619
NO_3^--N	ug L^{-1}	4.7 -41.8
NH_4^+-N	ug L^{-1}	3.1 - 77.2
SO_4	mg L^{-1}	27.7 - 60.3
P	mg L^{-1}	0 - 0.17*

*Values were below detection limit.

TABLE III-2: Association table resulting from an application of TWINSPAN to the rich fen site species. Values denote categories of percent cover: 1, 0-1% 2, 2-4% 3, 5-9% 4, 10-19% and 5, 20-100%. Number of quadrats indicated at bottom.

	flark				string		forest
Scorpidium scorpioides (Hedw.) Limpr.	2	4	4	1	2	1	
Drosera anglica Huds.	1	2	2		1	1	
Tofieldia glutinosa (Michx.) Pers.		1	1				
Carex pauperaula Michx.			2				
Utricularia intermedia Hayne	2	2	1	1	1	2	
Lobelia kalmii L.		1	1	1	1	1	
Scirpus validus Vahl.	3		1	4	3	5	
Viola spp.				1	1	3	
Carex spp.				2	1	1	
Juncus nodosus L.				2			
Juncus tenuis Willd.					2		
Scirpus acutus Muhl. ex Bigel.			1				
Campylium stellatum (Hedw.) C. Jens.	3	5	4	5	5	5	3
Muhlenbergia glomerata (Willd.) Trin.		1	1	2	1	2	1
Scirpus cespitosus L.	2	4	4	4	4	4	2
Salix candida Fluegge ex Willd.	1	1	1	1	2	1	1
Drepanocladus revolvens (Sw.) Warnst.	1	1	2	5	5	5	3
Galium boreale L.				1	1	2	1
Gentianella crinita (Froel.) G. Don		1		1	1	1	1
Triglochin maritima L.		2		2	2	2	2
Betula pumila L. var. *glandulifera* Regel	1	1		2	5	2	2
Parnassia palustris L.	1	1	1		1	1	1
Aster puniceus L.			1	1	1		1
Juncus balticus Willd.			1		1	1	1
Triglochin palustris L.	1	1	1	1	2		1
Tomenthypnum nitens (Hedw.) Loeske	2			3	3		5
Oxycoccus microcarpus Turcz.				2	1		2
Pyrola asarifolia Michx.					1		1
Drosera rotundifolia L.				1	1		2
Dodecatheon pulchellum (Raf.) Merr.				1		1	2
Picea mariana (Mill.) BSP		1	2	1	1	1	5
Larix laricina (Du Roi) K. Koch	2	2	1	3	1		4
Carex viridula Michx.		1			1	1	2
Sphagnum fuscum (Schimp.) Klinggr.							2
Sphagnum warnstorfii Russ.							2
Pleurozium schreberi (Brid.) Mitt.							3
Cladina mitis (Sandst.) Hale & Culb.							2
Ptilium crista-castrensis (Hedw.) De Not							2
Fragaria virginiana Duchesne							4
Vaccinium vitis-idaea L. spp. *minus* (Lodd.) Hult.							2
Linnaea borealis L. spp. *americana* (Forbes) Hult.							3
Cornus canadensis L.							1
Maianthemum canadense Desf. var. *interius* Fern.							1
Carex capillaris L.							2
Carex aquatilis Wahlenb.							2
Habenaria hyperborea (L.) R. Br.							1
Ledum groenlandicum Oeder				1			2
Cornus stolonifera Michx.							2
Number of quadrats	3	6	3	4	5	4	5

TABLE III-3: Elemental composition of rainwater treatment based on the mean data of the years 1982-83 from Fort McMurray, Edson, and Rocky Mountain House CANSAP stations (AES 1982-83).

	spray medium	CANSAP
Ca^{++}	0.95 mg L^{-1}	1.59
Cl^{-}	0.84 mg L^{-1}	0.52
NH_4^{+}	0.35 mg L^{-1}	0.35
NO_3^{-}	1.20 mg L^{-1}	1.20
Mg^{++}	0.31 mg L^{-1}	0.31
SO_4^{--}	2.62 mg L^{-1}	2.32
K^{+}	0.23 mg L^{-1}	0.23

TABLE III-4: Results of a one-way ANOVA comparing the effect of treatment on the growth of *Tomenthypnum nitens*.

Source	df	Sum of squares	Mean squares	F ratio	F prob.
between groups	2	5222.2	2611.1	3.51	0.0484
within groups	21	15622.4	743.9		
total	23	20844.6			

TABLE III-5: Results of a one-way ANOVA comparing the effect of treatment on chlorophyll a and chlorophyll b content of *Tomenthypnum nitens*.

Source	df	Sum of squares	Mean squares	F ratio	F prob.
Chlorophyll a					
between groups	2	1002.9	501.4	2.17	0.136
within groups	23	5297.3	230.3		
total	25	6300.2			
Chlorophyll b					
between groups	2	336.2	168.1	7.79	0.0026
within groups	23	496.4	21.6		
total	25	832.7			

TABLE III-6: Seasonal variation in chlorophyll a and b for *Tomenthypnum nitens* and *Scorpidium scorpioides* analyzed from the control plots ($\bar{x}$ in mg Chl. g^{-1} dw ± S.E., n = 3 x 9 treatment).

Month	Chlorophyll a		Chlorophyll b	
	T. nitens	*S. scorp.*	*T. nitens*	*S. scorp.*
May	0.28 ± 0.02	0.24 ± 0.06	0.09 ± 0.01	0.05 ± 0.01
July	0.57 ± 0.07	0.33 ± 0.04	0.15 ± 0.03	0.09 ± 0.01
[illegible]tober	0.31 ± 0.08	0.17 ± 0.03	0.08 ± 0.01	0.03 ± 0.01

TABLE III-7: Comparison of growth between dominant mosses of a poor fen (Ontario) and a rich fen (Alberta) occupying the same microhabitat in 1986 ($\bar{x}$ mm ± S.E. (n); Ontario data taken from chapter IV).

	acid rain	water	control
Hummocks			
Sphagnum fuscum			
oligotrophic	22.1 ± 1.5 (66)	11.8 ± 1.0 (55)	6.7 ± 0.7 (30)
minerotrophic	20.8 ± 1.7 (46)	17.9 ± 1.9 (37)	
T. nitens	6.2 ± 1.1 (49)	4.0 ± 2.8 (56)	2.6 ± 2.7 (63)
Hollows			
Sphagnum angustifolium			
oligotrophic	33.0 ± 2.1 (75)	33.1 ± 4.1 (54)	21.3 ± 2.5 (30)
minerotrophic	38.8 ± 2.6 (58)	19.7 ± 1.5 (40)	
S. scorpioides	9.8 ± 5.9 (56)	9.7 ± 6.9 (63)	13.0 ± 7.6 (63)

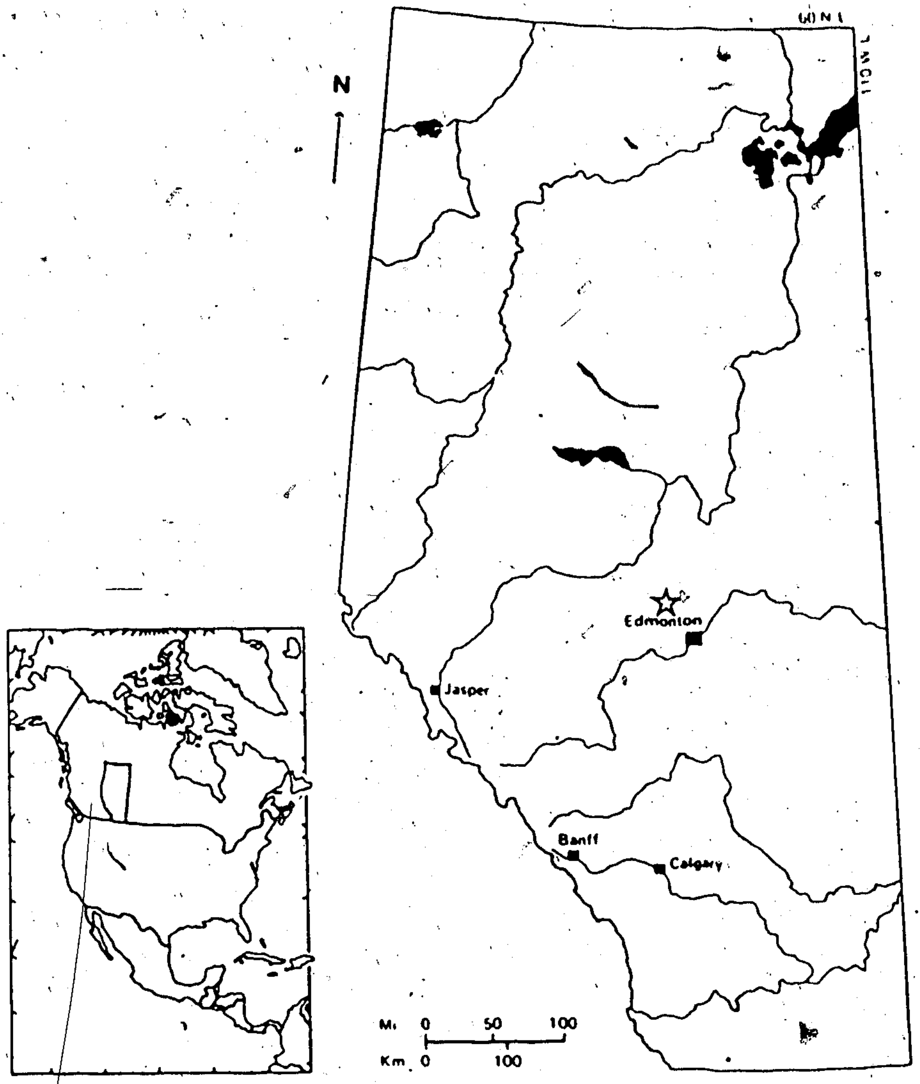

Figure III-1: Location of the study area in central Alberta.

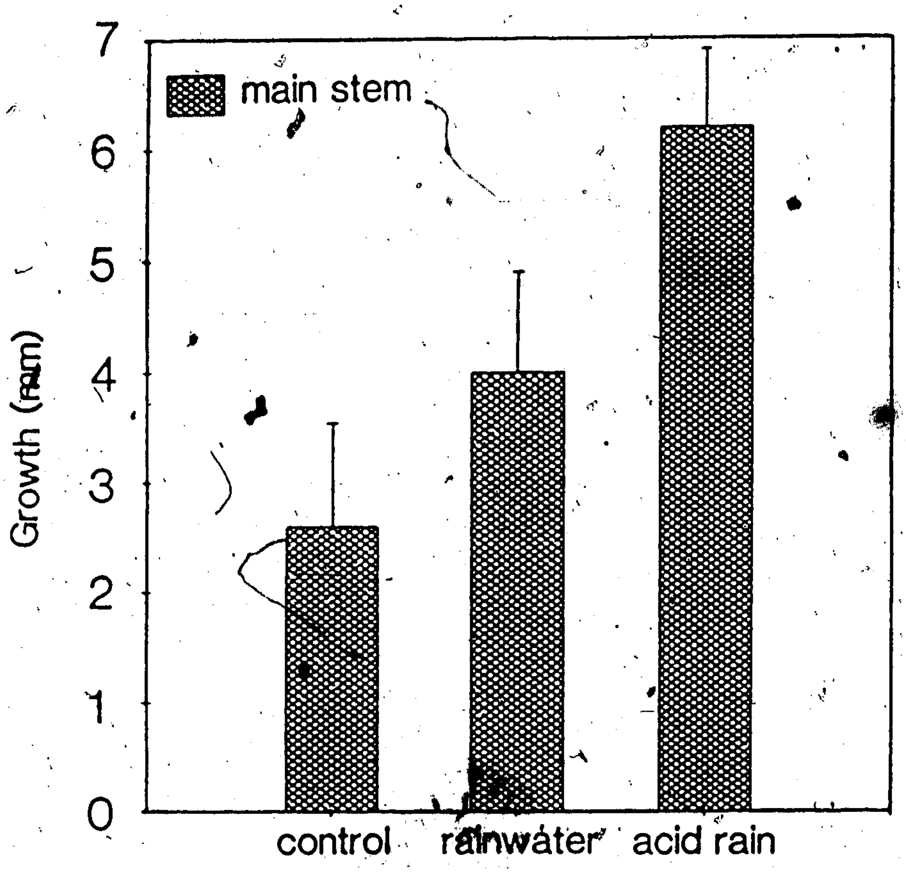

Figure III-2: Growth of *Tomenthypnum nitens* after one season of exposure to simulated acid rain of pH 3.5. Each histogram represents the mean and S.E. of 7 x 9 measured mosses marked at the beginning of the experiment. Means from the acid rain groups and control groups were significantly different.

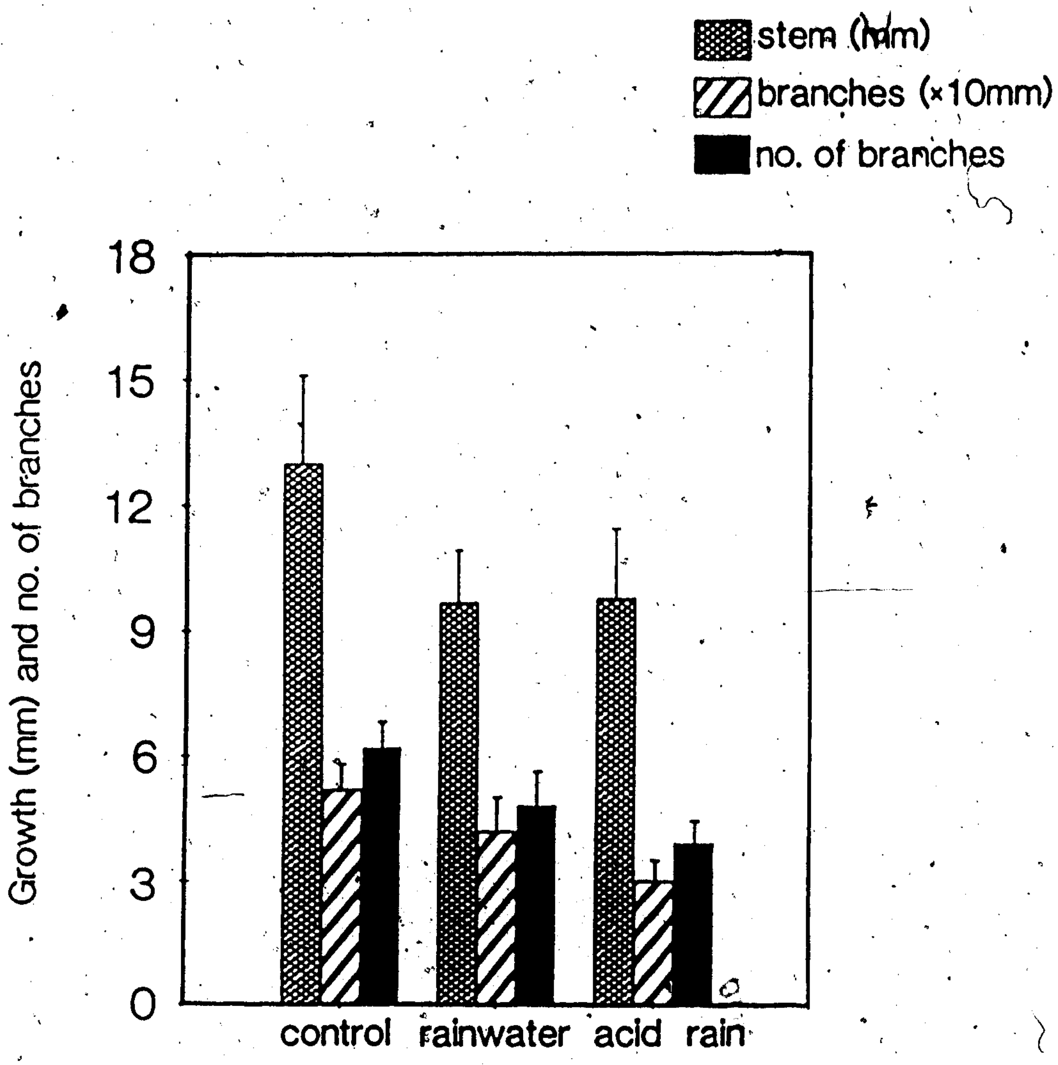

Figure III-3: Main stem length, number of branches, and total length of branches of *S. scorpioides* after one season of exposure to simulated acid rain at pH 3.5. Each histogram represents the mean and S.E. of 7 x 9 measured mosses marked at the beginning of the experiment. Treatment mean groups were not significantly different.

