# DEPOSITION OF SULPHUR AND ITS INFLUENCE ON SOILS IN THE AOSERP STUDY AREA

by

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# ABSTRACT

In the summers of 1975, 1976, and 1977, several field investigations were carried out to determine the amounts of sulphur deposited in rain, in rain washing off trees, and by direct absorption of $SO_2$ by soil. The impact of this sulphur deposition on soils in the AOSERP study area was also determined in both field and laboratory experiments. Rain collected at several sites in 1977 was acidic, with some monthly rain samples having pH values below 5.0. The sulphur content of rain was low and there was a gradient of decreasing $SO_4^{2-}$-S deposition in rain with increasing distance from the emission source. Scarcely, any of the sulphur in rain occurred in an acidic form. When instead the rain dripped through jack pine or trembling aspen trees (throughfall and stemflow) more sulphur was deposited. The effect was greater at sites near the emission source as compared to remote sites. Total amount of sulphur in net precipitation (throughfall and stemflow) beneath jack pine and trembling aspen was greater than that in rain. For both jack pine and trembling aspen larger quantities of the cations $K^+$, $Ca^{2+}$, and $Mg^{2+}$ were removed from the canopies at sites exposed to $SO_2$ compared to control sites. Both bare soils and soils with intact lichen cover were found to absorb $SO_2$ directly from the air. This absorption process amounted to the most important mechanism for removal of sulphur from the atmosphere in the AOSERP study area, particularly in areas close to the emission source. The absorption of $SO_2$ by soils was also shown to result in increased acidity of the top layer (0 to 1 cm) of some soils. Field experiments showed that sulphate sulphur (applied as $K_2SO_4$) was mobile in forest soils of the AOSERP study area. Applied sulphuric acid was also found to move quite rapidly through the soils and cause an increase in the acidity of the soil as it moved downward. Ground limestone was an effective method of counteracting the effects of the applied sulphuric acid on soil acidity.

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# 1. INTRODUCTION

Soils are dynamic natural bodies which constitute an important part of forest ecosystems. They are open systems to which substances may be added and removed. Soil processes and properties are therefore greatly influenced by the external chemical climate. Any direct change in the external chemical climate such as in the chemical composition of precipitation, or any indirect change such as an altered vegetative cover, will result in changes in the soil. Conversely, any changes in the soil will produce changes in vegetation and the chemical composition of drainage water. The effects of atmospheric sulphur on soils is therefore only one facet of atmosphere-plant-soil interactions.

Anthropogenic sources of atmospheric sulphur may affect forest soils via several pathways, namely:

1. In rain and snow;
2 In rainfall washing off vegetation;
3. By direct absorption of sulphur dioxide by soils; and
4. By impaction of particulate matter on soil and plant surfaces.

The first two processes are referred to as "wet deposition" and the latter two as "dry deposition". In order to better understand the influence of sulphur emissions on soil properties, it is necessary to quantify these external parameters which influence soil processes.

It is for this reason the study established a network of field sites in the Alberta Oil Sands Environmental Research Program (AOSERP) study area to monitor the chemical composition of rain, rain dripping of trees, and snow. The deposition of sulphur in particulates was determined in 1976 by Nipher gauges at several of the field sites, and the ambient sulphur dioxide concentrations were estimated in 1976 and 1977 by the use of sulphation discs set out at each field site.

The fundamental questions with which this project was concerned were:

1. How much sulphur was deposited and found its way into soil?
2. What were the resultant forms of this sulphur in soil; and
3. To what extent were soils acidified by this deposition of sulphur?

Measurement was made of the amounts of sulphur deposited by each of the above mechanisms, and of the total deposition on soils. The change in soil soluble sulphur and total sulphur contents was measured, together with changes in soil pH.

This report is a summary of several field investigations and laboratory experiments concerning the influence of anthropogenic sulphur on soils in the AOSERP study area.

## 1.1 STUDY OBJECTIVES

The principal objective of this project was to study the effects of anthropogenic sulphur on soils in the AOSERP study area. The major components of the objective were specifically:

1. Determine the mechanisms and rate of sulphur absorption by soils;
2. Characterize the chemical form of deposited sulphur and the proportional distribution of the various forms of sulphur in soil;
3. Predict the chemical changes in soil caused by sulphur emissions, including the rate, direction, and magnitude of such changes;
4. Study measures to reduce any soil damage; and
5. Develop recommendations for monitoring the long-term impact of emissions on soils.

The project was designed to answer broad, important questions regarding the potential effect of sulphur emissions on soils in the AOSERP study area. The experiments were not intricate and dealt with the amounts of sulphur deposition and any resultant changes in soils.

## 2. CURRENT KNOWLEDGE

In the past few decades, serious environmental problems have become apparent with increasing emissions of atmospheric sulphur dioxide. On a global scale, anthropogenic emissions of sulphur compounds are estimated to be $78 \times 10^6$ tonnes S/year (Erickson 1963, Kellogg et al. 1972) with approximately an equivalent amount arising from natural emissions. Canada has five percent of the world total anthropogenic emissions (Katz 1977), while 0.23 million tonnes per year (or approximately 0.4 percent of the world total) are emitted in Alberta (Tollefson 1972).

In Alberta, the main source of sulphur oxides is the processing of natural gas (Summers and Whelpdale 1976). This $SO_2$ may be oxidized and hydrolyzed to $H_2SO_4$ which can give rise to acid rain (Brosset 1973). A trend towards increased acidity of precipitation has been found in the heavily industrialized regions of the world, namely northwestern Europe and the northeastern United States. Slightly acid precipitation has been reported in a region downwind of gas processing plants in the foothills belt of Alberta (Summers and Whelpdale 1976).

Sulphur dioxide may also give rise to acid particulates, depending on the ammonia content of the air, which may be transported long distances (Brossett 1976a). These may impinge directly on the ground surface or onto the forest vegetation and be subsequently washed off by rain (Brosset 1976b).

Overrein (1972) found in lysimeter experiments that the leaching of calcium in different soil types increased considerably when the acidity of the precipitation increased. Similar increases for both calcium and magnesium were noted by Abrahamsen et al. (1976). Tamm et al. found that treatment of soil in lysimeters with fertilizer ($NH_4NO_3$) resulted in a marked increases in the degree of leaching, especially when the fertilizer was combined with dilute acid. They also found that much of the sulphur, added as sulphuric acid, was retained in the lysimeters even through the degree of leaching of calcium increased by about 25 percent. Wiklander (1975) showed that neutral salts in precipitation may reduce the acidification of soils by acid precipitation.

The chemical composition of rain is altered when it penetrates tree crowns. Adsorbed dry deposits are washed from surfaces and nutrients are leached from leaves (Madgwick and Ovington 1959, Nihlgard 1970, Eaton et al.

1973, and many others). Abrahamsen et al. (1976) found that the total deposition of sulphuric acid beneath Norway spruce (Picea abies (L.) Karst.) and scots pine (Pinus sylvestris (L.) was twice that deposited in incident rain. Baker et al. (1977) found that throughfall and stemflow was depressed in pH at sites close to sources of sulphur dioxide. Nyborg et al. (1977) found increased levels of sulphur in white spruce (Picea glauca (Moench) Voss.) throughfall at exposed sites in Alberta. Stemflow and throughfall are an important influence on the physico-chemical properties of soils (Mina 1967, Gersper and Holowaychuk 1971). Field studies on forest ecosystems in southern Sweden have shown that acid canopy drip gives rise to an increase in the degre of leaching of calcium from the soil (Nihlgard 1971). In Alberta, Baker et al. (1977) found higher potassium chloride extractable acidity and aluminum, and lower exchangeable calcium and magnesium in soils exposed to sulphur dioxide compared with control site soils.

Emissions of sulphur dioxide can be directly absorbed by soils. Johansson (1959) set out bare potted soils downwind from a $SO_2$ source for six years. The ratio of sulphur gained by the soil through direct absorption from the air to that gained through precipitation ranged from 2 to 7, depending on the site. The pH of the soil was also lowered by between 0.3 and 1.4 pH units. In Ontario, Cox (1975) set containers of three soils under canopies downwind from two $SO_2$-emitting smelters. At sites 15 to 25 km from the emission source, the pH of the top 1 cm of a silty clay loam soil was depressed 0.2 to 0.4 units after 19 weeks of exposure. The soluble sulphate content of the soils increased by 15 to 70 ppm. In Alberta, Nyborg and Walker (1977) reported a correlation between soluble sulphate and pH depression for soils exposed to $SO_2$ emissions in the field. The maximum increase in sulphate sulphur (8.8 ppm) was not sufficient to account for the pH depressions.

Laboratory experiments have demonstrated that soils have a large capacity for the absorption of sulphur dioxide (Abeles et al. 1971). The effect of sulphur dioxide on soil pH and sulphate content was related to the concentration of sulphur dioxide and the time of exposure (Yee et al. 1975). It was also related to the moisture content (Terraglio and Manganelli 1966, Smith et al. 1973, Cox 1975), texture (Cox 1975) and calcium carbonate content (Cox 1975, Yee et al. 1975) and calcium carbonate content (Cox 1975, Yee et al. 1975) of the soil used.

Ghiorse and Alexander (1976) found that sulphur dioxide was rapidly removed from the gas phase by both sterile and non-sterile soil indicating viable micro-organisms are not directly involved in its removal from the atmosphere. Sulphur dioxide was rapidly oxidized to sulphate in the soil and soil pH was depressed slightly. In both sterile and non-sterile soil, about one quarter of the sulphur introduced as sulphur dioxide could not be recovered as sulphite or sulphate. However, if the soil was first ignited in a furnace to destroy organic matter, the recovery was complete. Apparently, this investigation indicated that sulphur dioxide can react directly with soil organic matter.

Direct absorption of sulphur dioxide by soils was found by Nyborg et al. (1977) to be the most important means of sulphur deposition in central Alberta. They estimated that as much as 50 kg sulphur (S)/ha was deposited for 20 to 30 km downwind from large single emissions sources over the summer period. A small but measurable decrease in soil pH accompanied the increase in sulphur content of the soils, and much of the absorbed sulphur was found in non-sulphate form.

# 3. EXPERIMENTAL PROCEDURES

## 3.1 DESCRIPTION OF THE STUDY SURVEY

The AOSERP study area (**Figure 1**) is part of the mixedwood section of the boreal forest region (Rowe 1972). The growing season, based on a $4^{o}C$ index, occurs from the end of April to early October, and lasts an average of 165 days yearly. The average annual precipitation is 432 mm with 280 mm falling during the period from May to October.

At the time of this study, the only sources of sulphur emissions in the study area were located at the Great Canadian Oil Sands processing plant (now Suncor Inc.) located at Tar Island, about 70 km north of the town of Fort McMurray. At this plant, there are two main sources of sulphur emissions: (1) the power house stack; and (2) the incinerator stack. The power house stack is estimated to emit an average of 120 tonnes S/day and the incinerator stack about 15 tonnes S/day. In addition, there are two flares which are intermittent sources of smaller amounts of sulphur oxides (personnel communication from M. Strosher, Pollution Control Division Alberta Environment, Edmonton).

### 3.1.1 Field Sites

A network of field sites were erected in May and June 1976. These sites occurred in four zones corresponding to increasing distances from the emission source: (1) less than 25 km; (2) 25 to 50 km; (3) 50 to 100 km; and (4) over 100 km (remote or control sites). The position of these sites relation to the emission source is shown in **Figure 2** and **Table 1**. A site was also located at Canwood, Saskatchewan (502 km SE of the emissions source) which served as a distant control site. In addition, there were two more distant controls, Loon Lake, Saskatchewan (356 km SSE) and Beaverlodge, Alberta (527 km WSW). In this report the terms exposed, control, and remote sites are used more to designate relative distance from the Oil Sands plant rather than in the precise meaning of the terms with respect to deposition of sulphur emissions.

The sites, excepting Hangingstone River (Site No. 15) and Canwood (Loon Lake and Beaverlodge) consisted of a 3.7 m x 3.7 m enclosure surrounded

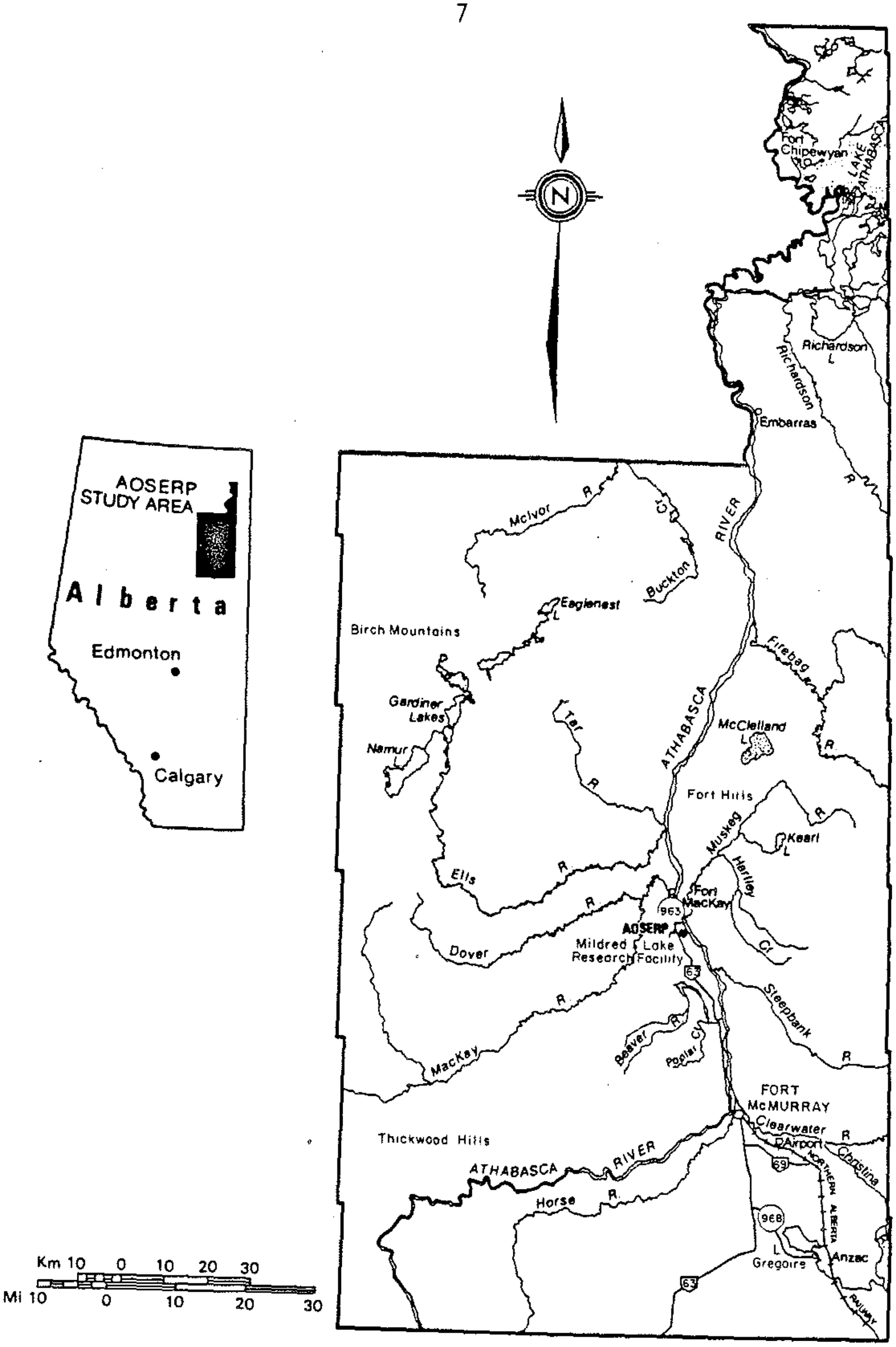


Figure 1. Location of the AOSERP Study Area.

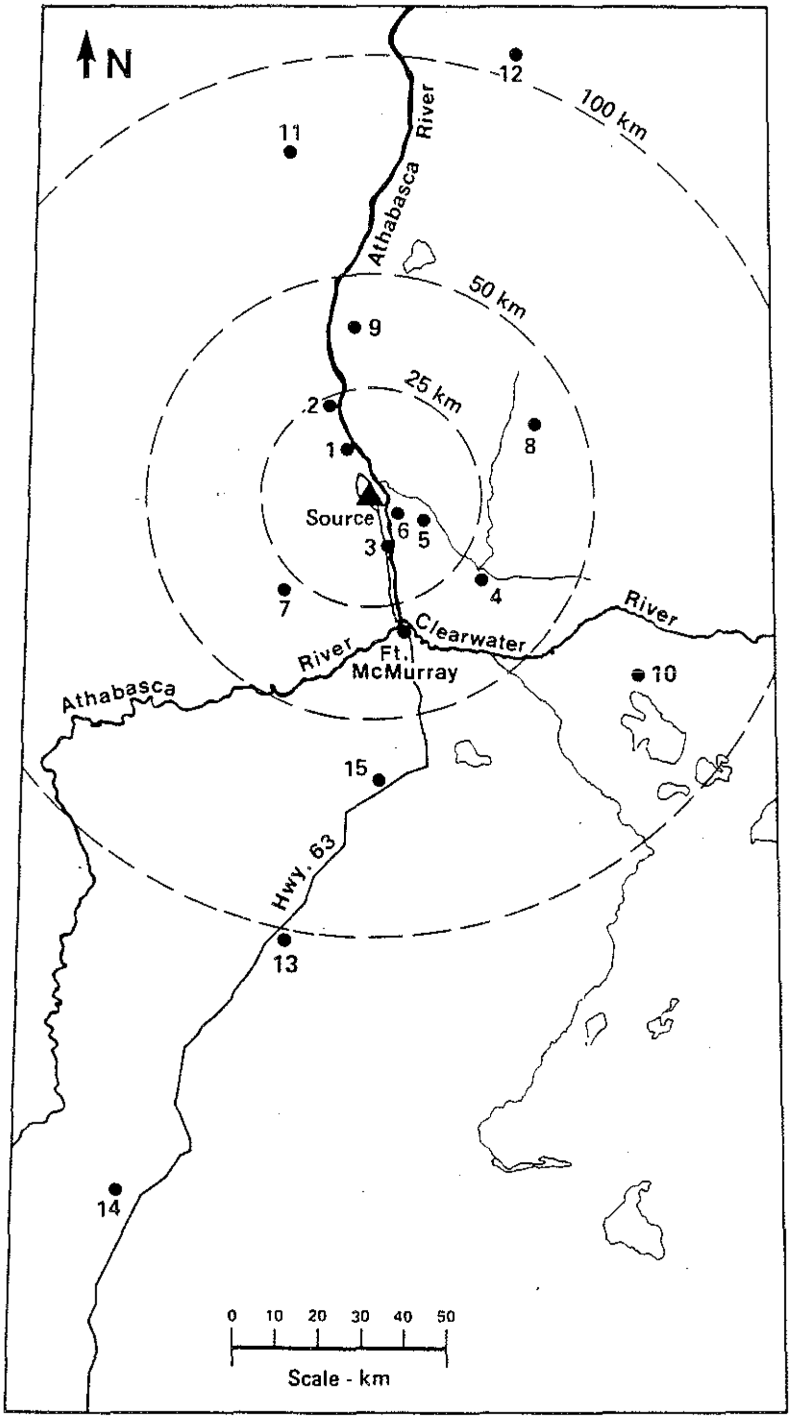


Figure 2. Location of sulphur dioxide monitoring sites (shown by full circles and numbers), in relation to emission source ( Δ ), and the four zones at designated distances from the source (as shown by dashed lines).

Table 1. Distances (km) and Direction of the Research Sites from the Sulphur Dioxide Emission Source.

| Site No. | Site | Direction from Source | Distance (km) from Emission Source |
|---|---|---|---|
| Northerly Sites | | | |
| 1 | Mildred Lake | NW | 11 |
| 2 | MacKay River | NW | 21 |
| 9 | Bitumount | N | 39 |
| 11 | Birch Mountain | NNW | 79 |
| 12 | Richardson | NNE | 102 |
| Southerly Sites | | | |
| 3 | Supertest Hill | S | 7 |
| 7 | Thickwood Hills | SW | 31 |
| 15 | Hangingstone River | S | 67 |
| 13 | Algar | SSW | 101 |
| 14 | May | SW | 173 |
| Easterly Sites | | | |
| 6 | Steepbank 2 | ESE | 4 |
| 5 | Steepbank 1 | ESE | 17 |
| 4 | Steepbank A | SE | 32 |
| 8 | Muskeg Mountain | ENE | 38 |
| 10 | Gordon Lake | SE | 75 |

by a 1.8 m high link chain fence equipped with a door. Within this enclosure was a 1.8 m x 1.2 m rain shelter raised 0.9 m above ground level.

In 1976 and 1977, each field site was equipped with a Taylor 11 inch "clear-vu" rain gauge (Sybon Corporation, N.C.). It was positioned 40 cm above the ground surface.

During the summer of 1976 and 1977, a rain sample collection gauge was also set up at each site. They consisted of 5 L polyethylene bottles fitted with polyethylene funnels of 21 cm inside diameter. This provided rain water samples for chemical analysis. Each funnel was equipped with a screen to prevent contamination of the sample with debris. The sample collector was placed 40 cm above the ground surface. In 1976 only, modified Nipher gauges were installed at several sites to determine both the deposited particulate matter and the rain over the summer period. The Nipher gauge is a standard item for measuring fresh snowfall at meteorological stations, but with modifications the gauge will accumulate any dry particulates which are deposited from the air (Nyborg et al. 1977). Other experiments established at the field sites during the 1977 field season will be described in subsequent sections of this report.

### 3.1.2 Nutrient Cycling Study

The study was established in 1976 to compare the chemical composition of throughfall, stemflow, and litterfall of several indigenous tree species of the AOSERP study area, and to evaluate the influences of atmospheric sulphur dioxide on the foliar leaching rates of these same species. The tree species studied were black spruce (Picea mariana (Mill.) B.S.P.), jack pine (Pinus banksiana Lamb.), and trembling aspen (Populus tremuloides Michx.). The three species were chosen because they are the predominant tree species in the region and because they represent three different types with regard to tree form, bark texture, and site preferences.

It should be noted that in the AOSERP study area, there is some hybridization between jack pine and lodgepole pine (Pinus contorta Dougl. var. latifolia. Engelm.) where their ranges overlap (Hosie 1975). Branch and cone samples from all the jack pine sites used in this study were examined in the laboratory. It was evident that the variability between sites was no greater than the natural variability of jack pine populations. The jack pine trees at each site exhibited predominantly jack pine characteristics. In further discussion in this report, these hybrid trees will be referred to as jack pine.

Two study sites were chosen in 1976. The "control site" was established near the Algar forestry air strip (Site No. 13) 101 km SSW of the emission source. The "exposed site" was situated near Site No. 4 at 32 km SE of the emission source (**Figure 2**). At each site, three plots were established, one for each species. Thus, there were three control plots and three exposed plots.

It was not possible to have two plots for each species at each of the control and exposed sites. Difficulty in locating similar stands, lack of time to establish the plots, and the prohibitive number of sample collectors, precluded the use of this more desirable experimental design.

Each plot consisted of a pure stand of each tree species. A description of the study plots is given in **Table 2**. Ten trees were sampled in each plot. For jack pine and trembling aspen the control and exposed plots had similar tree heights and stand densities. The difference in the diametres of trees selected for stemflow gauges was significant (Student's t-test) for trembling aspen ($p<0.05$) but was not significant for jack pine. The spruce plots were quite different in stand density, tree heights and stem diameters.

At both exposed and control sites, plots were chosen to be as close together as possible. This minimized topographic differences and ensured each plot received similar amounts of precipitation. This also ensured that the exposed plots received similar levels of sulphur dioxide emissions.

Each plot (except the exposed black spruce plot) measured 30 m x 30 m (approximately 0.1 ha) and was divided into 36 quadrats of 5 m x 5 m. Twenty of the quadrats were selected using a random number table and a throughfall gauge was set up in the centre of each (**Figure 3**). The throughfall collectors consisted of 5 L polyethylene bottles fitted with polyethylene funnels with an inside diameter of 21 cm. On plots where the crown closure was less than 80%, throughfall gauges were placed under the tree nearest the centre of the quadrat. This was to ensure that there was an adequate number of collectors to obtain samples of throughfall. Ten stemflow collectors were attached to randomly selected trees in each experimental plot

Table 2. Description of the Plots Used for the Nutrient Cycling Study 1976.

| Plot | No. of Stems/ha[b] | Basal Area ($m^2$/ha) | Average Tree Height (m) | Average Age (Years) | Estimated Canopy Closure (%) | Mean Tree Diameter (cm) | Diam. of Trees Selected for Stemflow Gauges[a] Mean | Diam. of Trees Selected for Stemflow Gauges[a] Signif. Level |
|---|---|---|---|---|---|---|---|---|
| Control Aspen | 2180 | 47.0 | 20.7 | 69 | 90 | 15.8 | 18.9 | |
| Exposed Aspen | 3180 | 30.8 | 19.8 | 37 | 95 | 10.9 | 13.9 | 0.042 |
| Control Pine | 800 | 22.7 | 15.9 | 120 | 38 | 18.4 | 21.5 | |
| Exposed Pine | 400 | 14.8 | 18.3 | 37 | 51 | 21.5 | 22.0 | 0.787 |
| Control Spruce | 1190 | 14.0 | 11.6 | 73 | 48 | 11.4 | 13.6 | |
| Exposed Spruce | 7500 | 27.0 | 6.1 | 57 | 80 | 6.5 | 7.2 | 0.001 |

[a] For each species, the mean diameter of 10 trees selected for stemflow gauges at the control plot was compared (Student's t-test) with the mean diameter of the corresponding exposed plot.

[b] Tree stem was defined as having a DBH ≥ 5 cm.

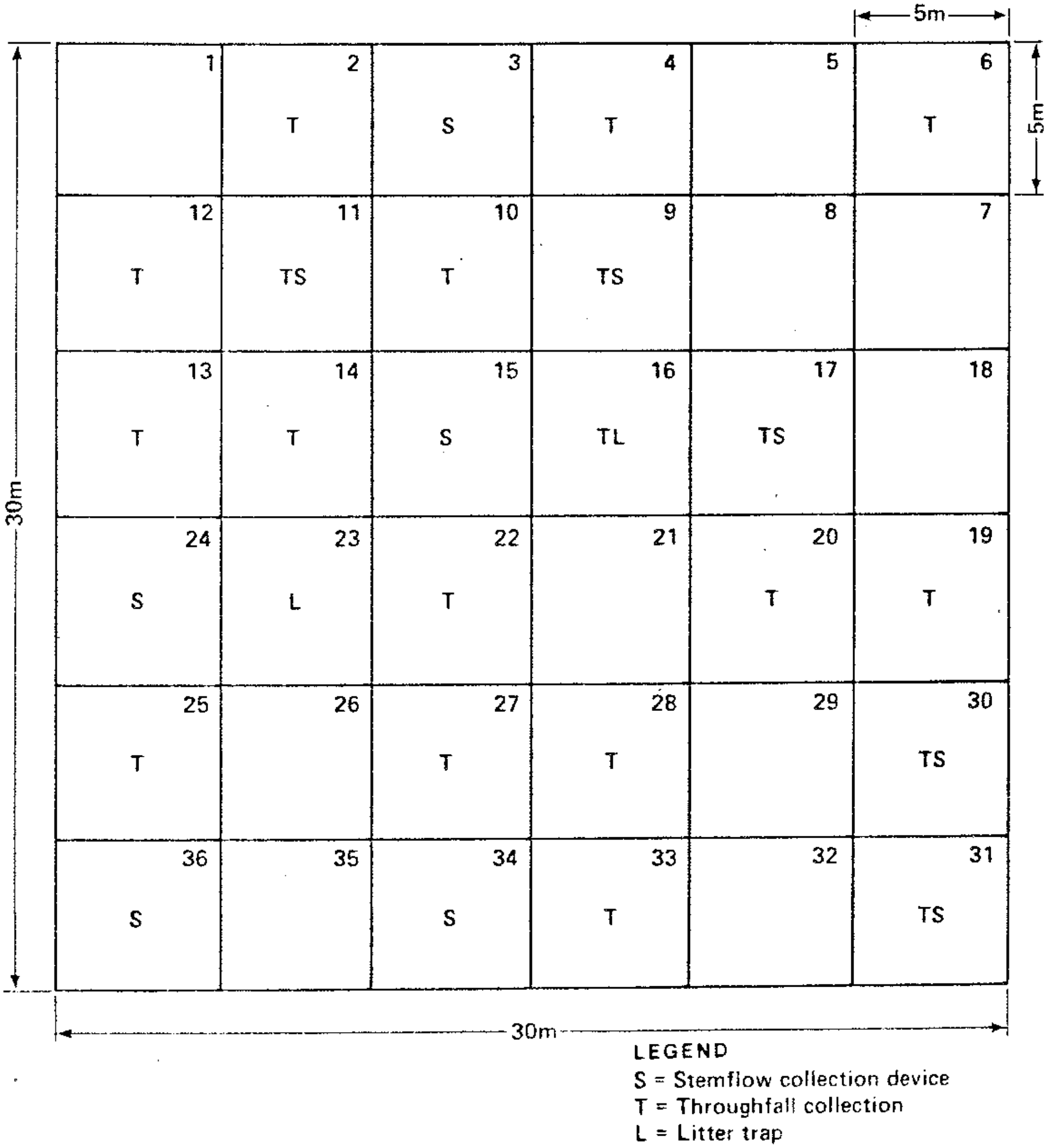


Figure 3. Layout of a Typical Plot Used in the Nutrient Cycling Study.

(Figure 3). The stemflow collectors consisted of split plastic piping fastened to the tree in a spiral fashion and sealed with an inert caulking compound. The piping led into 23 L polyethylene "jerry" cans placed on the ground. Each device was fited with a nylon screen to trap out insects and other debris. Two litter traps were randomly positioned in each plot (Figure 3). The litter traps were made up of 1 m x 1 m x 15 cm wooden frames with fine (18 mesh) fiberglass screen bottoms. They were set on legs 15 cm above the ground surface. This number of collection devices per plot (20 throughfall, 10 stemflow, and 2 litter) was considered the minimum necessary for comparisons to be made between the plots at a reasonable confidence level (Kimmins 1973).

The black spruce exposed plot measured 20 m x 20 m and had a narrow path cut through the centre and around the outside edges to provide access for sampling. This plot design was necessary because the density of the trees made a larger plot difficult to set up. Each 5 m x 5 m quadrat was divided into four subquadrats and a throughfall collector was positioned in two of these by random selection. The stemflow collection devices and litter traps were positioned as for the other plots.

Each plot had two rain gauges in a nearby clearing and a rain collection gauge to provide samples of incident rain for chemical analysis. The rain gauges were Taylor 11 inch "clear-vu" rain gauges (Sybon Corporation N.C.). They were positioned approximately 40 cm above the ground surface. The rain sample collectors consisted of 5 L polyethylene bottles fitted with polyethylene funnels with an inside diameter of 21 cm. Each funnel was equipped with a fine mesh screen to prevent debris from contaminating the samples. The collection devices were placed inside wooden boxes attached to wooden stakes so that the gauges were approximately 40 cm above the ground surface. Sulphation discs were also located at each plot in a wooden shelter box located in an adjacent opening.

### 3.1.3 Jack Pine Stemflow Study

In June 1977, four sites were established to study the influence of sulphur dioxide emissions on the chemical composition of jack pine stemflow. Data from the 1976 nutrient cycling study had shown that there was a marked depression in the pH of jack pine stemflow and throughfall at the site exposed to sulphur dioxide. Further investigation was needed.

The two control sites were located near field site No. 13, 27 km south of field site No. 14. The site south of site No. 14 is referred to as site No. 14A and named May 2 (Table 3), althought that site does not appear on Figure 2. The two exposed sites were located at site No. 8, about 1.6 km northwest of site No. 6. The site near site No. 6 is referred to as site No. 6A and named Steepbank 3 (Table 3), but does not appear on Figure 2. The sites were located at least 300 m from the highway to prevent contamination of the rain samples by motor vehicle exhaust fumes.

Pure stands of jack pine were chosen for each plot. A description of the sites is given in Table 3. At each site, stemflow collector devices were attached to five randomly selected trees. Rain gauges, rain sample collection gauges, and sulphation discs were set out at each site as for the 1976 nutrient cycling study (Section 3.1.2).

### 3.1.4 Movement of Applied Sulphate Sulphur in Forest Soils

The experiment was established to determine the rate of movement of sulphate sulphur through natural undisturbed soils of the AOSERP study area. There were sites for the experiment (Figure 4).

3.1.4.1 Mildred Lake Research Facility Site. The site is located 11 km northwest of the emission source on well-drained aeolian sand. The principal tree species is jack pine with a sparse understory of bearberry (*Arctostaphylos uva-ursi* (L.) Spreng.), bog cranberry (*Vaccinium vitis-idaea* (L.) var. *minus* Lodd), and blueberry (*Vaccinium myrtilloides* Michx.). There is also a nearly continuous lichen stratum principally of *Cladina mitis* (Sandst.) Hale & W. Culb.) and *Cladina arbuscula* (Wallr.) Hale and W. Culb.

3.1.4.2 Ruth Lake Site. The site is located 6 km south of the emission source on poorly-drained aeolian sand with a water table situated less than 1 m from the surface during the summer months.