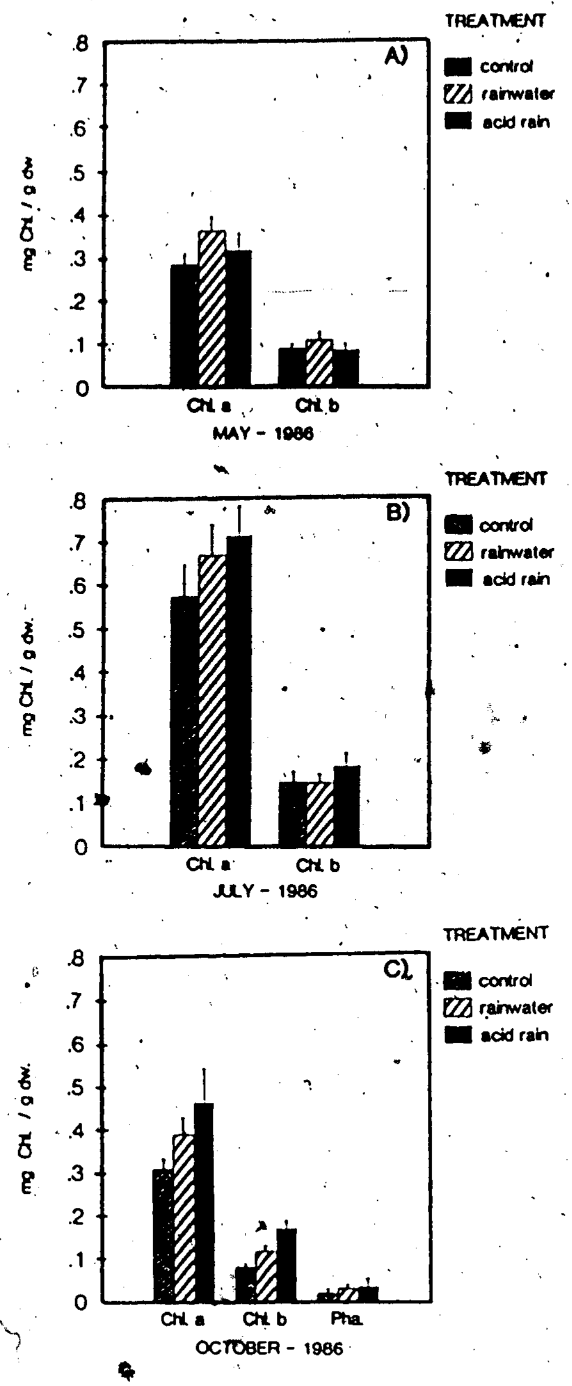

Figure III-4: The chlorophyll a and chlorophyll b content of *Tomenthypnum nitens* A) prior to any spray treatment, B) during growing season, and C) after one season of exposure to simulated acid rain of pH 3.5. Values represent the mean and S.E. of 3 x 9 plants per treatment. Chlorophyll b was significantly higher in simulated acid rain groups compare to the control groups.

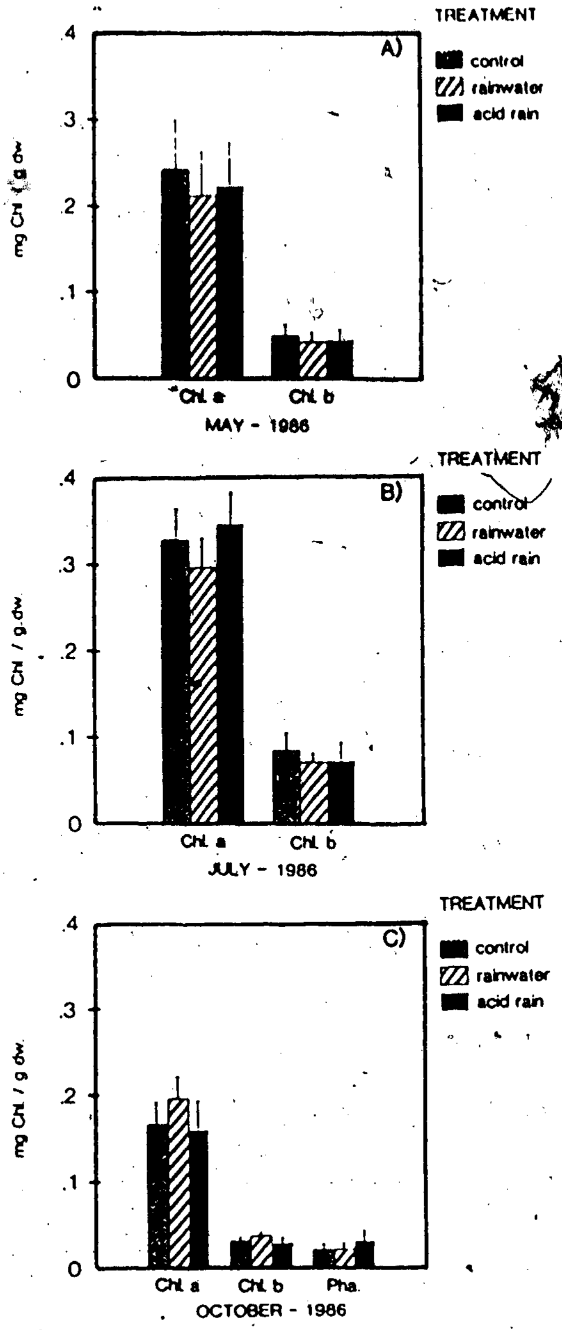

Figure III-5: The chlorophyll a and chlorophyll b content of *Scorpidium scorpioides* A) prior to any spray treatment, B) during growing season, and C) after one season of exposure to simulated acid rain of pH 3.5. Values represent the mean and S.E. of 3 x 9 plants per treatment. No mean groups resulted to be significantly different.

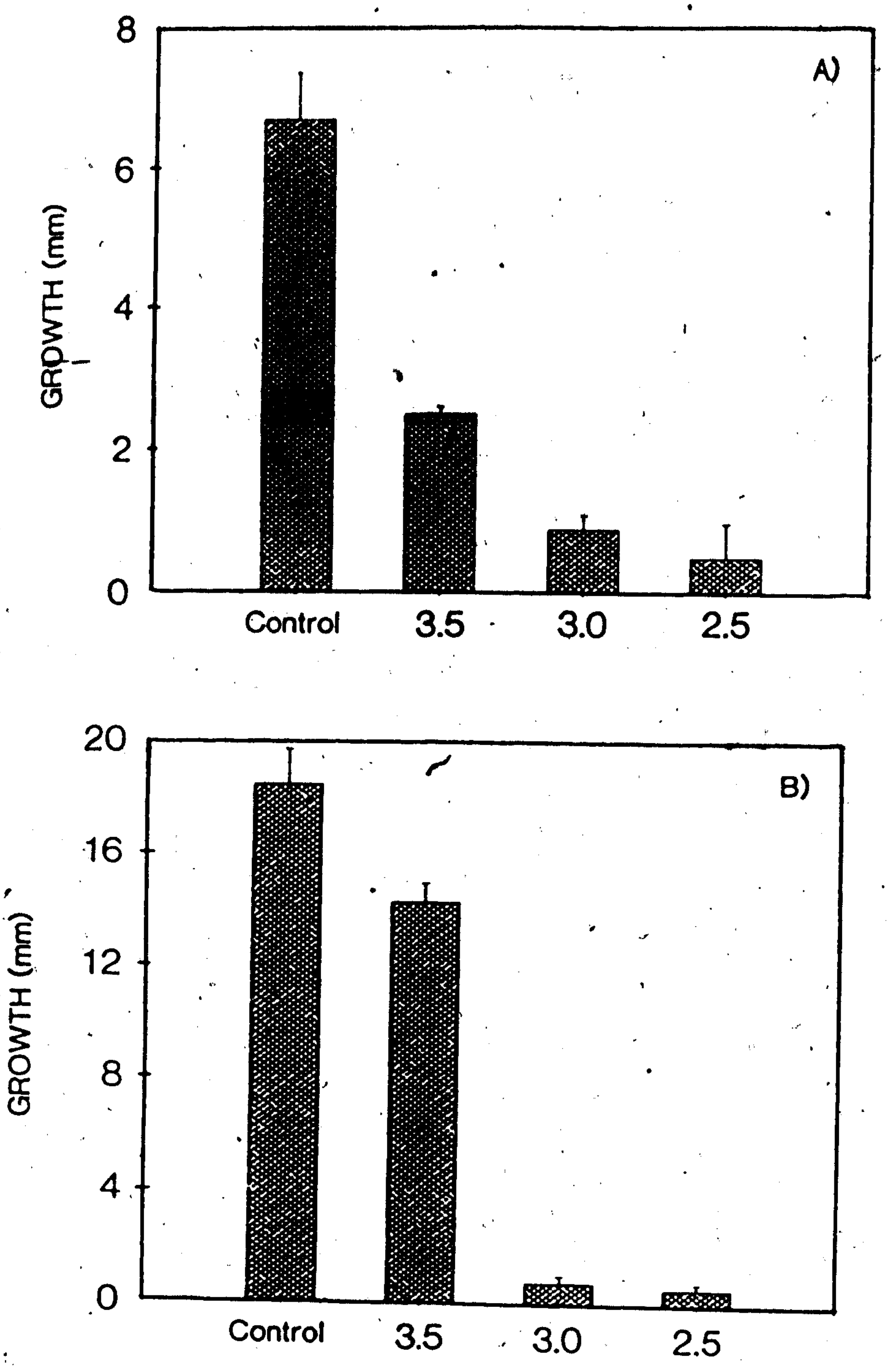

Figure III-6: The growth of A) *Scorpidium scorpioides* and B) *Tomenthypnum nitens* after two months exposure to acidic water of pH 2.5, 3.0, and 3.5 compared with natural fen water. Each histogram represents the mean and S.E. of 15 measurements.

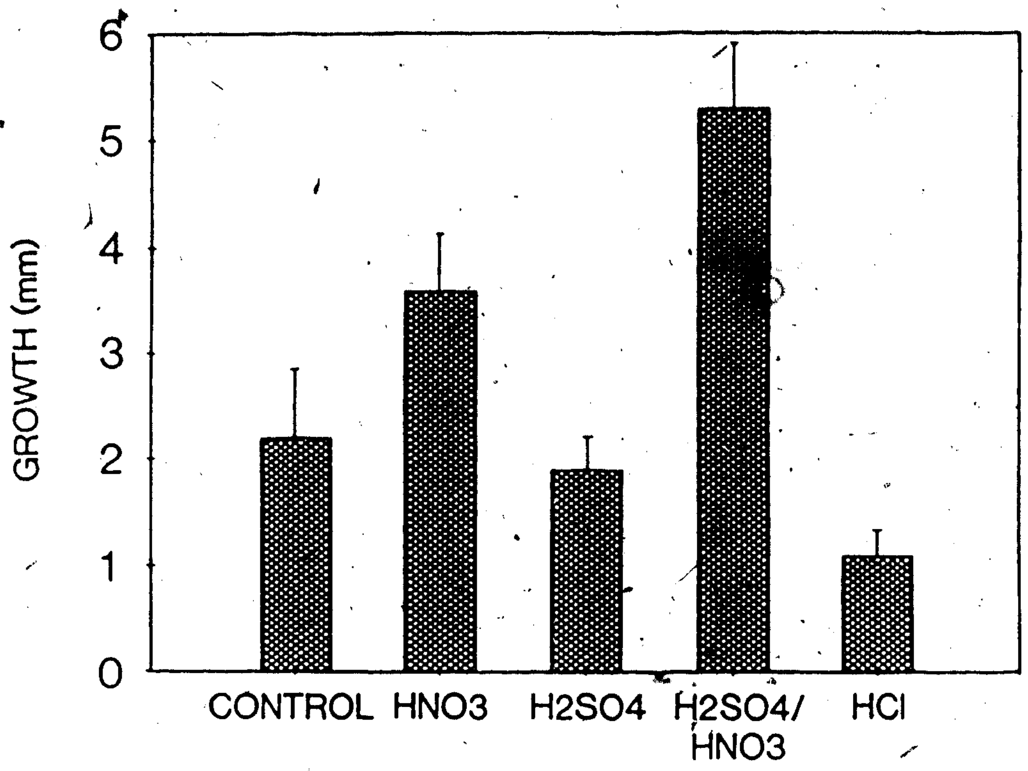

Figure III-7: The growth of *Tomenthypnum nitens* after 13 weeks with one of five acidic treatments. Values are the means of 7 x 3 treatment ± S.E.. Kruskal-Wallis non-parametric analysis of variance demonstrated a significative difference between means (chi-square = 9.9667; *P* = 0.0410).

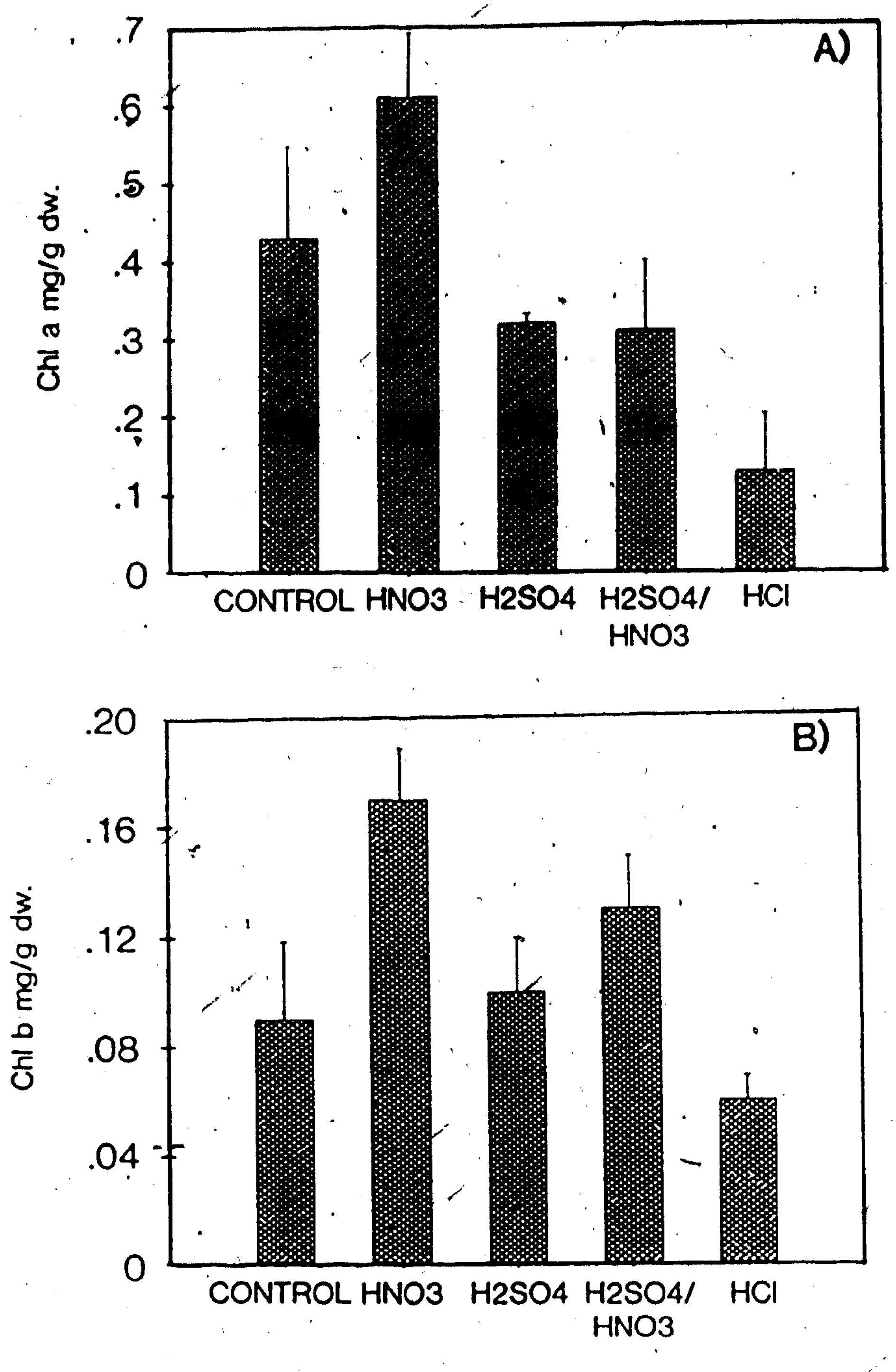

Figure III-8: A) The chlorophyll a content of *Tomenthypnum nitens* after 13 weeks treatment with one of five acidic treatments. Values are the means of 3 x 3 samples ± S.E.. One-way ANOVA and Duncan's Multiple Range test indicated significative differences between means (F ratio = 6.90; P = 0.0062). Four treatment pairs (control and HCl; HNO_3 and HCl; HNO_3 and H_2SO_4; HNO_3 and H_2SO_4 + HNO_3) also showed significant differences. B) Chlorophyll b (F ratio = 3.62; P = 0451). Two treatment pairs (HNO_3 and control; HNO_3 and HCl) showed significant differences.

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IV. EFFECTS OF LONG TERM EXPERIMENTAL ACIDIFICATION ON *SPHAGNUM* - GROWTH, PRODUCTION, DECOMPOSITION AND SPECIES COMPOSITION.[1]

Introduction

Attempts to understand the ecological effects of acid rain in North America have largely concentrated on aquatic and terrestrial ecosystems (Harvey *et al.* 1981; Schindler *et al.* 1980b, 1985, 1986; Abrahamsen 1980; Hutchinson and Havas 1980; Overein *et al.* 1980) Peatlands, which cover approximately 12% of Canada's surface area (Zoltai and Pollet 1981) have long been neglected in acid rain research (Gorham *et al.* 1984). In response to this deficiency, a long-term wetland acidification study was started in 1983 at the Experimental Lakes Area in northwestern Ontario, Canada (Bayley *et al.* 1987). The experimental peatland is a boreal mire dominated by the single moss genus, *Sphagnum*. Partly, this study will investigate the dynamic responses of peat mosses after 3 1/2 years of experimental acidification.

The balance between annual net primary production and annual decomposition ultimately regulates the accumulation and maintenance of peat in a peatland, regardless of geographic location (Wieder and Lang

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[1] A version of this chapter will be submitted for publication. Rochefort, L., D. H. Vitt, and S. E. Bayley. Journal of Ecology.

1983). Because of the importance of these two fundamental biological processes, production and decomposition must be evaluated in order to fully understand peat formation.

Attempts to explain the surface reliefs (sometime referred as surface roughness) in peatland have interested several workers. Malmer (1962a) reported that the variation among microsites was clearly related to oscillations in water level. He also found that decomposition of the plant litter on hummocks was more complete than in adjacent wetter parts, but he did not report rates of decomposition. Height above water table was found to be an important environmental gradient in sorting of bryophyte species along the hummock-hollow microtopography (Vitt and Slack 1984; Slack *et al.* 1980). Water supply to the capitulum (related to the structure of the *Sphagnum* plant) and shade were two parameters used to explain a relationship between water-table depth and surface roughness (Clymo 1973; Hayward and Clymo 1983). The surface roughness of a *Sphagnum* carpet should be smaller the higher it is above the water table. An examination of production and decomposition along hummock-hollow gradients will attempt to establish the state of our surface mire microtopography.

The objectives of this study were two fold. Firstly, to assess the effect of acid deposition on a) the growth and production of the three dominant species of *Sphagnum*, b) the decomposition rates of these three Sphagna, and c) the *Sphagnum* community structure. Secondly, to compare production and decomposition dynamics between *Sphagnum* species (*S. angustifolium, S. magellanicum* and *S. fuscum*) along the hummock-hollow gradient.

Study Area and Experimental Design

The experimental peatland was a 3.67 ha poor fen (sensu Sjörs 1950) located at the Experimental Lakes Area (ELA) of northwestern Ontario, Canada (Lat. 49° 40′ N, Long. 93° 43′ W). The study site (mire 239) was dominated by *Picea mariana* with a shrub layer of *Ledum groenlandicum* and *Chamaedaphne calyculata*, a herb layer of *Carex trisperma* and *Smilacina trifolia*, and a ground layer of *Sphagnum*. The dominant *Sphagnum* species were *Sphagnum angustifolium* (C. Jens. *ex* Russ) C. Jens. *in* Tolf forming carpets and lawns and *Sphagnum magellanicum* Brid. on lawns and hummock-sides. *Sphagnum fuscum* (Schimp.) Klinggr. was present, but less abundant. *S. fuscum* was always the dominant species of well-developed dry hummocks. In 1974, the watershed and one half of the peatland burned. In the burned portion of the peatland, the vegetation was dominated by juvenile individuals of *Pinus banksiana* and a ground layer of herbs and *Sphagnum* similar to the unburned area. Detailed descriptions of vegetation and physico-chemical conditions were documented in Vitt and Bayley (1984), while the vegetation of the upland watershed (8.76 ha) was described by Bayley *et al* (1987).

Based on vegetation and water chemistry, Vitt and Bayley (1984) and Bayley *et al.* (1987) recognized two distinct physiographic zones, (1) a lagg fen zone, which was called the <u>minerotrophic</u> zone of the mire and (2) a central portion of the mire which was nearly ombrotrophic called the <u>oligotrophic</u> zone (Figure IV-1). The minerotrophic zone was under a greater degree of soil water influence than the oligotrophic zone. The surface water chemistry of this minerotrophic zone averaged pH 4.45, 1.80 ± 0.36 mg Ca L^{-1}, 0.67 ± 0.05 mg Mg L^{-1}, and contained such minerotrophic indicator species as *Equisetum sylvaticum, Alnus rugosa, Salix cf. planifolia,* and *Calamagrostis canadensis* (Vitt and Bayley 1984). This ion-enriched zone was characterized by shallow peat (0 - 1.5 m; D. H. Vitt, pers. comm.) whereas in the oligotrophic zone peat depth reached 14 m (Beaty 1986). Mean values of surface water in the oligotrophic zone were pH 4.09, 1.26 ± 0.15 mg Ca L^{-1}, and 0.51 ± 0.06 mg Mg L^{-1}. This oligotrophic zone was characterized by an abundance of *Andromeda glaucophylla, Kalmia polifolia,* and *Vaccinium vitis-idaea*. Water chemistry and vegetation data indicated that this oligotrophic zone was more nutrient-poor than the minerotrophic zone and poorly influenced by minerotrophic water. For the sake of clarity, the oligotrophic zone will be considered as ombrotrophic (for the remainder of the paper). The two zones, minerotrophic and oligotrophic, will also be referred to as conditions.

For the experiment, the mire received two treatments; a control area (0.85 ha - upslope) was sprayed with lake-water only and an acidified area (2.66 ha) was sprayed with lake-water plus strong acids (Figure IV-1). Since the ecosystem experimental design (one control area and one experimental area) was too costly to replicate, no inferential statistics have been used in this paper to test for treatment effects (Hurlbert 1984). The purpose of the experiment wa to simulate acidic rain equivalent to the pH precipitation in the eastern U.S. and Canada (pH ± 4.0). To achieve this, a 1:1 mixture of concentrated sulfuric and nitric acid was added to lake water and sprayed once a month (at pH 3.0) on the peatland during the growing season (six times per year). For further details on the acidification design and irrigation system see Bayley *et al.* (1987) and Beaty (1986).

A sampling plot for each of the four areas of the mire was established in August 1983 to study *Sphagnum* growth and decomposition. Each plot contained 120 sampling points positioned along four hummock-hollow transects. In 1985, four additional plots were added, each containing 50 new sampling points. The eight plots (2 per area) corresponded to the four areas of the mire (Figure IV-1): oligotrophic control (OC), minerotrophic control (MC), oligotrophic experimental (OE), and minerotrophic experimental (ME). Plot selection required hummocks sufficiently developed to be vegetated on the top by *Sphagnum fuscum*. All plots were located within the unburned portion of the mire, so no variance was introduced due to abiotic factors such as light intensity.

Methods

Production

Parameters necessary to determine productivity for *Sphagnum* included the surface area of the species, its rate of linear growth, and the relationship of linear growth to mass increment. For the study site, the microtopography was idealized as an assemblage of hemiellipsoids as described by Grigal (1985).

Surface area

Two quadrats (10 m x 10 m) were randomly selected in the sampling area. Within each quadrat, hummocks were counted and the dimensions of each hemiellipsoid taken. Measurements included diameter of the long and short axis and height from the top of the hemiellipsoid to the lowest adjacent point. To compute the total surface, the plane ellipsoid area was substracted from the volumetric ellipsoid area. The percent cover of *Sphagnum* species was estimated visually within each quadrat in order to estimate the proportion of the total surface area that was occupied by the three dominant species of *Sphagnum*.

Differences in net production and growth in length between the three *Sphagnum* species were examined with one-way parametric analysis of variance (ANOVA). Multiple comparisons between species means were then made with the Student-Newman-Keuls (SNK) procedure (alpha = 0.05).

Linear growth

Sphagnum elongation was determined by the cranked wire method (Clymo 1970). The wires were stainless steel and 30 cm long. Length increment of the three dominant *Sphagnum* species were measured during the growing season (May to October) of 1984, 1985, and 1986. In 1986, we used innate time markers of *Sphagnum angustifolium* to verify the accuracy of the cranked wire method. The annual growth pattern of *S. angustifolium* is produced by the weight of snow cover, which causes a permanent bend of the main stem.

Mass increment

When growth in length was measured the weight of plants per unit area and depth (bulk density) was needed to obtain production values. The relationship between linear growth of *Sphagnum* and mass increment was determined from surface cores (ca. 85 cm^2) collected in each sampling area (OC-MC-OE-ME). Four replicates per species and per sampling area for a total of 48 cores were sampled. The number of plants in the sample was counted, and each plant was separated into capitulum and the next 3 cm of stem. Dry weight at 60 °C of the 3 cm of stem (excluding capitula) was measured. All results were related to a unit of 1 cm length. Estimates of production were obtained by multiplying length increment (cm), mean weight of *Sphagnum* per unit depth (g cm^{-1}) and the surface area per vertically projected area. For this conversion it is assumed that there has been no change in the size of the capitulum during the experiment.

Increase N-loading experiment

Previous investigations indicated that a NO_3-N loading of 0.46 g m^{-2} yr^{-1} to the acidified area of mire 239 had a stimulative effect on the growth of the dominant *Sphagnum* species (Bayley *et al.* 1987). This N-loading was supplemented by adding NH_4NO_3 and NH_4Cl over small portions of mire 239 up to 3.6 g m^{-2} yr^{-1}. In 1986, eight quadrats of 50 cm x 50 cm (4 in OE and 4 in ME) were set up in carpets of *Sphagnum magellanicum*. Fifteen cranked-wires were established per quadrat. Six quadrats (4 in OE, 2 in ME) were delimited by ropes and two (in ME) by a plexiglass enclosures (50 cm deep). The quadrats were sprayed manually once a month, at the same time as the acidification events. In the results and discussion section, we refer to these quadrats as the ammonium-sprayed plots.

Decomposition

Decomposition bags (approximately 2.5 x 2.5 cm) were made using 0.8 mm nylon mesh. Samples of *Sphagnum angustifolium, S. magellanicum* and *S. fuscum* were autoclaved, air dried for 24 to 48 h, and approximately 0.3 to 0.8 g dry weight of monospecific material placed in each bag. The decomposition bags were placed 10 cm below the peat surface (within aerobic zone) in August 1983. The bags were collected every 6 months for 1984, 1985 and 1986, with usually three replicates or more per species per area on each sampling date. Differences in the decay constant between species were tested for significance with a one-way analysis of variance (ANOVA) for each sampling period and for Scheffé multiple contrasts for pairwise comparisons.

Species composition

For three years, cranked wires for measuring growth were kept at exactly the same position along hummock-hollow transects. Species presence at each stake was recorded for Aug. 1983, Oct. 1984 and May 1986 under control and experimental conditions. A R x C test of independence using the G-test statistic (Sokal and Rohlf 1981) was performed to examine whether the *Sphagnum* species proportions exhibited were independent of the years at which the individuals at each stake were sampled.

Results

Linear growth

For the measurement of linear growth (in this paper growth refers to length increment), Clymo (1970) emphasized the fact that close agreement between mean results is the best evidence of accuracy. The comparison of length increment between the innate biological marker and the cranked wire methods proved to be statistically similar (U-test, P = 0.854, df = 141). Thus the less consuming-time cranked wire method was used to relate linear growth to mass increment. Agreement between the two methods (cranked wire and innate time marker) was satisfactory, because no very wet hollows occurred in the mire and the Sphagnum plants grow vertically.

The effect of acidification *Sphagnum fuscum* was most pronounced in the oligotrophic zone where growth was 2 to 3 time that of mosses in the control area. Under oligotrophic conditions, the growth of *S. fuscum* in the experimental area was 217% greater in 1984, 180% in 1985, and 87% in 1986 compared to the control area (Figure IV-2). Under minerotrophic conditions, no difference was found for the growth of *S. fuscum* between the experimental and control areas (Figure IV-2). The growth in length of *S. fuscum* for the oligotrophic control area ranged from 7 to 12 mm a year and 18 to 31 mm a year for the other areas.