Vegetation consists of scattered individuals of jack pine seedlings with a low shrub stratum comprised of mainly leather leaf (*Chamaedaphne*

Table 3. Description of the Four Jack Pine Stemflow Study Sites.

| Site No. | Site | Distance from Source (km) | Direction from Source | Total Precipitation (mm) | Mean Tree Height (m) | DBH |  |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Mean (cm) | Minimum (cm) | Maximum (cm) |
| 6A | Steepbank 3 | 2.4 | ESE | 51.7 | 13.2 | 16.8 | 11.3 | 23.0 |
| 8 | Muskeg Mountain | 38.0 | ENE | 49.3 | 7.7 | 12.9 | 12.1 | 14.0 |
| 13 | Algar | 101.0 | SSW | 43.0 | 15.9 | 21.4 | 18.3 | 28.1 |
| 14A | May 2 | 200.0 | SW | 52.8 | 9.1 | 16.7 | 11.5 | 20.3 |

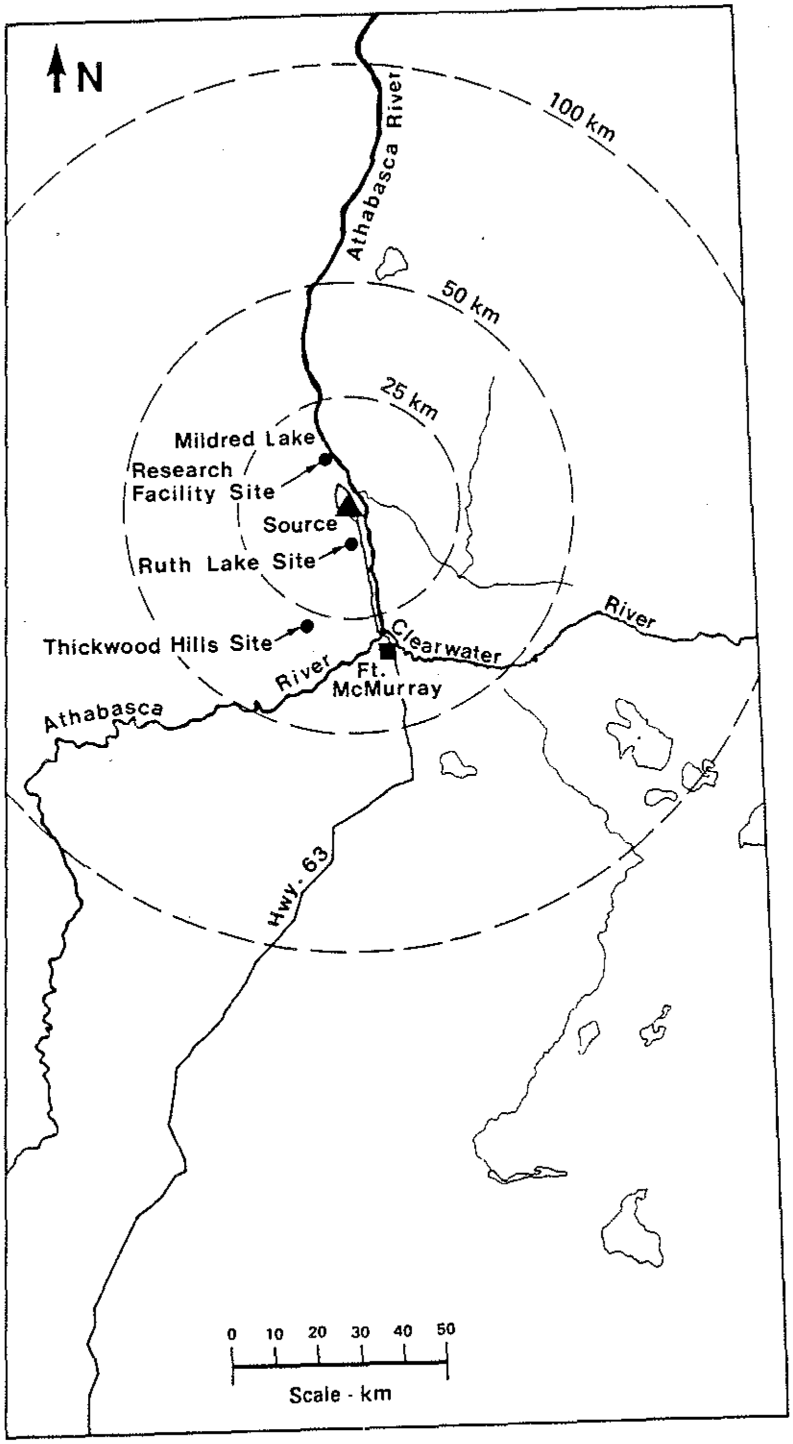


Figure 4. Location of Three Sites with Experimental Plots on Undisturbed Soil, with Applications of Elemental Sulphur, Sulphuric Acid, and Potassium Sulphate.

calyculata Moench.) and bog rosemary (Andromeda polifolia L.). The bryophyte stratum is diverse but consists mainly of Polytrichum strictum Brid.

#### 3.1.4.3 Thickwood Hills Site.

The site is a well-drained upland site on glacial till located approximately 27 km southwest of the emission source. The tree species present are large jack pine individuals in a dense stand of smaller trembling aspen trees. There are also a few small white spruce trees. The sparse tall shrub stratum consists of green alder (Alnus crispa (Ait.) Pursch). The lichen stratum is almost continuous and comprised principally of Cladina mitis (Sandst.) Hale & W.Culb.

The texture and bulk density of the soils at these sites is given in Table 4. The soils at the Mildred Lake Research Facility and Ruth Lake sites are sandy; while the soil at Thickwood Hills contains more clay. The first soil was an Orthic Eutric Brunisol. The soil at Ruth Lake site was not classified. The soil at Thickwood Hills was an Orthic Gray Luvisol.

### 3.1.5 Permanent Soil Plots

The plots were laid out in mid-August, 1976, at each of the field sites (Figure 2). These plots were established to provide baseline information on soils in the AOSERP study area, and to provide a means of monitoring the long-term effect of sulphur deposition on soils. These plots allow soil sampling from specific micro-plots (1 m x 2 m) replicated three times, with allowance to take soil samples in nine different years (Figure 5).

## 3.2 SAMPLE COLLECTION AND ANALYSIS

### 3.2.1 Wet Deposition

#### 3.2.1.1 Precipitation Measurements.

The amount of precipitation at each field site was recorded during the first and second halves of each month (approximately 15 days apart) from June to September 1976. During 1977, precipitation was measured during the first week of each month from May to

Table 4. Soil Texture and Bulk Density of Soils from Sites of the Applied Sulphur Movement Experiment.

| Sites | Depth (cm) | Sand (%) | Silt (%) | Clay (%) | Textural Class | Bulk Density ($g/cm^3$) |
|---|---|---|---|---|---|---|
| Mildred Lake Site | 0.0 to 2.5 | 93.0 | 2.7 | 4.3 | S | 1.28 |
| | 2.5 to 15 | 89.8 | 4.9 | 5.3 | S | 1.72 |
| | 15 to 30 | 91.8 | 2.8 | 5.4 | S | 1.96 |
| | 30 to 60 | 93.4 | 0.4 | 6.2 | S | 2.12 |
| | 60 to 90 | 92.0 | 1.7 | 6.3 | S | 2.33 |
| Ruth Lake Site | 0.0 to 2.5 | 89.6 | 3.7 | 6.7 | S | 1.50 |
| | 2.5 to 15 | 93.4 | 0.4 | 6.2 | S | 1.76 |
| | 15 to 30 | 90.5 | 1.0 | 8.5 | S | 1.97 |
| | 30 to 60 | 92.4 | 0.7 | 6.9 | S | 2.12 |
| | 60 to 90 | 92.1 | 0.6 | 7.3 | S | 2.23 |
| Thickwood Hills Site | 0.0 to 2.5 | 33.3 | 48.8 | 17.8 | L | 1.00 |
| | 2.5 to 15 | 27.6 | 27.2 | 45.2 | CL | 1.23 |
| | 15 to 30 | 32.0 | 32.6 | 35.4 | CL | 1.44 |
| | 30 to 60 | 63.5 | 25.2 | 11.3 | SCL | 1.55 |

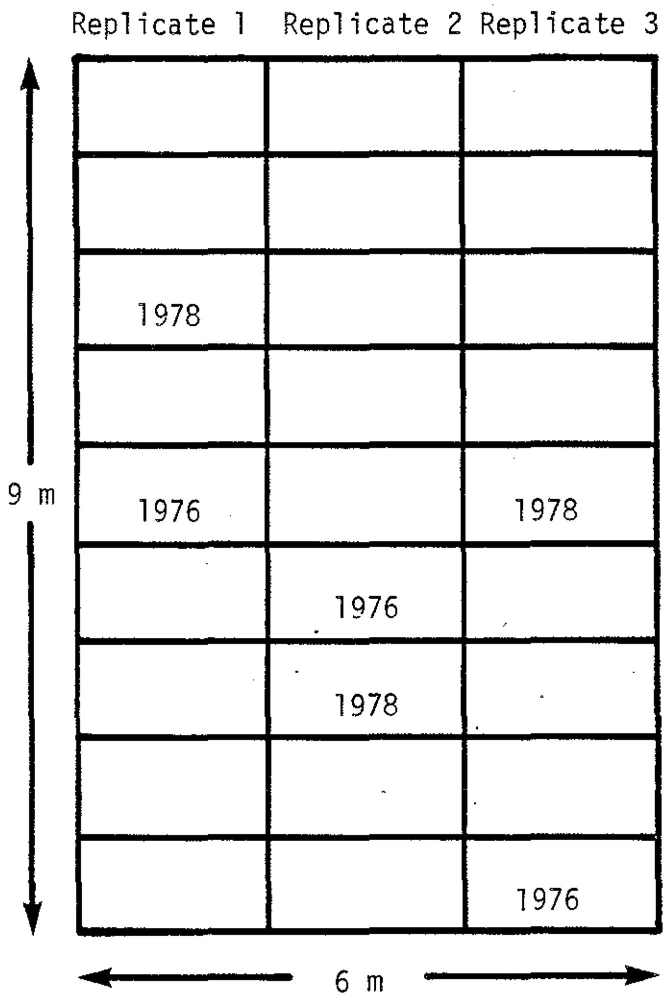


Figure 5. Field Plan of a Permanent Soil Plot. Samples were taken in 1976 and 1978.

September. Small quantities of mineral oil was placed in the emptied rain gauges after measurements were obtained to minimized evaporation between readings.

3.2.1.2 Precipitation Sampling. Incident rain samples were collected from the rain funnel-type sample gauge at each field site at the same time as the rain gauge was read. The volume of the rain sample was recorded and a 250 mL sample taken. Samples were stored in the dark at $0^oC$ to $+4^oC$ so that any growth of microorganism would be reduced until analyses were completed. Samples were filtered before the analyses.

The rain samples from the Nipher gauges, which included deposted water-soluble particulate matter, were handled in a similar way as the rain from the funnel-type gauges. The sulphate sulphur content of the Nipher sample minus the sulphate sulphur content of the funnel-type gauge gave the estimate of the amount of sulphate sulphur in dry deposition.

Accumulated snow samples were collected in 1976 March 17 and 18 at seven sites in the AOSERP study area. Duplicate samples were taken at each site. Snow volume per unit area was measured. The pH, sulphate sulphur concentrations, and cation content were determined on the melted samples.

The cations $Ca^{2+}$, $Mg^{2+}$, $Na^+$, and $K^+$ were determined by atomic absorption using a Perkin-Elmer model 503 atomic absorption spectrophotometer with an air-acetylene flame. Samples for $Ca^{2+}$ and $Mg^{2+}$ determination were first diluted with 1% $La_2O_3$ solution to reduce chemical interference. The pH of precipitation samples was determined using a Fisher Acumet model 250 digital pH meter.

Sulphate sulphur was determined using Dean's (Dean 1966) modification of the spectrophotometric method of Johnson and Nishita (1952). Precision of the determination of sulphur sulphate normally fell within ±5% of the average, but when the concentration of sulphur sulphate in precipitation samples was less than 0.5 ppm, precision was only ±10%.

3.2.1.3 Nutrient Cycling Study. Throughfall and stemflow were sampled approximately every two weeks for the control plots and monthly for the exposed plots. The exposed plots were sampled less frequently than the control plots because the only means of access to the exposed plots was by helicopter. Sampling frequency was increased with more frequent rain storms.

On each sample date, the volume of water in each collector was recorded and a 250 mL sample taken. Rain water samples were collected in a similar fashion. The filters were cleaned at each sampling and 1 mL of chloroform was added to the polyethylene collection vessels and the sample bottles to prevent algal growth (Carlisle et al. 1966).

The $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$, and $SO_4^{2-}$-S concentrations were determined as for the precipitation samples (Section 3.2.1.2). The mean nutrient concentrations presented are geometric means with each concentration value being weighted according to the sample volume. To calculate such a mean for the pH values, the pH numbers were first converted to their negative antilogarithms (hydrogen ion concentration). These were then multiplied by the sample volume and summed. This sum was divided by the sum of the sample volumes and the resulting concentration value was converted back to a pH value. This pH represents the strength of a solution of a completely ionized acid which could have brought the same amount of hydrogen ions per unit area to the ground as was brought by the rainfall.

The pH was determined using glass electrodes. Titratable acidity was determined by titrating a 25 mL aliquot of the degassed sample against 0.001 N KOH (standardized against $H_2SO_4$) to pH 7.00 using a combination glass electrode and a Fisher automatic titrimetre.

It should be noted here that in any water sample there are two types of acidity that can be measured, free and total. Free acidity is a measure of the concentration of protons in solution. They could have originated from the dissociation of weak or strong acids. Free acid is determined by measurement of the solution pH. Total acidity is determined by titration and is a measure of the concentration of protons, both those in solution and those still undissociated.

3.2.1.4 Jack Pine Stemflow Study. Stemflow was collected on three occasions during the summer of 1977: (1) 19 to 20 May; (2) 06 to 07 June; and (3) 03 to 05 July. At each sample period all four sites were serviced. The amount of precipitation was recorded at each sample date and a sample of rainwater was collected from the rain sample collection gauge. The volume of stemflow was recorded and a 250 mL subsample taken for analysis. The pH, titratable acidity, and $SO_4^{2-}$-S were determined on all samples as for the nutrient cycling study samples (Section 3.2.1.3).

### 3.2.2 Dry Deposition

3.2.2.1 Sulphur Dioxide Absorption by Sulphation Discs. Two sulphation discs were maintained under the rain shelter at each field site during the summer of 1976 and 1977. Each consisted of plastic petri dishes of 4.8 cm inside diameter and contained a $PbO_2$ compound.

The discs were left for an exposure period of one month at each field site before being replaced by fresh discs. They were analysed for sulphur by digesting the insoluble lead sulphate with sodium carbonate and then the $SO_4^{2-}$-S was determined by the method of Johnson and Nishita (1952). The data were expressed as mg $SO_3$ per 100 $cm^2$ of plate surface area per day.

3.2.2.2 Sulphur Uptake by Bare Soils - Field Experiments. In 1975, a peat and two mineral soils from the AOSERP study area, and three agricultural soils were set out in canisters at a number of different sites. The purpose of this experiment was to measure the amounts of sulphur absorbed directly from the air by soils in the AOSERP study area and to measure the effect of this absorbed sulphur on soil pH. Agricultural soils were used to provide a simple means of comparison with studies elsewhere in the province. The soils were as follows:

1. Soil 1: An Orthic Black Chernozem, Malmo series, silty clay loam texture, 10% organic matter. The soil is cultivated, and the sample was taken from the cultivated layer. This soil will be referred to as O.BL soil.
2. Soil 2: An Orthic Dark Gray Chernozem, silty loam texture. The soil is cultivated, and the sample was taken from the cultivated layer. This soil will be alternatively referred to as O.DG soil.

3. Soil 3: An Orthic Black Chernozem, sandy loam texture. The soil is cultivated, and the sample was taken from the cultivated layer. This soil will be alternatively referred to as the sandy O.BL soil.
4. Soil 4: An Orthic Eutric Brunisol, sand texture. Sample taken approximately 2 km south from the AOSERP Mildred Lake Research Facility Site. Tree cover was jack pine. The soil sample was obtained from the top 25 cm of the Bm horizon. This soil will be alternatively referred to as the sandy O.EB soil.
5. Soil 5: An Orthic Gray Luvisol, sandy loam texture. Sample taken approximately 5 km north of Fort MacKay. Tree cover was trembling aspen. Sample was taken from the top 15 cm. The soil will be alternatively referred to as the O.GL soil.
6. Soil 6: A Typic Mesisol. sample was taken 25 km south of Fort MacKay. The soil be alternatively referred to as the TY.M soil.

Soils were ground to pass through a 2 mm sieve and equal weights of each soil were placed in canisters of dimensions 9.5 cm x 9.5 cm x 13.5 cm. The soil surface area exposed to the air was therefore 90.3 $cm^2$. Three canisters of each soil were placed under the rain shelter at each field site. This was to ensure that the only source of sulphur for the soils was that in the ambient air. The rain shelter was open on all sides so as to provide unrestricted air flow over the soil samples. Most of these soils were brought to field capacity water content weekly by addition of distilled $H_2O$. A few were kept air-dry at all times.

In 1976, the above experiment was repeated with more sites. In this report, however, results are given only for the sandy O.EB soil and the TY.M soil. Soils were set out in canisters at each of 14 field sites from June to September. The soils were watered twice a month to 10% above their predetermined field capacity moisture content with distilled water.

After the summer exposure period, the soil canisters were returned to the laboratory and the soils were separated into layers: (1) 0 to 1 cm; (2) 1 to 3 cm; (3) 3 to 5 cm; and (4) 5 to 12 cm. They were then air dried. The pH was determined using a Fisher Acumet 250 pH metre. The soil:water and peat:water ratios used were 20 g soil:50 mL water and 2 g peat:50 mL water, respectively. Soluble sulphate was extracted by shaking with 0.1 M $CaCl_2$ for 30 minutes. The mixture was then filtered (Whatman No. 40) and the $SO_4^{2-}$-S content of the filtrate was determined by the method of Johnson and Nishita (1952). The extractant ratios used were 10 g soil:20 mL $CaCl_2$, and 2 g peat:30 mL $CaCl_2$. Total sulphur was determined by the alkaline oxidation method of Tabatabai and Bremner (1970). Soil samples were finely ground (less than 425 um) and 0.1 to 0.2 g was digested depending on the total sulphur content. Analyses were performed with a bank of six digestion-distillation units. A recovery test showed that the method used gave a 97 to 99% recovery of $K_2SO_4$ and elemental sulphur added to test soils. In addition, the precision of soil total sulphur determination was within ±3%.

3.2.2.3 Sulphur Uptake by Lichen Covered Soils - Field Experiment. The soil samples used for this experiment were obtained from an area close to field site No. 14 (Figure 2). The samples were removed from th ground in such a manner that the lichen layer on the soil sample surface remained undisturbed. A description of a typical soil sample is given in Table 5.

The intact soil samples were placed in plastic pots of 16.5 cm inside diameter and 13.0 cm in height. Six replicates of each were set out under the rain shelters at four of the field sites Nos. 6, 8, 13, and 14 (Figure 2), from May to October, 1977. Every month the soils were brought to predetermined field capacity moisture content by the addition of distilled water.

At the end of the exposure period, the plots were sealed in plastic bags and returned to the laboratory for analysis. The lichen material and the top 2.5 cm of soil were separated, dried, ground, and analysed for pH, $SO_4^{2-}$-S, and total S as for the bare soil experiment (Section 3.2.2.2). Results were expressed on an area basis (kg/ha) by multiplying the results in ug/g soil by the soil bulk density and exposed surface area.

3.2.2.4 Sulphur Uptake by Lichen Covered Soils - Controlled Atmosphere Experiment. Intact lichen covered soil samples taken from an area near field site No. 12 (Figure 2) were placed into round plastic containers 11 cm in

**Table 5.** Analysis of Lichen Covered Soils Used in a Field Experiment on Sulphur Uptake by Undisturbed Soils.

| Horizon | Thickness (cm) | pH | Sand (%) | Silt (%) | Clay (%) | Bulk Density (g/cm$^3$) | Organic Matter (%) |
|---|---|---|---|---|---|---|---|
| Lichen | 3.8 | 4.5 | N/A[a] | N/A | N/A | 0.02 | N/A |
| LFH | 0.5 | 4.1 | N/A | N/A | N/A | 0.53 | 15.2 |
| Ae | 8.0 | 4.6 | 51.5 | 37.5 | 11.0 | 0.95 | ND[b] |

[a] N/A = Not Applicable.

[b] ND = No Data.

diameter and 6.5 cm high. The soil used was sandy in texture with a thin FH horizon (5 mm) below the lichen cover (Table 6).

Samples were exposed to sulphur dioxide for seven days in a controlled atmosphere apparatus (Figure 6). The average air flow rate used was 685 L/hr and the average air temperature was 22°C. The average sulphur dioxide concentration in the exposure chamber was 100 ppb. Similar samples were placed in a chamber which had identical conditions except sulphur dioxide was excluded -- this served as a control. The experiment was conducted at both high (80%) and low (20%) relative humidity to determine the effect of air moisture levels on soil sulphur uptake. There were six replicated used for each run.

After the exposure period the soils were divided into two layers, lichen material, and the top 2.5 cm of soil (including then thin FH horizon). These were air dried, ground, and analysed for pH, $SO_4^{2-}$-S, and total S as for the bare soils experiment (Section 3.2.2.2).

### 3.2.3 Movement of Applied Sulphate Sulphur in Forest Soils

3.2.3.1 Treatments. All three sites received the following treatments on 1976 June 30:

T1 = nil
T2 = 56 kg S/ha as $K_2SO_4$
T3 = 112 kg S/ha as $K_2SO_4$

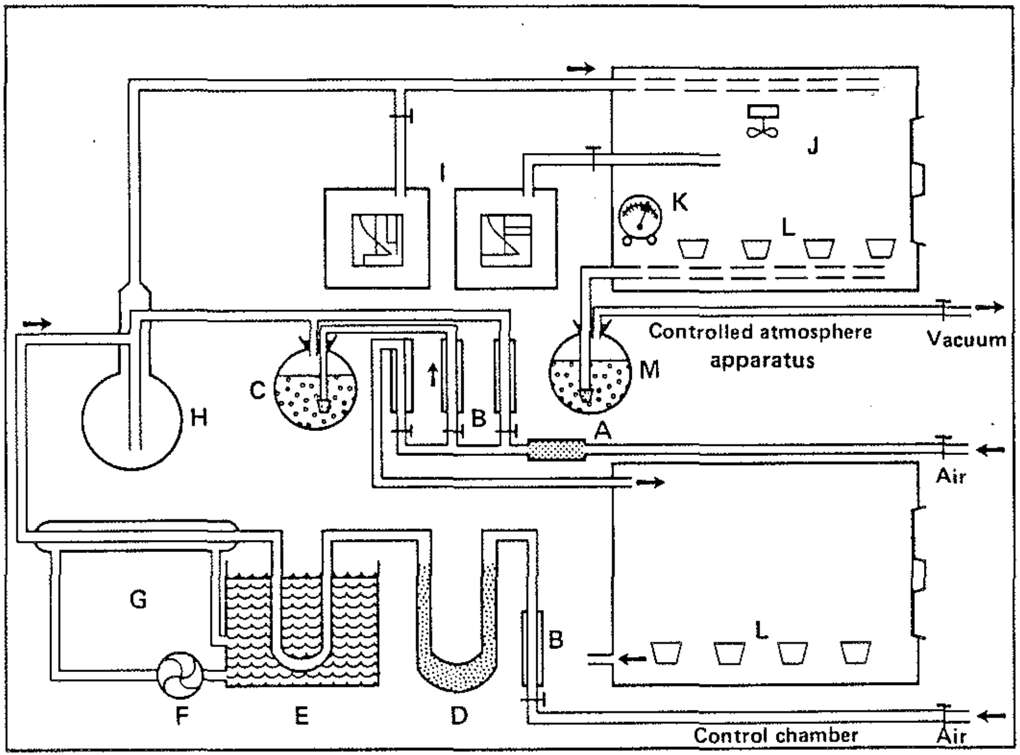
The $K_2SO_4$ was applied as crystals broadcast by hand. At the Thickwood Hills site, each treatment was replicated three times while at the other sites (Mildred Lake Research Facility and the Ruth Lake sites) there were four replicates of each treatment (see Section 3.1.4 for site descriptions).

3.2.3.2 Soil Sampling and Analysis. A custom made soil sampler of 3.5 cm core diameter was used for taking the soil samples. The soil was sampled by depth as follows:

Table 6. Analysis of Lichen Covered Soils Used in the Controlled Atmosphere Experiment on Sulphur Uptake by Undisturbed Soils.

| Horizon | Thickness (cm) | pH | Sand (%) | Silt (%) | Clay (%) | Bulk Density (g/cm$^3$) | Organic Matter (%) |
|---|---|---|---|---|---|---|---|
| Lichen | 5.0 | 4.1 | N/A[a] | N/A | N/A | 0.02 | N/A |
| FH/Ae | 2.5 | 4.7 | 90.5 | 2.2 | 7.3 | 1.07 | 5.7 |

[a] N/A = Not Applicable.



A. Air drying agent (silica gel)
B. Flowmeters
C. Air saturator
D. $SO_2$ absorbing crystals
E. Constant temperature bath
F. Pump
G. Permeation tube chamber
H. Mixing bulb
I. $SO_2$ Analyzers (Scientific Industries Inc. Model No. 67)
J. Fan
K. % relative humidity meter
L. Plastic pots with lichens and soils
M. $SO_2$ trap (30% $H_2O_2$)

Figure 6. Controlled Atmosphere Apparatus.

1. 0 to 2.5 cm;
2. 2.5 to 15.0 cm;
3. 15.0 to 30.0 cm;
4. 30.0 to 60.0 cm;
5. 60.0 to 90.0 cm; and
6. 90.0 to 120.0 cm (where possible)

The lichen or moss layer was sampled by removing a 15 cm square block with a knife.

Samples were obtained three times during the course of the experiment:

1. June 1976 (before the treatments were applied);
2. September 1976; and
3. June 1977.

Soil samples were air dried and ground (20 mesh) before analysis. Soluble sulphate and pH were determined as for the bare soil experiment (Section 3.2.2.2). Soluble potassium was determined from the saturated paste extract and extractable potassium was determined from the 2N NaCl soil extract using atomic absorption spectrophotometry.

### 3.2.4 Effects of Applied Elemental Sulphur, Sulphuric Acid, and Lime on Soil Acidity

3.2.4.1 Site Locations. Three sites were used for this experiment:

1. Mildred Lake Research Facility site;
2. Ruth Lake site; and
3. Thickwood Hills site.

The location and description of these sites are given in Figure 4 and Section 3.1.4.

3.2.4.2 Treatments. The treatments applied to the three sites are shown in Table 7. The Mildred Lake site received all the treatments while the Thickwood Hills site and the Ruth Lake site received treatments 1, 3, 6, and 9 only. All the treatments except 4 and 7 were applied on 1976 June 30. For treatments 4 and 7, half the amounts were applied on 1976 June 30 and the remainder on 1976 September 27. All treatments were replicated four times.

Table 7. Rates of Elemental Sulphur, Sulphuric Acid, and Lime Applied to the Soil.

| Treatment No. | Treatment Description |
|---|---|
| 1 | control |
| 2 | elemental sulphur at 56 kg S/ha + inoculant |
| 3 | elemental sulphur at 280 kg S/ha + inoculant |
| 4 | elemental sulphur at 560 kg S/ha + inoculant |
| 5 | 0.1 N $H_2SO_4$ at 56 kg S/ha |
| 6 | 0.5 N $H_2SO_4$ at 280 kg S/ha |
| 7 | 0.5 N $H_2SO_4$ at 560 kg S/ha |
| 8 | lime at 2500 kg/ha |
| 9 | lime at 2500 kg/ha + elemental sulphur at 280 kg S/ha + inoculant |

Notes: Elemental sulphur was very fine (passing through a sieve with 4 openings per each mm) and was spread by hand. The inoculant was a water extract of a peat which had become acid because of exposure to windblown sulphur dust. For the acid treatment each plot received 21.2 L of the various strength acid solutions. This was equivalent to 0.3 cm of rain. The lime was finely ground $CaCO_3$ (passing through a sieve with 4 openings per each mm) and was spread by hand.

3.2.4.3 Soil Sampling and Analysis. The soils were sampled and analysed for $SO_4^{2-}$-S and pH as for the movement of applied sulphate sulphur in forest soils experiment (Section 3.2.3.2).

### 3.2.5 Lysimeter Experiment

This experiment was conducted to determine the amounts of sulphate sulphur and cations leached from intact forest soils and to establish if there is a relationship between leaching losses of plant nutrient and sulphur deposition in the AOSERP study area.

Two soils from the AOSERP study area, a sandy Eutric Brunisol and a sandy loam Orthic Gray Luvisol, were set up in closed-bottomed lysimeters as shown in Figure 7. The lysimeters were placed on the surface of the soil. Three replicates of each soil type were set out at nine of the field sites during July 1976. The leachate was collected from July to September 1976 and from May to October 1977. The leachate was analysed for the cations $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$-S and pH as for the rain samples (Section 3.2.1.2).

In August 1978, the lysimeters were brought in from the various sites. Soil solums were taken apart by layers, dried, and ground for analysis. The organic horizons were separated into five components: (1) moss, (2) vascular plants, (3) lichen, (4) fresh litter (L), and (5) decomposed litter (FH). The mineral horizons were sampled by depth: (1) 0 to 3 cm; (2) 3 to 8 cm; (3) 8 to 15 cm; and (4) $15^+$ cm. They were analysed for pH, $SO_4^{2-}$-S, and total sulphur as for the other soil samples (Section 3.2.2.3).

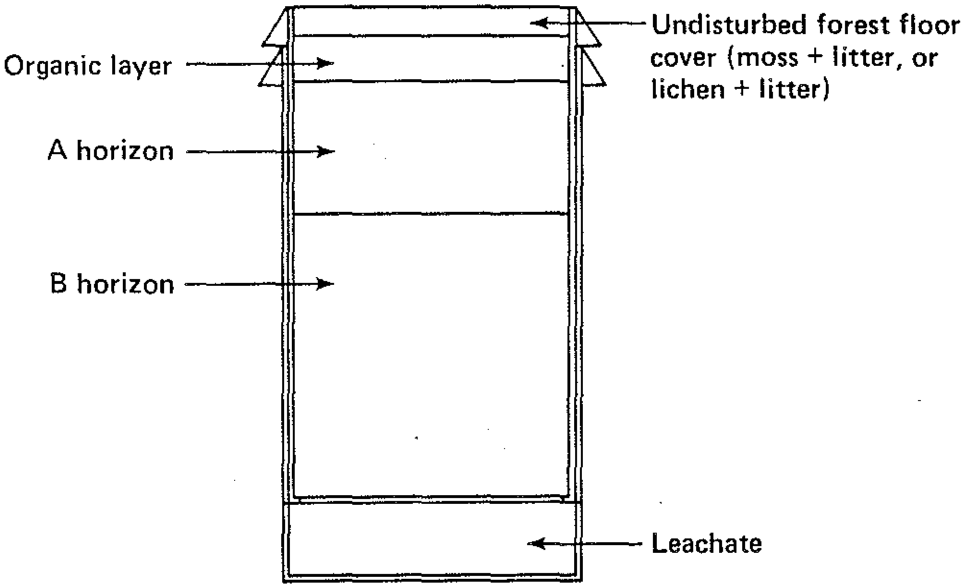


Figure 7. Lysimeter Design. Inside Diameter and Depth are 22 cm and 50 cm, respectively.

# 4. RESULTS AND DISCUSSION

## 4.1 WET DEPOSITION

### 4.1.1 Rain

4.1.1.1 Precipitation Pattern. The total precipitation for each month recorded at each of the field sites over the summers of 1976 and 1977 is given in Section 8.1. In general, field sites located along the river valley (Bitumount and MacKay River) received the least precipitation. The southern sites (Algar and May) and a northwestern site (Birth Mountain), which are located at the greatest elevations in the AOSERP study area, received the most precipitation. Detailed description of the climatology of the AOSERP study area was given by Longley and Janz (1978).

4.1.1.2 Acidity and Sulphur Content of Rain. The pH and sulphate sulphur content of rain samples taken weekly during the summer of 1975 are given in Section 8.2. The average pH at sites within 25 km of the emission source was similar to the average pH at the three remote sites (pH 6.0 and 6.2, respectively). Sulphate sulphur concentrations at sites within 25 km of the emissions source averaged 1.3 ppm compared to an average of 0.6 ppm at the remote sites.

The pH and sulphate sulphur content of rainfall samples taken monthly from 1976 June to September, are given in **Table 8.** Corresponding values from 1977 May to September, are given in **Table 9.** Field site No. 3 (Supertest Hill) had consistently high pH and $SO_4^{2-}$-S levels. This would be due to samples at this site being contaminated with trembling aspen throughfall (Section 4.1.3). The rain sample gauge at this site was located in a small clearing in a stand of trembling aspen. Values from this site were therefore excluded in the calculation of the mean values. On several occasions, field site Nos. 1 (Mildred Lake) and 2 (Mackay River) also had high pH values. These high values could be because of sample contamination from alkaline dust. Both of these sites were located within 200 m of a gravel road. The rain gauges used were not covered between rainfall events so rain

Table 8. Sulphur Concentrations (ppm) and pH of Rain Sampled Monthly from 1976 June to September.

| Site No. | Site | Month: June | | July | | August | | September | | $SO_4^{2-}$-S | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | pH | $SO_4^{2-}$-S | pH | $SO_4^{2-}$-S | pH | $SO_4^{2-}$-S | pH | $SO_4^{2-}$-S | Site Mean[b] | Site Mean[c] |
| | 0 to 25 km | | | | | | | | | | |
| 1 | Mildred Lake | 6.79 | 0.84 | 6.70 | 0.38 | 6.90 | 0.40 | 6.75 | 0.25 | 0.39 | 6.76 |
| 2 | MacKay River | 6.75 | 0.66 | 6.58 | 0.83 | 6.66 | 0.27 | 6.68 | 0.10 | 0.47 | 6.65 |
| 3 | Supertest | 7.52 | 2.80 | 7.49 | 1.23 | 8.07 | 1.36 | 7.59 | 2.50 | 2.01 | 7.67 |
| 5 | Steepbank 1 | 6.16 | 0.69 | 6.45 | 0.25 | 6.04 | 0.35 | 6.33 | 0.10 | 0.26 | 6.30 |
| 6 | Steepbank 2 | 5.95 | 1.20 | 6.34 | 0.50 | 6.07 | 1.00 | 6.35 | 0.10 | 0.52 | 6.27 |
| | mean | | | | | | | | | 0.41[a] | |
| | 25 to 50 km | | | | | | | | | | |
| 9 | Bitumount | 6.41 | 0.46 | 6.12 | 0.41 | 6.40 | 0.25 | 5.36 | 0.25 | 0.35 | 5.98 |
| 8 | Muskeg Mtn. | 5.99 | 0.32 | 6.15 | 0.34 | 6.40 | 0.25 | 6.56 | 0.35 | 0.34 | 6.40 |
| 4 | Steepbank A | 5.10 | 0.39 | 6.45 | 0.32 | 6.60 | 0.29 | 6.30 | 0.10 | 0.25 | 6.11 |
| 7 | Thickwood Hills | 5.33 | 0.85 | 6.24 | 0.37 | 6.44 | 0.27 | 6.40 | 1.75 | 0.49 | 5.95 |
| | mean | | | | | | | | | 0.36 | |
| | 50 to 100 km | | | | | | | | | | |
| 11 | Birch Mountain | 5.58 | 0.44 | 6.15 | 0.25 | 6.44 | 0.25 | 6.10 | 0.56 | 0.36 | 5.69 |
| 10 | Gordon Lake | 6.10 | 0.50 | 5.82 | 0.23 | 6.28 | 0.17 | 6.16 | 0.25 | 0.27 | 6.05 |
| | mean | | | | | | | | | 0.32 | |
| | > 100 km | | | | | | | | | | |
| 12 | Richardson | 5.90 | 0.83 | 6.17 | 0.20 | 6.30 | 0.20 | 5.78 | 0.10 | 0.28 | 6.10 |
| 13 | Algar | 5.67 | 0.30 | 5.96 | 0.42 | 6.33 | 0.15 | 6.39 | 0.05 | 0.23 | 5.99 |
| 14 | May | 5.87 | 0.30 | 5.61 | 0.39 | 5.95 | 0.14 | 5.76 | 0.05 | 0.23 | 5.61 |
| | mean | | | | | | | | | 0.25 | |
| | monthly means[d] | | 0.60 | | 0.38 | | 0.31 | | 0.31 | | |

[a] Value excludes Supertest site.