Under oligotrophic conditions, *Sphagnum magellanicum* exhibited an increase in growth due to acid applications only in 1986 (74% more). Under minerotrophic conditions, growth of *S. magellanicum* was greater in the experimental treatment for the growing seasons of 1985

(149% more) and 1986 (104% more). From 1984 to 1986, annual growth of *S. magellanicum* varied greatly for all areas (OC- MC-OE-ME), ranging from 11 to 45 mm (Figure IV-2).

In most years of acid application, *Sphagnum angustifolium* growth was enhanced. Under oligotrophic conditions, the growth of *S. angustifolium* in the experimental area was greater for the three years of acidification compared to control area. However in successive years of treatment, the growth of *S. angustifolium* tended to decrease (Figure IV-2) with growth 79% greater in the experimental area than the control in 1984, 27% in 1985, and only 0.3% in 1986. Under minerotrophic conditions, growth of *S. angustifolium* was greater in the experimental conditions (≥ 57%) than in the control area for all years of treatment. Growth in length of *S. angustifolium* for the control area ranged from 20-39 mm a year and 33-57 mm for the experimental area.

To verify if the growth of the Sphagna was affected by the lake-water addition in the experimental mire (239), we compared the growth of Sphagna in the control areas with that of the nearby mire 661. Mire 661 vegetation and water chemistry was described by Vitt and Bayley (1984). *Sphagnum angustifolium* and *S. magellanicum* were compared only in the field season 1986. We found no significant difference (U-test, all $\underline{P} \geq 0.2847$) between the growth of the mosses of mire 661 and the control areas in mire 239 (Figure IV-3). No difference was expected since only 10% of the precipitation was added over the experimental poor fen per year. For *S. fuscum*, the growth was compared for the 1984, 1985 and 1986 field season (Figure IV-4). The growth of *S. fuscum* was significantly greater in the minerotrophic zone of mire 239 than in mire 661 (U-test, all $P \leq 0.0003$). For the 1984 and 1985 growing seasons, *S. fuscum* growth was significantly lower in the oligotrophic zone than in mire 661 (U-test, all $P \leq 0.0017$) but the reverse occurred in 1986 where *S. fuscum* grew more in the oligotrophic zone than in mire 661. The difference might be related to the nutrient status of the hummocks. For further details, refer to the discussion on *S. fuscum* in the production section.

Production (as affected by acid rain)

Mean of eighteen hummocks was recorded for each quadrat of 100 m^2. The average long diameter and short diameter for the hemiellipsoids were 160 ± 7.4[2] and 90 ± 5.4 cm respectively. Their heights above the lowest adjacent point are 28 ± 1.7 cm. Our hummocks were longer but not as high as the ones described by Grigal (1985) for bogs of northern Minnesota. For each 1.00 m^2 of vertical area, *Sphagnum fuscum* had a surface area of 0.06 m^2, *S. magellanicum* of 0.75 m^2 and *S. angustifolium* of 0.57 m^2. Overall our estimate of 1.38 m^2 for total surface area was well within the range of published data (see Grigal 1985).

The mass per unit length per unit area was determined twice, for each of the *Sphagnum* species studied (once in 1984 and once in 1986; see Table IV-1). These values were used to relate linear growth to mass increment. My mass values were higher than those of Grigal (1985) (Table IV-1), but the ratio of about 1:2 of mass per unit length per unit area between hollow species and hummock species (*S. fuscum*) still hold true.

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[2] Mean (S.E.)

Net production of *S. fuscum* in the oligotrophic control area was consistently lower (69 to 116 g m^{-2} yr^{-1}) when compared to all the other areas (175 to 303 g m^{-2} yr^{-1} for OE, MC, ME; see Figure IV-5). Production values of *S. fuscum* in the experimental area were similar between the years and the zones, and were also similar to the *S. fuscum* growing in the minerotrophic control zone. For *S. magellanicum*, production varied greatly between the years and between the oligotrophic and minerotrophic zones (Figure IV-5). In the oligotrophic control (OC) area, production was promoted by acid sprays only in 1984 for *S. angustifolium* (Figure IV-5). In the minerotrophic zone, *S. angustifolium* had more production in the experimental (ME) area (range values from 157 to 280 g m^{-2} yr^{-1}) than in the control (MC) area (100 to 198 g m^{-2} yr^{-1}) for the three years studied.

Comparisons of growth and production were made between the three dominant species in the control area, including oligotrophic and minerotrophic conditions, to study the dynamics of hummocks and hollows. In the oligotrophic control production and linear growth were significantly greater for two years (1984, 1985) for the hollow and mid-hummock species (186-230 mg m^{-2} yr^{-1}; 25-33 mm) than for the hummock species (69-91 mg m^{-2} yr^{-1}; 7-9 mm). In 1986, production and growth of *S. angustifolium* (157 mg m^{-2} yr^{-1}; 31 mm) were significantly greater than production and growth of *S. magellanicum* and *S. fuscum* (73-116 mg m^{-2} yr^{-1}; 12-13 mm) (Table IV-5). In the minerotrophic control, growth and net production of the three *Sphagnum* species were not significantly different in 1984 (Table IV-5). In 1985 and 1986, growth of *S. magellanicum* was significantly less than growth of *S. angustifolium* and *S. fuscum*. For the same period (1985-1986), net production was significantly greater for hummock species (175 - 303 g m^{-2} yr^{-1}) than hollow and mid-hummock species (59 - 198 g m^{-2} yr^{-1}) (Table IV-5).

Increase N-loading experiment

No increase in growth was detected for *Sphagnum magellanicum* with a total N-loading of 3.6 g m^{-2} yr^{-1} (with 1.8 g m^{-2} yr^{-1} of NO_3^--N and 1.8 g m^{-2} yr^{-1} of NH_4^+-N). *S. magellanicum* did not grow inside the plexiglass enclosures, therefore the data from these quadrats were excluded. The plexiglass frame may have disturbed the water relations of the mosses, as most dried out. Two one-way analyses of variance (Appendix 1) followed by the Scheffé multiple contrasts for pairwise comparison revealed that for both conditions, oligotrophic and minerotrophic mosses from the experimental area with the N-loading of 0.5 g m^{-2} yr^{-1} grew significantly more than the ammonium-sprayed plots or the control area plots. No difference in growth was detected between the control area, mire 661 and the ammonium-sprayed *Sphagnum* (Figure IV-6).

Decomposition

The decomposition rate of the *Sphagnum* mosses was not different between experimental and control areas for any species (Figure IV-7). Hence, low level of acidification with nitric and sulfuric acid did not affect the decomposition rate. Rates of decay were similar within a species, hence the data from the different sampling plots were pooled together to obtain a mean decay constant for each species (Table IV-2).

Sphagnum angustifolium colonizing hollows and lawns had a significantly higher rate of decay than *S. magellanicum* growing on hummock-sides. The latter two species had significantly higher rates of decomposition than *S. fuscum*, which colonized the top of hummocks, except for the sampling period May 1984 and May 1985 where no significant difference was found between *S. magellanicum* and *S. fuscum*, and in October 1985 when significant differences were not observed (Appendix 2).

Species composition

The species composition of the three dominant Sphagna was not influenced by 3.5 years of experimental acidification. Highest G-value had a $P > 0.55$ (Figure IV-8).

Discussion

1 - Effect of acidification

Species composition

Each individual *Sphagnum* species has its own distinct chemical ecology (Vitt and Slack 1984). As well, some *Sphagnum* plants are more sensitive to atmospheric pollution than others (Lee *et al.* 1986; Press *et al.* 1983; Tallis 1964). Consequently, it is of interest to monitor the species composition under experimental acidification to observe if any change occurs in abundance or frequency of the dominant plants. Changes may occur by deleterious chemical effects (disappearance of one species) or by plants growing more rapidly under acid applications, replacing neighboring species (area extension of one species). After three and half years of acidification, no changes in the *Sphagnum* community were observed. However this short time span may be too brief to determine if some species will disappear after cumulative years of acidification, as was observed in Britain (Tallis 1964). It may be that a clear change in the species composition will occur as has been reported in a fertilization experiment (Vasander 1982).

Decomposition

The finding of no difference in the decay rate of *Sphagnum* between experimental and control areas contrasts with results from experimentally acidified water wherein leaf litter decomposition was retarded by acidification (Allard and Moreau 1986; McKinley and Vestal 1982; Traaen 1980). This difference may be due to the fact that *Sphagnum* mosses are already adapted to an acid habitat where the rate of decay is unusually slow (Clymo and Hayward 1982). Spraying with mineral acids for 3.5 years did not change the overall acidity of the poor fen (see Bayley *et al.* (1987) for 1984 data, and Figure IV-9 for 1985-1986 data), thus no change in the rate of decomposition was expected due to acidity. Coulson and Butterfield (1978) found that nitrogen enrichment increased the rates of decay of *Sphagnum*. This specific effect of nitrogen enrichment was not observed in this experimental acidification. Likewise, Clymo (1965) reported no marked effect of experimental irrigation with chemicals including NO_3 (e.g. $NaNO_3$, $CaNO_3$) on the rate of breakdown of *Sphagnum*. Behr (1985) demonstrated that sulfate reduction was stimulated by the acidic additions on mire 239. Hemond (1980) estimated that approximately 2 g dry mass m^{-2} yr^{-1} of plant material is oxidized to CO_2 and water in the process of sulfate reduction. Therefore theoretically one would expect to see an increase in the rate of decomposition in the experimental area but this effect was not observed.

Growth and production

Sphagnum fuscum grew equally well in the oligotrophic experimental area as it did in the minerotrophic experimental and control areas (see Figure IV-2). This suggests that *S. fuscum* hummocks in the oligotrophic control area may be limited in their growth by a lack of nutrients. In ombrotrophic conditions, K, N, and P are available only in low quantities and limit the growth of *Sphagnum* (Damman 1986; Malmer 1962b, 1964). By supplying nitrates and sulfates through the acid treatment, the *Sphagnum fuscum* mosses were able to grow as much as those in minerotrophic conditions. This suggests that *S. fuscum* (at the top of hummocks) in the minerotrophic control area was able to obtain nutrients from the underlying water table. Damman (1978) pointed out that certain elements (N, K, P, and Na) were somehow recycled to the peat surface and suggested that a capillary flow driven by evapotranspiration could be one mechanism.

In general, growth of *Sphagnum angustifolium* was greater in the experimental area of the mire compared to the control area sprayed with lake-water only (Figure IV-2). This fertilizing effect was probably caused by nitrate, a limiting nutrient in peatlands (Damman 1986), which when supplied by acid sprays (nitric and sulfuric acids) initiated a primary growth burst. However it appears that after the initial rapid growth in response to acidification, this stimulation effect decreased (see Figure IV-2, oligotrophic conditions). More years of experimental acidification are needed to test if this "fertilizing" effect will become detrimental to *Sphagnum* as reported in England (Lee *et al.* 1986).

In the first years of acidification 1984 to 1985, we observed no response of *Sphagnum magellanicum* to the acidification. Linear growth and production were similar in control and experimental areas (Figure IV-2 and IV-5). In 1986 growth of *S. magellanicum* in the acidified portion of the poor fen was greater than that in the control portion was observed. This species appeared to react more slowly to the acidified treatment than *S. angustifolium*, but after 3.5 years of acidification, the same effect of fertilization noticed in *S. angustifolium* also occurred with *S. magellanicum*.

2 - Hummock-hollow dynamics.

Decomposition

In this study, hummock species had a slower rate of break down than hollow species (this study). This contrasts with results of Farrish and Grigal (1985) where litter in hummocks lost significantly more mass than similar material from hollows. The content of their litter bags and the depth at which they were placed in peat were not specified. Differences in rate of loss between the three dominant *Sphagnum* species might be due to a number of factors. (1) Different species of *Sphagnum* might be composed of different chemical constituents which disappear at different rates. It would be expected in consequence that the rate of decomposition would be different for different species. (2) When the pH of the environment drops below 5, organisms responsible for decomposition of organic matter may diminish in activity (Williams and Gray 1974). This effect might be due to the hydrogen ion concentration itself through interference with enzyme and membrane function. Nutrients are more abundant and pH highest in the hollows and both progressively decrease to the top of the hummock as uronic acids increase (Clymo 1963; Vitt, Crum and Snider 1975; Clymo 1986). Therefore if microbial activity is proportional to the concentration of H^+ (pH), it would be expected for the hummock-top species to have the lowest rate of decay and for the hollow inhabiting species the highest one. (3) Malmer (1986) pointed out that peat decomposition was enhanced when the water table varied greatly in the season and is low for seasonal periods. The faster rate of decomposition of *S. angustifolium* might be explained by its closer position to the water table in the zone of water level variation. The water table of mire 239 had an amplitude of fluctuation of 30 cm in 1984 season (Beaty 1986). The peat of *S. fuscum* 10 cm below the surface is usually drier than the peat of *S. angustifolium* (both still being in the aerobic zone) and probably less favorable for the activity of decomposing microorganisms. Rosswall *et al.* (1975) thought moisture to be the most important factor limiting decomposition rates.

Our results shows that losses in hummock-top (*S. fuscum*), mid-hummock (*S. magellanicum*) and hollow (*S. angustifolium*) are roughly in the ratio 7:9:13. All the decomposition bags were placed in the aerobic zone but the bags of *S. angustifolium* were closer to the water table and subject to periodic submersion. Thus, it seemed that decomposition in the zone of the water table fluctuation was enhanced by a cycle of moisture-dryness. Decomposition of *Sphagnum fuscum* on hummocks was probably lower due to a combination of low pH, high uronic acid content, dryer peat, and a different chemical composition. None of these parameters were evaluated in this study.

Production

Sphagnum fuscum and *S. magellanicum* production data for the control areas fell within the range of published production values (see Table IV-3). However there was considerable variation between the years and even the areas (OC versus MC) within the mire (Figure IV-5). A variety of factors have been suggested to explain variability in production within small geographic areas including distance to water table, degree of dwarf shrub cover and lichens, depth and duration of snow cover, degree of exposure to wind and solar radiation (Pakarinen 1978), different habitats, i.e. hummocks vs. lawns, method of measurement (Clymo 1970; Clymo and Reddaway 1971), or different supply of inorganic ions (Clymo 1973). The different amounts of production of *S. fuscum* hummocks between the oligotrophic and minerotrophic conditions suggests that the nutrient status of the micro-habitat may ~~also~~ affect the productivity of a given species.

Our production values for *S. angustifolium* from the control areas were among the lowest ones published (Table IV-3). This was true, even when our production values were corrected for convexity (see methods), which overestimated our values when compared to other studies (except Grigal 1985). These low production results do not support the suggestion of Wieder and Lang (1983) and Damman (1979) where that annual production of *Sphagnum* should increase along a gradient from northern to southern latitudes. To verify the statement that *Sphagnum* production increases with decreasing latitude, *S. angustifolium*, *S. magellanicum* and *S. fuscum* were tested for trend using the same method as described in Wieder and Lang 1983 (Daniels Test for Trend, Conover 1980), adding our data and five other studies (Table IV-3). Only *S. magellanicum* showed a significant ($P = 0.025$) trend of increasing production with decreasing latitude. No significant trend was found for *S. fuscum* or *S. angustifolium (= S. recurvum)* as reported by Wieder and Lang (1983). Moreover, Damman (1979) suggested that *Sphagnum* production should increase along a gradient from continental to maritime climate. Precipitation, a parameter often closely associate with a continental-maritime gradient, was paired with *Sphagnum* production values. No positive significant trend for any species was found, implying that precipitation is not the key climatic parameter that would enhance production along a continental to maritime gradient.

For both conditions, oligotrophic and minerotrophic, *Sphagnum angustifolium* grew more than *S. fuscum* in 1984 to 1986. These results corroborate the statement that annual growth (length increment) is less in hummock species than in hollow species (Clymo 1970; Pedersen 1975; Pakarinen 1978; Wieder and Lang 1983). Clymo (1970) has discussed the differences in growth between the peat mosses and suggested that chlorophyll distribution might be correlated with the different growth rates of *Sphagnum* species. Thus loose hollow species with a large horizontal surface to receive radiation might be expected to grow better than compact hummock species.

From comparisons of growth and production of *S. fuscum* between oligotrophic and minerotrophic conditions (see Table IV-3), it can be seen that hummocks have a better performance in the minerotrophic zone than the oligotrophic zone. Hummock species inhabiting bogs and poor fens i.e. being in ombrotrophic or very oligotrophic conditions seem to be limited in growth by a lack of nutrients, but if the same hummock species are found in more nutrient rich conditions (as occurs in the minerotrophic zone) these hummock species have better growth and net production per unit area.

In the oligotrophic central zone of mire 239, production and growth were generally greater for hollow and mid-hummock species than hummock species (Table IV-4), but decomposition rate was slower in hummocks and mid-hummocks compared to hollows, meaning that hummock-hollow relief seems established in a somewhat constant state.

Under minerotrophic conditions (in the lagg zone) net production was either not different between the *Sphagnum* species or hummock production was greater than hollow or mid-hummock production (Table IV-4). Decomposition rate was the slowest in hummocks, indicating that the peat accumulation rate was different between these habitats. Theoretically hummocks should be expanding in the lagg zone. For now the percent cover of *S. fuscum* was 4% and only two hummocks of *S. nemoreum* were noted in the fen. This percentage of hummock species may increase in the next years if present climatic conditions persist. Mire 239 is believed to have a positive balance of peat accumulation. Since the fen is confined within a basin, peat should be able to increase a 5-6 m.

Total *Sphagnum* production for this poor fen was obtained by combining production of each species and its surface percent cover. *Sphagnum* cover was 100% for the bryophyte layer. Estimates of net production of *Sphagnum* varied greatly between the years but was more or less constant within a year (Table IV-5). These estimates were the lowest value published to date. Net production of *Sphagnum* varied from 320 to 380 g m^{-2} yr^{-1} in a forested bog of northern Minnesota (Grigal 1985) and was 390 g m^{-2} yr^{-1} in an open bog in Minnesota (Elling and Knighton 1984). At Moor House, in England, Forrest and Smith (1975) estimated *Sphagnum* productivity to be 213 g m^{-2} yr^{-1} for a site covered by 80% *Sphagnum*.

Conclusion:

In summary, after three years of acidification, all species grew more in the acidified portion of the mire compared to the control portion. The loading rates of NO_3-N and SO_4 to the experimental mire were annually 0.46 and 1.81 g m^{-2} yr^{-1} respectively. When the loading rate of SO_4 was kept the same but nitrogen (including ammonium) was increased to 1.5 g m^{-2} yr^{-1}, the growth of the *Sphagnum* species was not significantly different than in the control portion of the mire.

Three years of artificial application of sulfuric and nitric acids did not change the *Sphagnum* community structure of the mire. Although acidification promoted primary production of all the *Sphagnum* species for most years, decomposition of the system remained similar to pre-acidification conditions. Because the balance between production and decomposition determines rates of peat accumulation, the experimental acidification will theoretically result in greater peat accumulation in the system. These observations support the suggestion of Urban and Bayley (1986), that in the initial years, acid deposition acts as a fertilizer for mires of boreal North America.

Hummocks species had a slower rate of decomposition than hollow species, whereas production rate was similar between the species. It appeared that hummocks may be expanding, at least in the lagg zone.

Acknowledgments

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TABLE IV-1: Mass per unit length per unit area of each *Sphagnum* species over the 1-to 4-cm increment. Values are in g m^{-2} yr^{-1}.

	S. *fuscum*	S. *magellanicum*	S. *angustifolium*
1984	92	78	55
1986	92	44	40
Grigal (1985)	61		30

TABLE IV-2: Calculated linear decay constants ($K = X_o - X/X_o \times 100$, where X_o = initial *Sphagnum* mass and X = final *Sphagnum* mass) for the three *Sphagnum* species after merging together the data of the different physiographic areas and experimental conditions. K (S.E., n).

	May 84	Oct. 84	May 85	Oct. 85	Oct. 86
S. angustifolium	20 (1,16)	25 (1,16)	29 (1,16)	24 (1,6)	26 (2,14)
S. magellanicum	10 (1,16)	18 (2,16)	21 (2,16)	21 (2,13)	20 (2,21)
S. fuscum	9 (1,16)	12 (1,16)	17 (2,16)	16 (1,12)	14 (1,28)

TABLE IV-3: Comparison of selected data on the production of Sphagnum angustifolium, Sphagnum magellanicum, and Sphagnum fuscum in order of decreasing latitude.

Species	Growth mm / year	Production g m^{-2}/yr	Latitude	Longitude	Location	Annual precipitation (mm)	Source
S. fuscum	1.4-3.2	70	68° 22'N	19° 03'W	N Sweden	300	Rosswall et al. 1975
S. fuscum	-	250	63° 09'N		S Finland	550	Silvola & Hanski 1979
S. fuscum	-	220-290	63° 09'N	-	Finland	300	Tolonen (unpubl.)
S. fuscum	7-16	195	60°-62°N	22°-26°W	S Finland	650	Pakarinen 1978
S. magell.	9.5	70	59° 50'N		S Norway	1250	Pedersen 1975
S. angust.	147	500	-	-	-	-	-
S. fuscum	9.8	90	56° 05'N	13° 10'W	S Sweden	800	Damman 1978
S. magell.	7.8	100	-	-	-	-	-
S. magell.	10.4-17.5	50-100	55° 09'N	-	England	1270	Chapman 1965
S. angust.	28-34	110-240	54° 46'N	2° 21'W	England	1980	Clymo & Reddaway 1971
S. magell.	14-14.9	230	54° 46'N	2° 21'W	England	1980	Forrest & Smith 1975
S. angust.	-	240-330	-	-	-	-	-
S. angust.	38-43	110-440	54° 46'N	2° 21'W	England	1980	Clymo 1970'58
S. angust.	4.0-8.9	19-58	54° 43'N	66° 42'W	Québec	700	Bartch & Moore 1985
S. fuscum	-	270	54° 28'N	-	England	1375	Bellamy & Rieley 1967
S. fuscum	-	50	49° 53'N	95° 54'W	S Manitoba	500	Reader & Stewart 1971
S. fuscum	17-24	240	49° 52'N	80° 36'W	NE Ontario	700	Pakarinen & Gorham 1983
S. fuscum	7-31	69-303	49° 40'N	93° 43'W	NW Ontario	625	ELA - this study
S. magell.	11-34	59-246	-	-	-	-	-
S. angust.	20-39	100-198	-	-	-	-	-
S. fuscum	30	424-801	-	-	N Germany	725	Overbeck & Happach 1957
S. magell.	35-51	252-794	-	-	-	-	-
S. angust.	120-160	488-1656	-	-	-	-	-
S. fuscum +							
S. magell.	36-39	310	47° 09'N	93° 30'W	Minnesota	640	Grigal 1985
S. angust.	91-131	420	-	-	-	-	-
S. magell.	62	540	39° 07'N	79° 35'W	Virginia-USA	1330	Wieder & Lang 1983
S. angust.	75	610	-	-	-	-	-

TABLE IV-4: Ranges of production values (growth in parentheses) of *Sphagnum* in mire 239 for 1984, 1985, and 1986. Values are in g m^{-2} yr^{-1} for production and mm for growth.

	1984		1985		1986	
OLIGOTROPHIC ZONE						
S. fuscum	69	(7)	91	(9)	116	(12)
S. magellanicum	230	(25)	186	(34)	73	(13)
S. angustifolium	186	(28)	198	(33)	157	(31)
F value[1]	10.6	(12.6)	5.2	(12.6)	6.7	(16.7)
P[2]	0.000	(0.000)	0.007	(0.000)	0.002	(0.000)
MINEROTROPHIC ZONE						
S. fuscum	240	(25)	303	(31)	175	(18)
S. magellanicum	246	(27)	103	(19)	59	(11)
S. angustifolium	191	(29)	198	(39)	100	(20)
F value	1.6	(0.2)	20.4	(9.8)	17.3	(7.8)
P	0.211	(0.805)	0.000	(0.000)	0.000	(0.001)

1. Value of F based on a parametric ANOVA between species
2. Probability level

Table IV-5: Total *Sphagnum* production in a poor fen of northwestern Ontario. (OC) Oligotrophic Control (MC) Minerotrophic Control. Note: surface area per vertically projected area is taken into account.

Estimates of net production g m^{-2} yr^{-1}		
Year/area	OC	MC
1984	206	223
1985	175	150
1986	109	80

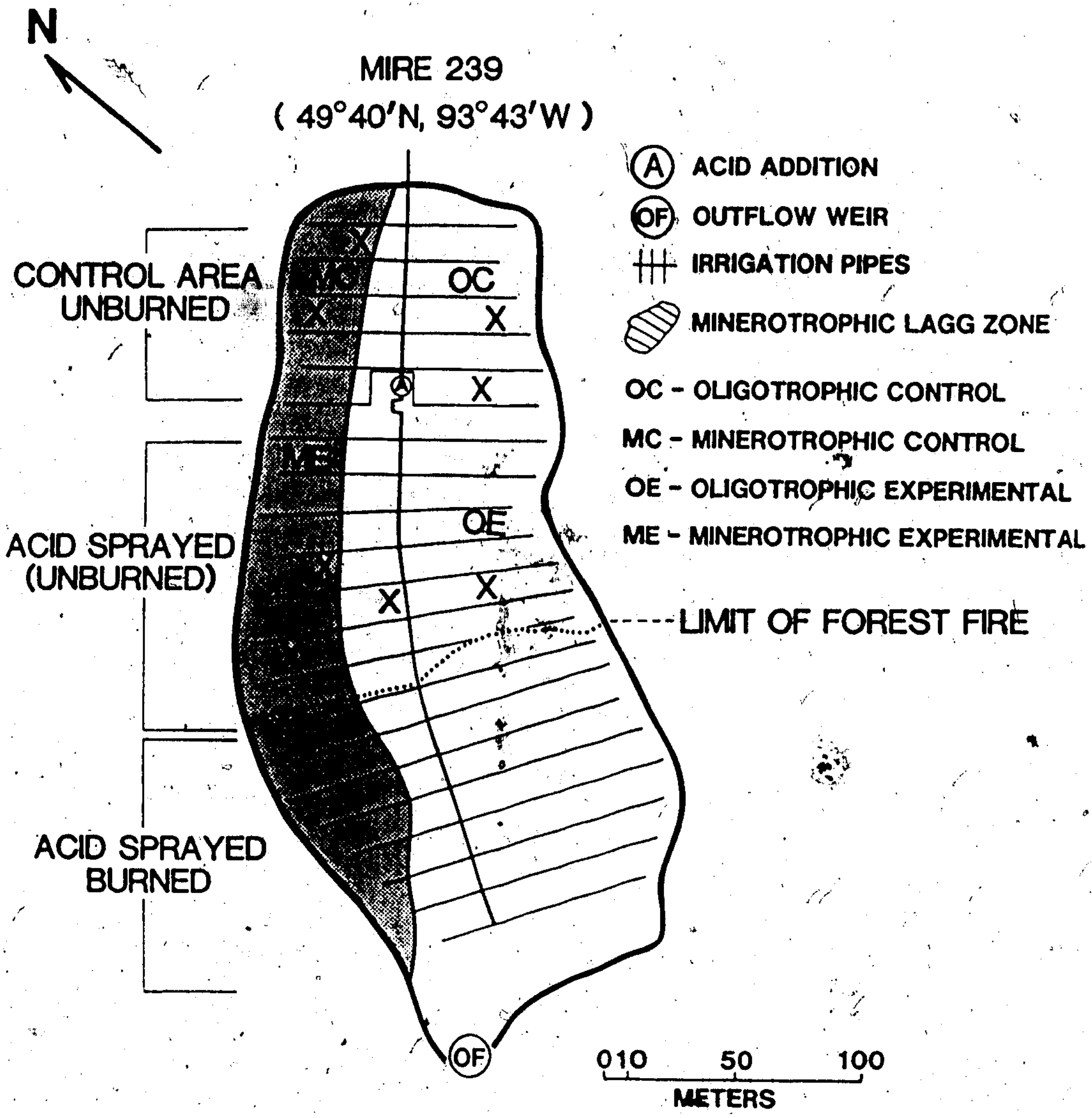

Figure IV-1: A map of mire 239 with the irrigation system for acidification, limit of forest fire, and delimitations of the four areas: OC - oligotrophic control, MC - minerotrophic control, OE - oligotrophic experimental, and ME - minerotrophic experimental.

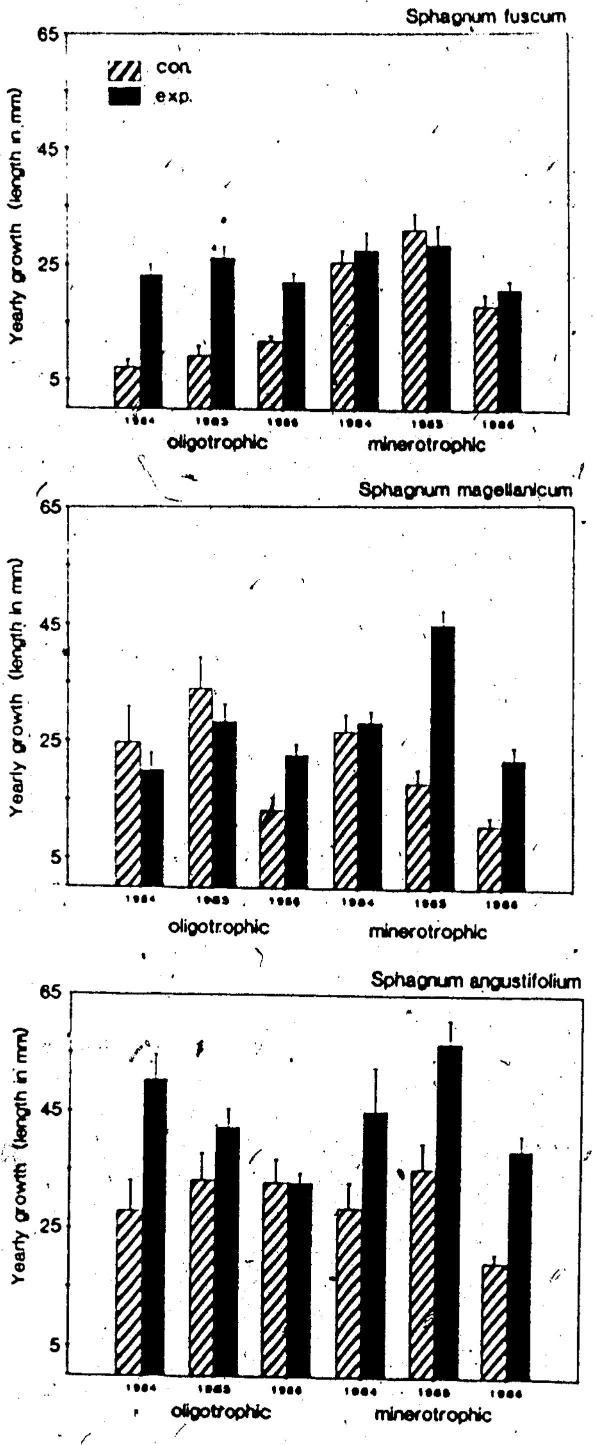

Figure IV-2: Comparison of growth (mm ± S.E.) of the three dominant *Sphagnum* species for three years of acidification (1984, 1985, and 1986). con. - control area and exp. - experimental area.