[b] Excepting the Supertest site, the difference among the site means were not statistically different ($p = 0.05$).

[c] pH weighted by sample volume

[d] Least significant different ($p = 0.05$) was 0.22 ppm for comparing monthly means (Supertest site was excluded).

Table 9. Sulphur Concentrations (ppm) and pH of Rain Sampled Monthly from 1977 May to September.

| Site No. | Site | Month | | | | | | | | | | $SO_4^{2-}$-S | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | May | | June | | July | | August | | September | | | |
| | | pH | $SO_4^{2-}$-S | pH | $SO_4^{2-}$-S | pH | $SO_4^{2-}$-S | pH | $SO_4^{2-}$-S | pH | $SO_4^{2-}$-S | Site Mean[b] | Site Mean[c] |
| | 0 to 25 km | | | | | | | | | | | | |
| 1 | Mildred Lake | 5.98 | 0.34 | 4.77 | 0.40 | 5.18 | 0.40 | 5.21 | 0.39 | 6.21 | 0.38 | 0.38 | 5.12 |
| 2 | MacKay River | ND[e] | ND | 6.14 | 0.39 | 6.19 | 0.28 | 5.89 | 0.53 | 6.33 | 0.54 | 0.44 | 6.09 |
| 3 | Supertest | 7.57 | 2.20 | 7.41 | 0.98 | 7.10 | 1.10 | 6.79 | 1.30 | 7.33 | 1.90 | 1.51 | 7.26 |
| 5 | Steepbank 1 | 5.44 | 0.33 | 4.97 | 0.20 | 5.10 | 0.32 | ND | ND | 5.25 | 0.35 | 0.30 | 5.12 |
| 6 | Steepbank 2 | 6.18 | 0.50 | 4.64 | 0.50 | 5.60 | 0.40 | 5.16 | 0.82 | 5.69 | 0.55 | 0.55 | 5.07 |
| | mean | | | | | | | | | | | 0.42[a] | |
| | 25 to 50 km | | | | | | | | | | | | |
| 9 | Bitumount | 6.01 | 0.30 | 5.22 | 0.75 | 4.99 | 0.07 | 3.94 | 0.13 | 5.11 | 0.28 | 0.31 | 4.59 |
| 8 | Muskeg Mtn. | 5.21 | 0.17 | 5.17 | 0.31 | 5.18 | 0.65 | 5.01 | 0.10 | 5.27 | 0.26 | 0.30 | 5.15 |
| 4 | Steepbank A | 4.54 | 0.73 | 5.78 | 0.18 | 5.18 | 0.25 | 5.40 | 0.44 | 5.77 | 0.20 | 0.36 | 4.99 |
| 7 | Thickwood Hills | 5.38 | 0.28 | 4.67 | 0.35 | 5.09 | 0.15 | 4.86 | 0.18 | 5.00 | 0.35 | 0.26 | 4.96 |
| | mean | | | | | | | | | | | 0.31 | |
| | 50 to 100 km | | | | | | | | | | | | |
| 11 | Birch Mountain | 6.36 | 0.24 | 5.30 | 0.28 | 5.46 | 0.10 | 5.31 | 0.15 | 4.95 | 0.20 | 0.19 | 5.32 |
| 10 | Gordon Lake | 5.78 | 0.23 | 5.96 | 0.20 | 5.45 | 0.18 | 4.94 | 0.15 | 5.34 | 0.40 | 0.23 | 5.39 |
| | mean | | | | | | | | | | | 0.21 | |
| | > 100 km | | | | | | | | | | | | |
| 12 | Richardson | 5.71 | 0.29 | 5.15 | 0.20 | 5.21 | 0.29 | 4.05 | 0.25 | 5.04 | 0.10 | 0.23 | 4.62 |
| 13 | Algar | 6.53 | 0.42 | 5.08 | 0.30 | 5.08 | 0.10 | 5.59 | 0.25 | 6.29 | 0.20 | 0.25 | 5.33 |
| 14 | May | 5.45 | 0.19 | 5.66 | 0.30 | 5.42 | 0.18 | 4.91 | 0.35 | 4.31 | 0.15 | 0.23 | 4.92 |
| | mean | | | | | | | | | | | 0.24 | |
| | monthly means[d] | | 0.34 | | 0.31 | | 0.26 | | 0.31 | | 0.30 | | |

[a] Values excludes Supertest site.

[b] Least significant different ($p = 0.05$) was 0.21 ppm for comparing site means (Supertest site was excluded).

[c] pH weighted by sample volume.

[d] Excepting the Supertest site, the differences among the monthly means were not statistically different ($p = 0.05$).

[e] ND = No data.

samples contained any road-derived dust, in addition to any conventional dry deposition deposited between sample collection dates.

Distilled water in equilibrium with atmospheric $CO_2$ at $25^oC$ has a pH of 5.7. This may be regarded as the neutral point for rainwater (Barrett and Brodin 1955). Rain was therefore acid at several sites in the AOSERP study area in 1977. A rain sample of pH 3.9 was recorded at field site No. 9 (Bitumount) in August and the July sample had a pH of 5.0. Rain samples with pH values below 5.0 were also recorded at eight other field sites on one or more occasions (Table 9).

Because of the localized nature of the plume during storm events, the sparse network of field sites, and the fact that only monthly samples were obtained, accurate interpretation of this wet deposition pattern is not possible. The network does, however, provide 'baseline' wet deposition rates of sulphate sulphur in the AOSERP study area (Section 8.2, Tables 38, 39, and 40). The average monthly concentration of $SO_4^{2-}$-S in rain in the AOSERP study area ranged from 0.0 to 4.0 ppm in 1975, 0.05 to 1.75 ppm in 1976, and from 0.07 to 0.82 in 1977. This is low in comparison to a mean annual (1974) concentration of 1.08 ppm for Birkenes, Norway (Semb 1976). The values reported here are also lower than those found in rain sampled near natural gas processing plants in west central Alberta by Walker (1969). He found most samples contained 0.4 to 1.5 ppm $SO_4^{2-}$-S. Summers and Hitchon (1973) reported a mean value 0.9 ppm $SO_4^{2-}$-S for rain samples in the region of sulphur gas extraction plants in Central Alberta. This value is somewhat higher than that reported by Walker (1969) for the same general area.

The results for the Nipher gauges indicated that there was little deposition of sulphate sulphur in dry particulates, at least east of the Athabasca River. There was less particulate sulphate sulphur than there was sulphate sulphur brought down in rain. The Nipher gauge data is given in this report, but the few data together with more recent and extensive data will be made available through another publication (Nyborg et al. 1977).

4.1.1.3 Cation Content of Rain. The concentration of cations in the 1977 rain samples are shown in **Table 10**. Rain at field site No. 3 (Supertest Hill) had unusually high concentrations of calcium, magnesium, and potassium.

Table 10. Concentration (ppm) of Cations in Rain Sampled Monthly from 1977 May to September.

| Site No. | Site | Month |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | Weighted Mean[b] |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | May |  |  |  | June |  |  |  | July |  |  |  | August |  |  |  | September |  |  |  |  |  |  |  |
|  |  | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg |
|  | 0 to 25 km |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 1 | AOSERP | 0.3 | 0.4 | 1.1 | 0.3 | 0.2 | 0.1 | 0.9 | 0.2 | 0.2 | 0.1 | 1.0 | 0.4 | 0.3 | 0.1 | 1.0 | 0.3 | 0.2 | 0.2 | 0.8 | 0.2 | 0.2 | 0.2 | 1.0 | 0.2 |
| 2 | MacKay | ND[c] | ND | ND | ND | 0.4 | 0.5 | 1.4 | 0.3 | 0.2 | 0.2 | 1.0 | 0.2 | 0.1 | 0.3 | 0.6 | 0.1 | 0.2 | 0.7 | 1.2 | 0.3 | 0.3 | 0.4 | 1.0 | 0.3 |
| 3 | Supertest[a] | 0.8 | 9.3 | 8.7 | 1.2 | 0.3 | 1.4 | 6.4 | 0.8 | 0.2 | 1.5 | 5.9 | 0.7 | 0.2 | 2.0 | 4.1 | 0.8 | 0.2 | 5.0 | 6.9 | 2.0 | 0.4 | 4.0 | 6.5 | 1.1 |
| 5 | Steepbank 1 | 0.3 | 0.5 | 0.6 | 0.2 | 0.3 | 0.1 | 0.5 | 0.1 | 0.5 | 0.1 | 0.3 | 0.1 | ND | ND | ND | ND | 0.3 | 0.1 | 0.6 | 0.1 | 0.3 | 0.2 | 0.4 | 0.1 |
| 6 | Steepbank 2 | 0.3 | 0.6 | 1.2 | 0.2 | 0.2 | 0.2 | 0.8 | 0.2 | 0.4 | 0.1 | 0.7 | 0.1 | 0.3 | 0.1 | 0.9 | 0.1 | 0.2 | 0.3 | 0.9 | 0.2 | 0.3 | 0.3 | 0.9 | 0.2 |
|  | mean |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 0.3 | 0.3 | 0.8 | 0.2 |
|  | 25 to 50 km |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 9 | Bitumount | 0.3 | 0.4 | 0.6 | 0.1 | 0.1 | 0.1 | 0.3 | 0.1 | 0.1 | 0.0 | 0.2 | 0.0 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.4 | 0.0 | 0.2 | 0.1 | 0.3 | 0.1 |
| 8 | Muskg Mtn. | 0.6 | 0.3 | 0.3 | 0.0 | 0.5 | 0.1 | 0.4 | 0.1 | 0.4 | 0.1 | 0.2 | 0.1 | 0.2 | 0.0 | 0.3 | 0.0 | 0.2 | 0.1 | 0.5 | 0.1 | 0.4 | 0.1 | 0.3 | 0.1 |
| 4 | Steepbank A | 0.3 | 0.5 | 0.3 | 0.1 | 0.2 | 0.1 | 0.4 | 0.1 | 0.2 | 0.1 | 0.3 | 0.1 | 0.2 | 0.1 | 0.3 | 0.1 | 0.2 | 0.4 | 0.4 | 0.1 | 0.2 | 0.2 | 0.3 | 0.1 |
| 7 | Thickwood | 0.2 | 0.3 | 0.3 | 0.1 | 0.2 | 0.2 | 0.3 | 0.1 | 0.2 | 0.1 | 0.4 | 0.0 | 0.1 | 0.1 | 0.3 | 0.0 | 0.2 | 0.4 | 0.5 | 0.1 | 0.2 | 0.2 | 0.3 | 0.1 |
|  | mean |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 0.2 | 0.2 | 0.3 | 0.1 |
|  | 50 to 100 km |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 11 | Birch Mtn. | 0.9 | 0.2 | 0.4 | 0.1 | 0.1 | 0.1 | 0.2 | 0.0 | 0.3 | 0.1 | 0.2 | 0.0 | 0.2 | 0.1 | 0.2 | 0.1 | 0.2 | 0.1 | 0.2 | 0.1 | 0.4 | 0.1 | 0.2 | 0.1 |
| 10 | Gordon Lake | 0.6 | 0.6 | 0.5 | 0.1 | 0.3 | 0.1 | 0.5 | 0.1 | 0.3 | 0.1 | 0.4 | 0.0 | 0.2 | 0.1 | 0.3 | 0.0 | 0.2 | 0.3 | 0.4 | 0.1 | 0.4 | 0.2 | 0.4 | 0.1 |
|  | mean |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 0.4 | 0.2 | 0.3 | 0.1 |
|  | > 100 km |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 12 | Richardson | 0.4 | 0.3 | 0.4 | 0.1 | 0.2 | 0.1 | 0.3 | 0.1 | 0.1 | 0.1 | 0.2 | 0.0 | 0.1 | 0.1 | 0.2 | 0.0 | 0.2 | 0.1 | 0.3 | 0.0 | 0.2 | 0.1 | 0.3 | 0.1 |
| 13 | Algar | 0.3 | 0.4 | 0.5 | 0.1 | 0.2 | 0.2 | 0.8 | 0.2 | 0.2 | 0.1 | 0.3 | 0.0 | 0.3 | 0.1 | 0.4 | 0.1 | 0.2 | 0.6 | 0.7 | 0.2 | 0.2 | 0.2 | 0.5 | 0.1 |
| 14 | May | 0.4 | 0.2 | 0.4 | 0.1 | 0.2 | 0.1 | 0.5 | 0.1 | 0.2 | 0.1 | 0.3 | 0.0 | 0.1 | 0.1 | 0.2 | 0.0 | 0.2 | 0.1 | 0.3 | 0.0 | 0.2 | 0.1 | 0.3 | 0.1 |
|  | mean |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 0.2 | 0.2 | 0.4 | 0.1 |

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[a] Values for Supertest Hill not included in the calculation of the mean, because the rain samples at Supertest Hill were probably contaminated by road dust.

[b] Weighted by sample volume.

[c] ND = No data.

This may be due to contamination by aspen throughfall as mentioned earlier (Section 4.1.1.2).

Barrie and Kovalick (1980) found that during a two-week field study in June 1977, particulate calcium and magnesium content collected at the AOSERP Research Facility, originated mainly from windblown dust sources. This could explain the high calcium content in rain samples collected at field sites Nos. 1 (Mildred Lake) and 2 (MacKay River). Both of these field sites are located within 200 m of a gravel road.

### 4.1.2 Snow

The pH of snow sampled in 1976 was not related to the distance from the emission source (Table 11). If all the sulphate sulphur measured in the snow was present as sulphuric acid, and if no other acids were present, then snow having concentrations of 0.16 and 0.51 ppm $SO_4^{2-}$-S would be expected to have pH values of 5.0 and 4.5, respectively. However, at all sites snow pH was greater than 5.0 despite $SO_4^{2-}$-S concentrations greater than 0.25 ppm. This suggests that sulphur in snow was deposited as a neutral salt, or the sulphuric acid was neutralized by alkaline particulates. This is consistent with the cation content of the snow (Table 11). There is essentially a balance between cations and $SO_4^{2-}$-S at all sites except at the Mildred Lake where calcium concentration (and pH) was high.

Considering that the estimated amounts deposited by snow represent the total deposited between the sampling date and the time snow started to accumulate (about three- and one-half months), the amounts of sulphur deposited in snow (0.1 to 0.2 kg/ha/month) in the AOSERP study area were low.

### 4.1.3 Nutrient Cycling Study

The mean amount of precipitation for each individual sample period was similar for both control and exposed plots (Table 12). Individual rainfall events were sampled on most occassions and dthe range in storm sizes sampled was considerable (Table 12). The measurement period for the exposed black spruce plot was shorter than for the other plots because of difficulty in locating a suitable study area, and with problems setting up the plot collectors (Section 3.1.2).

Table 11. Chemical Determinations on Accumulated Snow Sampled on 1976 March 17 and 18.

| Site No. | Site | Distance (km) /direction from Source | Snow Depth (cm) | pH | Cond.[a] (umho/cm) | $SO_4^{2-}$-S (ppm) | Basic Cations |  |  |  | Excess Cations |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  | Ca (ppm) | Mg (ppm) | Na (ppm) | K ppm) | mmol($p^+$)/L |
| 6A | Steepbank 3 | 2/ESE | 38 | 5.5 | 8 | 0.53 | 0.31 | 0.10 | 0.23 | 0.23 | 0.01 |
| 6 | Steepbank 2 | 4/ESE | 41 to 43 | 5.4 | 7 | 0.40 | 0.31 | 0.11 | 0.23 | 0.17 | 0.01 |
| 5 | Steepbank 1 | 17/ESE | 38 | 5.1 | 6 | 0.32 | 0.26 | 0.06 | 0.23 | 0.15 | 0.00 |
| 1 | Mildred Lake | 11/NW | 30 to 41 | 6.3 | 7 | 0.52 | 0.75 | 0.21 | 0.20 | 0.22 | 0.05 |
| 7 | Thickwood Hills | 31/SW | 38 to 41 | 5.6 | 7 | 0.25 | 0.27 | 0.08 | 0.28 | 0.67 | 0.03 |
| 15 | Hangingstone River | 67/S | 33 to 38 | 6.0 | 6 | 0.40 | 0.29 | 0.12 | 0.50 | 0.40 | 0.03 |
| 14 | May[b] | 172/SW | 38 to 43 | 5.6 | 6 | 0.28 | 0.32 | 0.08 | 0.51 | 0.32 | 0.03 |

[a] Electrical conductivity.

[b] Sampled 6 km east of site No. 14.

Table 12. Precipitation (mm) at the Control Site and the Exposed Site of the Nutrient Cycling Study, Summer of 1976.

| Experimental Plot | Duration of Measurement Period | Number of Sample Periods | Precipitation (mm) | | | | |
|---|---|---|---|---|---|---|---|
| | | | Total | Mean Value Per Period | SD[a] | Min. | Max. |
| Control Aspen | 24/6 to 2/10 | 8 | 318.4 | 39.8 | 43.6 | 3.7 | 138.8 |
| Exposed Aspen | 22/6 to 10/10 | 7 | 286.0 | 40.9 | 29.8 | 20.8 | 105.2 |
| Control Pine | 24/6 to 2/10 | 8 | 299.5 | 37.4 | 38.1 | 5.2 | 121.6 |
| Exposed Pine | 22/6 to 10/10 | 7 | 286.0 | 40.9 | 29.8 | 20.8 | 105.2 |
| Control Spruce | 24/6 to 2/10 | 8 | 328.5 | 41.1 | 43.6 | 3.7 | 138.8 |
| Exposed Spruce | 22/7 to 10/10 | 4 | 156.1 | 39.0 | 42.6 | 7.6 | 101.6 |

[a] Standard deviation.

The mean concentrations and pH or rain for the control and exposed sites are given in **Table 13**. The mean sulphate sulphur concentration in rain at the exposed site was nearly twice as great as the concentration in rain at the control site. A t-test indicated that the mean volume, nutrient concentrations and mean pH of rain at the exposed site were not significantly ($p > 0.05$) different from rain at the control site. On the average, rain was not acid at either site. Sulphation discs maintained at each plot showed that the exposed plots received, on the average, more than twice the amount of sulphur emissions than the control plots (**Table 14**).

The amount of net precipitation (expressed as a percentage of incident rain) reaching the forest floor under trembling aspen, jack pine, and black spruce was 91% and 85%, respectively. Throughfall averaged about 85% of incident precipitation for both trembling aspen and jack pine. Stemflow averaged 7 to 8% of incident precipitation in trembling aspen, and 0.2 to 0.3% in jack pine (Section 8.3).

Assuming that the chemical composition of the rain at each site was on the average the same (except $SO_4^{2-}$-S), it can be seen that there are differences in the nutrient content of throughfall and stemflow between the two sites (**Table 15**). For aspen throughfall, there was a greater concentration of $Ca^{2+}$. $Mg^{2+}$, and $SO_4^{2-}$-S at the exposed site than the control site. This greater nutrient concentration was associated with a higher throughfall pH at the exposed site. Aspen stemflow at the exposed site had higher $K^+$, $Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$-S concentrations and higher pH despite the higher average volume at the exposed site. The concentrations of $K^+$, $Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$-S in jack pine throughfall were higher at the exposed site than at the control site. The pH of the exposed site throughfall was lower. Jack pine stemflow, like the throughfall, had higher concentrations of $K^+$, $Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$-S at the exposed site than the control site. The pH of exposed pine stemflow was also markedly lower than for the control site. For black spruce, differences between the control and exposed sites were smaller than for the other two species.

**Table 16** shows the weighted mean nutrient concentration and weighted mean pH for jack pine and aspen throughfall and stemflow for a given sample period when the amount of precipitation at each site was

Table 13. Mean Nutrient Concentration (ppm) and Mean pH of Incident Rain in the Summer of 1976 at Plots of Nutrient Cycling Study.[a]

| | Site | | | |
|---|---|---|---|---|
| | Control | | Exposed | |
| | Mean | SD[b] | Mean | SD |
| $Na^+$ | 0.14 | 0.09 | 0.15 | 0.12 |
| $K^+$ | 0.17 | 0.18 | 0.17 | 0.13 |
| $Ca^{2+}$ | 0.44 | 0.10 | 0.45 | 0.15 |
| $Mg^{2+}$ | 0.08 | 0.05 | 0.06 | 0.03 |
| $SO_4^{2-}$-S | 0.16 | 0.10 | 0.31 | 0.21 |
| pH | 5.73 | | 5.72 | |

[a] Geometric means weighted by the sample volumes.

[b] Standard deviation.

Table 14. Mean total Sulphation for the Control Site and the Exposed Site of the Nutrient Cycling Study.

| mg $SO_3$/100 $cm^2$/day | |
|---|---|
| Control Site | Exposed Site |
| 0.023 | 0.053 |

Table 15. Mean Nutrient Concentrations (ppm) and Mean pH of Throughfall and Stemflow in Summer of 1976.[a]

| | Trembling Aspen | | | | Jack Pine | | | | Black Spruce | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | | Exposed | | Control | | Exposed | | Control | | Exposed | |
| | Mean | SD[b] | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD |
| Throughfall | | | | | | | | | | | | |
| $Na^+$ | 0.12 | 0.04 | 0.12 | 0.03 | 0.18 | 0.04 | 0.19 | 0.12 | 0.13 | 0.02 | 0.17 | 0.05 |
| $K^+$ | 1.43 | 0.68 | 3.76 | 6.24 | 0.71 | 0.22 | 1.78 | 0.88 | 1.00 | 0.22 | 1.09 | 0.65 |
| $Ca^{2+}$ | 0.97 | 0.31 | 3.08 | 3.24 | 1.30 | 0.24 | 1.82 | 1.49 | 0.81 | 0.15 | 1.41 | 1.12 |
| $Mg^{2+}$ | 0.16 | 0.05 | 0.57 | 0.97 | 0.32 | 0.05 | 0.47 | 0.57 | 0.18 | 0.04 | 0.20 | 0.08 |
| $SO_4^{2-}$-S | 0.39 | 0.21 | 0.42 | 0.18 | 0.75 | 0.39 | 1.54 | 1.48 | 0.68 | 0.24 | 0.77 | 0.32 |
| pH | 6.14 | 0.32 | 6.49 | 0.22 | 5.09 | 0.22 | 4.78 | 0.28 | 5.03 | 0.22 | 5.14 | 0.29 |
| Volume (mL) | 1164 | 1173 | 1243 | 891 | 1279 | 1438 | 1165 | 988 | 1210 | 1370 | 1173 | 1213 |
| Stemflow | | | | | | | | | | | | |
| $Na^+$ | 0.12 | 0.02 | 0.14 | 0.04 | 0.48 | 0.15 | 0.65 | 0.33 | 0.90 | 0.79 | 0.84 | 0.61 |
| $K^+$ | 2.53 | 0.44 | 4.29 | 1.53 | 1.91 | 0.57 | 8.48 | 3.87 | 6.32 | 1.84 | 5.34 | 2.35 |
| $Ca^{2+}$ | 8.84 | 3.13 | 16.87 | 7.13 | 9.41 | 5.18 | 11.76 | 8.94 | 10.66 | 2.83 | 11.10 | 11.19 |
| $Mg^{2+}$ | 1.22 | 0.46 | 2.08 | 0.26 | 1.70 | 1.19 | 3.08 | 1.94 | 1.91 | 0.99 | 1.41 | 0.53 |
| $SO_4^{2-}$-S | 0.62 | 0.39 | 2.25 | 0.96 | 4.84 | 3.45 | 15.88 | 10.27 | 5.59 | 4.71 | 6.92 | 1.82 |
| pH | 7.55 | 0.14 | 7.82 | 0.09 | 4.58 | 0.14 | 3.48 | 0.25 | 4.23 | 0.19 | 4.19 | 0.23 |
| Volume (mL) | 11357 | 8198 | 11850 | 6115 | 2802 | 4560 | 5097 | 7968 | 676 | 1471 | 815 | 1456 |

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[a] Geometric means weighted by the sample volumes.

[b] Standard deviation.

Table 16. Mean Nutrient Concentrations (ppm) and pH of Rain; and of Trembling Aspen and Jack Pine Throughfall and Stemflow.[a]

| | Trembling Aspen | | Jack Pine | |
|---|---|---|---|---|
| | Control[b] | Exposed[c] | Control[d] | Exposed[e] |
| Precip. (mm) | 45.0 | 43.0 | 45.4 | 41.6 |
| Throughfall | | | | |
| $Na^+$ | 0.19 | 0.10 | 0.19 | 0.24 |
| $K^+$ | 0.86 | 1.03 | 0.99 | 2.26[f] |
| $Ca^{2+}$ | 0.88 | 1.48[f] | 1.49 | 1.77 |
| $Mg^{2+}$ | 0.13 | 0.18[f] | 0.39 | 0.57 |
| $SO_4^{2-}$-S | 0.16 | 0.49[f] | 1.09 | 1.78 |
| pH | 6.03 | 6.41[f] | 5.04 | 4.72[f] |
| Volume (mL) | 1037 | 1266[f] | 1344 | 1055[f] |
| Stemflow | | | | |
| $Na^+$ | 0.15 | 0.19 | 0.73 | 0.91 |
| $K^+$ | 2.83 | 4.51[f] | 2.82 | 11.79 |
| $Ca^{2+}$ | 11.69 | 26.37[f] | 18.31 | 28.76 |
| $Mg^{2+}$ | 1.64 | 3.89[f] | 2.59 | 5.75[f] |
| $SO_4^{2-}$-S | 0.52 | 4.21[f] | 12.87 | 33.00[f] |
| pH | 7.56 | 8.03[f] | 4.99 | 3.50[f] |
| Volume (mL) | 16025 | 11138 | 1266 | 2544 |
| Rain | | | | |
| $Na^+$ | 0.10 | 0.09 | 0.09 | 0.23 |
| $K^+$ | 0.07 | 0.10 | 0.10 | 0.21 |
| $Ca^{2+}$ | 0.47 | 0.49 | 0.21 | 0.44 |
| $Mg^{2+}$ | 0.08 | 0.06 | 0.02 | 0.04 |
| $SO_4^{2-}$-S | 0.08 | 0.10 | 0.19 | 0.60 |
| pH | 5.65 | 5.03 | 5.82 | 5.30 |

[a] Values are from a single sampling period. The mean value of a given variable ($Na^+$, $K^+$, etc.) at the control site was compared to the corresponding mean value at the exposed site according to Student's t-test. Pairs of values which are significantly different ($p = 0.05$) are indicated by [f] beside the exposed site values.

[b] From 28 August to 05 September.

[c] From 15 July to 29 July.

[d] From 29 June to 16 July.

[e] From 30 June to 15 July.

[f] Value for exposed site is statistically different compared to the value for the control site ( $p = 0.05$).

similar. A similar comparison was not possible for black spruce because there was not a sample period when the amount of precipitation for each plot was the same. The concentrations of nutrients at the exposed site were generally higher than at the control site for both species. The differences which are statistically significant (0 = 0.5) are indicated. Aspen throughfall and stemflow had a higher pH at the exposed site whereas jack pine throughfall and stemflow were lower in pH at the exposed site.

The total amounts of nutrients returned to the soil in incident rain, throughfall and stemflow for jack pine and trembling aspen at both sites are given in Section 8.4.

Since nutrient quantities in dry fallout were not determined separately, these quantities are included in the amounts of nutrients recorded in the throughfall and stemflow. A number of researchers have recognized the possibility that aerosols and dust may adhere to leaves, branches, and stems and then add significantly to the chemical composition of throughfall and stemflow (Eriksson 1958, Tamm and Troedsson 1955, Hart and Parent 1974, and Nihlgard 1970). In this study, particulate deposition from the emissions source could be an important component of the nutrient content of throughfall and stemflow at the exposed site, particularly for sulphate sulphur. This component represents the filtering action of the forest canopy on airborne particulates and aerosols. A detailed discussion of these results is given by Parker (1978).

### 4.1.3.1 Deposition of Sulphate Sulphur in Aspen Throughfall and Stemflow.

The average pH and sulphate sulphur concentrations in throughfall and stemflow of different tree species at the various field sites are shown in Section 8.5. These samples were collected every two weeks from nine throughfall collections and three stemflow collections at each site during the summer of 1975 and 1976.

The deposition of $SO_4^{2-}$-S in trembling aspen throughfall and stemflow measured in 1976 at the nutrient cycling study plots is given in **Table 17**. At both the control site and the exposed site the amount of sulphur deposited in throughfall and stemflow was higher than that deposited in incident rain. The amount deposited in both the incident rain and the

Table 17. Deposition of Sulphate Sulphur in Trembling Aspen Throughfall and Stemflow at Control Site and Exposed Site, Summer 1976.

| Month | Sample Period | Deposition in Throughfall and Stemflow | | | | Total Monthly Deposition in Net Precipitation[c] | Total Monthly Deposition in Rain |
|---|---|---|---|---|---|---|---|
| | (days) | TF[a] (kg/ha) | SF[b] (kg/ha) | Total (kg/ha) | Fraction as SF (%) | (kg/ha/mo) | (kg/ha/mo) |
| | | | | Control Site | | | |
| June | 5 | 0.134 | 0.016 | 0.150 | 10.7 | 0.900 | 0.456 |
| July | 17 | 0.225 | 0.035 | 0.260 | 13.5 | 0.474 | 0.170 |
| July | 7 | 0.049 | 0.011 | 0.060 | 18.3 | 0.266 | 0.080 |
| July | 7 | 0.046 | 0.012 | 0.058 | 20.7 | 0.257 | 0.159 |
| August | 23 | 0.229 | 0.009 | 0.238 | 3.8 | 0.321 | 0.000 |
| September | 13 | 0.104 | 0.012 | 0.116 | 10.3 | 0.268 | 0.261 |
| Mean | | | | | 12.9 | 0.41 | 0.19 |
| | | | | Exposed Site | | | |
| June | 8 | 0.172 | ND[d] | 0.172 | ND | 0.645 | 0.424 |
| July | 15 | 0.101 | 0.097 | 0.198 | 49.0 | 0.409 | 0.517 |
| July | 14 | 0.178 | 0.134 | 0.312 | 42.9 | 0.691 | 0.095 |
| August | 12 | 0.046 | 0.034 | 0.080 | 42.5 | 0.207 | ND |
| August | 15 | 0.066 | 0.032 | 0.098 | 32.7 | 0.203 | 0.060 |
| September | 14 | 0.297 | 0.077 | 0.374 | 20.6 | 0.801 | 0.632 |
| Mean | | | | | 37.5 | 0.49 | 0.35 |

[a] Throughfall.

[b] Stemflow.

[c] Net precipitation is the sum of throughfall and stemflow.

[d] ND = No data.

throughfall and stemflow was greater at the site exposed to sulphur dioxide than at the control site. The deposition expressed as kg/ha/month was calculated from the deposition in kg/ha at each sample period by weighting each value by the number of days in the month divided by the number of days over which the sampled was collected. This method assumes that the precipitation over the sample period represents the mean precipitation/day over the month. This may not be the case particularly where only one sample per month was obtained. This method allows comparison with other forms of sulphur dioxide.

The fraction of precipitation returned to the soil (throughfall plus stemflow) as stemflow was 7% and 8% at the control aspen plot and exposed aspen plot, respectively (Section 8.3). The fraction of sulphate sulphur deposited as stemflow was much greater at the exposed plot (38%) than at the control plot (13%). The difference in the amount of the sulphate sulphur deposited in stemflow must therefore reflect the influence of atmospheric sulphur on aspen trees at the exposed site. When the amount of sulphate sulphur deposited in incident rain, throughfall, and stemflow at each site is weighted by the amounts of each particular precipitation fraction at each site (in mm), a direct comparison between sites is possible. Such a calculation reveals that, if equivalent amounts of precipitation occurred at each site, an estimated 53% more sulphate sulphur would be removed from the tree canopy (throughfall plus stemflow minus incident rain) at the exposed site compared to the control site. Values for this calculation were taken from the tables in Sections 8.3 and 8.4, and detailed steps to the method of calculation are given in Section 8.4.

4.1.3.2 <u>Deposition of Sulphur in Jack Pine Throughfall and Stemflow</u>. The deposition of sulphate sulphur in jack pine throughfall and stemflow are shown in Table 18. As for trembling aspen, there were greater quantities of $SO_4^{2-}$-S deposited in the throughfall and stemflow than in incident rain. Amounts of $SO_4^{2-}$-S deposited under jack pine were also greater than amounts deposited under aspen at both the control and exposed sites.