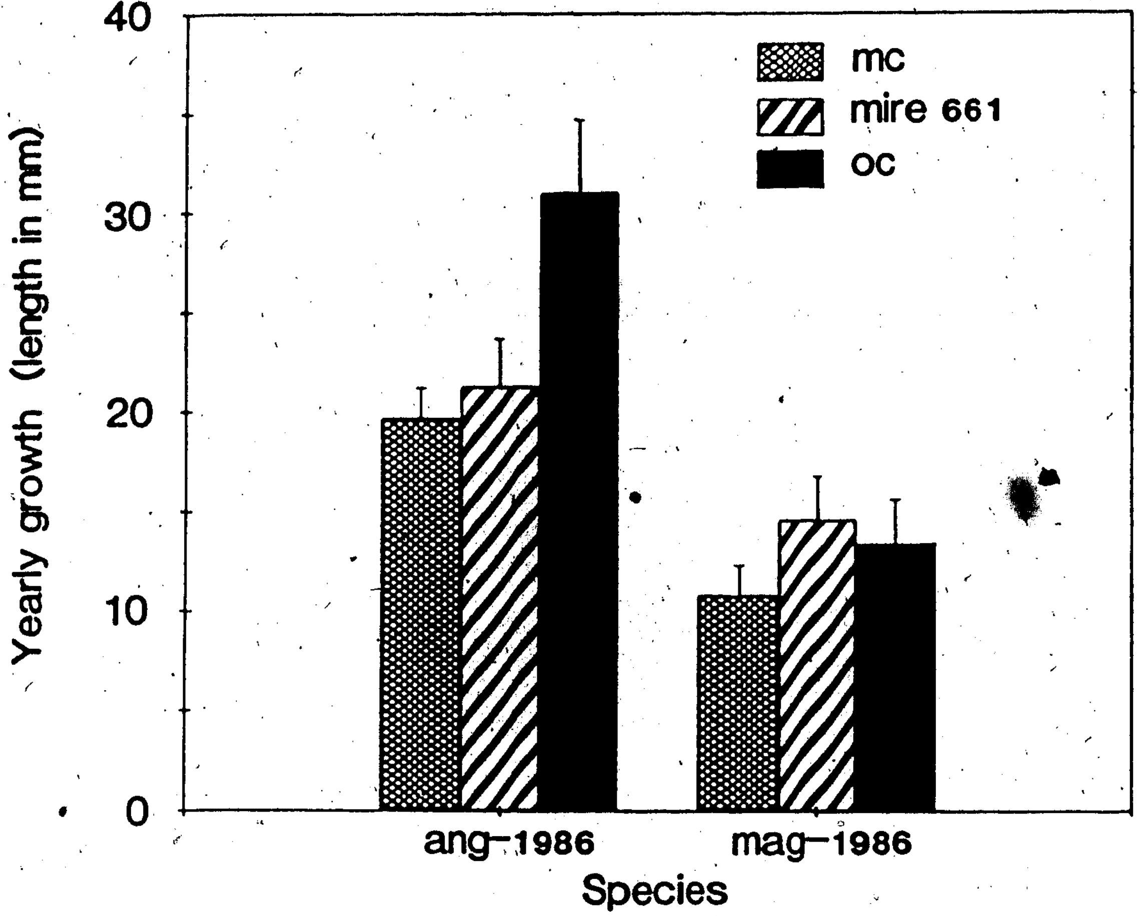

Figure IV-3: Comparison of growth (mm ± S.E.) of *Sphagnum angustifolium* (ang - 1986) and *Sphagnum magellanicum* (mag - 1986) between the control areas of mire 239 and a similar nearby poor fen, mire 661 for 1986 season. MC - minerotrophic control area OC - oligotrophic control area.

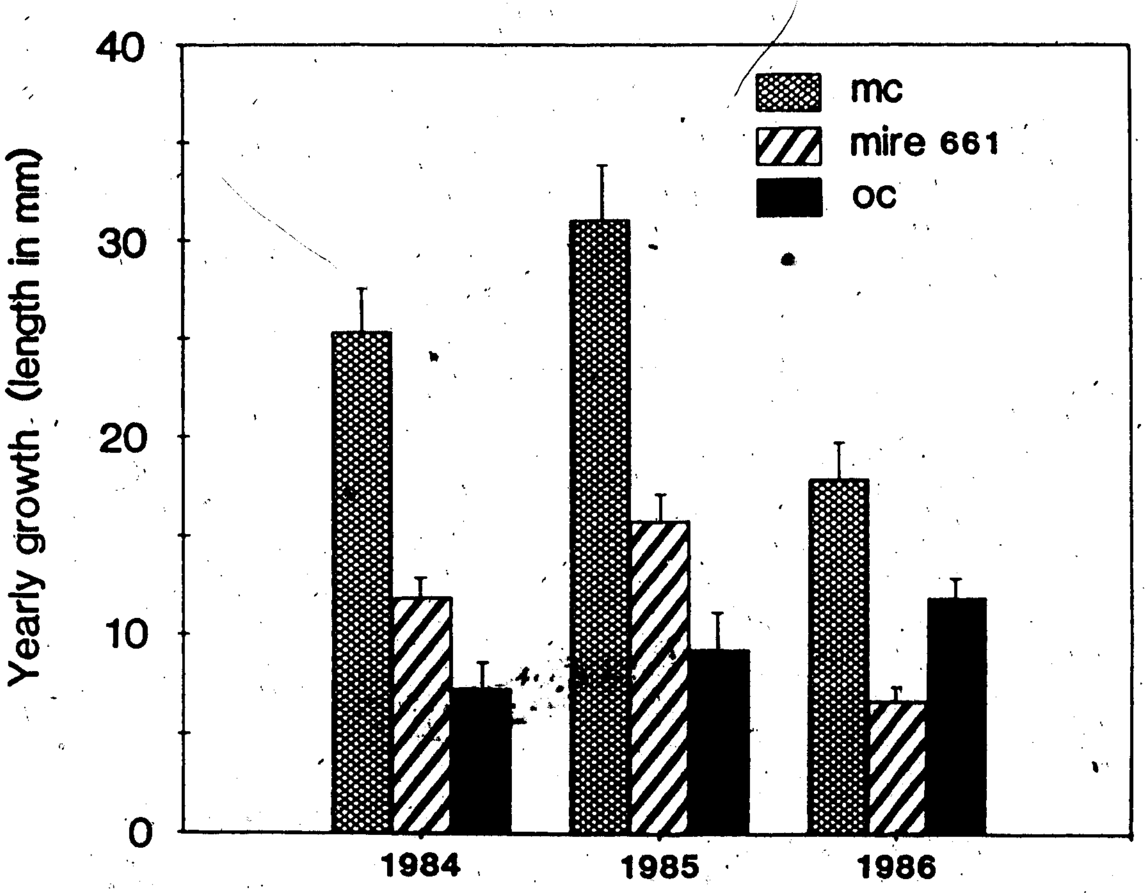

Figure IV-4: Comparison of growth of *Sphagnum fuscum* (mm ± S.E.) between the control zones of mire 239 and a similar nearly poor fen, mire 661 for 1984, 1985, and 1986 seasons. MC - minerotrophic control area, OC - oligotrophic control area.

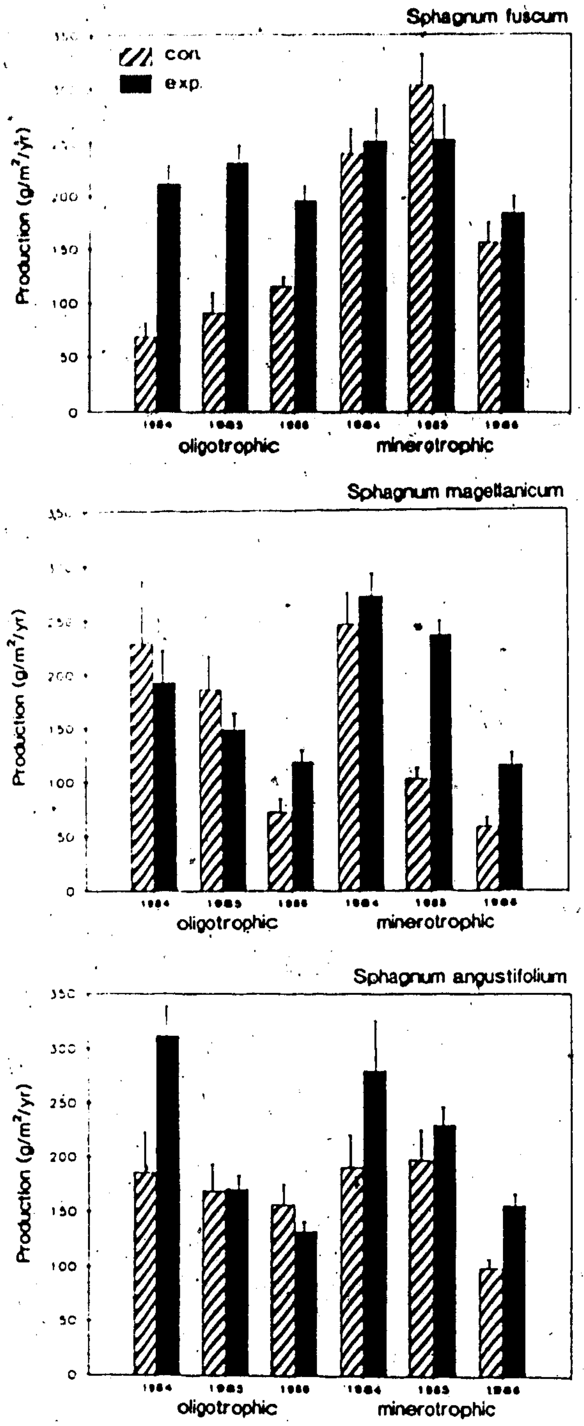

Figure IV-5: Comparison of production (g m^{-2} yr $^{-1}$ ± S.E.) of the three dominant *Sphagnum* species for three years of acidification (1984, 1985, and 1986). con. - control area and exp. - experimental area.

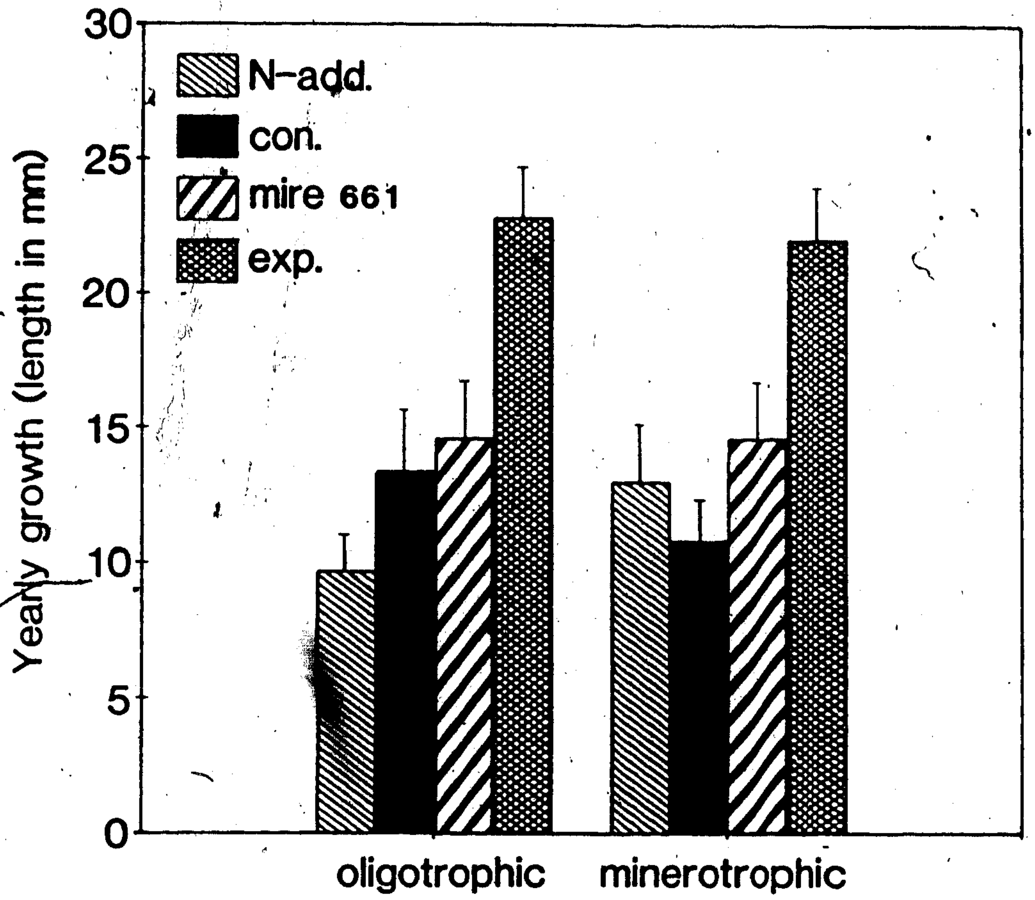

Figure IV-6: Comparison of growth (mm ± S.E.) of *Sphagnum magellanicum* receiving different nitrogen-loading. N-add. (NO_3^- + NH_4^+) - 1.5 g-N m^{-2} yr^{-1}; con. - "natural loading"; mire 661 - "natural loading"; exp. (NO_3^-) - .5 g-N m^{-2} yr^{-1}.