The fraction of precipitation returned to the soil (throughfall plus stemflow) as stemflow was on the average less than 1% for both the control and

Table 18. Deposition of Sulphate Sulphur in Jack Pine Throughfall and Stemflow at Control Site and Exposed Site, Summer 1976.

| Month | Sample Period | Deposition in Throughfall and Stemflow | | | | Total Monthly Deposition in Net Precipitation[c] | Total Monthly Deposition in Rain |
|---|---|---|---|---|---|---|---|
| | (days) | TF[a] (kg/ha) | SF[b] (kg/ha) | Total (kg/ha) | Fraction as SF[b] (%) | (kg/ha/mo) | (kg/ha/mo) |
| | | | | Control Site | | | |
| June | 11 | 0.335 | ND[d] | ND | ND | ND | 0.325 |
| July | 17 | 0.414 | 0.012 | 0.426 | 2.9 | 0.752 | 0.152 |
| July | 7 | 0.083 | 0.001 | 0.084 | 0.8 | 0.356 | 0.100 |
| July | 7 | 0.071 | 0.013 | 0.084 | 0.7 | 0.789 | 0.135 |
| August | 23 | 0.504 | 0.028 | 0.532 | 5.3 | 0.694 | 0.000 |
| September | 13 | 0.148 | 0.005 | 0.153 | 3.1 | 0.353 | 0.000 |
| Mean | | | | | 2.7 | 0.59 | 0.12 |
| | | | | Exposed Site | | | |
| June | 8 | 0.670 | ND | ND | ND | ND | 0.423 |
| July | 15 | 0.416 | 0.072 | 0.488 | 14.7 | 0.976 | 0.533 |
| July | 14 | 0.336 | 0.025 | 0.362 | 7.0 | 0.776 | 0.093 |
| August | 12 | 0.117 | 0.008 | 0.124 | 6.1 | 0.310 | ND |
| August | 15 | 0.146 | 0.003 | 0.149 | 1.7 | 0.298 | 0.036 |
| September | 14 | 0.450 | 0.084 | 0.534 | 15.6 | 1.144 | 0.655 |
| Mean | | | | | 9.0 | 0.70 | 0.35 |

[a] Throughfall.

[b] Stemflow.

[c] Net precipitation is the sum of throughfall and stemflow.

[d] ND = No data.

exposed jack pine plots (Section 8.3). The corresponding fractions of $SO_4^{2-}$-S deposited in stemflow was 3% for the control plot and 9.0% for the exposed plot (Table 18). As for trembling aspen, the larger proportion of $SO_4^{2-}$-S deposited in stemflow at the exposed plot apparently represents removal of anthropogenic sulphur from the tree stems.

### 4.1.4 Effect of Sulphur Dioxide on Jack Pine Stemflow Chemistry.

Jack pine stemflow sampled during June and July 1977 was progressively less acidic and contained lower levels of sulphate sulphur with increasing distance from the emission source (**Table 19**). The low concentrations of $SO_4^{2-}$-S at the Muskeg Mountain site (exposed) could be due to the higher stemflow volume and similarly the higher $SO_4^{2-}$-S concentration at Algar (control) could be due to the low stemflow volumes recorded. When these concentration values were converted to sulphate sulphur deposition as kg/ha/month, they were multiplied by the respective stemflow volumes and the number of stems/ha. These values show the general decrease with increasing distance from the emission source. Ths is coincident with a decrease in the average $SO_2$ concentrations in the air at each site as determined by the total sulphation discs.

The difference in pH, titratable acidity, sulphate sulphur and total sulphation were significant ($p = 0.05$) between sites (**Table 20**). The trends in stemflow acidity and sulphate sulphur content as illustrated in **Figure 8**. This figure includes data from a remote site in Canwood, Saskatchewan.

The $SO_4^{2-}$-S concentrations and free acid concentrations in jack pine stemflow are highly correlated at sites close to the emission source and are not correlated at the remote sites (**Table 21**). A similar relationship was found for jack pine throughfall in the nutrient cycling study (Section 4.1.3). The hydrogen ion concentration was highly correlated with $SO_4^{2-}$-S concentrations at the exposed plot ($r^2 = 0.86$) and poorly correlated with $SO_4^{2-}$-S concentrations at the control site ($r^2 = 0.12$). These results show that there was a greater deposition of sulphuric acid beneath jack pine at sites close to the emissions source as compared to the more remote sites.

Table 19. Acidity and Sulphate Sulphur Content of Jack Pine Stemflow Sampled at Four Sites During 1977 and July.

| Site No. | Site | Distance (km) /direction from Source | Mean Sample volume/tree (mL) |  | pH |  | Titratable Acidity[a] (ug $H^+$/mL) |  | $SO_4^{2-}$-S (ppm) |  | Total $SO_4^{2-}$-S[b] |  | Total Sulphation ($mgSO_3$/100 $cm^2$/day) |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Mean | SE[c] | Mean | SE | Mean | SE | Mean | SE | Mean | SE | Mean | SE |
| 6A | Steepbank 3 | 2.4/ESE | 2729 | 1205 | 3.97 | 0.07 | 0.76 | 0.16 | 17.49 | 3.30 | 0.025 | 0.006 | 0.058 | 0.011 |
| 8 | Muskeg Mountain | 38.0/ENE | 8841 | 3225 | 3.91 | 0.08 | 0.59 | 0.16 | 4.37 | 1.03 | 0.020 | 0.006 | 0.056 | 0.004 |
| 13 | Algar | 101.0/SSW | 1409 | 408 | 4.68 | 0.22 | 0.33 | 0.06 | 5.66 | 1.04 | 0.015 | 0.005 | 0.016 | 0.002 |
| 14A | May 2 | 200.0/SW | 9891 | 2142 | 4.32 | 0.11 | 0.34 | 0.10 | 1.03 | 0.28 | 0.008 | 0.001 | 0.011 | 0.001 |

[a] Titrated with 0.001 N KOH to pH 7.00.

[b] Calculated on the basis of 100 stems/ha.

[c] Standard error.

Table 20. Analysis of Variance Between Sites.

| | pH | Titratable Acidity | $SO_4^{2-}$-S | Total Sulphation |
|---|---|---|---|---|
| df | 53 | 53 | 53 | 54 |
| F ratio | 6.716 | 2.903 | 14.572 | 27.204 |
| F probability | b | a | b | b |

a signficant at $p > 0.05$.

b significant at $p > 0.001$.

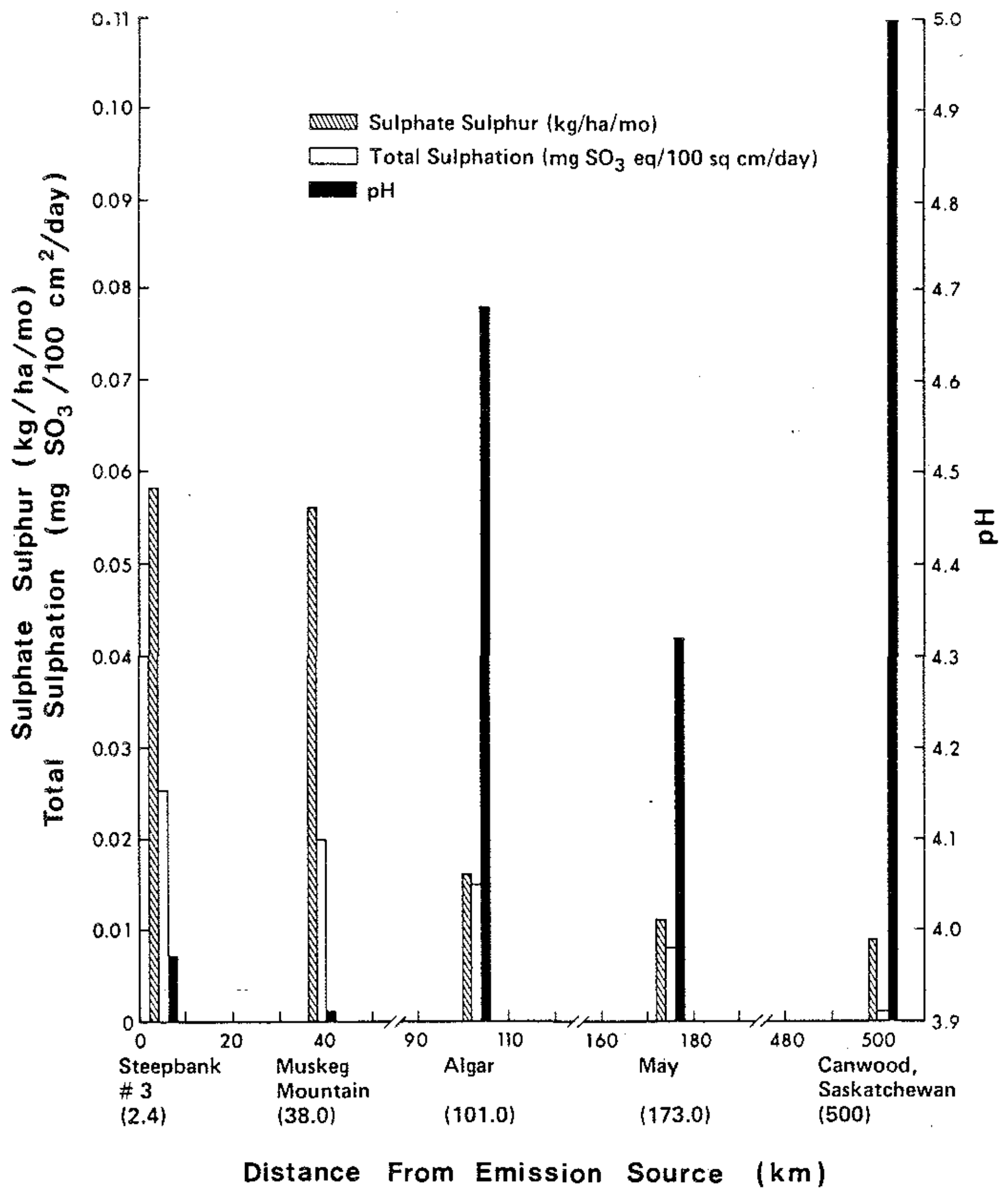

Figure 8. The Variation in Sulphate Sulphur and Acidity of Jack Pine (P. banksiana Lamb.) Stemflow with Increasing Distance from a Sulphur Dioxide Emission Source.

Table 21. Relationship of Acidity and Sulphate Sulphur Content of Jack Pine Stemflow Sampled at Four Sites During June and July 1977.

| Site No. | Site | Distance Direction from Source (km) | Correlation of Hydrogen Ion Concentration versus $SO_4^{2-}$-S Content[a] | | |
|---|---|---|---|---|---|
| | | | Correlation Coefficient (r) | $r^2$ | Significance level |
| 6A | Steepbank 3 | 2.4/ESE | 0.80 | 0.64 | 0.001 |
| 8 | Muskeg Mountain | 38.0/ENE | 0.76 | 0.58 | 0.01 |
| 13 | Algar | 101.0/SSW | 0.23 | 0.05 | 0.22 |
| 14A | May 2 | 200.0/SW | -0.12 | 0.01 | 0.34 |

[a] Calculated from the pH (hydrogen ion concentration = $10^{-pH}$).

### 4.1.5 Impact of Sulphur Dioxide on Bark Leachate Acidity and Sulphur Content

To further investigate the field findings, bark samples from jack pine, trembling aspen, and black spruce were exposed to sulphur dioxide in a controlled atmosphere experiment. The results (Table 22) show that jack pine bark leachate was more acid and contained higher amounts of $SO_4^{2-}$-S after exposure to sulphur dioxide. The pH of jack pine bark leachate decreased from about 5.5 to 4.8, a change of 0.7 pH units. This decrease in pH was associated with a large increase in the $SO_4^{2-}$-S concentration. For the jack pine bark samples from Algar, the hydrogen ion concentration (as calculated from the pH values) increased 279% while the $SO_4^{2-}$-S concentration increased by 405% upon exposure to $SO_2$. Spruce bark showed a similar trend as for jack pine but the changes were not as large.

The reduction in pH of the aspen bark leachate is contrary to the field results where aspen stemflow increased in pH at the site exposed to sulphur dioxide (Table 15). However, the increased sulphate sulphur concentration of the exposed bark leachate is consistent with the increased $SO_4^{2-}$-S concentration of aspen stemflow at the exposed site (Table 15). The difference in the laboratory findings with respect to pH may be because aspen stemflow consists of rainwater which has been intercepted by the foliage and then runs down the branches and down the stem. The smooth bark of aspen and the acutely angled branches cause a channelling of water down the tree trunk. This could alter the composition of any bark leachate and is responsible for the high stemflow volume found in aspen. Thomas (1969) sampled stemflow on dogwood which had been tagged with $^{45}Ca$ and found that after leaf abscission, stemflow contained $^{45}Ca$ at much lower concentrations than when trees supported foliage, indicating that direct leaching from the bark did not contribute as much to the chemical composition of the stemflow as did leaching of the leaves. However, the laboratory experiments here indicate that a substantial amount of the stemflow $SO_4^{2-}$-S content would be derived from leaching of bark.

Table 22. pH and $SO_4^{2-}$-S Content of Bark Washings Exposed to $SO_2$ in a Controlled Environment Chamber for Seven Days.[a]

| Sample[c] | pH | Change in pH | $SO_4^{2-}$-S[b] (ppm) | Area ($cm^2$) |
|---|---|---|---|---|
| Exposed Aspen | 5.53 | -0.34 | 1.97 | 56.3 |
| Control Aspen | 5.87 | | 0.29 | 56.3 |
| Exposed Spruce | 4.75 | | 1.43 | 56.3 |
| Control Spruce | 5.06 | -0.31 | 0.30 | 56.3 |
| Exposed Pine (May) | 4.87 | | 0.56 (0.70) | 30.0 |
| Control Pine (May) | 5.64 | -0.77 | 0.23 | 37.5 |
| Exposed Pine (Algar) | 4.81 | | 1.87 (0.83) | 25.0 |
| Control Pine (Algar) | 5.49 | -0.68 | 0.37 | 56.3 |

[a] Average $SO_2$ concentration = 0.1 ppm.
Average humidity concentration = 80%.
Average air temperature = 22°C.

[b] $SO_4^{2-}$-S concentration weighted according to bark sample area with control bark sample area considered equal to one. Actual concentration value is given in brackets.

[c] Site where bark was sampled is given in brackets.

### 4.1.6 Summary - Wet Deposition

The amount of sulphur deposition in rain in the AOSERP study area was low. In 1976 and 1977 at sites close to the emission source, the amount of $SO_4^{2-}$-S deposited averaged 0.3 to 0.6 kg/ha/month while at remote sites than 0.25 kg/ha/month was deposited. Deposition of $SO_4^{2-}$-S in snow was also very low with about 0.15 kg/ha/month being deposited at sites close to the emission source compared to less than 0.10 kg/ha/month at more distance sites in 1976.

Greater quantities of $SO_4^{2-}$-S were deposited in throughfall and stemflow than in rain. There was also increased deposition of $SO_4^{2-}$-S in throughfall and stemflow at exposed sites compared to remote sites. In 1976, approximately 0.5 to 4.7 kg/ha/month was deposited in throughfall and stemflow at exposed sites compared 0.4 to 0.6 kg/ha/month at control sites, depending on the tree species.

The acidity of rain decreased as it passed through the canopy of trembling aspen whereas rainfall acidity increased as it passed through the canopy of jack pine. The acidity of jack pine throughfall and stemflow increased at sites exposed to sulphur dioxide compared to control sites. Throughfall decreased in pH by about 0.3 pH units and stemflow decreased by about 0.8 to 1.1 pH units.

For both jack pine and trembling aspen, larger quantities of the cations $K^+$, $Ca^{2+}$, and $Mg^{2+}$ were removed from the canopy at the site closer to the emission source compared to the remote site.

Further research is needed into the mechanism of the influence of $SO_2$ on nutrient cycling. These results pose the question as to what effects these differences between species have on forest ecosystems in the AOSERP study area. In particular, how do changes in the chemistry of throughfall and stemflow affect nutrient cycling and soil properties? The nutrients in throughfall and stemflow become part of the available nutrient pool in the soil (Figure 9). Is the increased input in throughfall and stemflow the result of leaching of nutrients from the tree canopy? Is there an increase in plant nutrient uptake to compensate for this or are these nutrients lost by leaching from the soil?

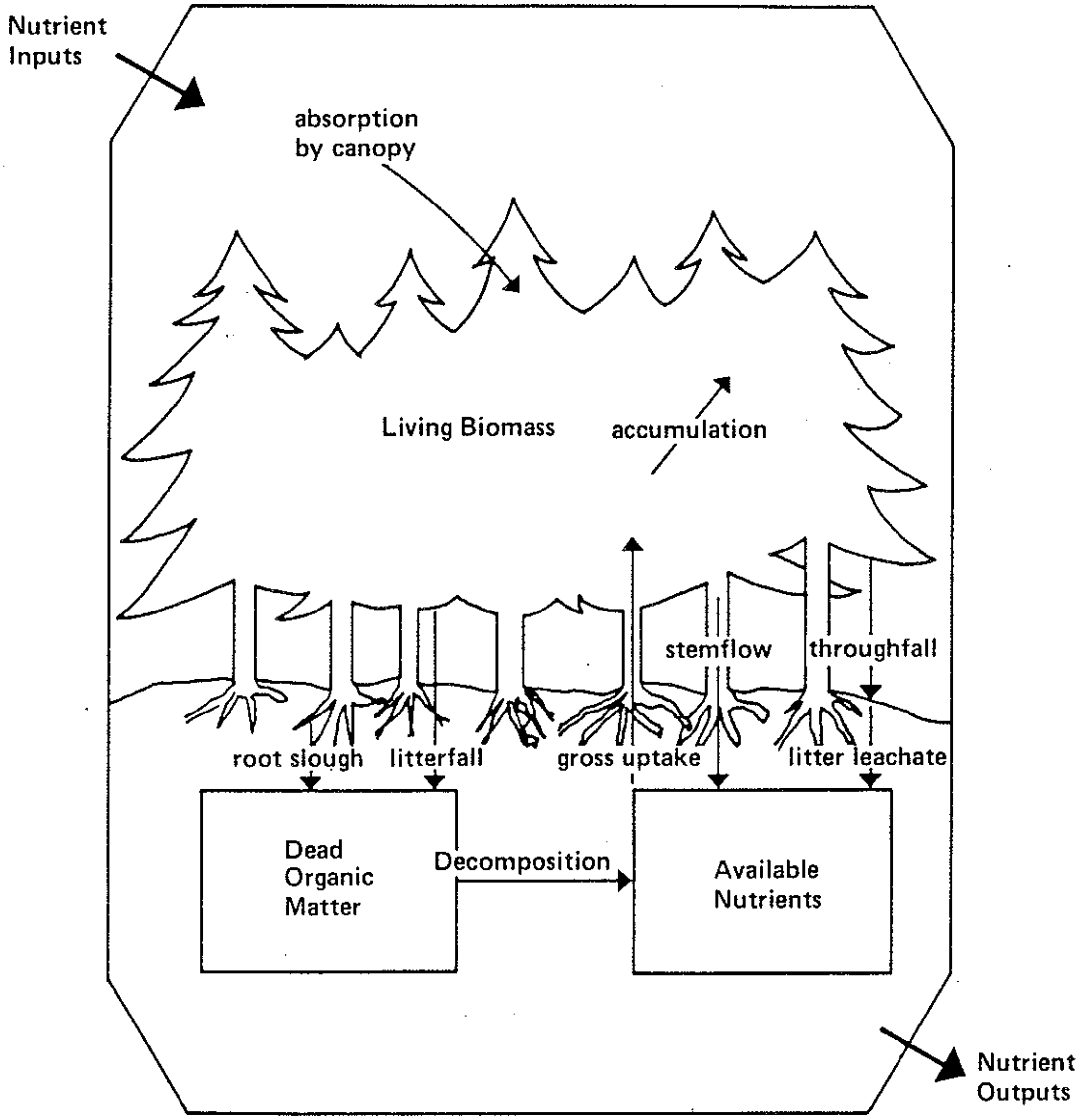

Figure 9. Components of the Nutrient Cycle for a Forest Ecosystem Showed Sites of Nutrients Accumulation and Major Pathways. (After Eaton et al. 1973)

## 4.2 DRY DEPOSITION

### 4.2.1 Sulphur Dioxide Absorption by Sulphation Discs.

The total sulphation values of sulphation discs set out over the summers of 1976 and 1977 are given in Section 8.6. The network of sulphation discs became part of an extended network maintained by the Pollution Control Division, Alberta Department of the Environment in June 1974 (Strosher 1978).

### 4.2.2 Sulphur Uptake by Bare Soils - Field Experiments

The average pH values of several soils exposed under rain shelters from June to September 1975 are given in **Table 23**. All of the soils within 30 km of the emission source increased in acidity over the summer compared to soils located at remote sites. The moist soils had a greater increase in acidity than the soils kept dry. This is consistent with the observation of Terraglio and Manganelli (1966) that increased soil moisture content increases the amount ot sulphur dioxide absorbed by soil.

The pH of the 0 to 1 cm layer of the sandy O.EB soil set out at 13 field sites during the summer of 1976 is shown in **Figure 10**. After being exposed to sulphur emissions for a period of four months, the pH of soils located within 50 km of the emission source was lower by about 0.2 pH units than that of soils located at greater distances from the emission source.

It is important to note that short-term field experiments on the effect of $SO_2$ emissions on soil pH must take into consideration the natural fluctuation in pH from site to site which may mask changes caused by $SO_2$. Differences in soil moisture content and temperature will result in changes in the rates of ammonification and nitrification of soil nitrogen which will alter the soil pH. This effect is greatest in bare soils where ammonium or nitrates accumulate instead of being taken up by plants. In our field experiments, the moisture contents of the soils were kept as uniform as possible by watering the soils to field capacity every week in 1975 and every two weeks in 1976.

The amounts of sulphur absorbed (as indicated by $SO_4^{2-}$-S analyses) by the top 1 cm of the sandy O.EB soil and the TY.M soil set under rain shelters at 13 field sites is shown in **Figures 11 and 12**. The

Table 23. pH Values of the Top 1 cm of Soils Exposed Under Rain Shelters from 1975 June to September.

| Site | Distance /direction from Source | 0.BL Soil, Moist | 0.BL Soil, Dry | 0.DG Soil, Moist | 0.DG Soil, Dry | 0.BL Soil Moist | 0.GL Soil Moist | TY.M Soil Moist | Mean pH Change |
|---|---|---|---|---|---|---|---|---|---|
| Syncrude | 1.6/N | 5.85 | 5.88 | ND[d] | 6.09 | 5.14 | 5.49 | 5.85 | -0.12 |
| Steepbank 3 | 2.4/ENE | 5.45 | 5.77 | 5.64 | 6.03 | 4.95 | 5.45 | 5.80 | -0.26 |
| Steepbank 2 | 4.0/ENE | 5.59 | 5.88 | 5.96 | 6.24 | 4.99 | 5.26 | 5.81 | -0.17 |
| Mildred Lake | 7.2/NNW | 5.64 | 5.84 | 5.72 | 6.16 | 5.05 | 5.36 | 5.86 | -0.18 |
| Supertest Hill | 8.0/S | 5.59 | 5.84 | 5.74 | 6.13 | 5.05 | 5.63 | 5.88 | -0.15 |
| Steepbank 1 | 8.8/ESE | 5.64 | 5.82 | 5.87 | 6.03 | 5.26 | 5.21 | 5.88 | -0.17 |
| Thickwood Hills | 30.5/SW | 5.76 | 5.93 | 5.95 | 6.01 | 5.26 | 5.27 | 5.88 | -0.12 |
| Mean | | 5.64 | 5.85 | 5.81 | 6.10 | 5.10 | 5.38 | 5.85 | -0.17 |
| Remote Sites[a] (mean) | | 5.74[b] | 6.14 | 5.97 | 6.26 | 5.23 | 5.55[c] | 5.98[c] | 0.00 |
| L.S.D.[d] | | 0.08 | 0.26 | 0.21 | N.S.[d] | 0.26 | 0.11 | 0.07 | |

[a] Loon Lake, Saskatchewan (356 km SSE); Canwood, Saskatchewan (502 km SE); and Beaverlodge, Alberta (527 km WSW).

[b] Beaverlodge, Alberta only.

[c] Canwood, Saskatchewan only.

[d] ND = No data; N.S. = Not significant; L.S.D. = Least significant difference (p = 0.05).

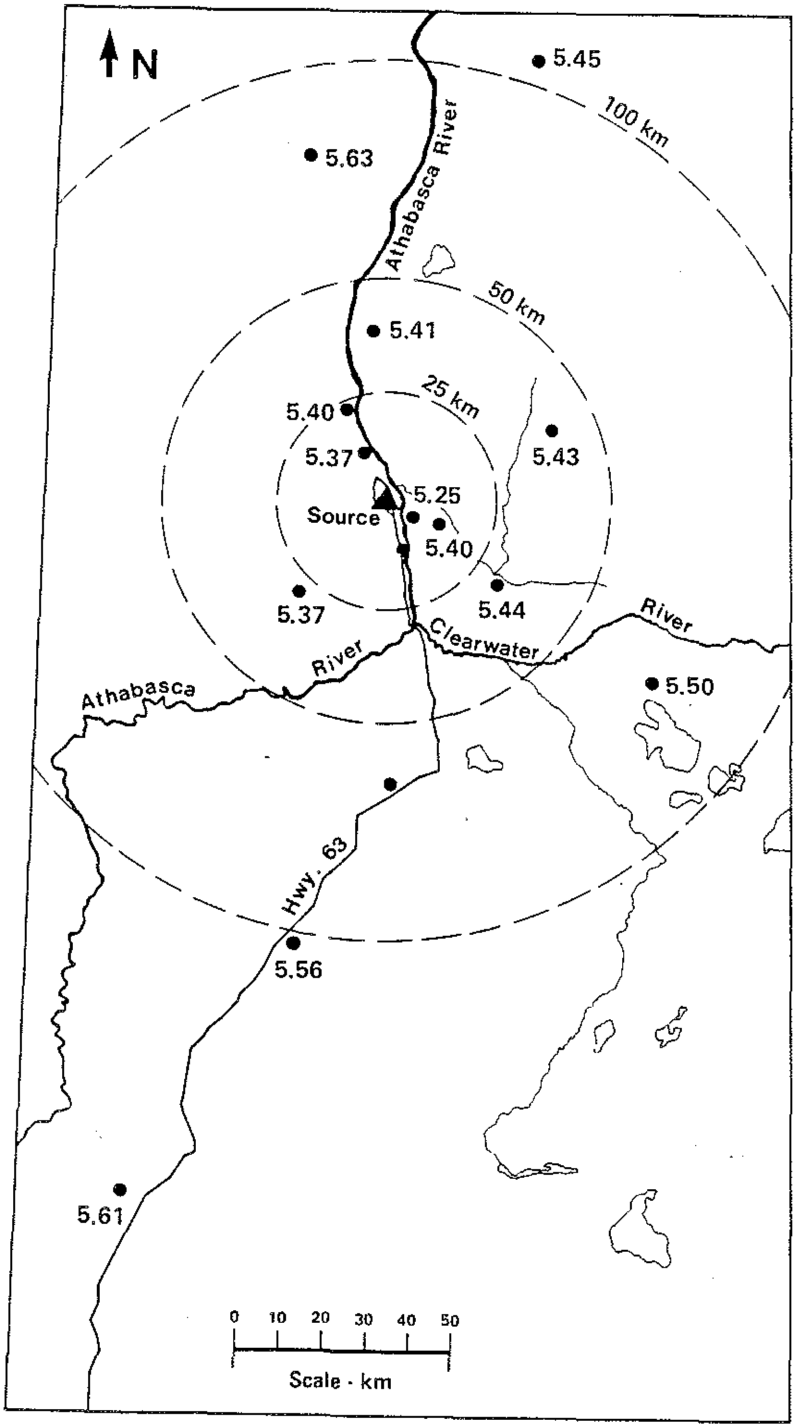

Figure 10. pH Values of 1 cm Top of the Sandy O.EB Soil Kept Under Rain Shelters from 1976 June to September.

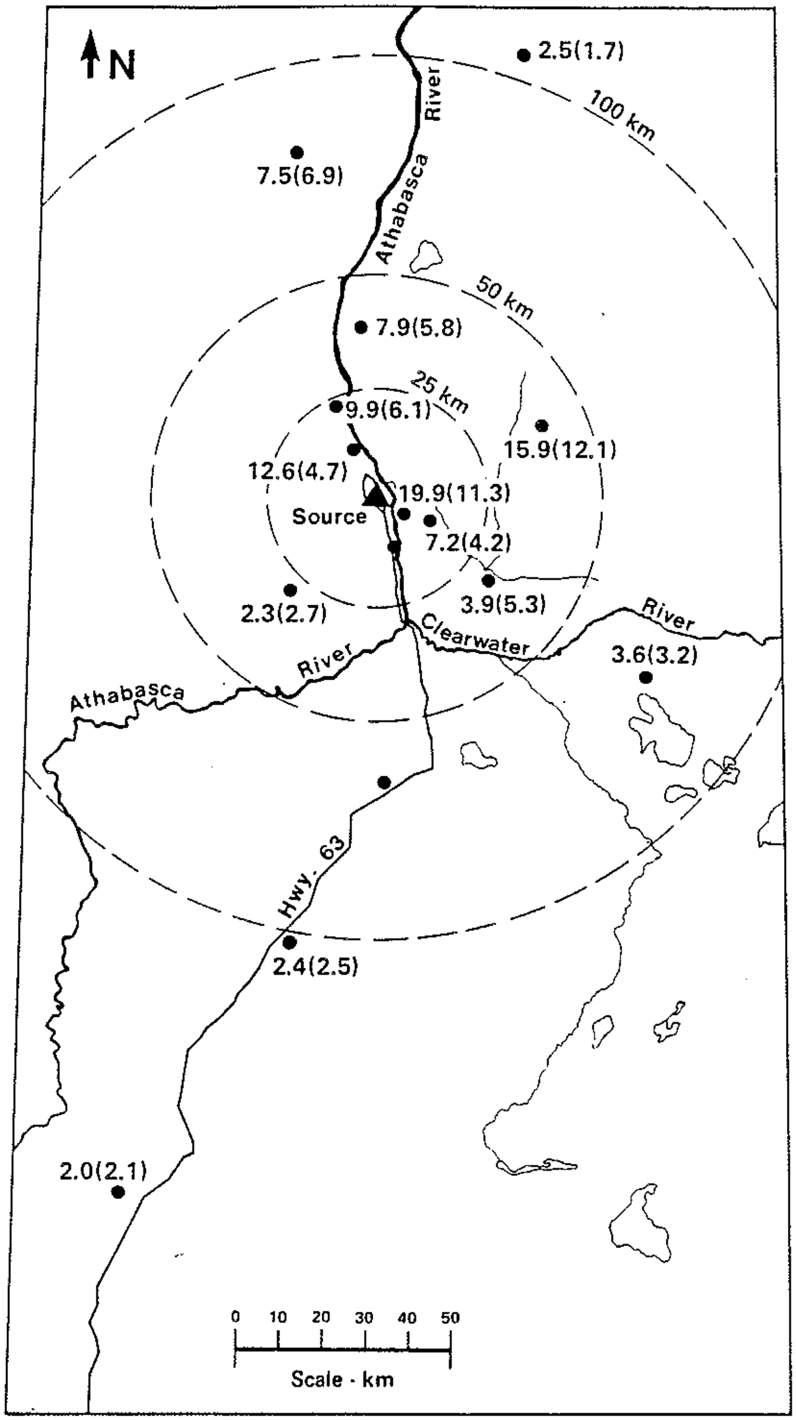

Figure 11. Sulphur (ug/cm$^2$/mo) Adsorbed by Sulphation Discs from 1976 June 01 to September 30, and in Brackets the Sulphate Sulphur (ppm) Content of the Surface of 1 cm of the Sandy O.EB Soil Set Out for the Same Period.

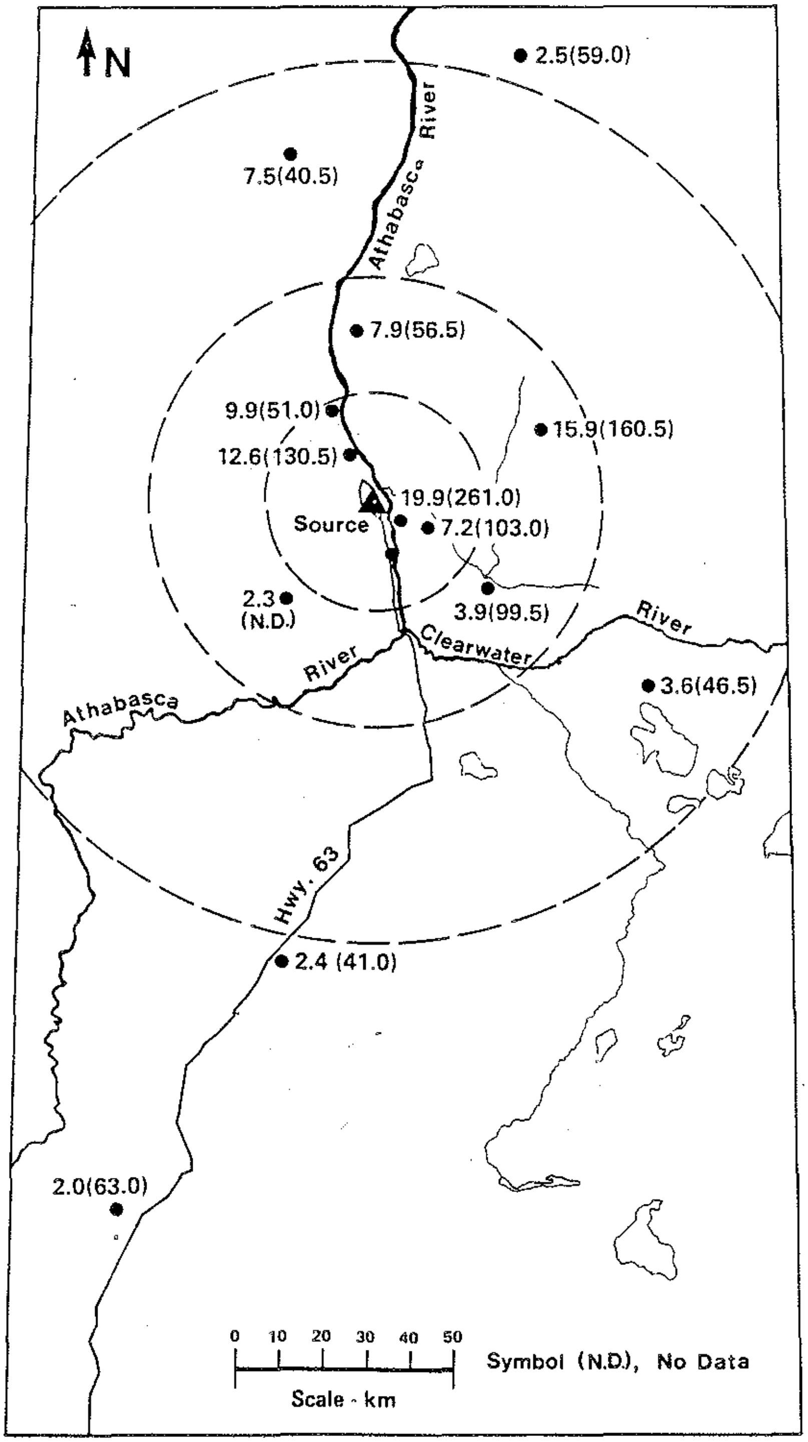

Figure 12. Sulphate Sulphur (ug/cm$^2$/mo) Absorbed by Sulphation Discs from 1976 June to September, and in Brackets the Sulphate Sulphur (ppm) Content of the Surface of 1 cm of the TY.M Soil Set Out for the Same Period.