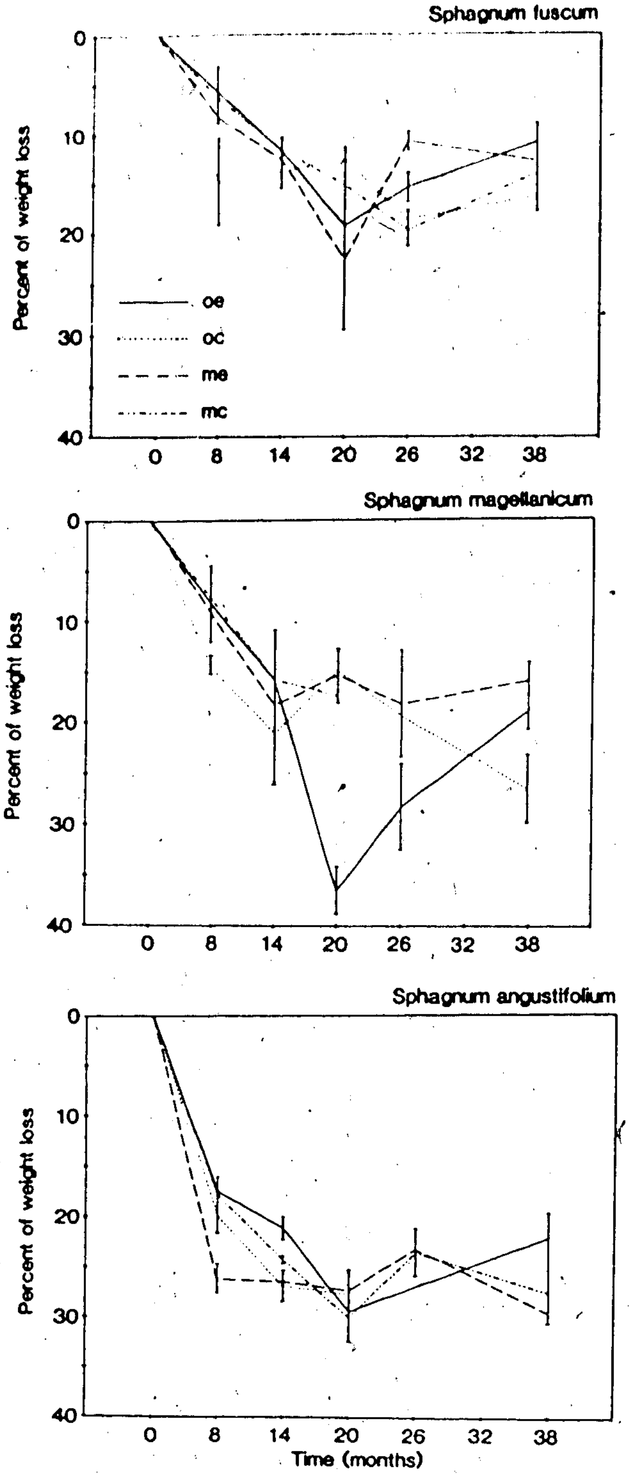

Figure IV-7: Comparison of decomposition (% of weight loss ± S.E.) for the 3.5-years study period. OC - oligotrophic control, MC - minerotrophic control, OE - oligotrophic experimental, ME - minerotrophic experimental.

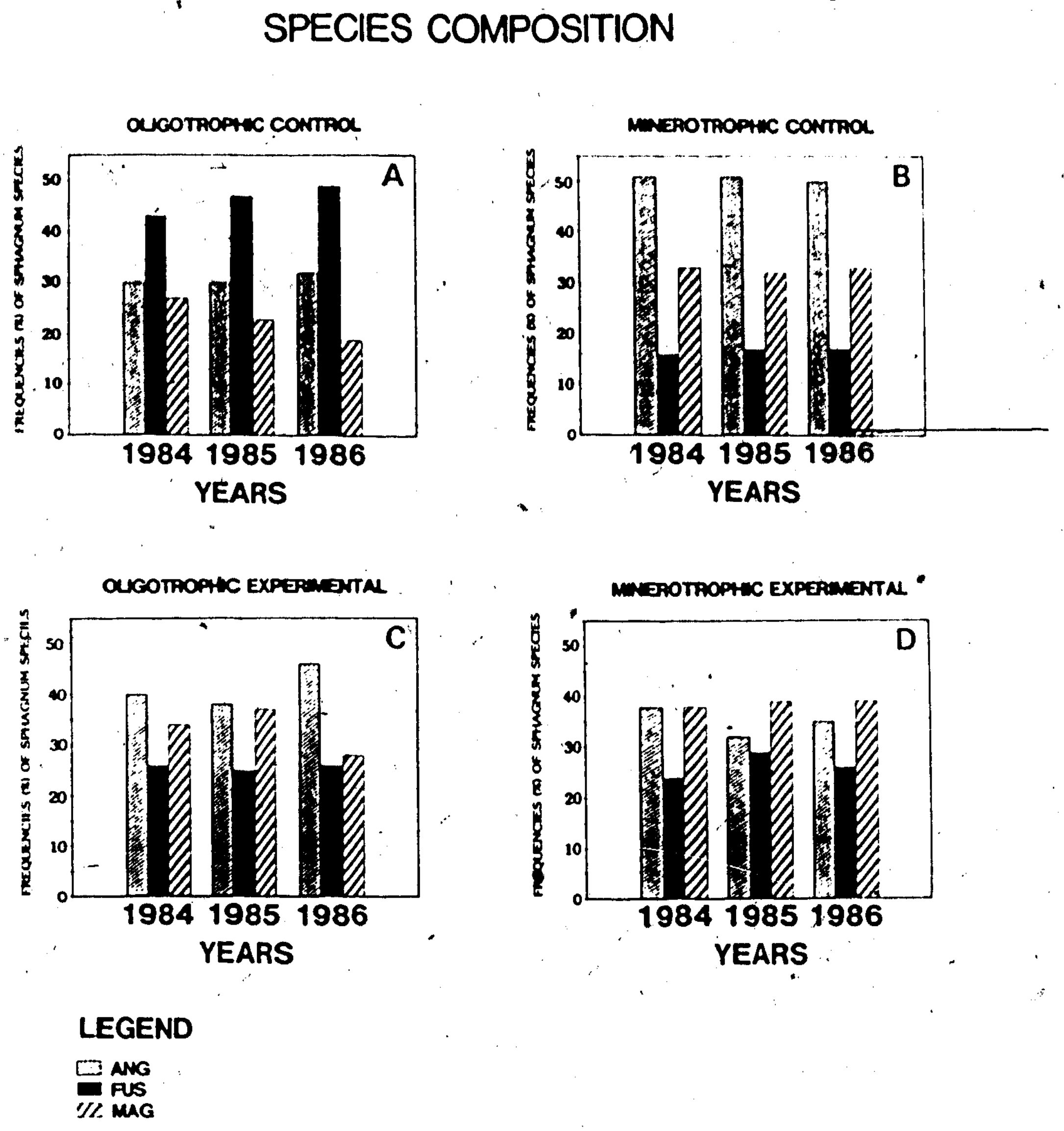

Figure IV-8: Yearly variation of the frequencies of *Sphagnum* species for each treatment zone. A) Oligotrophic Control; G = 3.274, P = 0.55 - B) Minerotrophic Control; G = 0.226, P = 0.995 - C) Oligotrophic Experimental; G = 3.625, P = 0.55 - D) Minerotrophic Experimental; G = 0.85, P = 0.999. Legend: ang = *Sphagnum angustifolium*, fus = *Sphagnum fuscum*, mag = *Sphagnum magellanicum*.

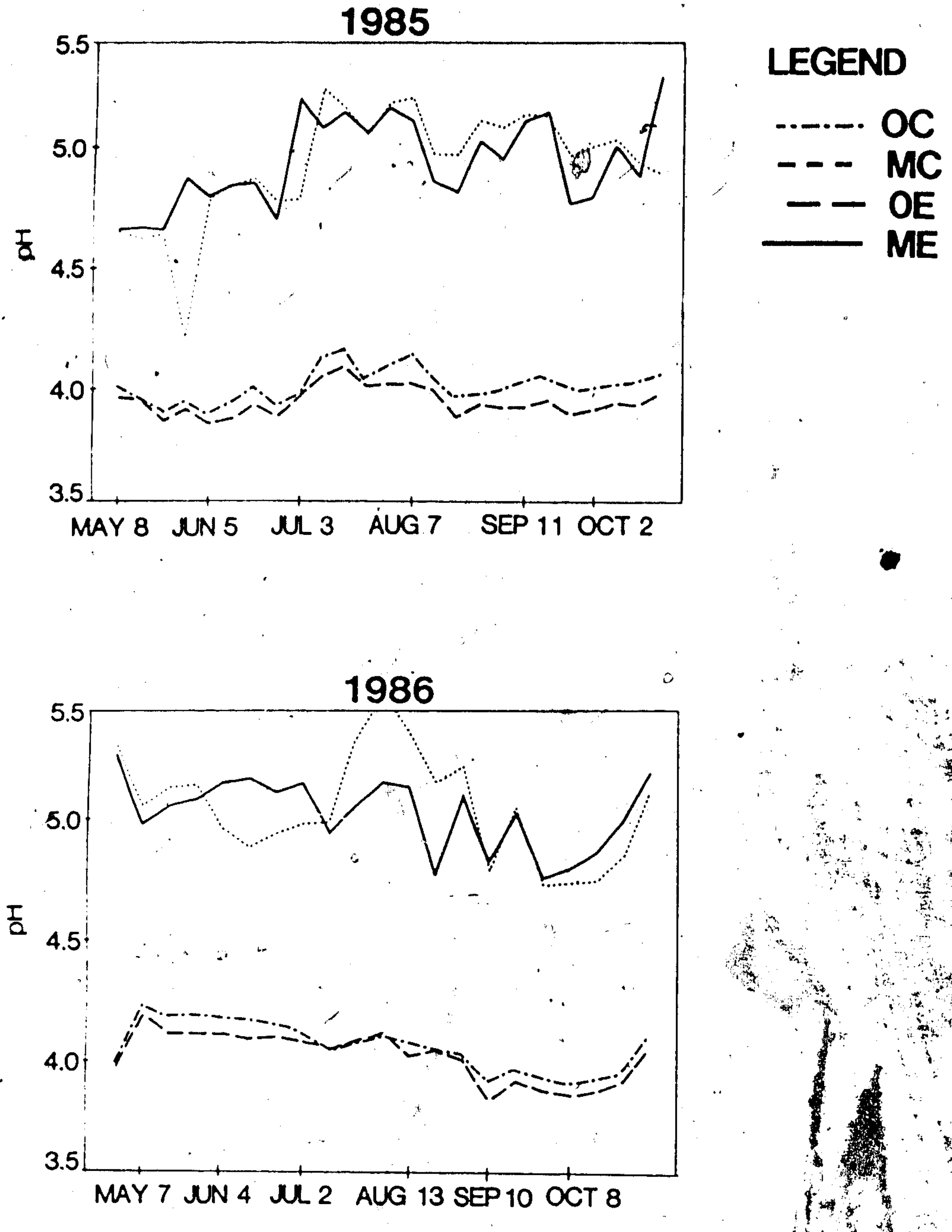

Figure IV-9: Weekly pH of OC - oligotrophic control area, OE - oligotrophic experimental area, MC - minerotrophic control area, and ME - minerotrophic experimental area.

Appendix 1: Results of a one-way ANOVA comparing the production of *Sphagnum* species in the control area.

Source	D.F.	Sum of squares	Mean squares	F ratio	F prob.
Oligotrophic					
Between groups	3	3358.15	1119.38	8.58	0.0000
Within groups	146	19058.79	130.54		
Total	149	22416.94			
Minerotrophic					
Between groups	3	3143.36	1047.79	6.98	0.0002
Within groups	143	21453.09	150.02		
Total	146	24596.45			

Appendix 2: Results of a one-way ANOVA comparing the decomposition rates of *Sphagnum* species.

Source	D.F.	Sum of squares	Mean squares	F ratio	F prob.
May 1984					
Between groups	2	1251.42	625.71	25.22	0.0000
Within groups	44	1091.62	24.81		
Total	46	2343.04			
Oct 1984					
Between groups	2	1216.73	608.36	23.11	0.0000
Within groups	45	1184.60	26.32		
Total	47	2401.33			
May 1985					
Between groups	2	1055.28	527.64	8.78	0.0006
Within groups	45	2704.84	60.11		
Total	47	3760.12			
Oct 1985					
Between groups	2	249.13	124.57	3.60	0.0422
Within groups	25	2864.22	34.57		
Total	27	1113.36			
Oct 1986					
Between groups	2	1481.34	740.67	20.57	0.0000
Within groups	58	2088.78	36.01		
Total	60	3570.12			

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V. THE ROLE OF SPHAGNUM IN THE RETENTION OF NITROGEN BY AN EXPERIMENTAL ACIDIFIED PEATLAND.

Introduction

Nitrogen is often considered a limiting nutrient in many North American bogs (Damman 1986; Watt and Heinselman 1965; Moizuk and Livingstone 1966; Tilton 1978). Bogs are nitrogen deficient habitats because of their complete dependence on atmospheric nutrient supply. *Sphagnum*-dominated poor fens also have minimal influence of soil water. Thus, they also rely on atmospheric supply and are frequently nitrogen and phosphorus deficient. Nitrogen cycling in bogs is minimized by anaerobic conditions, acidity, and slow decomposition, which when combined with continuous growth restricts mineralization and nitrification (Damman 1986; Lee *et al*. 1986).

Surprisingly, high rates of nitrogen supply in British precipitation is known to reduce *Sphagnum* growth (Press *et al*. 1986), possibly by exceeding its ability to retain inorganic nitrogen (Woodin and Lee 1987). This may prevent many bryophyte species from re-establishing in the mires of southern England (Ferguson *et al*. 1984; Lee *et al*. 1986). *Sphagnum* is adapted to a low supply of nitrogen and is sensitive to excessive ammonium (Press and Lee 1982; Woodin *et al*. 1985; Rudolph and Voigt 1986).

Increases in the concentration of NOx air and nitrate in rain and snow have been observed in recent decades in North America (Brimblecombe and Stedman 1982). The response of a *Sphagnum*-dominated peatland to high nitrogen inputs has received little attention (Press *et al*. 1986; Urban *et al*. 1987). Nitrate is known to be efficiently retained within peatlands (Moore 1978; Rosswall and Granhall 1980; Hemond 1983) and an experimentally acidified peatland at the Experimental Lakes Area (ELA) in Ontario, proved to be an efficient sink for nitrate (Urban and Bayley 1986; Bayley *et al*. 1987). This study is concerned with the major mechanism of nitrogen uptake in this acidified peatland.

Three possible mechanisms of nitrate transformation in peatlands have been proposed: denitrification, assimilation by plants, and dissimilatory reduction to ammonium (Hemond 1983; Urban *et al*. 1987). Bayley *et al*. (1987) observed little increase in ammonium in surface water after acidification events, indicating that the process of dissimilatory NO_3^- reduction is probably of minor importance, although no direct measurement of this process has yet been made. Rates of denitrification were measured in the field at the ELA site in 1985 (Urban *et al*. 1987). Background rates of denitrification were low (0.08 g m^{-2} as N) and no response to the acid application was detected. These latter results suggest that plant uptake may be the major sink for NO_3^- at ELA.

Vascular plants in acidic habitats, chiefly *Ericaceae*, have a restricted ability to utilize NO_3^- (Havill *et al*. 1974; Lee and Stewart 1978). *Sphagnum* species have been shown to utilize N in the NO_3^- form (Press and Lee 1982; Woodin *et al*. 1985). The objective of this study was to determine the importance of the *Sphagnum* mat in immobilization of deposited inorganic nitrogen in a poor fen which was being experimentally acidified with nitric and sulfuric acids.

Study Area

The experimental peatland is a 3.67 ha poor fen located in the Experimental Lakes Area (ELA) of northwestern Ontario, Canada (Lat. 49° 40′ N, Long. 93° 43′ W). In 1974 the watershed and one half of the peatland burned. The study site was dominated by *Picea mariana* with a shrub layer of *Ledum groenlandicum* and *Chamaedaphne calyculata*, a herb layer of *Carex trisperma* and *Smilacina trifolia*, and a ground layer of peat mosses. The dominant mosses were *Sphagnum angustifolium* (C. Jens. ex Russ) C. Jens. *in* Tolf colonizing hollows and lawns and *Sphagnum magellanicum* Brid. on hummocks.

A portion of the ELA site has been experimentally acidified since 1983. Once a month for 6 months of the year, 2.7 ha of the mire are sprayed with a 1:1 (equivalent basis) mixture of nitric and sulfuric acid at a pH of 3. The acid application was designed to increase the acid-loading to the site 10-fold, to simulate acidic rain from the eastern U.S. and Canada. The simulated acid precipitation was equivalent to reducing the mean pH of precipitation from on the bog 5.0 to 4.0 (Bayley *et al*. 1987) The unacidified portion of the site served as a control and received an equal volume of water without acid.

Methods

Nitrate reductase assay

To obtain a measure of nitrate reductase potential a technique similar to that described by Urban *et al*. (1987) was used. Three sets of assays were performed throughout the summer 1986. Twelve capitula plus stalks (5 cm) of green *S. angustifolium* were placed in vial tubes with 20 ml of assay medium (100 mM phosphate buffer, pH 7.34 containing 75 mM potassium nitrate and 0.75% propan-1-ol). The tubes were stoppered, wrapped in aluminum foil and incubated in the dark in the field for 1.5 h. The field incubation temperatures were in the range of 15-19 °C in June, 17-21 °C in July and 9-13 °C in October. After incubation, the tubes were placed in a boiling water bath for 20 min. After extraction, the liquid was decanted for measurement of nitrite, and the moss dried and weighed. A set of tubes with mosses extracted immediately without incubation was used to determine initial nitrite concentrations. Eight replicates for the experimental area and four replicates for the control area of the mire were processed. All assays were performed in the afternoon. Nitrite samples were analyzed within 16 h using a Technicon Autoanalyser as described in Stainton *et al.* (1977).

Results

Activity of nitrate reductase in *S. angustifolium* responded immediately following the acidification events of June and July (Figure V-1 a,b). A 7 to 12 fold induction of enzyme activity was observed within two hours after the acidification event, followed within four days by a fall in activity to initial levels. The fall in NR-activity after 2 to 4 days was related to the disappearance of free nitrate from surface water (Figure V-2). Results of the October assay (Figure V-1 c) did not show an induction of the enzyme activity as pronounced as in June or in July. At the time of the last acidification event in October, frost was occurring at night. This may have slowed metabolism, even though days were still warm and sunny. In field conditions, rates of NRA (constitutive and induced) measured at ELA (0.016 - 0.8 umol g^{-1} hr^{-1}) were higher than NRA measured by Urban *et al.* (1987) at Marcell bog in Minnesota (0.0004 - 0.013 umol g^{-1} hr^{-1}), but lower than values measured by Press and Lee (1982) in England and Wales (0.3 - 2.8 umol g^{-1} hr^{-1}), or by Woodin *et al.* (1985) in Sweden (1.0 - 4.0 umol g^{-1} hr^{-1}). The lower rates of NRA of Urban *et al.* (1987) are probably explained by the lack of nitrate in their phosphate buffer. This may have impeded the full expression of nitrate reductase enzymes.

Discussion

Minimum nitrate reductase activity (0.016 - 0.16 umol g^{-1} hr^{-1}) coincided with periods where nitrate was very low or non-detectable in surface water in mire 239. When nitrate became available through experimental acidification, an induction of NRA and utilization of nitrate was observed (Figure V-1 a,b). After three years of acid applications at ELA (at an average N-loading of 0.08 g m^{-2} per acidification event), there was still a tight coupling between nitrate deposition and the induction of NRA of *Sphagnum*. These results differ from the experiments of Press and Lee (1982) and Woodin *et al.* (1985), where they found a decline in NRA induced with successive nitrate additions. The supply of inorganic nitrogen in British studies, however, were more frequent (every four days) than in this experimental study (once a month). The decline in NRA of the British studies was believed to be due to the ammonium accumulation in the tissues, which inhibited enzyme induction or enhanced the degradation of the induced enzyme. I did observe a concurrent increase in cellular ammonium concentrations of *S. angustifolium* as NRA was induced (data not shown). The lack of a close relationship, between nitrate supply and induction of NRA in *Sphagnum* populations when nitrate is provided at high concentrations or frequently, may reflect a mechanism to limit the assimilation of nitrogen and prevent the build up of toxic concentrations of nitrogenous compounds such as NH_4^+ (Lee et *al.* 1986).

A breakdown in the induction of NRA of *Sphagnum* within peatland ecosystems can lead to a loss of the ability of peat mosses to retain nitrate. The loss of nitrate retention by the *Sphagnum* mat may have uncertain ecological consequences. Lee et *al.* (1986) suggested that it may alter the competitive balance in favor of species with a higher potential to utilize nitrate, modify microbial populations in the underlying peat, and/or affect the leaching of cations from the peat or from the underlying mineral substrata. At the level of NO_3^- sprayed onto mire 239, none of the effects listed above was observed. Further field investigations (with maybe an increase in nitrogen loading) may permit early identification of such effects in peatland ecosystems affected by acidification.

Conclusion

In the experimentally acidified peatland, the nitrate sprayed onto the mire surface was retained by the bryophyte layer i.e. *Sphagnum* mat. This observation agreed with the failure to detect denitrification activity after acidification (Urban *et al.* 1987) or ammonium and nitrate in pools (Bayley *et al.* 1987) in previous studies. Higher plants of ombrotrophic habitats have an ammonium base nitrogen nutrition, probably due to the fact that nitrate ions are efficiently taken up by the *Sphagnum* mat and thus nitrate is rarely available.

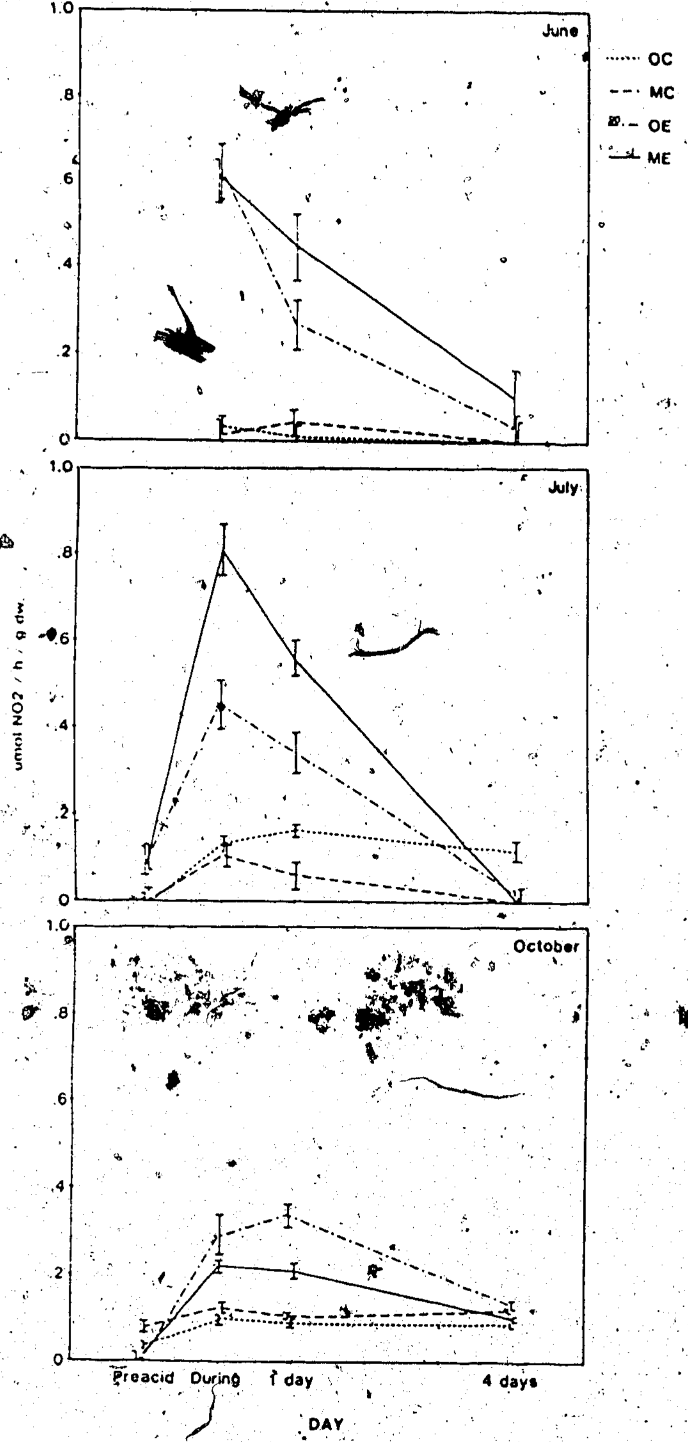

Figure V-1: Nitrate reductase activity (umol NO_2^- h^{-1} g^{-1} dw) in *Sphagnum angustifolium* one day before (Preacid), one hour after (During), one day after (1 day), and four days after (4 days) an acidification event at ELA site. Figures are means of four replicates for control plants and eight replicates for experimental plants, vertical bars represent ± S.E.

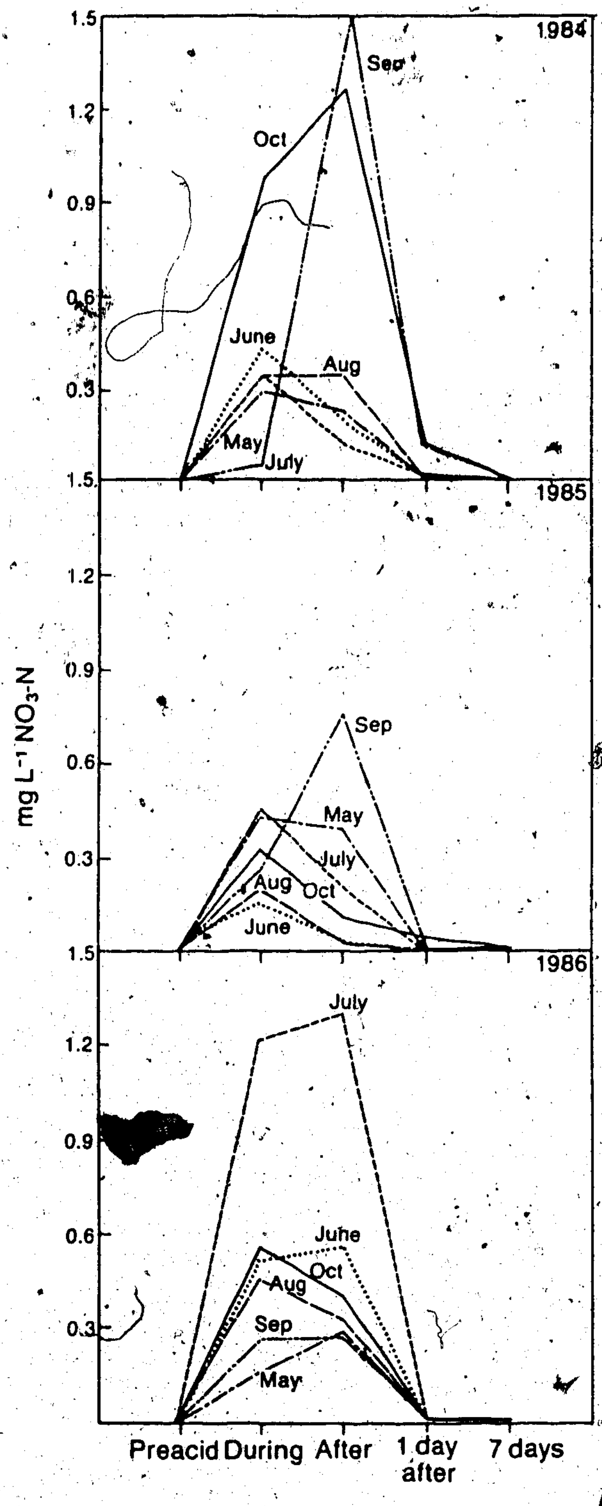

Figure V-2: Concentration of NO_3-N in the oligotrophic experimental area before and after acidification experiments. Samples collected prior to acidification (Preacid), two hours after the start of acidification (During), just after (After), 1 day after and 7 days after acidification.

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VI. CONCLUDING DISCUSSION

The study of the effect of acid deposition on peatland bryophytes is interesting because acidity is known to be detrimental to plant growth (Hutchinson t al. 1986; Raeymaekers and Glime 1986; Ferguson *et al.* 1978) and forest and lake (e.g. Hutchinson and Havas 1980; Schindler *et al.* 1985), but peat mosses are typically nitrogen limited (Damman 1986) and adapted to acidity, thus one might expect either a reduction or stimulation of plant growth of an experimentally acidified peatland.

The effect of acidic deposition on bryophytes of an extreme rich fen was studied for the first time. Growth and chlorophyll b content of *Tomenthypnum nitens* was stimulated by artificial acid sprays, contrasting with earlier findings that acid deposition was detrimental to mosses (Ferguson *et al.* 1978; Hutchinson *et al.* 1986; Raeymaekers and Glime 1986). Treatment with simulated acid rain had no effect on *Scorpidium scorpioides*, possibly because this moss was well protected when growing in flarks or in wet hollows where the surrounding water was highly ionic and well buffered.

Laboratory experiments on *Tomenthypnum nitens* and *Scorpidium scorpioides* revealed that *S. scorpioides* is more sensitive to acidity than *T. nitens* even though if it was not affected by acid rain in the field. *S. scorpioides* barely thrived at pH 3.5, whereas *T. nitens* growth was affected by pH lower than 3.5. Further experimentation with *T. nitens* proved that the nitrate component of acid rain was the stimulating agent improving growth and chlorophyll production.

These results did not identy the sulfuric acid component as having deleterious effect on the performance of *T. nitens*, as reported by Hutchinson *et al.* 1986 for upland, terrestrial feather mosses or by Glime *et al.* 1986 for boreal mosses,

After three years of treatment, in an experimentally acidified peatland, it was found that *Sphagnum* growth and production were still stimulated by acid applications, as also reported by Bayley *et al.* 1987 for the year of acid-loading at pH 3.0. Decomposition was not affected by acid deposition and *Sphagnum* community structure did not change. Theoretically peat accumulation was promoted in the acidified mire. These observations supported the suggestion of Urban *et al.* (1987), that in the initial years, acid deposition acts as a fertilizer for mires of boreal North America.

Within the experimentally acidified peatland, hummocks species showed a slower rate of decomposition than hollow species whereas production rate was more or less the same between the species. It appeared that hummocks were increasing in size, at least in the lagg zones.

A strong relationship between nitrate additions and the induction of nitrate reductase activity *Sphagnum* was found. The *Sphagnum* mat retained most of the nitrate sprayed onto the mire, an observation consistent with the failure to detect denitrification activity after acidification (Urban *et al.* 1987) or ammonium and nitrate in pools (Bayley *et al.* 1987).

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