$SO_4^{2-}$-S concentrations in the sandy O.EB soil and the TY.M soil were signficantly ($p = 0.001$) correlated with the total sulphation values at each site ($r^2 = 0.79$ and 0.80, respectively).

Table 24 shows the final pH values of the two soils after being set out at nine field sites over the summer of 1976. The main source of sulphur for these soils was from gaseous emissions since the soils were kept under the rain shelters. The surface layer (0 to 1 cm) of both the peat and pine sand became more acid than the layer beneath (1 to 3 cm) at all sites. The pH of the surface layer of both soils was depressed in those soils nearest the emission source. The 0 to 1 cm layer of pine sand had decreased in pH by 0.34 units at the site nearest the emission source (Steepbank 2) as compared to the corresponding layer of pine sand located at the site furthest from the emission source (May). The 0 to 1 cm layer of peat at Steepbank 2 had a decrease in pH of 0.15 units compared to a corresponding layer of peat at May. These differences in pH for a given soil and depth were significant ($p = 0.05$) between sites. The depression in pH over the summer period may be small, but the trends are clear--soil pH is depressed nearer the emission source. Other researchers have shown similar results in both field (Johansson 1959, Cox 1975) and laboratory experiments (Ghiorse and Alexander 1976).

The $SO_4^{2-}$-S content of the 0 to 1 cm and 1 to 3 cm layers of both soils increased at those soils placed closest to the emission source (Table 24). Analysis of variance indicated that for a given soil and depth, $SO_4^{2-}$-S content was significantly ($p = 0.05$) different between sites. The hydrogen ion concentrations (calculated from soil pH) in the top 1 cm of the sandy O.EB soil were significantly ($p = 0.01$) correlated ($r^2 = 0.65$) with the total sulphation values at each site (Section 8.7).

Analysis of the soils for total sulphur in 1977 revealed that the soils nearest the emission source had absorbed larger quantities of $SO_2$ from the air than had been indicated by the $SO_4^{2-}$-S results (Table 24). The total S content of both soils was very variable and most likely reflects differing amounts of organic matter in the soil samples selected for each site. The total S values for both peat and pine sand are unusually high at Algar and May where low values would be exptected. However, the total S

Table 24. pH Values and Sulphur Content (kg/ha) of the Sandy O.EB Soil and TY.M Soil Set Out Under Rain Shelters from 1976 June to September.[a]

| Site | Distance (km) /direction from Source | 0 to 1 cm | | | 1 to 3 cm | | | 0 to 3 cm | |
|---|---|---|---|---|---|---|---|---|---|
| | | pH | $SO_4^{2-}$-S (kg/ha) | Total S kg/ha) | pH | $SO_4^{2-}$-S (kg/ha) | Total S (kg/ha) | $SO_4^{2-}$-S (kg/ha) | Total S (kg/ha) |
| Sandy O.EB Soil | | | | | | | | | |
| Steepbank 2 | 4.0/ESE | 5.25 | 1.3 | 25.1 | 5.48 | 0.4 | 23.8 | 1.7 | 49.0 |
| Mildred Lake | 11.0/NW | 5.37 | 1.1 | 5.1 | 5.38 | 0.3 | 7.2 | 1.4 | 12.3 |
| Steepbank 1 | 17.0/ESE | 5.40 | 0.8 | 5.1 | 5.55 | 0.5 | 8.5 | 1.3 | 13.6 |
| Steepbank A | 32.0/SE | 5.44 | 1.0 | 6.1 | 5.54 | 0.4 | 5.5 | 1.4 | 11.6 |
| Muskeg Mountain | 38.0/ENE | 5.43 | 1.3 | 24.2 | 5.54 | 0.4 | 21.5 | 1.7 | 45.7 |
| Bitumount | 39.0/N | 5.41 | 1.0 | 5.3 | 5.47 | 0.5 | 8.3 | 1.5 | 13.6 |
| Algar | 101.0/SSW | 5.56 | 0.5 | 14.6 | 5.65 | 0.3 | 20.2 | 0.8 | 34.8 |
| Richardson | 102.0/NNE | 5.45 | 0.6 | 4.6 | 5.51 | 0.3 | 5.4 | 0.9 | 10.0 |
| May | 173.0/SW | 5.60 | 0.5 | 16.1 | 5.67 | 0.4 | 21.3 | 0.9 | 37.4 |
| L.S.D.[b] | | 0.06 | 0.1 | 0.5 | 0.09 | 0.1 | 0.9 | | |
| TY.M Soil | | | | | | | | | |
| Steepbank 2 | 4.0/ESE | 5.40 | 3.9 | 18.9 | 5.84 | 0.5 | 39.3 | 4.4 | 58.2 |
| Mildred Lake | 11.0/NW | 5.48 | 3.0 | 19.0 | 5.81 | 0.4 | 33.7 | 3.4 | 51.3 |
| Steepbank 1 | 17.0/ESE | 5.43 | 1.1 | 13.2 | 5.81 | 0.2 | 32.3 | 1.3 | 45.5 |
| Steepbank A | 32.0/SE | 5.46 | 0.7 | 14.9 | 5.81 | 0.1 | 29.6 | 0.8 | 44.5 |
| Muskeg Mountain | 38.0/ENE | 5.40 | 2.3 | 18.1 | 5.83 | 0.3 | 34.0 | 2.6 | 52.1 |
| Bitumount | 39.0/N | 5.46 | 0.6 | 14.6 | 5.79 | 0.2 | 33.9 | 0.8 | 48.5 |
| Algar | 101.0/SSW | 5.49 | 1.1 | 14.4 | 5.78 | 0.1 | 38.0 | 1.2 | 52.4 |
| Richardson | 102.0/NNE | 5.57 | 0.4 | 13.9 | 5.83 | 0.2 | 30.7 | 0.6 | 44.6 |
| May | 173.0/SW | 5.52 | 0.8 | 16.9 | 5.78 | 0.2 | 35.2 | 1.0 | 52.1 |
| L.S.D.[b] | | 0.07 | 0.1 | 0.6 | 0.05 | 0.1 | 1.0 | | |

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[a] Values are means of three replications.

[b] L.S.D. = Least significant difference (p = 0.05).

content of both pine sand and peat was correlated to the average total sulphation values at each site (Section 8.7). This correlation explained 54% of the variance in total S content of peat. The hydrogen ion and $SO_4^{2-}$-S concentration in both the peat and pine sand were correlated with distance from the sulphur dioxide emission source and average total sulphation values at each site.

### 4.2.3 Sulphur Uptake by Bare Soils - Controlled Atmosphere Experiment

The capacity of soils to absorb $SO_2$ and the consequent depression of soil pH was demonstrated in a controlled atmosphere experiment in 1976. The pH and total S values are shown in **Table 25**. All three soils decreased in pH and increased in total S content after being exposed to sulphur dioxide for a period of 30 days. A t-test indicated that the decrease in pH was significant ($p = 0.05$) for both the O.BL soil and sandy O.EB soil but was not significant for the TY.M soil. The increase in total S was significant for sandy O.EB soil but not significant for the other two soils.

### 4.2.4 Sulphur Uptake by Lichen Covered Soils - Field Experiment

This experiment was designed to determine the rate of uptake of sulphur by an intact forest soil from the AOSERP study area. The soil was sampled so that the natural lichen cover and mineral soil remained undisturbed. Pots of this soil were set out in the field under rain shelters from May to October 1976. They had therefore been exposed to sulphur emissions for a period of five months.

The results (**Table 26**) indicate that the $SO_4^{2-}$-S and total S content of soils set out at the two field sites located nearest the emission source (Steepbank 2 and Muskeg Mountain) increased substantially over the exposure period. Although the live lichen material had the largest increase in $SO_4^{2-}$-S and total S when expressed in ug S/g material, the increase on an area basis was small because of the low bulk density of the lichen material. The layer below five cm depth (Ae horizon) did not absorb sulphur from the atmosphere. The live lichen material at both control sites increased in total S content but this increase was much smaller than for the lichen material which had been exposed at two sites nearer the emission source.

Table 25. Effect of $SO_2$ Exposure, Under Controlled Conditions[a], on Soil pH Values and Total Sulphur Concentration.[b]

| | Control | | | Exposed to $SO_2$ [e] | | |
|---|---|---|---|---|---|---|
| Soil | pH[c] ($H_2O$) | pH[d] ($CaCl_2$) | Total S (ppm) | pH ($H_2O$) | pH ($CaCl_2$) | Total S (ppm) |
| O.BL Soil | 5.89 | 4.78 | 641 | 5.81 | 4.58 | 674 |
| Sandy O.EB Soil | 5.82 | 4.46 | 30 | 5.33 | 4.37 | 55 |
| TY.M Soil | 5.68 | 4.40 | 1126 | 5.47 | 4.37 | 1142 |

[a] Air temperature = 22°C.
Average $SO_2$ concentration = 70 ppb.
Average relative humidity = 60%.
Length of exposure = 30 days.

[b] Values are means of 3 replications for pH, and 6 replications for total sulphur.

[c] pH in water.

[d] pH in 0.01 M $CaCl_2$.

[e] Concerning statistical differences (0 = 0.05) between control and $SO_2$ exposed soil samples: pH values in water, all 3 soils were statistically less when exposed to $SO_2$; for pH values in $CaCl_2$ solution, only the O.BL soil and the sandy O.EB soil were statistically less when exposed; and for total S, only the sandy O.EB soil was statistically greater when exposed.

Table 26. Sulphur Dioxide Uptake by Intact Lichen Covered Soil Samples Set Out Under Rain Shelters from 1977 May to October.[a]

| Site No. | Site | Layer | pH |  | $SO_4^{2-}$-S (ppm) |  | Total S (ppm) |  | $SO_4^{2-}$-S (kg/ha) |  |  | Total S (kg/ha) |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | May | Oct. | May | Oct. | May | Oct. | May | Oct. | Incr.[b] | May | Oct. | Incr.[b] |
| 6 | Steepbank | lichen | 4.46 | 4.38 | 22.6 | 38.7 | 447.0 | 721.7 | 0.7 | 0.8 | 0.1 | 8.9 | 14.4 | 5.5 |
|  |  | LFH | 4.26 | 4.25 | 14.3 | 28.8 | 160.5 | 226.0 | 11.6 | 23.3 | 11.7 | 129.8 | 182.5 | 52.7 |
|  |  | AE | 4.86 | 4.88 | 2.7 | 2.9 | 1.3 | 7.3 | 3.9 | 4.2 | 0.3 | 10.6 | 10.6 | 0.0 |
|  |  | total |  |  |  |  |  |  |  |  | 12.1 |  |  | 58.2 |
| 8 | Muskeg Mountain | lichen | 4.49 | 4.44 | 23.1 | 30.1 | 430.0 | 574.0 | 0.5 | 0.6 | 0.1 | 8.6 | 11.5 | 2.9 |
|  |  | LFH | 4.02 | 4.00 | 14.5 | 20.7 | 181.1 | 190.0 | 11.8 | 16.8 | 5.0 | 146.7 | 153.9 | 7.2 |
|  |  | Ae | 4.59 | 4.58 | 2.4 | 2.5 | 7.8 | 8.0 | 2.9 | 3.6 | 0.1 | 11.3 | 11.6 | 0.3 |
|  |  | total |  |  |  |  |  |  |  |  | 5.2 |  |  | 10.4 |
| 13 | Algar | lichen | 4.43 | 4.40 | 25.2 | 31.6 | 439.9 | 480.0 | 0.5 | 0.6 | 0.1 | 8.8 | 9.6 | 0.8 |
|  |  | LFH | 4.10 | 4.08 | 14.5 | 13.2 | 162.5 | 150.0 | 11.8 | 10.7 | -1.1 | 131.6 | 121.5 | -10.1 |
|  |  | Ae | 4.62 | 4.60 | 2.0 | 2.5 | 6.0 | 6.0 | 2.9 | 3.6 | 0.7 | 8.7 | 8.7 | 0.0 |
|  |  | total |  |  |  |  |  |  |  |  | 0.3 |  |  | -9.3 |
| 14 | May | lichen | 4.43 | 4.43 | 23.0 | 24.1 | 421.0 | 460.0 | 0.5 | 0.5 | 0.0 | 8.4 | 9.2 | 0.8 |
|  |  | LFH | 4.14 | 4.16 | 14.0 | 14.0 | 196.0 | 200.0 | 11.3 | 11.3 | 0.0 | 158.8 | 162.0 | 3.2 |
|  |  | Ae | 5.49 | 5.50 | 2.0 | 2.0 | 6.3 | 6.5 | 2.9 | 2.9 | 0.0 | 9.1 | 9.4 | 0.3 |
|  |  | total |  |  |  |  |  |  |  |  | 0.0 |  |  | 4.3 |

[a] Values are means of six replications.

[b] Incr. = Increase from May to October.

Inexplicably, the sulphur content of the LFH layer located at one of the control sites (Algar) decreased.

The $SO_4^{2-}$-S and total S content of a given layer at a given site was significantly different (p = 0.05) between the two sample dates. Analysis of variance also showed that the two-way interactions; site by layer, site by date, and layer by date, were significant (p = 0.05) for both $SO_4^{2-}$-S and total S.

In contrast to the experiments with bare soils, the pH of the lichen covered soil was not depressed (Table 26). There tended to be a decrease in the pH of the lichen material at the two sites nearest the emission source (Steepbank 2 and Muskeg Mountain). However, analysis of variance shows that differences in pH for a given layer, at a given site, were not significantly ($p < 0.05$) different between the two sample dates.

The considerable increase in total S by the soils located nearest the emission source (particularly field site No. 6) demonstrates that an undisturbed sandy forest soil can absorb appreciable quantities of $SO_2$ directly from the air. This absorption amounted to a net increase of total S of 10.8 kg/ha/month and 1.2 kg/ha/month for field site Nos. 6 and 8, respectively. When this is compared to the sulphur deposition (as $SO_4^{2-}$-S) in rainwater of 0.3 kg/ha/month for field site No. 6 and 0.2 kg/ha/month for field site No. 8, it is evident that dry deposition of sulphur by direct absorption of $SO_2$ by soils is a major mechanism for the removal of sulphur from the atmosphere. This is particularly important in areas close to the emission source.

### 4.2.5 Sulphur Uptake by Lichen Covered Soils - Controlled Atmosphere Experiment

Data obtained from the controlled atmosphere experiment coroborates data from the field experiment (Table 27). After an exposure period of seven days, there was a significant (p = 0.05) increase in the $SO_4^{2-}$-S content of the lichen layer and top 2.5 cm of soil. There was a larger (but non-significant) increase in the total sulphur content of the lichen layer and mineral soil at both humidity levels. A significantly larger amount of sulphur was absorbed by the lichen layer and mineral soil at the 80% humidity

Table 27. pH Values and Sulphur Content of a Lichen Covered Sandy Soil Exposed to 0.1 ppm Sulphur Dioxide for Seven days Under Controlled Conditions.[a]

| | pH | | $SO_4^{2-}$-S (ppm) | | Total S (ppm) | | $SO_4^{2-}$-S (ppm) | | | Total S (kg/ha) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | control | exposed | control | exposed | control | exposed | control | exposed | Incr.[b] | control | exposed | Incr.[b] |
| | | | | | 80% RH | | | | | | | |
| Lichen Layer | 4.13 | 3.97 | 6.0 | 40.4 | 680.5 | 790.5 | 0.2 | 1.2 | 1.0 | 31.1 | 36.1 | 5.0 |
| Top 2.5 cm Soil | 4.68 | 4.65 | 3.4 | 5.3 | 58.3 | 63.5 | 3.6 | 5.7 | 2.1 | 95.0 | 103.5 | 8.5 |
| Total | | | | | | | | | 3.1 | | | 13.5 |
| | | | | | 20% RH | | | | | | | |
| Lichen Layer | 4.11 | 4.08 | 3.2 | 16.3 | 570.0 | 648.0 | 0.2 | 0.8 | 0.6 | 26.1 | 29.6 | 3.5 |
| Top 2.5 cm Soil | 4.74 | 4.52 | 1.6 | 2.5 | 55.0 | 62.0 | 2.6 | 4.1 | 1.5 | 89.7 | 101.1 | 11.4 |
| Total | | | | | | | | | 1.1 | | | 14.9 |

[a] Air temperature = 22°C.
Average $SO_2$ concentration = 100 ppb.

[b] Incr. = Increase over the exposure period.

level compared to the 20% humidity level. This may be due to the increased moisture hastening the oxidation of $SO_2$ and the reactions of its oxidation products with soil bases. Other researchers have shown an increase in the absorption of $SO_2$ with increasing moisture content of soil (Terraglio et al. 1966) and the air moisture content (Yee et al. 1975). These studies, however, only analysed the soils for $SO_4^{2-}$-S and Faller and Herwig (1969/70) stated that the end product of soil $SO_2$ absorption is sulphate. Our results show that for peat (Section 4.2.3), sulphate sulphur appears as the main end product. In this case, the absorption could be related to the moderate solubility of $SO_2$ in water.

The larger increase in total S indicates that only a fraction of the absorbed $SO_2$ is recovered as $SO_4^{2-}$-S. The $SO_2$ was also able to penetrate the lichen layer and be absorbed by the mineral soil beneath (Table 27).

### 4.2.6 Sulphur Content of Lysimeter Soils

In July 1976, two soils in three replicates were set out at nine sites. The soils, an Orthic Gray Luvisol and an Orthic Eutric Brunisol were placed in lysimeters so that the plant cover and organic layers remained undisturbed (Section 3.2.5). The lysimeters were left out in the field until August 1978. They were then removed from the field and both soils were separated into layers. Each layer was analysed for pH, $SO_4^{2-}$-S and total S (Sectio 8.8).

The total S concentrations in the plants and organic layers of both soils are given in **Table 28**. The grasses and moss covering the O.GL soil show a clear trend of decreasing total S concentration with increasing distance from the emission source. The organic layers also show this trend. The concentrations of total S in the organic layers are considerably larger at the two sites nearest the emission source compared to the two remote sites. The lichen and FH layers of the sandy O.EB soil do not show a trend of decreasing total S concentration with increasing distance from the emission source.

The $SO_4^{2-}$-S and total S content of the organic layers and top 3 cm of mineral soil for both soils is shown in **Table 29**. The $SO_4^{2-}$-S

Table 28. Total S (ppm) of the Plants and Organic Layers of the Two Lysimeter Soils Kept Out from July 1976 to August 1978.[a]

| Site | Distance (km) and Direction from Emission Source | Sandy O.EB Soil | | O.GL Soil | | | |
|---|---|---|---|---|---|---|---|
| | | Lichen (ppm) | FH (ppm) | Grasses (ppm) | Moss (ppm) | Litter (L) (ppm) | FH (ppm) |
| Steepbank 2 | 4 ESE | 432 | 157 | 2200 | 1897 | 1400 | 1133 |
| Mildred Lake | 11 NW | 354 | 251 | 1690 | 1643 | 1800 | 1120 |
| Mean | | 393 | 204 | 1945 | 1770 | 1600 | 1127 |
| Thickwood Hills | 31 SW | 370 | 220 | 1373 | 1343 | 1367 | 1023 |
| Steepbank A | 32 SE | 309 | 396 | 2050 | 2017 | 1509 | 1040 |
| Bitumount | 39 N | 412 | 331 | 1200 | 1367 | 1360 | 1140 |
| Gordon Lake | 75 SE | 317 | 349 | 1380 | 2007 | 1416 | 1267 |
| Mean | | 352 | 324 | 1501 | 1684 | 1413 | 1118 |
| Algar | 101 SSW | 255 | 155 | 1285 | 1277 | 883 | 888 |
| May | 173 SW | 302 | 142 | 1123 | 1367 | 1093 | 447 |
| Mean | | 279 | 149 | 1204 | 1322 | 988 | 668 |
| L.S.D.[b] | - | 19 | 29 | 190 | 115 | 108 | 57 |

[a] Values are mean of three replicates.

[b] L.S.D. = Least significant difference (p = 0.05) to compare site values within a column.

Table 29. Sulphate Sulphur and Total S Content of Plants and Soils in Lysimeters Kept Out from July 1976 to August 1978.[a]

| Site | Distance (km) and Direction from Emission Source | $SO_4^{2-}$-S content of litter (FH) layer and top 3 cm of mineral soil | | Total S content of plants plus litter layers plus top 3 cm of mineral soil | |
|---|---|---|---|---|---|
| | | O.EB Soil (kg/ha) | O.GL Soil (kg/ha) | O.EB Soil[b] (kg/ha) | O.GL Soil (kg/ha) |
| Steepbank 2 | 4 ENE | 0.31 | 2.18 | 103.7 | 182.1 |
| Mildred Lake | 11 NW | 0.33 | 1.71 | 96.8 | 158.9 |
| Mean | | 0.32 | 1.95 | 100.3 | 170.5 |
| Thickwood Hills | 31 SW | 0.36 | 1.15 | 77.9 | 177.0 |
| Steepbank A | 32 SE | 0.28 | 1.09 | 89.8 | 133.4 |
| Bitumount | 39 N | 0.38 | 1.58 | 64.6 | 152.2 |
| Gordon Lake | 75 SE | 0.41 | 0.87 | 76.5 | 147.4 |
| Mean | | 0.36 | 1.17 | 77.2 | 152.5 |
| Algar | 101 SSW | 0.54 | 0.82 | 94.0 | 144.1 |
| May | 173 SW | 0.34 | 1.18 | 70.4 | 92.2 |
| Mean | | 0.44 | 1.00 | 82.2 | 118.2 |

[a] Values are means of three replicates.

[b] Litter layer was FH only.

content of the top layers of the O.EB soil do not show any relation to distance from the emission source whereas the O.GL soil shows such a trend. The $SO_4^{2-}$-S content of the surface layers of the O.EB soil increased by approximately 1 kg/ha at the sites nearest the emission source compared to the remote sites.

The total S content of O.EB soil also showed a clear trend of increasing with decreasing distance from the emission source. The total S content of the surface layers of this soil increased by approximately 50 kg/ha at the sites nearest the emission source compared to the remote sites.

There were no significant differences in the pH of both soils at sites near the emission source as compared to the remote sites (Section 8.8)

## 4.3 MOVEMENT OF APPLIED SULPHATE SULPHUR IN FOREST SOILS

### 4.3.1 Sandy Soil (Mildred Lake Research Facility Site)

Potassium sulphate was applied to the surface of a forest soil at two rates (56 kg/ha S and 112 kg/ha S). To determine changes over the summer period, the soil was sampled before (June) and four months after (September) the potassium sulphate was applied.

Preliminary results (Section 8.9) indicated that soil pH was not affected by the application of the potassium sulphate. At the low rate of application (56 kg/ha S), $SO_4^{2-}$-S had moved down about 60 cm into the soil while soluble K had moved down about 15 cm. At the high application rate (112 kg/ha S), $SO_4^{2-}$-S and $K^+$ appeared to have moved about the same rate as for the low rate of application. Most of the recovered $SO_4^{2-}$-S was found in the top 30 cm of soil. Potassium appeared to be less mobile than $SO_4^{2-}$-S. The low recovery of $SO_4^{2-}$-S and particularly $K^+$ makes interpretation of these results difficult.

The $SO_4^{2-}$-S, total S, and extractable potassium content of the soil one year after application of potassium sulphate is given in **Table 30.** The $SO_4^{2-}$-S values indicate that the applied $SO_4^{2-}$-S had moved down at least 60 cm. Very little of the applied $SO_4^{2-}$-S was recovered as $SO_4^{2-}$-S and, if considered in isolation, this would suggest that much of the $SO_4^{2-}$-S had been leached to depths greater than was sampled or much

Table 30. Soluble Sulphate, Total S, and Extractable Potassium Content of Soil One Year After Application of Potassium Sulphate (Mildred Lake Research Facility Site).

| Treatment | Depth (cm) | $SO_4^{2-}$-S (kg/ha) | | Total S (kg/ha) | | K (kg/ha) | |
|---|---|---|---|---|---|---|---|
| | | June 1977 | Increase[a] | June 1977 | Increase | June 1977 | Increase |
| Control | 2.5 to 0.0 | 4.0 | | 31 | | 46 | |
| | 0.0 to 2.5 | 25.6 | | 55 | | 128 | |
| | 2.5 to 15.0 | 4.1 | | 34 | | 113 | |
| | 15.0 to 30.0 | 7.4 | | 35 | | 116 | |
| | 30.0 to 60.0 | 2.3 | | 39 | | 94 | |
| | 60.0 to 90.0 | 4.4 | | 31 | | 110 | |
| $K_2SO_4$ [c] | 2.5 to 0.0 | 2.2 | -2.0 | 31 | 0 | 54 | 8 |
| | 0.0 to 2.5 | 26.0 | 0.4 | 62 | 7 | 136 | 8 |
| | 2.5 to 15.0 | 4.2 | 0.1 | 45 | 11 | 123 | 10 |
| | 15.0 to 30.0 | 7.9 | 0.5 | 49 | 12 | 125 | 9 |
| | 30.0 to 60.0 | 7.1 | 4.8 | 44 | 5 | 100 | 6 |
| | 60.0 to 90.0 | 8.2 | 3.8 | 32 | 8 | 121 | 11 |
| Recovery[b] | | | 14 | | 77 | | 38 |
| $K_2SO_4$ [d] | 2.5 to 0.0 | 3.9 | -0.1 | 37 | 6 | 62 | 16 |
| | 0.0 to 2.5 | 24.8 | -0.8 | 19 | 44 | 152 | 24 |
| | 2.5 to 15.0 | 8.7 | 4.6 | 68 | 34 | 131 | 18 |
| | 15.0 to 30.0 | 10.5 | 3.1 | 46 | 11 | 134 | 18 |
| | 30.0 to 60.0 | 7.4 | 5.1 | 41 | 3 | 113 | 19 |
| | 60.0 to 90.0 | 5.7 | 1.3 | 33 | 2 | 124 | 14 |
| Recovery | | | 12 | | 89 | | 40 |

[a] Increase (compared to control) from June 1976 to June 1977.

[b] Expressed as a percentage of the amount applied.

[c] Rate of 56 kg/ha of sulphur.

[d] Rate of 112 kg/ha of sulphur.

was taken up by vegetation (primarily jack pine trees). The total S values also indicate that the applied $SO_4^{2-}$-S had moved down at least 60 cm soil depth. However, the total S values show that a much higher proportion of the applied sulphur had remained within the sampling depth. The differences in the $SO_4^{2-}$-S and total S values at each soil depth suggest that much of the applied $SO_4^{2-}$-S was converted to a non-extractable form.

The applied $K^+$ leached dowan at least to 60 cm, but only a small fraction of the applied $K^+$ was recovered in the 2N NaCl soil extract. This suggests that a large amount of the applied $K^+$ was taken up by vegetation.

### 4.3.2 Clay Loam Soil (Thickwood Hills Site)

Four months after the application of $K_2SO_4$, the $SO_4^{2-}$-S had moved down into the soil about 30 cm at this site compared to about 60 cm at the Mildred Lake site (Section 8.9). A much larger proportion of the $SO_4^{2-}$-S applied was recovered at this site compared to the Mildred Lake site. These differences may be due to the higher clay content of the soil at the Thickwood Hills site (Table 4). MacIntire et al. (1952) have demonstrated that silicate clays strongly absorb $SO_4^{2-}$-S.

After one year, very little of the applied $SO_4^{2-}$-S was recovered (Table 31). The total S analyses show that some of the applied $SO_4^{2-}$-S had moved down to a depth of at least 60 cm. Most of the recovered $SO_4^{2-}$-S was, however, found in the top 30 cm of soil. As for the sandy soil, there was a large difference in the recovery of applied $SO_4^{2-}$-S as indicated by the $SO_4^{2-}$-S analyses and the total S analyses. This suggests that much of the applied $SO_4^{2-}$-S was converted to a non-extractable form. This discrepancy was largest in the top 30 cm of soil (Tables 30 and 31). The applied $SO_4^{2-}$-S may have become incorporated into the soil organic matter where it would not be recovered as soluble $SO_4^{2-}$-S but would be recovered in the total S analyses.

As for the Mildred Lake site, the applied $K^+$ was leached down to at least the 60 cm depth and only a small fraction of the applied $K^+$ was recovered.

The results of this experiment show that $SO_4^{2-}$-S applied to the surface of a sandy soil and clay loam soil in the AOSERP study area is rapidly

Table 31. Soluble Sulphate, Total S, and Extractable Potassium Content of Soil One Year After Application of Potassium Sulphate. (Thickwood Hills Site).

| Treatment | Depth (cm) | $SO_4^{2-}$-S (kg/ha) June 1977 | $SO_4^{2-}$-S (kg/ha) Increase[a] | Total S (kg/ha) June 1977 | Total S (kg/ha) Increase | K (kg/ha) June 1977 | K (kg/ha) Increase |
|---|---|---|---|---|---|---|---|
| Control | 2.5 to 0.0 | 2.0 | | 60 | | 94 | |
| | 0.0 to 2.5 | 45.3 | | 63 | | 387 | |
| | 2.5 to 15.0 | 9.9 | | 54 | | 433 | |
| | 15.0 to 30.0 | 9.5 | | 46 | | 495 | |
| | 30.0 to 60.0 | 7.2 | | 47 | | 411 | |
| | 60.1 to 90.0 | 6.7 | | 39 | | 207 | |
| $K_2SO_4$ [c] | 2.5 to 0.0 | 3.7 | 1.7 | 60 | 0 | 96 | 2 |
| | 0.0 to 2.5 | 47.6 | 2.3 | 80 | 17 | 393 | 6 |
| | 2.5 to 15.0 | 9.6 | -0.3 | 65 | 11 | 444 | 11 |
| | 15.0 to 30.0 | 9.6 | 0.1 | 54 | 8 | 504 | 9 |
| | 30.0 to 60.0 | 6.8 | -0.4 | 53 | 6 | 422 | 11 |
| | 60.0 to 90.0 | 8.4 | 1.7 | 45 | 6 | 214 | 7 |
| Recovery[b] | | | 9 | | 86 | | 34 |
| $K_sSO_4$ [d] | 2.5 to 0.0 | 5.7 | 3.7 | 65 | 5 | 104 | 10 |
| | 0.0 to 2.5 | 46.8 | 1.5 | 107 | 44 | 422 | 35 |
| | 2.5 to 15.0 | 19.1 | 9.2 | 80 | 26 | 448 | 15 |
| | 15.0 to 30.0 | 15.5 | 6.0 | 56 | 10 | 510 | 15 |
| | 30.0 to 60.0 | 11.6 | 4.4 | 56 | 9 | 427 | 16 |
| | 0.0 to 90.0 | 3.2 | -3.5 | 44 | 5 | 214 | 7 |
| Recovery | | | 24 | | 88 | | 36 |

[a] Increase (compared to control) from June 1976 to June 1977.

[b] Expressed as a percentage of the amount applied.

[c] Rate of 56 kg/ha of sulphur.

[d] Rate of 112 kg/ha of sulphur.

leached downward. It has also shown that the traditional method of analysing soil for sulphur content (soluble $SO_4^{2-}$-S) is not an accurate method for determining the fate of deposited $SO_4^{2-}$-S in soil. Much of the applied $SO_4^{2-}$-S was transformed into an unextractable form.

## 4.4 EFFECTS OF APPLIED ELEMENTAL SULPHUR, SULPHURIC ACID, AND LIME IN SOIL ACIDITY

The aim of these experiments was to obtain information on the effects of simulated acid precipitation on forest soils in the AOSERP study area. The effects of acid precipitation on soil properties and processes are undoubtedly very complex. Long-term field experiments were therefore established so that the interactions of climate, vegetation, and organic and inorgganic matter were largely undisturbed. Liming experiments were also established as this will most likely be the primary method used to counteract excessive soil acidity.

### 4.4.1 Effects of Applied Sulphuric Acid

**4.4.1.1 Sandy Soil (Mildred Lake Research Facility Site).** The change in pH and the $SO_4^{2-}$-S content of the sandy soil four months after application of $H_2SO_4$ is shown in **Table 32**. For both application rates, pH has been depressed and the $SO_4^{2-}$-S content increased down to at least 60 cm. The change in pH which resulted from the addition of $H_2SO_4$ reflects the low buffering capacity of the sandy soil at this site.

4.4.1.2 Clay Loam Soil (Thickwood Hills Site). As for the sandy soil, the application of $H_2SO_4$ at 280 kg/ha lowered soil pH to a depth of 90 cm. Sulphate sulphur was also found to have moved down at about 90 cm (**Table 33**). The decrease in pH of the top 15 cm of soil was less at this site than at the Mildred Lake site. This reflects the higher buffering capacity of this clay loam soil as compared to the sandy soil at the Mildred Lake site.

The bulge in $SO_4^{2-}$-S concentrations in the clay loam occurred at a depth of 15 to 30 cm, whereas the greatest pH decrease occured in the top 2.5 cm of soil. This suggests that in the top layers of soil, hydrogen ions

Table 32. pH Values and Soil $SO_4^{2-}$-S Content of Soil Four Months After the Application of Sulphuric Acid, Elemental Sulphur, and Lime Treatments. (Mildred Lake Research Facility Site).

| Depth (cm) | Treatment | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | | $H_2SO_4$ at 56 kg/ha.S | | $H_sSO_4$ at 280 kg/ha.S | | Elemental S at 56 kg/ha | Elemental S at 280 kg/ha | | Lime at 2500 kg/ha $CaCO_3$ | Lime at 2500 kg/ha $CaCO_3$ + elemental S at 280 kg/ha | |
| | pH | $SO_4^{2-}$-S (kg/ha) | pH | $\Delta SO_4^{2-}$-S (kg/ha) | ΔpH | $\Delta SO_4^{2-}$-S (kg/ha) | $\Delta SO_4^{2-}$-S (kg/ha) | ΔpH | $\Delta SO_4^{2-}$-S (kg/ha) | ΔpH | ΔpH | $\Delta SO_4^{2-}$-S (kg/ha) |
| 2.5 to 0.0 | 4.48 | 1.2 | -0.44 | +4.0 | -0.71 | +18.1 | +2.4 | -0.45 | +11.4 | +1.91 | +2.03 | 160.0 |
| 0.0 to 2.5 | 5.09 | 29.1 | -0.36 | +18.1 | -0.80 | +91.6 | +26.3 | -0.19 | +31.4 | +1.35 | +1.04 | 121.4 |
| 2.5 to 15.0 | 5.64 | 6.6 | -0.28 | +19.3 | -0.66 | +78.8 | +1.5 | -0.40 | +1.8 | +0.31 | +0.10 | 16.2 |
| 15.0 to 30.0 | 5.66 | 9.0 | -0.16 | +24.5 | -0.17 | +99.1 | -1.8 | -0.20 | +1.2 | +0.00 | +0.04 | 10.1 |
| 30.0 to 60.0 | 5.84 | 5.5 | -0.10 | +15.2 | -0.27 | +32.3 | -1.6 | -0.01 | +0.9 | -0.03 | -0.07 | 10.3 |
| 60.0 to 90.0 | 5.94 | 4.6 | -0.08 | +6.4 | -0.17 | +18.1 | N.S.[a] | N.S. | N.S. | N.S. | N.S. | N.S. |

[a] N.S. = Not sampled; Δ = change in.

Table 33. pH Values and $SO_4^{2-}$-S Content of Soil Four Months After the Application of Sulphuric Acid, Elemental Sulphur, and Lime Treatments. (Thickwood Hills Site).

| Depth (cm) | Treatment | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Control | | $H_2SO_4$ at 280 kg/ha S | | Elemental S at 280 kg/ha | | Lime at 2500 kg/ha $CaCO_3$ | |
| | pH | $SO_4^{2-}$-S (kg/ha) | $\Delta$pH | $\Delta SO_4^{2-}$-S (kg/ha) | $\Delta$pH | $\Delta SO_4^{2-}$-S (kg/ha) | $\Delta$pH | $\Delta SO_4^{2-}$-S (kg/ha) |
| 2.5 to 0.0 | 4.75 | 3.1 | -1.06 | +3.5 | -0.51 | +12.9 | +1.60 | +0.1 |
| 0.0 to 2.5 | 5.07 | 15.7 | -0.78 | +21.6 | -0.26 | +72.5 | +0.78 | +8.5 |
| 2.5 to 15.0 | 5.18 | 5.4 | -0.37 | +53.3 | -0.13 | +5.7 | +0.06 | -0.3 |
| 15.0 to 30.0 | 5.39 | 4.2 | -0.51 | +108.1 | +0.05 | +3.7 | -0.01 | -1.1 |
| 30.0 to 60.0 | 5.65 | 3.1 | -0.38 | +21.8 | +0.03 | +0.9 | -0.06 | -0.3 |
| 60.0 to 90.0 | 5.96 | 3.2 | -0.29 | +1.9 | N.S.[a] | N.S. | N.S. | N.S. |

[a] N.S. = Not sampled; $\Delta$ = change in.

have replaced cations on the exchange complex and the displaced cations have been leached as sulphates.

Abrahamsen et al. (1976) found that a significant reduction in the degree of base saturation occurred in the top layer of soil subject to 50 mm/month of "rain" of pH 3.0. The pH decrease at the lower depths indicates that hydrogen ions have also been leached downward.

### 4.4.2 Effects of Applied Elemental Sulphur

Elemental sulphur was applied in this experiment to give a slow release of sulphuric acid as the elemental sulphur was oxidized by microbes in the soil. This treatment was designed to simulate a lower rate of acid precipitation than that of the applied sulphuric acid treatments. The results presented here refer to the samples taken four months after the application of the elemental sulphur and therefore the oxidation of the elemental sulphur was not complete.

4.4.2.1 Sandy Soil (Mildred Lake Research Facility Site). Application of elemental sulphur at 280 kg/ha S caused a decrease in pH only down to a depth of 30 cm (Table 32). The decrease in pH cause by elemental sulphur was less than for applied $H_2SO_4$ and the downward movement of acid was also less. This was probably due to the slow oxidation of the elemental sulphur and is reflected in the low recovery of $SO_4^{2-}$-S in the soil. The addition of lime at a rate of 2500 kg/ha $CaCO_3$ fully negated any acidifying effect of the sulphur (Table 32) and the pH of the top 15 cm of soil was increased. There was a higher recovery of $SO_4^{2-}$-S in this treatment as compared to the application of elemental S only. This suggests that the addition of lime increased the rate of oxidation of elemental sulphur to sulphate sulphur.

4.4.2.2 Clay Loam Soil (Thickwood Hills Site). Application of 280 kg/ha S to this soil caused a decrease in pH down to a depth of about 15 cm (Table 33). Sulphate sulphur moved down to about 30 cm. The movement of $SO_4^{2-}$-S and the downward movement of hydrogen ions was much less for this treatment than for a similar amount of sulphur applied as $H_2SO_4$.

### 4.4.3 Effects of Applied Lime on Soil Acidity

4.4.3.1 Sandy Soil (Mildred Lake Research Facility Site). After a period of four months, application of lime at a rate of 2500 kg/ha had raised the soil pH down to a depth of about 15 cm (Table 32). Ths downward movement could have been achieved in part by small particles of $CaCO_3$ being washed into the soil pores by percolating water where the particles slowly dissolved. On this sandy soil, liming appears to be an effective method for counteracting soil acidity in the rooting zone of most shrubs and forbs.

4.4.3.2 Clay Loam Soil (Thickwood Hills Site). The downward movement of lime was much slower in this soil than for the sandy soil. The influence of lime on soil pH was largely restricted to the top 2.5 cm of soil four months after the application of the lime (Table 33). Soil pH was increased slightly in the 2.5 to 15.0 cm depth.

These results must be regarded as tentative at present as the full effects of liming on soil properties have yet to be investigated. Abrahamsen et al. (1976) found that the addition of lime to forest soils caused a decrease in the potassium content presumably from exchange with the added calcium. However, they found exchangeable Mn was decreased also, because of decreased solubility at the higher soil pH.

## 4.5 LYSIMETER EXPERIMENT

The pH and $SO_4^{2-}$-S concentrations in the lysimeters leachate from the Orthic Eutric Brunisolic and the Orthic Gray Luvisolic soils collected over the summer of 1977 are shown in Tables 60 and 61 (Section 8.10).

The pH of the leachate from both soils was not related to the pH of rainwater at each site. The pH and $SO_4^{2-}$-S concentrations in the leachate from both soils at Supertest Hill were, however, unusually high. These lysimeters were located under trembling aspen trees and most likely received additional $SO_4^{2-}$-S in aspen throughfall (Section 4.1.1.2)

For both soils, there was a decrease in leachate $SO_4^{2-}$-S concentrations with increasing distance from the emission source. The relative amounts of $SO_4^{2-}$-S leached from the lysimeters at each site are given in **Table 34.** These values are weighted so that the amount of rain and the amount of leachate were equivalent at each site. The relative amounts of $SO_4^{2-}$-S leached from the O.EB soil was strongly correlated with the amounts of $SO_4^{2-}$-S deposited in rain at each site ($r^2 = 0.96$, $p = 0.001$). This relationship was much weaker for the O.GL ($r^2 = 0.48$, $p = 0.05$).

The concentrations of cations in the lysimeter leachates are given in Tables 62 and 63 (Section 8.10). The soil leachate at Supertest Hill contained the highest concentrations of cations, particularly calcium. Calcium was the predominant cation in the leachate from both soils.

The relative amounts of calcium deposited in the lysimeter leachates at each site are shown in **Table 35.** The relative amounts of calcium deposited in the O.EB soil leachate and the O.GL soil leachate were not significantly correlated with the amounts of calcium deposited in rain at each site. The relative amounts of calcium in the O.EB soil leachate at each site was correlated to the amounts of $SO_4^{2-}$-S in the leachate ($r^2 = 0.71$, $p = 0.001$). There was no significant correlation between the amounts of calcium and $SO_4^{2-}$-S leached at each site for the O.GL soil.

Other experiments (Section 4.3) have demonstrated that $SO_4^{2-}$-S applied to the surface of sandy soils such as the O.EB soil used in this experiment is readily leached down through the soil column. These results imply that $SO_4^{2-}$-S deposited on the sandy O.EB soil in rain was washed down through the soil and collected as leachate. The strong correlation between the amounts of calcium and $SO_4^{2-}$-S in the leachate suggests that calcium was leached from the soil in association with the leached $SO_4^{2-}$-S. Such a process would cause a decrease in soil base content.

## 4.6 PERMANENT SOIL PLOTS

The pH and total S content of the permant plot soils is given in Section 8.11. Because of the change in sampling between 1976 and 1978, only the values for the litter layers are directly comparable.

The pH values are variable, and there is no clear trend to an increase or decrease. The total S values also indicate that there is no clear change in 1976 to 1978.

Table 34. Relative Amounts of Sulphate Sulphur Deposited in Rain and Leached from Lysimeters from 1977 June to September.

| Site | Distance (km) and Direction from Emission Source | Relative[a] amounts of $SO_4^{2-}$-S deposited in rain (kg/ha) | Relative[b] amounts of $SO_4^{2-}$-S in lysimeter leachate | |
|---|---|---|---|---|
| | | | O.EB Soil (kg/ha) | O.GL Soil (kg/ha) |
| Steepbank 2 | 4 ENE | 2.6 | 5.2 (2.2)[c] | 10.5 (1.9) |
| Mildred Lake | 11 NW | 1.9 | 4.0 (1.7) | 15.1 (2.7) |
| Thickwood Hills | 31 SW | 1.2 | 2.4 (1.0) | 3.0 (0.5) |
| Steepbank A | 32 SE | 1.7 | 3.1 (1.3) | 8.0 (1.4) |
| Bitumount | 39 N | 1.8 | 3.5 (1.5) | 7.5 (1.3) |
| Gordon Lake | 75 SE | 0.9 | 2.3 (1.0) | 6.7 (1.2) |
| Algar | 101 SSW | 1.0 | 2.1 (0.9) | 2.1 (0.4) |
| May | 173 SW | 1.0 | 2.4 (1.0) | 5.6 (1.0) |

[a] Weighted so that the amount of rain at each site is equivalent to that at the May site.

[b] Weighted so that the amount of leachate at each site is equivalent to that at the May site.

[c] Values in brackets are the amounts expressed relative to the amounts at the May site with the values for the May site set at 1.0.

Table 35. Relative Amounts of Calcium Deposited by Rain and Leached from Lysimeters from 1977 June to September.

| Site | Distance (km) and Direction from Emission Source | Relative[a] amounts of $Ca^{2+}$ deposited in rain (kg/ha) | $Ca^{2+}$ Relative[b] amounts of in lysimeter leachate | |
|---|---|---|---|---|
| | | | O.EB Soil (kg/ha) | O.GL Soil (kg/ha) |
| Steepbank 2 | 4 ENE | 3.9 (3.0)[c] | 19.0 (1.9) | 24.4 (1.5) |
| Mildred Lake | 11 NW | 4.3 (3.3) | 20.4 (2.0) | 27.4 (1.7) |
| Thickwood Hills | 31 SW | 1.3 (1.0) | 9.5 (1.0) | 22.3 (1.4) |
| Steepbank A | 32 SE | 1.3 (1.0) | 17.1 (1.7) | 24.1 (1.5) |
| Bitumount | 39 N | 1.3 (1.0) | 18.8 (1.9) | 21.8 (1.4) |
| Gordon Lake | 75 SE | 1.7 (1.3) | 12.8 (1.3) | 16.0 (1.0) |
| Algar | 101 SSW | 2.2 (1.7) | 9.5 (1.0) | 24.4 (1.6) |
| May | 173 SW | 1.3 (1.0) | 10.0 (1.0) | 16.0 (1.0) |

[a] Weighted so that the amount of rain at each site is equivalent to that at the May site.

[b] Weighted so that the amount of leachate at each site is equivalent to that at the May site.

[c] Values in brackets are the amounts expressed relative to the amounts at the May site, with the values for the May site set at 1.0.

Because of the variable nature in soil properties, no conclusions can be drawn from these initial results. These values will provide a baseline for the AOSERP study area, and it is recommended that these plots be sampled again every few years.

## 5. CONCLUSIONS

The results presented in this report concern the pathways by which anthropogenic sulphur may find its way into soil, how much sulphur was deposited, what were the resultant forms of this sulphur in soil, and if the soils were acidified by this deposition of sulphur. The mechanisms of sulphur deposition investigated were: rain, snow, rain washing off trees, and direct absorption of $SO_2$ by soil. The conclusions drawn from this study are as follows:

1. The amount of $SO_4^{2-}$-S deposited in rain in the AOSERP study area is low. In 1975, an average of 0.8 to 1.1 kg/ha/month was deposited at sites near the emission source compared to about a 0.3 kg/ha/month at remote sites. In 1976 and 1977, at sites close to the emission source, the amount of $SO_4^{2-}$-S deposited averaged 0.3 to 0.6 kg/ha/month while at remote sites about 0.25 kg/ha/month was deposited.
2. The amounts of $SO_4^{2-}$-S deposited in rain washing off trees were greater than that deposited in rain. There was also greater deposition of $SO_4^{2-}$-S in net precipitation (throughfall plus stemflow) at sites close to the emission source compared to remote sites. In 1976, approxiamtely 0.5 to 4.7 kg/ha/month, $SO_4^{2-}$-S was deposited at exposed sites compared to 0.4 to 0.6 kg/ha/month at remote sites, depending on the tree species. The amounts of sulphur deposited in net precipitation represents a more accurate measure of the amounts of sulphur deposited on soils in the AOSERP study area than that determined from incident precipitation samples.
3. The acidity of rain decreased as it passed through the canopy of trembling aspen. This removal of hydrogen ions by exchange in the canopy could lessen the potential impact of acid precipitation on soils under aspen stands in the AOSERP study area.

   The acidity of rain increased as it passed through the canopy of jack pine trees. The acidity of jack pine throughfall and stemflow also was greater at sites exposed to $SO_2$ as compared to control sites. Throughfall was lower in pH by about 0.3 units and stemflow was lower by about 0.8 to 1.1 pH units. At a site near the emission source, deposition of free acid ($H^+$) under jack pine trees was highly correlated with deposition of $SO_4^{2-}$-S. No such correlation was evident at a control site.

For both jack pine and trembling aspen, larger quantities of the cations $K^+$, $Ca^{2+}$, and $Mg^{2+}$ were removed from the canopies at a site close to the emission source compared to a more remote control site.

4. Deposition of $SO_4^{2-}$-S in snow is low. In 1976, about 0.15 kg/ha/month was deposted at sites close to the emission source compared to less than 0.10 kg/ha/month at more distant sites.
5. Bare soils were found to absorb $SO_2$ directly from the air. This absorption process resulted in the formation of compounds. In some soils, the increase in total S was greater than the increase in $SO_4^{2-}$-S. That is, the usual method of determining $SO_4$ absorption by soils ($SO_4^{2-}$-S analysis) leads to an underestimation in some cases. The absorption of $SO_2$ by bare soils was also shown to result in a significant increase in the acidity of the top layer (0 to 1 cm) of soil. The pH of the top 1 cm of a bare sandy soil decreased by approximately 0.25 pH units at a site 4 km from the emission source as compared to a site 100 km from the emission source.
6. Lichen covered soils, sampled in the AOSERP study area, were also found to absorb $SO_2$ directly from the air. The sulphur uptake was restricted to the live lichen material and top few centimetres of organic material. The amount of sulphur absorbed by lichen covered soils was of the order of 10 kg/ha/month at sites immediately downwind from the emission source. Corresponding values of sulphur deposition in rain and net precipitation (throughfall plus stemflow) at the same sites were approximately 0.3 kg/ha/month and 0.6 kg/ha/month, respectively.

The surface layers of a sandy soil (lysimeter experiment) increased in sulphur content by approximately 20 kg/ha at sites near the emission source over a two-year period. The surface layers of a clay loam soil increased by approximately 50 kg/ha over the same period. Corresponding amounts of sulphur deposited in rain and snow were of the order of 4.0 kg/ha and 2.0 kg/ha, respectively. Absorption of $SO_2$ directly from the air by soils therefore amounted to the most important sulphur deposition mechanism in the AOSERP study area, particularly in areas close to the emission source.

7. Field experiments demonstrated that $SO_4^{2-}$-S deposited on soils in the AOSERP study area was rapidly leached downward. Sulphate applied to the soil surface as a neutral salt ($K_2SO_4$) moved downward as much as 30 to 60 cm into a sandy soil and a clay loam soil over a 12-month period. Sulphuric acid applied, to the surface of two forest soils, also moved quite rapidly through the soil and caused an increase in the acidity of the soil as it moved downward. Ground limestone applied to the surface of these same soils effectively counteracted the acidifying effect of the applied sulphuric acid.

   A lysimeter experiment showed that calcium was the principal cation leached from a sandy and a clay loam soil from the AOSERP study area. In the leachate from the sandy soil, the relative amount of calcium was strongly correlated with the relative amounts of $SO_4^{2-}$-S.

8. The surface few centimetres of bare and lichen covered sandy soils set out in canisters in the AOSERP study area absorbed $SO_2$ and decreased in pH, particularly at sites nearest the emission source. The increase in soil acidity was of the order of 0.1 to 0.3 pH units over the summer period. However, soil acidity of lysimeter soils (with the surface layers undisturbed) set out for two years showed no significant difference between control and exposed sites. Soil pH tends to fluctuate with the

soil moisture content and soil temperature and changes in pH were only noted in carefully controlled experiments. Long-term monitoring of soils is needed to determine if the pH of forest soils is being decreased by sulphur emissions in the AOSERP study area.

9. In general, the soils associated with jack pine would be expected to be the most susceptible to acidification in the AOSERP study area. Jack pine stands are more open and have less dense lower vegetative cover than trenbling aspen or mixed wood stands. Sulphur dioxide would more readily be able to come into direct contact with the ground surface at these sites. In addition, increased deposition of acid beneath jack pine was shown to result from sulphur emissions in the AOSERP study area. Jack pine commonly grows on coarse, acidic soils (Pawluk and Arneman 1961). Such sandy soils sampled from jack pine areas in the AOSERP study area were found to be poorly buffered against acid and were depressed in pH upon exposure to $SO_2$ in both controlled atmosphere and field experiments. Sulphate sulphur was also shown to be mobile in the soils. Leaching of deposited sulphate sulphur through the soil would case a depletion of the already low base status of these soils. These facts indicate that the sandy soils associated with jack pine are the most susceptible to acidification caused by sulphur emissions. These soils should be carefully monitored to determine if the process of soil acidification is occurring in the AOSERP study area.

## 6. RECOMMENDATIONS FOR FURTHER RESEARCH

The most needed immediate research in soils, based on findings made under program LS 4.2, is the following:

1. The determination of the amount of sulphur deposition on vegetated soils in lysimeters, at different distances from the main sources of $SO_2$ in the AOSERP study area. These determinations were made in the LS 4.2 program, and total S deposition on vegetated soil in lysimeters was much greater (by factor of 3 to 8) than was sulphur deposition with precipitation. This needs verification. If this is borne out, a different complexion will be put on estimates of the sulphur deposition within the AOSERP study area.
2. The soil sampling every few years of the "Permanent Plots", initiated in 1976, to monitor any long-term changes of soil sulphur content and soil pH in the AOSERP study area. These replicated plots were placed at 17 locations, and the soils were sampled in 1976 and 1978 and the samples were analysed. Those analyses will serve as the starting point of monitoring of the soils. The monitoring of the "Permanent Plots", taken together with the results of lysimeters on the amounts of sulphur coming down, will tell in the long term how much sulphur is deposited, whether the sulphur stays in the soils, and whether the soils become acidified.
3. Little sulphur was deposited by rain and snow when the sulphur content was determined as soluble sulphate (which is the conventional method of determination the world over). However, when some of the samples from LS 4.2 and from another poject were analysed for total S, they gave averages of 1.5 to 2.0 times more sulphur. Therefore, it is strongly recommended that researchers analysing rain and snow from the AOSERP study area include the total S method. That is, the amounts of sulphur deposition by rain and snow may not be as small as they appear.

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# 8. APPENDICES

## 8.1 THE TOTAL PRECIPITATION FOR EACH MONTH RECORDED AT EACH OF THE FIELD SITES OVER THE SUMMERS OF 1976 AND 1977.

Table 36. Total Precipitation (mm) at Field Sites for the Months of 1976 June to September.

| Site No. | Site | Elevation (m) | Month | | | | Totals |
|---|---|---|---|---|---|---|---|
| | | | June | July | August | September | |
| 1 | Mildred Lake | 320 | 30.6 | 62.6 | 33.0 | 94.7 | 220.9 |
| 2 | MacKay River | 274 | 25.4 | 45.0 | 46.2 | 80.3 | 196.9 |
| 3 | Supertest Hill | 305 | 32.9 | 76.0 | 37.9 | 97.0 | 243.8 |
| 5 | Steepbank 1 | 396 | 33.7 | 78.5 | 23.2 | 91.4 | 227.0 |
| 6 | Steepbank 2 | 305 | 38.4 | 90.0 | 25.0 | 93.1 | 246.5 |
| 9 | Bitumount | 350 | 32.0 | 50.6 | 40.2 | 33.8 | 156.6 |
| 8 | Muskeg Mountain | 653 | 78.5 | 67.8 | 87.4 | 31.8 | 265.5 |
| 4 | Steepbank A | 427 | 34.2 | 74.6 | 38.3 | 101.2 | 248.3 |
| 7 | Thickwood Hills | 604 | 62.7 | 61.8 | 219.0 | 35.9 | 379.4 |
| 11 | Birch Mountain | 854 | 100.2 | 75.8 | 53.2 | 12.4 | 241.6 |
| 10 | Gordon Lake | 488 | 69.9 | 96.2 | 138.6 | 34.6 | 339.3 |
| 12 | Richardson | 305 | 48.3 | 90.0 | 43.2 | 21.6 | 198.1 |
| 13 | Algar | 781 | 121.9 | 68.6 | 162.4 | 49.5 | 402.4 |
| 14 | May | 897 | 145.1 | 69.7 | 124.1 | 48.2 | 387.1 |

Table 37. Total Precipitation (mm) at the Sites for the Months of 1977 May to September.

| Site No. | Site | Elevation (m) | Month | | | | | Totals |
|---|---|---|---|---|---|---|---|---|
| | | | May | June | July | August | September | |
| 1 | Mildred Lake | 320 | 62.3 | 72.4 | 42.8 | 48.0 | 37.0 | 262.5 |
| 2 | MacKay River | 274 | ND[a] | 57.2 | 41.4 | 49.0 | 30.0 | ND |
| 3 | Supertest Hill | 305 | 49.1 | 59.4 | 43.2 | 36.0 | 31.0 | 218.7 |
| 5 | Steepbank 1 | 396 | 45.4 | 72.4 | 57.4 | 36.0 | 41.0 | 252.2 |
| 6 | Steepbank 2 | 305 | 54.0 | 67.4 | 40.4 | 40.0 | 43.0 | 244.8 |
| 9 | Bitumount | 350 | 65.2 | 67.5 | 59.6 | 51.0 | 28.2 | 271.5 |
| 8 | Muskeg Mountain | 653 | 45.3 | 81.2 | 56.7 | 51.0 | 25.0 | 259.2 |
| 4 | Steepbank A | 427 | 69.6 | 62.7 | 54.2 | 41.0 | 36.0 | 263.5 |
| 7 | Thickwood Hills | 604 | 89.7 | 69.9 | 62.2 | 47.0 | 30.0 | 298.8 |
| 11 | Birch Mountain | 854 | 105.1 | 155.4 | 88.2 | 49.0 | 42.0 | 439.7 |
| 10 | Gordon Lake | 488 | 90.3 | 41.4 | 90.5 | 51.0 | 14.0 | 287.2 |
| 12 | Richardson | 305 | 67.0 | 64.4 | 35.2 | 54.8 | 37.0 | 258.4 |
| 13 | Algar | 781 | 86.6 | 35.2 | 137.2 | 30.4 | 38.0 | 327.4 |
| 14 | May | 897 | 148.6 | 38.2 | 114.6 | 76.0 | 55.0 | 432.4 |

[a] ND = No data.

## 8.2 SULPHATE SULPHUR DEPOSITION IN RAIN MEASURED AT EACH OF THE FIELD SITES IN 1975, 1976, AND 1977.

Table 38. Average pH and Sulphate Sulphur Concentration in Rain and Amount of Sulphate Sulphur Deposited in Rain, Summer 1975.

| Site | Distance (km) and Direction from Emission Source | pH | Average and Ranges of $SO_4^{2-}$-S Concentrations (ppm) | $SO_4^{2-}$-S Deposited (kg/ha/mo) |
|---|---|---|---|---|
| Steepbank 3 | 2.4 ESE | 6.1 | 1.4 (0.2 to 2.7) | 0.8 |
| Steepbank 2 | 4.0 ESE | 5.4 | 1.7 (0.6 to 3.9) | 1.0 |
| Mildred Lake | 11.0 NW | 6.3 | 1.4 (0.5 to 3.4) | 1.1 |
| Steepbank 1 | 17.0 ESE | 5.7 | 1.2 (0.3 to 3.0) | 1.0 |
| MacKay River | 21.0 NW | 6.3 | 0.9 (0.2 to 1.8) | 0.7 |
| Thickwood Hills | 31.0 SW | 6.0 | 0.5 (0.0 to 1.9) | 0.4 |
| South Fort McMurray | 67.0 S | 6.3 | 0.2 (0.0 to 0.3) | 0.2 |
| Loon Lake, Saskatchewan | 335.0 SSE | 6.3 | 0.5 (0.1 to 2.0) | 0.2 |
| Canwood, Saskatchewan | 502.0 SE | 6.3 | 0.5 (0.1 to 2.3) | 0.2 |
| Beaverlodge, Alberta | 526.9 WSW | 6.1 | 0.7 (0.1 to 1.8) | 0.3 |

Table 39. Sulphate Sulphur Deposited in Rain from 1976 July to Mid-September.

| Site | Distance (km) and Direction from Emission Source | $SO_4^{2-}$-S Deposited (kg/ha/mo) |
|---|---|---|
| Steepbank 2 | 4.0 ESE | 0.60 |
| Mildred Lake | 11.0 NW | 0.47 |
| Steepbank 1 | 17.0 ESE | 0.19 |
| MacKay River | 21.0 NW | 0.21 |
| Thickwood Hills | 31.0 SW | 0.56 |
| Steepbank A | 32.0 SE | 0.17 |
| Muskeg Mountain | 38.0 ENE | 0.29 |
| Bitumount | 39.0 N | 0.16 |
| Hangingstone River | 67.0 S | 0.25 |
| Gordon Lake | 75.0 SE | 0.25 |
| Birch Mountain | 79.0 NNW | 0.25 |
| Algar | 101.0 SSW | 0.25 |
| Richardson | 102.0 NNE | 0.18 |
| May | 173.0 SW | 0.25 |

Table 40. Sulphate Sulphur Deposited in Rain from 1977 June to September.

| Site | Distance (km) and Direction from Emission Source | $SO_4^{2-}$-S Deposited (kg/ha/mo) |
|---|---|---|
| Steepbank 2 | 4.0 ESE | 0.29 |
| Mildred Lake | 11.0 NW | 0.23 |
| Steepbank 1 | 17.0 ESE | 0.17 |
| MacKay River | 21.0 NW | 0.22 |
| Thickwood Hills | 31.0 SW | 0.17 |
| Steepbank A | 32.0 SE | 0.21 |
| Muskeg Mountain | 38.0 ENE | 0.18 |
| Bitumount | 39.0 N | 0.23 |
| Hangingstone River | 67.0 S | ND[a] |
| Gordon Lake | 75.0 SE | 0.12 |
| Birch Mountain | 79.0 NNW | 0.23 |
| Algar | 101.0 SSW | 0.16 |
| Richardson | 102.0 NNE | 0.13 |
| May | 173.0 SW | 0.20 |

[a] ND = No data.

## 8.3 DISTRIBUTION OF RAINFALL UNDER TREMBLING ASPEN AND JACK PINE STANDS USED IN THE NUTRIENT CYCLING STUDY, 1976.

Net precipitation is the portion of incident precipitation reaching the ground in the form of throughfall and stemflow. Interception is the portion of incident precipitation retained by the tree canopy which is absorbed by the trees and/or evaporated directly into the atmosphere. This is equal to the difference between incident precipitation and net rainfall. On several occasions at the control site, jack pine throughfall exceeded the incident rain. This has also been noted by several other researchers (Voigt 1960, Pressland 1973). This could be due to rain at an oblique angle being caught directly by the throughfall gauges without passing through the canopy. On the occasions when throughfall exceeded incident rain, the percentage stemflow was unusually high. This could be due to wind driven rain impinging directly onto the tree trunks to a greater extent. Black (1957) noted that stemflow was greater during storms accompanied by a high wind.

Table 41. Net Rainfall, Throughfall, Stemflow, and Interception Under a Trembling Aspen Stand (Control Site).[a]

| Date | Incident Rain | Throughfall | | Stemflow | | Net Rainfall | | Interception | |
|---|---|---|---|---|---|---|---|---|---|
| | mm | mm | % | mm | % | mm | % | mm | % |
| 18 June | 28.3 | 24.8 | 87.6 | 1.5[b] | 5.3 | 26.3 | 92.9 | 2.0 | 7.1 |
| 24 June | 41.2 | 35.9 | 87.1 | 3.8[b] | 9.2 | 39.7 | 96.4 | 1.5 | 3.6 |
| 29 June | 30.4 | 27.6 | 90.8 | 1.9 | 6.3 | 29.5 | 97.0 | 0.9 | 3.0 |
| 16 July | 48.8 | 43.5 | 89.1 | 3.6 | 7.4 | 47.1 | 96.5 | 1.7 | 3.5 |
| 23 July | 10.1 | 7.1 | 70.3 | 1.0 | 9.9 | 8.1 | 80.2 | 2.0 | 19.8 |
| 30 July | 34.9 | 29.7 | 85.1 | 3.5 | 7.8 | 33.2 | 95.1 | 1.7 | 4.9 |
| 04 August | 3.7 | 2.9 | 78.4 | 0.2 | 5.4 | 3.1 | 83.8 | 0.6[c] | 16.2[c] |
| 27 August | 138.8 | 120.2 | 86.6 | 5.0[d] | 3.6 | 125.2 | 90.2 | 13.6[d] | 9.8[d] |
| 09 September | 45.0 | 37.1 | 82.4 | 4.0[d] | 8.9 | 41.1 | 91.3 | 3.9[d] | 8.7[d] |
| 02 October[e] | 6.7 | 4.8 | 71.6 | 0.5 | 7.5 | 5.3 | 79.1 | 1.4 | 20.9 |
| Mean | | | 82.9 | | 7.1 | | 90.2 | 1.6 | 9.0 |

[a] Expressed as equivalent to rainfall depth (mm), and percentage of incident rain.

[b] Estimated.

[c] Collection gauges sampled during rain shower on previous sample date therefore interception is probably underestimated. Not included in the mean.

[d] Stemflow collection vessels overflowed therefore interception is overestimated. Not included in the mean.

[e] Freezing rain--no leaves left on the aspen trees.

Table 42. Net Rainfall, Throughfall, Stemflow, and Interception Under a Trembling Aspen Stand (Exposed Site).[a]

| Date | Incident Rain | Throughfall | | Stemflow | | Net Rainfall | | Interception | |
|---|---|---|---|---|---|---|---|---|---|
| | mm | mm | % | mm | % | mm | % | mm | % |
| 30 June | 26.2 | 22.5 | 85.9 | 2.0[b] | 7.6 | 24.5 | 93.5 | 1.7 | 6.5 |
| 15 July | 41.6 | 36.7 | 88.2 | 4.2 | 10.1 | 40.9 | 98.3 | 0.7 | 1.7 |
| 29 July | 43.0 | 36.4 | 84.7 | 3.5 | 8.1 | 39.9 | 92.8 | 3.1 | 7.2 |
| 10 August | 20.8 | 15.7 | 75.5 | 1.6 | 7.7 | 17.3 | 83.2 | 3.5 | 16.8 |
| 25 August | 21.4 | 17.9 | 83.6 | 1.7 | 7.9 | 19.6 | 91.6 | 1.8 | 8.4 |
| 08 September | 105.2 | 90.6 | 86.1 | 6.7 | 6.4 | 97.3 | 92.5 | 7.9[c] | 7.5[c] |
| Mean | | | 84.0 | | 8.0 | | 91.7 | 2.2 | 8.1 |

[a] Expressed as equivalent to rainfall depth (mm), and percentage of incident rain.

[b] Estimated.

[c] Stemflow collection vessels overflowed therefore interception is overestimated. Not included in the mean.

Table 43. Net Rainfall, Throughfall, Stemflow, and Interception Under a Jack Pine Stand (Control Site).[a]

| Date | Incident Rain | Throughfall | | Stemflow | | Net Rainfall | | Interception | |
|---|---|---|---|---|---|---|---|---|---|
| | mm | mm | % | mm | % | mm | % | mm | % |
| 29 June | 45.0 | 41.0 | 91.1 | 0.10[b] | 0.2 | 41.1 | 91.3 | 3.9 | 8.7 |
| 16 July | 45.4 | 38.4 | 84.6 | 0.10 | 0.2 | 38.5 | 84.8 | 6.9 | 15.2 |
| 23 July | 8.8 | 6.3 | 71.6 | 0.01 | 0.1 | 6.3 | 71.6 | 2.5 | 28.4 |
| 30 July | 31.5 | 32.1[c] | 101.9 | 0.15 | 0.5 | 32.2 | 102.2 | -1.1[d] | -3.5[d] |
| 04 August | 5.2 | 3.6 | 69.2 | 0.00 | 0.0 | 3.6 | 69.2 | 1.6 | 30.8 |
| 27 August | 121.6 | 129.9[c] | 106.8 | 1.02 | 0.8 | 130.9 | 107.6 | -9.3[d] | -7.6[d] |
| 09 September | 39.6 | 41.3[c] | 104.3 | 0.28 | 0.7 | 41.6 | 105.1 | -2.0[d] | -5.1[d] |
| 02 October | 5.2 | 2.0 | 38.5 | 0.01 | 0.2 | 2.0 | 38.5 | 3.2 | 61.5 |
| Mean | | | 83.5 | | 0.3 | | 83.8 | 3.6 | 28.9<br>(16.1)[e] |

[a] Expressed as equivalent to rainfall depth (mm), and percentage of incident rain.

[b] Estimated.

[c] Throughfall exceeded incident rain. This behaviour has occasionally been noted by other researchers, and apparently accompanies wind-driven, oblique rains.

[d] The negative values for interception of rain are not included in the interception mean.

[e] Including the negative values.

Table 44. Net Rainfall, Throughfall, Stemflow, and Interception Under a Jack Pine Stand (Exposed Site).[a]

| Date | Incident Rain | Throughfall | | Stemflow | | Net Rainfall | | Interception | |
|---|---|---|---|---|---|---|---|---|---|
| | mm | mm | % | mm | % | mm | % | mm | % |
| 30 June | 26.2 | 20.5 | 78.2 | 0.02[b] | 0.1 | 20.5 | 78.2 | 5.8 | 22.0 |
| 15 July | 41.6 | 35.9 | 86.3 | 0.10 | 0.2 | 36.0 | 86.5 | 5.6 | 13.5 |
| 29 July | 43.0 | 36.3 | 84.4 | 0.04 | 0.1 | 36.3 | 84.4 | 6.7 | 15.5 |
| 10 August | 20.8 | 17.1 | 82.2 | 0.02 | 0.1 | 17.1 | 82.2 | 3.7 | 17.8 |
| 25 August | 21.4 | 18.9 | 88.3 | 0.00 | 0.0 | 18.9 | 88.3 | 2.6 | 12.0 |
| 08 September | 105.2 | 100.1 | 95.2 | 0.83 | 0.8 | 100.9 | 95.9 | 4.3 | 4.1 |
| Mean | | | 85.8 | | 0.2 | | 85.9 | | 14.2 |

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[a] Expressed as equivalent to rainfall depth (mm), and percentage of incident rain.

[b] Estimated.

## 8.4 ACIDITY AND NUTRIENT CONTENT OF INCIDENT RAIN, AND JACK PINE, AND TREMBLING ASPEN THROUGHFALL AND STEMFLOW

The quantities of nutrients (kg/ha) in each rain type were calculated by multiplying the concentration values in mg/L by the volume of each rain type in L/ha. Throughfall data are means of 20 replicates and stemflow data are means of 10 replicates.

The amount of sulphate sulphur removed from the tree canopies by rain and deposited on the soil was calculated using the sums of the amounts of sulphate sulphur during the season in throughfall and in stemflow (Tables 17, 46, and 47), as well as in incident rain (Tables 46 and 47). The value obtained at the exposed site was then divided by the control site to give the deposition percentage increase at the exposed site.

Using the summed values for throughfall, stemflow, and incident rain obtained from Tables 17, 46, and 47, the calculation is as follows:

Control site with values in kg S ha$^{-1}$

Throughfall + stemflow - incident rain
= 0.787 + 0.095 - 0.336
- 0.564 kg S ha$^{-1}$ removed from tree canopy.

Exposed site with values kg S ha$^{-1}$

Throughfall + stemflow - (incident rain at exposed site
- incidental rain at control site)
= 0.860 + 0.374 - (0.733 - 0.336)
= 0.837 kg S ha$^{-1}$ removed from tree canopy.

Therefore, $\frac{0.837 - 0.564}{0.564} \times 100 = 53\%$ more S

removed from tree canopy and deposited on the soil at the exposed site as compared to the control site.

Table 45. Cation and Sulphate Sulphur Flux for Trembling Aspen and Jack Pine at Control and Exposed Sites, 1976.

| | Precipitation<br>mm | Total Cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$)<br>$mol(p^+)/ha$ | $SO_4^{2-}$-S<br>$mol(p^+)/ha$ | $H^+$ [a]<br>$mol(p^+)/ha$ | $H^+$ as Fraction of Total Cations<br>% |
|---|---|---|---|---|---|
| | | | **Control Aspen** | | |
| Rain | 318 | 116 | 21 | 70 | 38 |
| Throughfall | 265 | 226 | 49 | 57 | 20 |
| Stemflow | 19 | 113 | 6 | 0 | |
| Net | | 223 | 34 | -13 | |
| | | | **Exposed Aspen** | | |
| Rain | 258 | 68 | 46 | 54 | 44 |
| Throughfall | 220 | 384 | 54 | 34 | 8 |
| Stemflow | 18 | 198 | 23 | 0 | |
| Net | | 515 | 31 | -20 | |
| | | | **Control Pine** | | |
| Rain | 289 | 68 | 16 | 64 | 48 |
| Throughfall | 289[b] | 319 | 103 | 144 | 31 |
| Stemflow | 2 | 7 | 3 | 4 | |
| Net | 2 | 258 | 90 | 84 | |
| | | | **Exposed Pine** | | |
| Rain | 258 | 74 | 46 | 54 | 42 |
| Throughfall | 200 | 247 | 134 | 210 | 46 |
| Stemflow | 1 | 5 | 5 | 22 | |
| Net | | 178 | 93 | 178 | |

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[a] Free acidity calculated from the pH vaues.

[b] Throughfall exceeded incident precipitation on several occasions (Section 8.3)

Table 46. Acidity and Nutrient Content of Incident Rain and Trembling Aspen, Throughfall, and Stemflow at the Control Site, 1976.

| Date | Precipitation Type | Precipitation<br>mm | Na<br>kg/ha | K<br>kg/ha | Ca<br>kg/ha | Mg<br>kg/ha | $SO_4^{2-}$-S<br>kg/ha | pH | Total Acidity as $H^+$<br>kg/ha |
|---|---|---|---|---|---|---|---|---|---|
| 29 June | Incident Rain | 30.4 | 0.024 | 0.033 | 0.116 | 0.006 | 0.076 | 5.19 | ND[a] |
| | Throughfall | | 0.024 | 0.184 | 0.240 | 0.032 | 0.134 | 5.99 | 0.128 |
| | Stemflow | | 0.002 | 0.047 | 0.235 | 0.030 | 0.016 | 7.70 | 0.000 |
| 16 July | Incident Rain | 48.8 | 0.049 | 0.112 | 0.195 | 0.029 | 0.093 | 5.82 | ND |
| | Throughfall | | 0.054 | 0.530 | 0.450 | 0.074 | 0.225 | 6.51 | 0.328 |
| | Stemflow | | 0.005 | 0.119 | 0.465 | 0.067 | 0.035 | 7.78 | 0.000 |
| 23 July | Incident Rain | 10.1 | 0.034 | 0.057 | 0.065 | 0.010 | 0.018 | 5.63 | ND |
| | Throughfall | | 0.009 | 0.124 | 0.116 | 0.019 | 0.049 | 6.37 | 0.017 |
| | Stemflow | | 0.001 | 0.029 | 0.097 | 0.015 | 0.011 | 7.55 | 0.000 |
| 30 July | Incident Rain | 34.9 | 0.045 | 0.032 | 0.212 | 0.081 | 0.036 | 5.47 | ND |
| | Throughfall | | 0.056 | 0.256 | 0.265 | 0.038 | 0.046 | 5.03 | 0.187 |
| | Stemflow | | 0.005 | 0.091 | 0.352 | 0.051 | 0.012 | 7.56 | 0.000 |
| 28 August | Incident Rain | 138.8 | 0.208 | 0.097 | 0.555 | 0.111 | 0.000 | 5.90 | ND |
| | Throughfall | | 0.095 | 1.197 | 0.750 | 0.145 | 0.229 | 5.99 | 3.089 |
| | Stemflow | | 0.006 | 0.093 | 0.251 | 0.034 | 0.009 | 7.50 | 0.000 |
| 09 September | Incident Rain | 45.0 | 0.054 | 0.032 | 0.189 | 0.027 | 0.113 | 5.64 | ND |
| | Throughfall | | 0.038 | 0.732 | 0.321 | 0.056 | 0.104 | 6.74 | 0.177 |
| | Stemflow | | 0.004 | 0.092 | 0.231 | 0.029 | 0.012 | 7.47 | 0.000 |
| 02 October | Incident Rain | 6.7 | 0.007 | 0.005 | 0.024 | 0.003 | ND | 4.87 | ND |
| | Throughfall | | 0.006 | 0.234 | 0.045 | 0.009 | ND | 5.26 | ND |
| | Stemflow | | 0.001 | 0.012 | 0.033 | 0.005 | ND | 6.85 | ND |

[a] ND = No data.

Table 47. Acidity and Nutrient Content of Incident Rain and Trembling Aspen, Throughfall, and Stemflow at the Exposed Site, 1976.

| Date | Precipitation Type | Precipitation<br>mm | Na<br>kg/ha | K<br>kg/ha | Ca<br>kg/ha | Mg<br>kg/ha | $SO_4^{2-}$-S<br>kg/ha | pH | Total Acidity as $H^+$<br>kg/ha |
|---|---|---|---|---|---|---|---|---|---|
| 30 June | Incident Rain | 26.2 | 0.092 | 0.102 | 0.173 | 0.024 | 0.113 | 5.56 | ND[a] |
| | Throughfall | | 0.028 | 0.287 | 0.310 | 0.045 | 0.172 | 6.60 | 0.058 |
| | Stemflow | | ND | ND | ND | ND | ND | ND | ND |
| 15 July | Incident Rain | 41.6 | 0.096 | 0.087 | 0.183 | 0.017 | 0.250 | 5.32 | ND |
| | Throughfall | | 0.031 | 0.456 | 0.434 | 0.059 | 0.101 | 6.39 | 0.250 |
| | Stemflow | | 0.005 | 0.187 | 1.053 | 0.134 | 0.097 | 7.87 | 0.000 |
| 29 July | Incident Rain | 43.0 | 0.039 | 0.043 | 0.211 | 0.026 | 0.043 | 5.60 | ND |
| | Throughfall | | 0.035 | 0.367 | 0.531 | 0.065 | 0.178 | 6.41 | 0.237 |
| | Stemflow | | 0.005 | 0.164 | 0.909 | 0.133 | 0.134 | 8.03 | 0.000 |
| 10 August | Incident Rain | 20.8 | 0.030 | 0.030 | 0.081 | 0.020 | ND | 5.36 | ND |
| | Throughfall | | 0.023 | 0.252 | 0.286 | 0.046 | 0.046 | 6.46 | 0.054 |
| | Stemflow | | 0.003 | 0.061 | 0.247 | 0.030 | 0.034 | 8.12 | 0.000 |
| 25 August | Incident Rain | 21.4 | 0.015 | 0.041 | 0.011 | 0.017 | 0.032 | 5.39 | ND |
| | Throughfall | | 0.025 | 0.375 | 0.300 | 0.047 | 0.066 | 6.81 | 0.051 |
| | Stemflow | | 0.003 | 0.062 | 0.258 | 0.031 | 0.032 | 7.76 | 0.000 |
| 08 September | Incident Rain | 105.2 | 0.063 | 0.032 | 0.210 | 0.021 | 0.295 | 5.44 | ND |
| | Throughfall | | 0.072 | 1.101 | 3.564 | 0.127 | 0.297 | 6.78 | 0.724 |
| | Stemflow | | 0.006 | 0.150 | 0.605 | 0.015 | 0.077 | 7.81 | 0.000 |
| 10 October | Incident Rain | 27.8 | 0.025 | 0.022 | 0.117 | 0.022 | ND | 5.87 | ND |
| | Throughfall | | 0.043 | 5.380 | 3.040 | 0.834 | ND | 712 | ND |
| | Stemflow | | 0.006 | 0.340 | 0.523 | 0.075 | ND | 6.93 | ND |

[a] ND = No data.

[b] Throughfall values are unusually high because of leachates from leaf litter caught in the throughfall gauges.

Table 48. Acidity and Nutrient Content of Incident Rain and Jack Pine Throughfall and Stemflow at Control Site, 1976.

| Date | Precipitation Type | Precipitation<br>mm | Na<br>kg/ha | K<br>kg/ha | Ca<br>kg/ha | Mg<br>kg/ha | $SO_4^{2-}$-S<br>kg/ha | pH | Total Acidity as $H^+$<br>kg/ha |
|---|---|---|---|---|---|---|---|---|---|
| 29 June | Incident Rain | 45.0 | 0.041 | 0.036 | 0.234 | 0.027 | 0.113 | 5.19 | ND[a] |
|  | Throughfall |  | 0.074 | 0.323 | 0.564 | 0.116 | 0.335 | 5.10 | 0.747 |
|  | Stemflow |  | ND | ND | ND | ND | ND | ND | ND |
| 16 July | Incident Rain | 45.4 | 0.041 | 0.045 | 0.095 | 0.009 | 0.086 | 5.57 | ND |
|  | Throughfall |  | 0.070 | 0.357 | 0.561 | 0.143 | 0.414 | 5.04 | 0.791 |
|  | Stemflow |  | 0.001 | 0.003 | 0.015 | 0.002 | 0.010 | 5.00 | 0.018 |
| 23 July | Incident Rain | 8.8 | 0.011 | 0.009 | 0.056 | 0.007 | 0.025 | 5.63 | ND |
|  | Throughfall |  | 0.014 | 0.061 | 0.097 | 0.022 | 0.083 | 4.98 | 0.043 |
|  | Stemflow |  | 0.000 | 0.000 | 0.001 | 0.000 | 0.001 | 5.02 | 0.000 |
| 30 July | Incident Rain | 28.7 | 0.023 | 0.014 | 0.126 | 0.011 | 0.029 | 5.47 | ND |
|  | Throughfall |  | 0.054 | 0.214 | 0.447 | 0.111 | 0.171 | 5.00 | 0.860 |
|  | Stemflow |  | 0.001 | 0.003 | 0.021 | 0.005 | 0.010 | 4.65 | 0.035 |
| 27 August | Incident Rain | 121.6 | 0.316 | 0.170 | 0.389 | 0.024 | 0.000 | 5.90 | ND |
|  | Throughfall |  | 0.322 | 0.672 | 1.416 | 0.414 | 0.504 | 5.35 | 6.427 |
|  | Stemflow |  | 0.004 | 0.014 | 0.052 | 0.003 | 0.023 | 4.69 | 1.006 |
| 05 September | Incident Rain | 39.6 | 0.040 | 0.028 | 0.135 | 0.016 | 0.000 | 5.65 | ND |
|  | Throughfall |  | 0.048 | 0.168 | 0.383 | 0.104 | 0.148 | 5.40 | 0.576 |
|  | Stemflow |  | 0.001 | 0.003 | 0.010 | 0.002 | 0.004 | 4.65 | 0.038 |

[a] ND = No data.

Table 49. Acidity and Nutrient Content of Incident Rain and Jack Pine Throughfall and Stemflow at Exposed Site. 1976.

| Date | Precipitation Type | Precipitation | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $SO_4^{2-}$-S | pH | Total Acidity as $H^+$ |
|---|---|---|---|---|---|---|---|---|---|
| | | mm | kg/ha | kg/ha | kg/ha | kg/ha | kg/ha | | kg/ha |
| 30 June | Incident Rain | 26.2 | 0.092 | 0.102 | 0.173 | 0.024 | 0.113 | 5.56 | ND[a] |
| | Throughfall | | 0.067 | 0.467 | 0.690 | 0.260 | 0.672 | 4.31 | 0.478 |
| | Stemflow | | ND | ND | ND | ND | ND | ND | ND |
| 15 July | Incident Rain | 41.6 | 0.096 | 0.087 | 0.183 | 0.017 | 0.250 | 5.32 | ND |
| | Throughfall | | 0.067 | 0.583 | 0.459 | 0.130 | 0.417 | 4.72 | 1.205 |
| | Stemflow | | 0.001 | 0.012 | 0.025 | 0.005 | 0.029 | 3.50 | 0.155 |
| 29 July | Incident Rain | 43.0 | 0.039 | 0.043 | 0.211 | 0.026 | 0.043 | 5.60 | ND |
| | Throughfall | | 0.045 | 0.485 | 0.346 | 0.084 | 0.337 | 4.81 | 0.991 |
| | Stemflow | | 0.000 | 0.005 | 0.002 | 0.002 | 0.010 | 3.41 | 0.052 |
| 10 August | Incident Rain | 20.8 | 0.030 | 0.030 | 0.081 | 0.020 | ND | 5.36 | ND |
| | Throughfall | | 0.020 | 0.198 | 0.409 | 0.047 | 0.117 | 5.10 | 0.161 |
| | Stemflow | | 0.000 | 0.002 | 0.003 | 0.001 | 0.003 | 3.64 | 0.006 |
| 25 August | Incident Rain | 21.4 | 0.015 | 0.041 | 0.107 | 0.017 | 0.032 | 5.39 | ND |
| | Throughfall | | 0.021 | 0.204 | 0.194 | 0.044 | 0.147 | 5.09 | 0.219 |
| | Stemflow | | 0.000 | 0.001 | 0.001 | 0.000 | 0.001 | 3.66 | 0.001 |
| 08 September | Incident Rain | 105.2 | 0.063 | 0.032 | 0.210 | 0.021 | 0.295 | 5.44 | ND |
| | Throughfall | | 0.081 | 0.450 | 0.375 | 0.072 | 0.451 | 4.97 | 4.696 |
| | Stemflow | | 0.002 | 0.026 | 0.027 | 0.007 | 0.033 | 3.90 | 2.517 |
| 10 October | Incident Rain | 27.8 | 0.025 | 0.022 | 0.117 | 0.022 | ND | 5.87 | ND |
| | Throughfall | | 0.044 | 0.903 | 0.289 | 0.062 | ND | 5.51 | ND |
| | Stemflow | | 0.001 | 0.009 | 0.010 | 0.002 | 0.008 | 4.12 | ND |

[a] ND = No data.

## 8.5 ACIDITY AND SULPHATE SULPHUR CONCENTRATION IN THROUGHFALL AND STEMFLOW OF DIFFERENT TREE SPECIES.

Table 50. Average pH and Sulphate Sulphur Concentration in Throughfall and Stemflow of Different Tree Species Collected During the Summer Months of 1975.

| Site | Distance (km) and Direction from Emission Source | Tree Species | Throughfall | | Stemflow | |
|---|---|---|---|---|---|---|
| | | | pH | $SO_4^{2-}$-S (ppm) | pH | $SO_4^{2-}$-S (ppm) |
| Steepbank 3 | 2.4 ESE | white spruce | 6.4 | 1.8 | 5.0 | 8.3 |
| Steepbank 2 | 4.0 ESE | white spruce | 5.8 | 2.0 | 4.0 | 13.9 |
| Supertest Hill | 7.0 S | black spruce | 5.8 | 9.9 | 4.5 | 16.9 |
| Mildred Lake | 11.0 NW | black spruce | 6.5 | 7.6 | 5.0 | 8.6 |
| Steepbank 1 | 17.0 ESE | black spruce | 5.0 | 4.4 | 3.8 | 12.5 |
| MacKay River | 21.0 NW | jack pine | 6.2 | 2.0 | 4.0 | 4.7 |
| Thickwood Hills | 31.0 SW | white spruce | 6.2 | 2.1 | 5.2 | 8.1 |
| Hangingstone River | 67.0 S | white spruce | 6.7 | 4.7 | 6.2 | 17.3 |
| Canwood, Saskatchewan | 502.0 SE | white spruce | 6.7 | 1.2 | 6.4 | 3.2 |

Table 51. Average pH and Sulphate Sulphur Concentration in Throughfall and Stemflow of Different Tree Species Collected from 1976 July to Mid-September.[a]

| Site | Distance (km) and Direction from Emission Source | Tree Species and Size | Throughfall | | Stemflow |
|---|---|---|---|---|---|
| | | | pH | $SO_4^{2-}$-S (ppm) | $SO_4^{2-}$-S (ppm) |
| Steepbank 2 | 4.0 ESE | white spruce - small | 6.5(0.2)[b] | 1.7(1.1)[b] | 27.9(43.8)[b] |
| Mildred Lake | 11.0 NW | jack pine - large | 6.5(0.2) | 3.2(1.6) | 16.1(11.6) |
| Steepbank 1 | 17.0 ESE | black spruce - small | 5.5(0.4) | 2.7(2.3) | 13.8(8.0) |
| MacKay River | 21.0 NW | white spruce - large | 5.7(0.5) | 9.1(3.3) | 26.1(13.1) |
| Thickwood Hills | 31.0 SW | white spruce - large | 6.5(0.2) | 2.6(1.5) | 8.0(4.8) |
| Steepbank A | 32.0 SE | white spruce - large | 5.6(0.8) | 15.8(6.3) | ND[c] |
| Muskeg Mountain | 38.0 ENE | white spruce - small | 5.5(0.6) | 2.2(1.9) | 11.1(9.3) |
| Bitumount | 39.0 N | white spruce - large | 6.6(0.3) | 1.3(0.9) | 13.5(12.3) |
| Hangingstone River | 67.0 S | white spruce - large | 6.6(0.3) | 4.8(3.0) | 15.1(9.1) |
| Gordon Lake | 75.0 SE | white spruce - large | 6.3(0.3) | 2.1(1.1) | 6.1(4.0) |
| Birch Mountain | 79.0 NNW | black spruce - small | 5.5(0.7) | 3.2(2.1) | 6.1(3.0) |
| Algar | 101.0 SSW | white spruce - large | 5.4(0.6) | 2.1(0.5) | 12.0(12.6) |
| Richardson | 102.0 NNW | jack pine - large | 5.1(0.1) | 0.8(0.4) | 8.1(4.4) |
| May | 173.0 SW | white spruce - large | 5.9(0.4) | 1.2(0.7) | 5.8(2.8) |

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[a] Samples were collected every two weeks from nine throughfall collectors and three stemflow collectors at each site.

[b] Standard deviation.

[c] No data.

Table 52. Amounts of Sulphate Sulphur Deposited in Throughfall and Stemflow from 1976 July to Mid-September.[a]

| Site | Distance (km) and Direction from Emission Source | Tree Species and Size | Throughfall (kg/ha/mo) | Stemflow (kg/ha/mo) |
|---|---|---|---|---|
| Steepbank 2 | 4.0 ESE | white spruce - small | 0.8 | 0.19[c] |
| Mildred Lake | 11.0 NW | jack pine - large | 1.3 | 0.14[b] |
| Steepbank 1 | 17.0 ESE | black spruce - small | 1.5 | ND[d] |
| MacKay River | 21.0 NW | white spruce - large | 4.5 | 0.16[b] |
| Thickwood Hills | 31.0 SW | white spruce - large | 1.9 | 0.13[b] |
| Steepbank A | 32.0 SE | white spruce - large | 2.7 | ND[d] |
| Muskeg Mountain | 38.0 ENE | white spruce - small | 1.0 | 0.19[c] |
| Bitumount | 39.0 N | white spruce - large | 1.0 | 0.10[b] |
| Hangingstone River | 67.0 S | white spruce - large | 2.2 | 0.13[b] |
| Gordon Lake | 75.0 SE | white spruce - large | 1.2 | 0.01[b] |
| Birch Mountain | 79.0 NNW | black spruce - small | 1.3 | 0.01[c] |
| Algar | 101.0 SSW | white spruce - large | 1.6 | 0.06[b] |
| Richardson | 102.0 NNE | jack pine - large | 0.4 | 0.03[b] |
| May | 173.0 SW | white spruce - large | 0.6 | 0.04[b] |

[a] Values are expressed in kg/ha/mo and were calculated from the sulphate sulphur concentrations and amounts of precipitation as throughfall and stemflow at each site.

[b] Calculated on the basis of 1250 stems/ha.

[c] Calculated on the basis of 3750 stems/ha.

[d] ND = No data.

## 8.6 ABSORPTION OF SULPHUR DIOXIDE BY SULPHATION DISCS

Table 53. Sulphur Absorbed by Sulphation Discs Set Out Monthly from 1976 June to September.

| Site | Distance /Direction from Source | Sulphur Absorbed (mg $SO_3$/100 $cm^2$/day) |
|---|---|---|
| Steepbank 2 | 4 ESE | 0.17 |
| Mildred Lake | 11 SW | 0.11 |
| Steepbank 1 | 17 ESE | 0.06 |
| MacKay River | 21 NW | 0.08 |
| Thickwood Hills | 31 SW | 0.02 |
| Steepbank A | 32 SE | 0.03 |
| Muskeg Mountain | 38 ENE | 0.13 |
| Bitumount | 39 N | 0.07 |
| Gordon Lake | 75 SE | 0.03 |
| Birch Mountain | 79 NNW | 0.06 |
| Algar | 101 SSW | 0.02 |
| Richardson | 102 NNW | 0.02 |
| May | 173 SW | 0.02 |

Table 54. Sulphur Absorbed by Sulphation Discs Set Out Monthly from 1977 May to September.

| Site No. | Site | mg $SO_3$/100 $cm^2$/day | | | | | Mean |
|---|---|---|---|---|---|---|---|
| | | May | June | July | August | September | |
| | 0 to 25 km | | | | | | |
| 1 | Mildred Lake | 0.031 | 0.051 | 0.045 | 0.059 | 0.087 | 0.06 |
| 2 | MacKay River | 0.030 | 0.024 | 0.055 | 0.032 | 0.056 | 0.04 |
| 3 | Supertest Hill | 0.042 | 0.018 | 0.179 | 0.191 | 0.056 | 0.10 |
| 5 | Steepbank 1 | 0.035 | 0.026 | 0.204 | 0.232 | 0.053 | 0.11 |
| 6 | Steepbank 2 | 0.041 | 0.038 | 0.092 | 0.382 | 0.073 | 0.13 |
| | Mean | | | | | | 0.09 |
| | 25 to 50 km | | | | | | |
| 9 | Bitumount | 0.021 | 0.053 | 0.025 | 0.035 | 0.033 | 0.03 |
| 8 | Muskeg Mountain | 0.061 | 0.038 | 0.048 | 0.130 | 0.076 | 0.07 |
| 4 | Steepbank A | 0.019 | 0.013 | 0.038 | 0.130 | 0.041 | 0.05 |
| 7 | Thickwood Hills | 0.016 | 0.011 | 0.042 | 0.043 | 0.030 | 0.03 |
| | Mean | | | | | | 0.05 |
| | 50 to 100 km | | | | | | |
| 11 | Birch Mountain | 0.015 | 0.056 | 0.035 | 0.047 | 0.033 | 0.04 |
| 10 | Gordon Lake | 0.018 | 0.003 | 0.043 | 0.073 | 0.024 | 0.03 |
| | Mean | | | | | | 0.04 |
| | > 100 km | | | | | | |
| 12 | Richardson | 0.006 | 0.006 | 0.027 | 0.050 | 0.024 | 0.02 |
| 13 | Algar | 0.009 | 0.003 | 0.026 | 0.038 | 0.036 | 0.02 |
| 14 | May | 0.015 | 0.011 | 0.019 | 0.042 | ND[a] | 0.02 |
| | Canwood, Saskatchewan | 0.010 | 0.008 | 0.008 | ND | ND | 0.01 |
| | Mean | | | | | | 0.02 |

[a] ND = No data.

## 8.7 REGRESSION ANALYSIS OF SOIL FREE ACID, SULPHATE SULPHUR, AND TOTAL SULPHUR CONCENTRATIONS VERSUS DISTANCE FROM A SULPHUR DIOXIDE EMISSIONS SOURCE AND ESTIMATED AVERAGE SULPHUR DIOXIDE CONCENTRATIONS

Table 55. Regression Analysis of Soil Hydrogen Ion Concentration ($H^+$)[a], Sulphate Sulphur Concentration ($SO_4^{2-}$-S) and Total Sulphur Concentration (Total S) Versus Distance (km) from a Sulphur Dioxide Emission Source and Average Ambient Sulphur Dioxide Concentrations.[b]

| Soil | Linear Regression Equation | Coefficient of Determination ($r^2$) | Standard Error of Estimate | Degrees of Freedom |
|---|---|---|---|---|
| Sandy O.EB | $H^+ = 4.54 \times 10^{-6} - 1.32 \times 10^{-8}$ (Distance)[d] | 0.66 | ND[c] | 25 |
| | $SO_4^{2-}$-S = 8.31 - 0.03 (Distance)[d] | 0.74 | 1.10 | 26 |
| | Not significant for total S | | | |
| | $H^+ = 2.82 \times 10^{-6} + 10^{-5}$ ($SO_2$)[d] | 0.65 | ND | 25 |
| | $SO_4^{2-}$-S = 3.94 + 36.80 ($SO_2$)[d] | 0.79 | | 26 |
| | Total S = 40.01 + 658.75 ($SO_2$)[d] | 0.33 | 48.48 | 26 |
| Peat<br>TY.M | $H^+ = 3.73 \times 10^{-6} - 5.08 \times 10^{-9}$ (Distance)[d] | 0.33 | ND | 26 |
| | $SO_4^{2-}$-S = 204.09 - 1.09 (Distance) | 0.30 | 91.35 | 26 |
| | Not significant for total S | | | |
| | $H^+ = 3.04 \times 10^{-6} + 5.98 \times 10^{-6}$($SO_2$)[d] | 0.40 | ND | 26 |
| | $SO_4^{2-}$-S = 15.14 + 1893.12 ($SO_2$)[d] | 0.80 | 48.28 | 26 |
| | Total S = 1251.76 + 2852.11 ($SO_2$)[d] | 0.54 | 135.07 | 26 |

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[a] Calculated from soil pH (hydrogen ion concentration = $10^{-pH}$).

[b] Expressed as mg $SO_3$ equiv./100 $cm^2$/day. All other concentration values are in ppm.

[c] ND = No data.

[d] Regression is statistically significant upon distance or $SO_2$ ($p = 0.001$).

## 8.8 THE SULPHUR CONTENT AND pH OF LYSIMETER SOILS SET OUT IN THE FIELD FROM JULY 1976 TO AUGUST 1978.

Table 56. Sulphate Sulphur, Total Sulphur Content, and pH of the Sandy O.EB Soil Kept at Nine Sites from July 1976 to August 1978.[a]

| Site | Layer | pH | $SO_4^{2-}$-S (ppm) | Total S (ppm) | $SO_4^{2-}$-S (kg/ha) | Total S (kg/ha) |
|---|---|---|---|---|---|---|
| Steepbank 2 | Lichen | 4.55 | 14.3 (0.8)[b] | 432 (18) | 0.07 | 2.1 (0.4) |
| | FH | 5.03 | 5.0 (0.3) | 157 (9) | 0.16 | 5.2 (2.1) |
| | 0 to 3 | 5.55 | 0.3 (0.2) | 35 (5) | 0.08 | 9.6 (0.1) |
| | 3 to 8 | 5.63 | 0.6 (0.2) | 23 (5) | 0.34 | 12.9 (0.3) |
| | 8 to 15 | 5.55 | 2.6 (0.2) | 30 (6) | 2.41 | 27.1 (0.5) |
| | $15^{+}$ | 5.99 | 2.9 (0.2) | 38 (12) | 8.74 | 115.8 (3.6) |
| Mildred Lake | Lichen | 4.65 | 25.0 (1.3) | 354 (9) | 0.12 | 1.7 (0.2) |
| | FH | 5.12 | 6.1 (0.2) | 252 (8) | 0.15 | 6.2 (1.5) |
| | 0 to 3 | 5.69 | 0.2 (0.0) | 32 (10) | 0.06 | 8.9 (0.3) |
| | 3 to 8 | 5.64 | 1.3 (0.2) | 27 (4) | 0.73 | 15.2 (0.2) |
| | 8 to 15 | 5.59 | 1.1 (0.1) | 33 (13) | 1.04 | 29.9 (1.2) |
| | $15^{+}$ | 5.94 | 2.3 (0.1) | 39 (3) | 7.11 | 118.4 (0.9) |
| Supertest Hill | Lichen | 5.19 | 27.0 (0.9) | 595 (19) | 0.08 | 1.7 (0.3) |
| | FH | 5.77 | 3.2 (0.3) | 132 (5) | 0.13 | 5.6 (1.2) |
| | 0 to 3 | 5.53 | 0.7 (0.1) | 26 (10) | 0.19 | 7.3 (0.3) |
| | 3 to 8 | 5.36 | 1.6 (0.1) | 34 (14) | 0.88 | 19.2 (0.8) |
| | 8 to 15 | 5.37 | 1.9 (0.2) | 28 (14) | 1.71 | 26.0 (1.3) |
| | $15^{+}$ | 5.88 | 3.1 (0.2) | 36 (10) | 9.55 | 108.2 (3.1) |
| Thickwood Hills | Lichen | 4.51 | 19.3 (0.3) | 370 (7) | 0.08 | 1.5 (0.1) |
| | FH | 4.99 | 4.9 (0.3) | 220 (28) | 0.13 | 5.6 (1.2) |
| | 0 to 3 | 5.43 | 0.5 (0.1) | 25 (6) | 0.15 | 7.1 (0.2) |
| | 3 to 8 | 5.66 | 1.6 (0.1) | 28 (6) | 0.91 | 15.4 (0.3) |
| | 8 to 15 | 5.57 | 1.0 (0.2) | 26 (6) | 0.94 | 23.9 (0.5) |
| | $15^{+}$ | 6.05 | 1.2 (0.2) | 34 (10) | 3.66 | 103.1 (3.2) |

continued ...

Table 56. Continued.

| Site | Layer | pH | $SO_4^{2-}$-S (ppm) | Total S (ppm) | $SO_4^{2-}$-S (kg/ha) | Total S (kg/ha) |
|---|---|---|---|---|---|---|
| Steepbank A | Lichen | 4.53 | 13.0 (0.0) | 309 (8) | 0.05 | 1.3 (0.2) |
| | FH | 5.01 | 5.0 (0.3) | 396 (14) | 0.11 | 8.4 (1.4) |
| | 0 to 3 | 5.59 | 0.4 (0.1) | 29 (6) | 0.12 | 8.0 (0.2) |
| | 3 to 8 | 5.66 | 1.0 (0.1) | 18 (7) | 0.54 | 10.1 (0.4) |
| | 8 to 15 | 5.58 | 1.8 (0.2) | 30 (12) | 1.62 | 27.3 (1.1) |
| | $15^+$ | 6.03 | 1.9 (0.2) | 39 (18) | 5.89 | 118.9 (5.5) |
| Bitumount | Lichen | 4.53 | 16.2 (0.3) | 412 (11) | 0.08 | 1.9 (0.1) |
| | FH | 4.98 | 3.9 (0.4) | 331 (31) | 0.12 | 10.0 (1.5) |
| | 0 to 3 | 5.47 | 0.6 (0.1) | 19 (13) | 0.18 | 5.3 (0.4) |
| | 3 to 8 | 5.55 | 1.6 (0.2) | 22 (5) | 0.91 | 12.0 (0.3) |
| | 8 to 15 | 5.43 | 2.2 (0.3) | 32 (6) | 2.04 | 29.7 (0.6) |
| | $15^+$ | 5.93 | 2.2 (0.2) | 37 (1) | 6.60 | 113.0 (0.4) |
| Gordon Lake | Lichen | 4.50 | 17.8 (0.3) | 317 (12) | 0.08 | 1.4 (0.1) |
| | FH | 4.84 | 4.2 (0.3) | 349 (10) | 0.10 | 8.5 (1.5) |
| | 0 to 3 | 5.49 | 0.8 (0.2) | 24 (20) | 0.23 | 6.7 (0.6) |
| | 3 to 8 | 5.53 | 1.7 (0.3) | 33 (9) | 0.97 | 18.3 (0.5) |
| | 8 to 15 | 5.42 | 1.5 (0.4) | 30 (6) | 1.40 | 27.1 (0.5) |
| | $15^+$ | 6.02 | 2.9 (0.2) | 32 (3) | 8.74 | 98.3 (0.8) |
| Algar | Lichen | 4.44 | 13.2 (0.3) | 255 (8) | 0.07 | 1.3 (0.1) |
| | FH | 5.15 | 2.9 (0.2) | 155 (8) | 0.13 | 7.0 (1.9) |
| | 0 to 3 | 5.58 | 1.2 (0.2) | 31 (6) | 0.34 | 8.6 (0.2) |
| | 3 to 8 | 5.66 | 1.1 (0.1) | 26 (5) | 0.63 | 14.3 (0.3) |
| | 8 to 15 | 5.58 | 0.6 (0.1) | 28 (14) | 0.58 | 25.8 (1.3) |
| | $15^+$ | 5.96 | 3.0 (0.2) | 39 (16) | 9.25 | 119.5 (4.9) |

continued ...

Table 56. Concluded.

| Site | Layer | pH | $SO_4^{2-}$-S (ppm) | Total S (ppm) | $SO_4^{2-}$-S (kg/ha) | Total S (kg/ha) |
|---|---|---|---|---|---|---|
| May | Lichen | 4.48 | 11.3 (0.6) | 302 (11) | 0.05 | 1.4 (0.1) |
|  | FH | 4.92 | 4.2 (0.2) | 142 (8) | 0.14 | 4.8 (1.0) |
|  | 0 to 3 | 5.54 | 0.5 (0.1) | 23 (5) | 0.15 | 6.4 (0.1) |
|  | 3 to 8 | 5.60 | 1.5 (0.2) | 27 (14) | 0.84 | 15.4 (0.8) |
|  | 8 to 15 | 5.56 | 1.0 (0.3) | 27 (18) | 0.88 | 25.1 (1.6) |
|  | $15^+$ | 6.08 | 1.2 (0.2) | 30 (5) | 3.66 | 91.4 (1.5) |

[a] Values are means of three replicates.

[b] Standard deviation.

Table 57. Sulphate Sulphur, Total Sulphur Content, and pH of the O.GL Soil Kept At Nine Sites from July 1976 to August 1978.[a]

| Site | Layer | pH | $SO_4^{2-}$-S (ppm) | Total S (ppm) | $SO_4^{2-}$-S (kg/ha) | Total S (kg/ha) |
|---|---|---|---|---|---|---|
| Steepbank 2 | Moss | | | 1897 (85) | | 5.7 (1.4) |
| | Plants | | | 2200 (50) | | 6.9 (3.8) |
| | Litter (L) | | | 1400 (20) | | 33.0 (2.1) |
| | FH | 6.38 | 16.5 (0.6)[b] | 1133 (25) | 1.29 | 87.6 (21.9) |
| | 0 to 3 | 6.00 | 3.5 (0.9) | 193 (47) | 0.89 | 48.9 (12.0) |
| | 3 to 8 | 6.36 | 2.2 (0.0) | 87 (33) | 0.78 | 30.8 (11.8) |
| | 8 to 15 | 5.75 | 2.5 (0.1) | 127 (12) | 1.88 | 97.0 (8.9) |
| | $15^+$ | 5.87 | 2.5 (0.1) | 138 (3) | 5.51 | 308.5 (5.9) |
| Mildred Lake | Moss | | | 1643 (59) | | 2.8 (2.1) |
| | Plants | | | 1690 (128) | | 0.9 (1.1) |
| | Litter (L) | | | 1800 (69) | | 26.1 (9.2) |
| | FH | 6.09 | 9.8 (0.2) | 1120 (17) | 0.73 | 83.6 (24.7) |
| | 0 to 3 | 5.83 | 3.9 (0.6) | 179 (15) | 0.98 | 45.6 (3.8) |
| | 3 to 8 | 6.63 | 2.2 (0.1) | 115 (8) | 0.77 | 40.8 (2.9) |
| | 8 to 15 | 5.70 | 2.2 (0.1) | 123 (3) | 1.65 | 94.0 (2.2) |
| | $15^+$ | 5.68 | 2.3 (0.1) | 123 (4) | 5.22 | 275.7 (7.8) |
| Thickwood Hills | Moss | | | 1343 (93) | | 8.7 (2.2) |
| | Plants | | | 1373 (92) | | 3.2 (1.5) |
| | Litter (L) | | | 1367 (23) | | 19.9 (9.9) |
| | FH | 6.99 | 10.2 | 1023 (38) | 0.63 | 58.8 (29.0) |
| | 0 to 3 | 7.17 | 2.1 (0.1) | 340 (139) | 0.52 | 86.4 (35.2) |
| | 3 to 8 | 6.98 | 2.7 (0.4) | 315 (276) | 0.96 | 112.0 (98.1) |
| | 8 to 15 | 6.69 | 2.1 (0.1) | 134 (21) | 1.63 | 102.1 (15.8) |
| | $15^+$ | 5.76 | 2.1 (0.1) | 109 (4) | 4.62 | 245.1 (9.0) |

continued ...

Table 57. Continued.

| Site | Layer | pH | $SO_4^{2-}$-S<br>(ppm) | Total S<br>(ppm) | $SO_4^{2-}$-S<br>kg/ha) | Total S<br>(kg/ha) |
|---|---|---|---|---|---|---|
| Steepbank A | Moss | | | 2017 (58) | | 8.5 (6.1) |
| | Plants | | | 2050 (70) | | |
| | Litter (L) | | | 1509 (20) | | |
| | FH | 6.45 | 8.1 (0.3) | 1040 (52) | 0.44 | 55.3 (14.5) |
| | 0 to 3 | 6.26 | 2.6 (0.3) | 174 (17) | 0.65 | 44.2 (4.4) |
| | 3 to 8 | 5.96 | 2.2 (0.1) | 155 (8) | 0.77 | 55.0 ( 2.9) |
| | 8 to 15 | 5.73 | 2.1 (0.0) | 108 (16) | 1.60 | 82.0 (12.3) |
| | $15^+$ | 5.82 | 2.2 (0.0) | 117 (5) | 4.92 | 262.3 (10.3) |
| Bitumount | Moss | | | 1367 (76) | | 3.4 (2.2) |
| | Plants | | | 1200 (87) | | 2.7 (3.8) |
| | Litter (L) | | | 1360 (20) | | 30.9 (13.2) |
| | FH | 6.48 | 12.6 (0.3) | 1140 (35) | 0.78 | 70.0 (8.7) |
| | 0 to 3 | 6.08 | 3.2 (0.2) | 178 (13) | 0.80 | 45.2 (3.3) |
| | 3 to 8 | 6.20 | 2.7 (0.2) | 165 (15) | 0.95 | 58.6 (5.3) |
| | 8 to 15 | 5.73 | 2.7 (0.1) | 115 (0) | 2.01 | 87.6 (0.0) |
| | $15^+$ | 5.86 | 2.4 (0.1) | 137 (3) | 5.44 | 305.5 (6.5) |
| Gordon Lake | Moss | | | 2007 (51) | | 2.3 (2.4) |
| | Plants | | | 1380 (28) | | 0.2 (0.0) |
| | Litter (L) | | | 1416 (74) | | 34.8 (21.0) |
| | FH | 6.34 | 9.2 (0.4) | 1267 (32) | 0.35 | 49.2 (13.6) |
| | 0 to 3 | 6.68 | 2.0 (0.1) | 240 (10) | 0.52 | 61.0 (2.5) |
| | 3 to 8 | 6.26 | 2.3 (0.1) | 107 (29) | 0.81 | 38.0 (10.2) |
| | 8 to 15 | 5.75 | 2.4 (0.1) | 105 (23) | 1.85 | 80.3 (17.7) |
| | $15^+$ | 5.66 | 2.5 (0.1) | 113 (2) | 5.51 | 252.6 (3.9) |

continued ...

Table 57. Concluded.

| Site | Layer | pH | $SO_4^{2-}$-S (ppm) | Total S (ppm) | $SO_4^{2-}$-S (kg/ha) | Total S (kg/ha) |
|---|---|---|---|---|---|---|
| Algar | Moss | | | 1277 (25) | | 4.2 (3.4) |
| | Plants | | | 1285 (49) | | 7.1 (2.4) |
| | Litter (L) | | | 883 (136) | | 26.3 (6.9) |
| | FH | 6.90 | 4.7 (0.3) | 888 (31) | 0.24 | 44.8 (20.6) |
| | 0 to 3 | 6.89 | 2.3 (0.2) | 243 (49) | 0.58 | 61.8 (12.5) |
| | 3 to 8 | 6.26 | 2.1 (0.1) | 102 (13) | 0.73 | 36.4 (4.5) |
| | 8 to 15 | 6.60 | 2.2 (0.1) | 127 (4) | 1.65 | 97.0 (3.1) |
| | $15^+$ | 6.02 | 2.1 (0.1) | 127 (4) | 4.77 | 283.1 (7.8) |
| May | Moss | | | 1367 (505) | | 1.2 (0.6) |
| | Plants | | | 1123 (116) | | 0.1 (0.0) |
| | Litter (L) | | | 1093 (23) | | 23.0 (3.5) |
| | FH | 6.64 | 4.2 (0.3) | 447 (58) | 0.38 | 40.6 (13.0) |
| | 0 to 3 | 6.44 | 3.2 (0.2) | 151 (21) | 0.80 | 38.3 (3.3) |
| | 3 to 8 | 6.44 | 2.0 (0.1) | 183 (13) | 0.72 | 65.2 (10.1) |
| | 8 to 15 | 5.71 | 2.1 (0.1) | 120 (28) | 1.57 | 91.2 (3.5) |
| | $15^+$ | 6.69 | 2.1 (0.1) | 136 (5) | 4.62 | 304.7 (1.9) |

[a] Values are means of three replicates.

[b] Standard deviation.

## 8.9 PRELIMINARY RESULTS OF THE MOVEMENT OF APPLIED SULPHATE SULPHUR IN FOREST SOILS EXPERIMENT

Table 58. pH Values $SO_4^{2-}$-S Content, and Soluble Potassium Content in Soil Four Months After Application of Potassium Sulphate. (Mildred Lake Research Facility Site).

| Treatment | Depth (cm) | pH | | $SO_4^{2-}$-S (kg/ha) | | | K (kg/ha)[c] | | |
|---|---|---|---|---|---|---|---|---|---|
| | | June | Sept. | June | Sept. | Incr.[a] | June | Sept. | Incr.[a] |
| Control | 2.5 to 0.0 | 4.48 | 4.28 | 3.0 | 3.6 | | 1.1 | 0.9 | |
| | 0.0 to 2.5 | 5.39 | 5.32 | 23.4 | 21.9 | | 2.9 | 3.3 | |
| | 2.5 to 15.0 | 5.70 | 5.66 | 4.5 | 4.5 | | 3.7 | 3.9 | |
| | 15.0 to 30.0 | 5.64 | 5.82 | 7.8 | 7.6 | | 3.6 | 3.6 | |
| | 30.0 to 60.0 | 5.81 | 5.82 | 2.9 | 5.5 | | 3.2 | 5.8 | |
| | 60.0 to 90.0 | 5.79 | 5.87 | 6.0 | 5.0 | | 6.4 | 6.4 | |
| $K_2SO_4$ [d] | 2.5 to 0.0 | 4.50 | 4.37 | 3.6 | 3.9 | 0.3 | 1.3 | 2.8 | 1.5 |
| | 0.0 to 2.5 | 5.42 | 5.39 | 28.2 | 35.9 | 7.7 | 3.3 | 10.5 | 7.2 |
| | 2.5 to 15.0 | 5.59 | 5.68 | 7.6 | 11.8 | 4.2 | 3.4 | 5.2 | 1.8 |
| | 15.0 to 30.0 | 5.62 | 5.70 | 6.6 | 13.4 | 6.8 | 3.0 | 3.6 | 0.6 |
| | 30.0 to 60.0 | 5.64 | 5.74 | 6.1 | 12.0 | 5.9 | 2.9 | 4.2 | 1.3 |
| | 60.0 to 90.0 | 5.77 | 5.70 | 8.2 | 6.0 | -2.2 | ND[c] | 5.7 | NA[c] |
| Recovery [b] | | | | | | 44.0 | | | 6.9 |
| $K_2SO_4$ [e] | 2.5 to 0.0 | 4.56 | 4.50 | 3.3 | 5.1 | 1.8 | 1.8 | 6.0 | 4.2 |
| | 0.0 to 2.5 | 5.49 | 5.41 | 17.4 | 31.4 | 14.0 | 3.5 | 36.7 | 33.2 |
| | 2.5 to 15.0 | 5.76 | 5.65 | 6.8 | 26.2 | 19,4 | 4.2 | 10.2 | 6.0 |
| | 15.0 to 30.0 | 5.61 | 5.49 | 6.9 | 13.4 | 6.5 | 3.0 | 3.3 | 0.3 |
| | 30.0 to 60.0 | 5.76 | 5.73 | 6.2 | 8.1 | 1.9 | 3.9 | 3.6 | -0.3 |
| | 60.0 to 90.0 | 5.86 | 5.81 | 9.2 | 6.4 | -2.8 | 6.0 | 5.7 | -0.3 |
| Recovery | | | | | | 38.9 | | | 16.0 |

[a] Increase over the summer period (June to September).

[b] Expressed as a percentage of the amount applied.

[c] ND = Not data; NA = Not applicable.

[d] Rate of 56 kg/ha of sulphur.

[e] Rate of 112 kg/ha of sulhphur.

Table 59. pH Values, $SO_4^{2-}$-S Content, and Soluble Potassium Content in Soil Four Months After Application of Potassium Sulphate. (Thickwood Hills Site).

| Treatment | Depth (mm) | pH June | pH Sept. | $SO_4^{2-}$-S (kg/ha) June | $SO_4^{2-}$-S (kg/ha) Sept. | $SO_4^{2-}$-S (kg/ha) Incr.[a] | K (kg/ha) June | K (kg/ha) Sept. | K (kg/ha) Incr.[a] |
|---|---|---|---|---|---|---|---|---|---|
| Control | 2.5 to 0.0 | 5.11 | 5.76 | 3.1 | 3.0 | | 1.8 | 1.8 | |
| | 0.0 to 2.5 | 5.05 | 5.03 | 44.0 | 42.1 | | 9.8 | 13.4 | |
| | 2.5 to 15.0 | 5.16 | 5.30 | 7.6 | 9.2 | | 6.3 | 8.4 | |
| | 15.0 to 30.0 | 5.16 | 5.34 | 6.6 | 9.0 | | 9.8 | 10.7 | |
| | 30.0 to 60.0 | 5.44 | 5.49 | 9.9 | 7.3 | | 9.4 | 10.1 | |
| | 60.0 to 90.0 | 5.77 | 5.76 | 7.6 | 3.4 | | 7.6 | 6.6 | |
| $K_2SO_4$ [c] | 2.5 to 0.0 | 5.08 | 4.86 | 3.3 | 3.4 | 0.1 | 1.2 | 1.6 | 0.4 |
| | 0.0 to 2.5 | 5.06 | 5.18 | 30.8 | 45.3 | 14.5 | 7.3 | 9.4 | 2.1 |
| | 2.5 to 15.0 | 5.13 | 5.15 | 9.6 | 24.9 | 15.3 | 7.5 | 7.1 | -0.4 |
| | 15.0 to 30.0 | 5.20 | 5.21 | 6.8 | 14.7 | 7.9 | 10.3 | 14.9 | 4.6 |
| | 30.0 to 60.0 | 5.37 | 5.55 | 8.3 | 9.7 | 1.4 | 9.9 | 18.4 | 8.5 |
| | 60.0 to 90.0 | 5.83 | 5.92 | 8.8 | 10.3 | 1.5 | 8.8 | 9.0 | 0.2 |
| Recovery[b] | | | | | | 72.7 | | | 11.3 |
| $K_2SO_4$ [d] | 2.5 to 0.0 | 5.11 | 4.91 | 3.5 | 3.9 | 0.4 | 1.6 | 2.6 | 1.0 |
| | 0.0 to 2.5 | 5.12 | 5.30 | 31.8 | 53.3 | 21.5 | 6.6 | 15.7 | 9.1 |
| | 2.5 to 15.0 | 5.18 | 5.10 | 7.7 | 23.8 | 16.1 | 6.4 | 11.4 | 5.0 |
| | 15.0 to 30.0 | 5.16 | 5.07 | 7.7 | 36.6 | 28.9 | 9.0 | 17.5 | 8.5 |
| | 30.0 to 60.0 | 5.27 | 5.43 | 7.3 | 9.0 | 1.7 | 8.7 | 12.7 | 4.0 |
| | 60.0 to 90.0 | 5.57 | 5.84 | 9.0 | 8.0 | -1.0 | 7.8 | 8.3 | 0.5 |
| Recovery | | | | | | 60.4 | | | 10.3 |

[a] Increase over the summer period (June to September).

[b] Expressed as a percentage of the amount applied.

[c] Rate of 56 kg/ha of sulphur.

[d] Rate of 112 kg/ha of sulphur.

## 8.10 ANALYSIS OF LYSIMETER LEACHATES.

Table 60. Sulphate Sulphur Content and pH of Lysimeter Leachates Sampled Monthly from 1977 April to October. (O.GL Soil).

| Site No. | Site | Month | | | | | | | | | | | | Mean | Mean |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | April | | May | | June | | July | | August | | September | | | |
| | | pH | $SO_4^{2-}$-S (ppm) | pH | $SO_4^{2-}$-S (ppm) | pH | $SO_4^{2-}$-S (ppm) | pH | $SO_4^{2-}$-S (ppm) | pH | $SO_4^{2-}$-S (ppm) | pH | $SO_4^{2-}$-S (ppm) | pH | $SO_4^{2-}$-S (ppm) |
| | <u>0 to 25 km</u> | | | | | | | | | | | | | | |
| 6 | Steepbank 2 | 6.95 | 6.82 | 7.09 | 3.29 | 7.80 | 4.39 | 5.34 | 2.92 | 6.48 | 2.55 | 6.03 | 1.90 | 6.61 | 3.64 |
| 3 | Supertest Hill[a] | 7.48 | 7.02 | 7.83 | 2.20 | 7.59 | 4.85 | 8.05 | 3.54 | 5.46 | 6.05 | 7.75 | 4.39 | 7.36 | 4.67 |
| 1 | AOSERP | 7.59 | 4.16 | 7.36 | 4.67 | 7.61 | 6.14 | 7.35 | 4.71 | 6.97 | 2.00 | 6.07 | 2.35 | 7.16 | 4.00 |
| | Mean | | | | | | | | | | | | | 6.90 | 3.80 |
| | <u>25 to 50 km</u> | | | | | | | | | | | | | | |
| 7 | Thickwood Hills | 8.03 | 1.46 | 8.13 | 0.68 | 7.71 | 1.16 | 7.93 | 0.90 | 7.88 | 0.37 | 7.85 | 0.32 | 7.92 | 0.81 |
| 4 | Steepbank A | 8.88 | 2.77 | 7.69 | 2.88 | 7.11 | 3.35 | 7.10 | 2.34 | 7.45 | 2.78 | 7.08 | 1.63 | 7.55 | 2.62 |
| 9 | Bitumount | 8.10 | 5.67 | 7.10 | 1.47 | 7.41 | 2.93 | 7.24 | 3.35 | 7.09 | 5.16 | 6.81 | 0.75 | 7.29 | 2.72 |
| | Mean | | | | | | | | | | | | | 7.60 | 2.20 |
| | <u>50 to 100 km</u> | | | | | | | | | | | | | | |
| 10 | Gordon Lake | 7.64 | 1.80 | 6.82 | 2.40 | 7.06 | 1.63 | 7.17 | 2.82 | 7.11 | 2.83 | ND[b] | ND | 7.16 | 2.30 |
| | <u>> 100 km</u> | | | | | | | | | | | | | | |
| 13 | Algar | 8.07 | 1.28 | 7.80 | 1.53 | 7.97 | 1.15 | 8.41 | 0.44 | 7.98 | 0.44 | 8.00 | 0.11 | 8.03 | 0.82 |
| 14 | May | 6.91 | 4.06 | 7.18 | 2.78 | 6.27 | 0.33 | 7.24 | 1.87 | 7.40 | 1.45 | 7.57 | 1.07 | 7.09 | 1.93 |
| | Mean | | | | | | | | | | | | | 7.60 | 1.40 |

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[a] Values for Supertest Hill not included in the calculation of the mean, because of road dust contamination.

[b] ND = No data.

Table 61. Sulphate Sulphur Content and pH of Lysimeter Leachates Sampled Monthly from 1977 April to October. (Sandy O.EB Soil).

| Site No. | Site | April | | May | | June | | July | | August | | September | | Mean pH | Mean $SO_4^{2-}$-S (ppm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | pH | $SO_4^{2-}$-S (ppm) | pH | $SO_4^{2-}$-S (ppm) | pH | $SO_4^{2-}$-S (ppm) | pH | $SO_4^{2-}$-S (ppm) | pH | $SO_4^{2-}$-S (ppm) | pH | $SO_4^{2-}$-S (ppm) | | |
| | <u>0 to 25 km</u> | | | | | | | | | | | | | | |
| 6 | Steepbank 2 | 5.44 | 1.79 | 6.22 | 1.33 | 6.77 | 1.92 | 6.48 | 1.30 | 6.74 | 1.94 | 6.23 | 1.30 | 6.31 | 1.60 |
| 3 | Supertest Hill[a] | 7.14 | 2.58 | 7.23 | 2.33 | 7.15 | 1.82 | 6.89 | 1.32 | 6.85 | 2.18 | 6.88 | 1.67 | 7.02 | 1.98 |
| 1 | AOSERP | 6.20 | 1.10 | 6.68 | 1.08 | 6.58 | 1.33 | 6.75 | 1.05 | 6.84 | 1.43 | 6.71 | 1.45 | 6.63 | 1.24 |
| | Mean | | | | | | | | | | | | | 6.50 | 1.4 |
| | <u>25 to 50 km</u> | | | | | | | | | | | | | | |
| 7 | Thickwood Hills | 7.04 | 0.72 | 6.26 | 0.52 | 6.95 | 0.83 | 6.77 | 1.02 | 6.83 | 0.83 | 6.76 | 0.62 | 6.77 | 0.76 |
| 4 | Steepbank A | 6.23 | 0.65 | 5.65 | 0.58 | 6.34 | 0.75 | 7.10 | 6.22 | 0.49 | 6.24 | 6.31 | 0.63 | 6.16 | 0.60 |
| 9 | Bitumount | 5.58 | 0.96 | 6.49 | 1.28 | 6.28 | 1.05 | 6.37 | 1.35 | 6.17 | 0.67 | 5.77 | 0.77 | 6.11 | 1.01 |
| | Mean | | | | | | | | | | | | | 6.40 | 0.80 |
| | <u>50 to 100 km</u> | | | | | | | | | | | | | | |
| 10 | Gordon Lake | 5.63 | 1.00 | 6.54 | 0.88 | 6.70 | 0.79 | 6.52 | 0.48 | 6.02 | 0.77 | ND[b] | ND | 6.28 | 0.78 |
| | <u>> 100 km</u> | | | | | | | | | | | | | | |
| 13 | Algar | 6.72 | 0.55 | 6.88 | 0.89 | 6.62 | 0.70 | 6.62 | 0.56 | 6.57 | 0.83 | 6.75 | 0.41 | 6.69 | 0.66 |
| 14 | May | 5.94 | 0.72 | 6.64 | 0.82 | 5.92 | 1.11 | 6.44 | 0.63 | 6.40 | 0.51 | 7.09 | 0.91 | 6.40 | 0.78 |
| | Mean | | | | | | | | | | | | | 6.50 | 0.70 |

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[a] Values for Supertest Hill not included in the calculation of the mean, because of the road dust contamination.

[b] ND = No data.

Table 62. Concentrations (ppm) of Cations in Lysimeter Leachates Sampled Monthly from 1977 April to September. (O.GL Soil).

| Site No. | Site | April | | | | May | | | | June | | | | July | | | | August | | | | September | | | | Mean | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg |
| | 0 to 25 km | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6 | Steepbank 2 | 0.5 | 1.0 | 3.1 | 0.8 | 0.6 | 0.9 | 2.8 | 0.6 | 0.7 | 0.9 | 4.3 | 1.1 | 0.9 | 1.2 | 3.8 | 0.8 | 0.9 | 1.7 | 4.9 | 1.2 | 1.1 | 2.6 | 12.3 | 3.2 | 0.8 | 1.4 | 5.2 | 1.3 |
| 3 | Supertest Hill[b] | 0.7 | 1.2 | 5.9 | 1.1 | 0.7 | 1.8 | 7.2 | 1.1 | 0.9 | 2.2 | 8.5 | 1.5 | 0.7 | 1.6 | 6.7 | 1.1 | 1.1 | 2.6 | 13.3 | 3.1 | 1.2 | 3.2 | 18.8 | 4.0 | 0.7 | 2.1 | 10.1 | 2.0 |
| | AOSERP | 0.4 | 1.0 | 2.6 | 0.5 | 0.7 | 1.3 | 4.0 | 0.9 | 0.7 | 1.7 | 7.0 | 1.9 | 0.7 | 1.8 | 6.4 | 1.6 | 0.7 | 1.8 | 7.2 | 1.9 | 0.7 | 2.4 | 8.2 | 0.5 | 0.6 | 1.7 | 5.9 | 1.2 |
| | Mean | | | | | | | | | | | | | | | | | | | | | | | | | 0.7 | 1.6 | 5.5 | 1.2 |
| | 25 to 50 km | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 7 | Thickwood Hills | 0.3 | 0.9 | 3.2 | 0.6 | 0.4 | 1.1 | 3.3 | 0.6 | 0.5 | 1.2 | 2.9 | 0.8 | 0.4 | 1.9 | 2.6 | 0.4 | 0.4 | 1.4 | 2.8 | 0.7 | 0.4 | 3.5 | 2.7 | 0.5 | 0.4 | 1.7 | 2.9 | 0.6 |
| 4 | Steepbank A | 0.4 | 0.8 | 2.1 | 0.4 | 0.6 | 1.3 | 3.0 | 0.6 | 0.7 | 1.8 | 4.2 | 0.9 | 1.7 | 1.0 | 6.3 | 1.5 | 0.7 | 1.6 | 7.9 | 2.0 | 0.7 | 2.1 | 7.7 | 2.0 | 0.8 | 1.4 | 5.2 | 1.2 |
| 9 | Bitumount | 0.4 | 0.7 | 2.6 | 0.6 | 0.8 | 1.2 | 2.6 | 0.6 | 0.9 | 1.7 | 5.7 | 0.8 | 0.9 | 2.2 | 6.7 | 1.5 | 0.9 | 2.4 | 10.8 | 3.3 | 1.0 | 1.6 | 19.0 | 4.5 | 0.8 | 1.6 | 7.9 | 1.9 |
| | Mean | | | | | | | | | | | | | | | | | | | | | | | | | 0.7 | 1.6 | 5.3 | 1.2 |
| | 50 to 100 km | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 10 | Gordon Lake | 0.5 | 0.6 | 2.2 | 0.3 | 0.6 | 1.0 | 2.5 | 0.5 | 0.6 | 2.5 | 3.0 | 0.6 | 0.8 | 1.7 | 6.4 | 1.5 | 0.5 | 1.8 | 4.8 | 0.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 | 1.5 | 3.7 | 0.7 |
| | > 100 km | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 13 | Algar | 0.3 | 0.8 | 2.7 | 0.6 | 0.5 | 1.1 | 3.3 | 0.7 | 0.5 | 1.5 | 3.0 | 0.7 | 0.5 | 1.5 | 2.8 | 0.5 | 0.4 | 1.0 | 2.9 | 0.8 | 0.5 | 1.5 | 3.3 | 0.7 | 0.4 | 1.2 | 3.0 | 0.7 |
| 14 | May | 0.4 | 1.0 | 0.3 | 0.5 | 0.5 | 0.9 | 2.5 | 0.4 | 0.7 | 1.1 | 2.7 | 0.7 | 0.5 | 1.2 | 2.4 | 0.5 | 0.4 | 1.2 | 3.1 | 0.7 | 1.0 | 1.2 | 6.7 | 1.8 | 0.6 | 1.1 | 3.3 | 0.8 |
| | Mean | | | | | | | | | | | | | | | | | | | | | | | | | 0.5 | 1.1 | 3.1 | 0.7 |

[a] Geometric means weighted by the leachate volume.

[b] Mean value excludes values for Supertest Hill, because of road dust contamination.

Table 63. Concentrations (ppm) of Cations in Lysimeter Leachates Sampled Monthly from 1977 April to October. (O.EB Soil).

| Site No. | Site[a] | April | | | | May | | | | June | | | | July | | | | August | | | | September | | | | Mean | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg | Na | K | Ca | Mg |
| | 0 to 25 km | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6 | Steepbank 2 | 1.2 | 1.3 | 7.3 | 1.2 | 1.3 | 1.1 | 7.6 | 1.8 | 1.7 | 1.3 | 10.7 | 2.6 | 1.3 | 0.6 | 6.2 | 1.5 | 0.4 | 1.2 | 2.3 | 0.5 | 0.5 | 2.1 | 3.1 | 0.8 | 1.1 | 1.3 | 4.6 | 1.4 |
| 3 | Supertest Hill[b] | 1.6 | 1.8 | 12.2 | 2.4 | 1.1 | 1.8 | 11.0 | 1.7 | 1.4 | 1.9 | 11.1 | 1.9 | 1.5 | 2.2 | 11.0 | 1.2 | 2.3 | 2.9 | 16.5 | 2.5 | 0.9 | 2.6 | 15.5 | 1.0 | 1.5 | 2.2 | 12.9 | 1.8 |
| 1 | AOSERP | 1.8 | 1.5 | 14.2 | 2.7 | 0.9 | 1.5 | 7.5 | 2.0 | 2.0 | 1.3 | 11.0 | 2.5 | 2.0 | 0.9 | 10.6 | 2.6 | 0.7 | 0.8 | 5.2 | 1.6 | 0.4 | 2.6 | 5.4 | 1.4 | 1.3 | 1.6 | 9.0 | 2.1 |
| | Mean | | | | | | | | | | | | | | | | | | | | | | | | | 1.2 | 1.4 | 6.8 | 1.7 |
| | 25 to 50 km | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 7 | Thickwood Hills | 1.2 | 1.2 | 7.7 | 1.7 | 1.3 | 1.4 | 8.3 | 1.9 | 1.6 | 1.5 | 8.2 | 2.2 | 1.7 | 2.3 | 7.1 | 0.7 | 1.3 | 2.0 | 7.8 | 2.1 | 1.3 | 2.0 | 7.7 | 1.7 | 1.4 | 1.7 | 7.8 | 1.7 |
| 4 | Steepbank A | 1.3 | 1.0 | 10.5 | 2.3 | 1.5 | 1.3 | 9.9 | 2.1 | 1.6 | 1.5 | 8.6 | 1.7 | 1.1 | 1.7 | 8.1 | 1.9 | 0.8 | 0.9 | 5.9 | 1.5 | 1.1 | 1.4 | 5.6 | 1.5 | 1.2 | 1.3 | 8.1 | 1.8 |
| 9 | Bitumount | 1.6 | 1.2 | 2.5 | 0.6 | 1.0 | 1.1 | 6.6 | 1.2 | 1.2 | 1.2 | 8.5 | 1.7 | 1.4 | 1.0 | 9.3 | 1.5 | 1.2 | 2.4 | 9.5 | 2.1 | 0.7 | 3.1 | 5.2 | 0.8 | 1.2 | 1.7 | 6.9 | 1.3 |
| | Mean | | | | | | | | | | | | | | | | | | | | | | | | | 1.3 | 1.6 | 7.6 | 1.6 |
| | 50 to 100 km | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 10 | Gordon Lake | 1.3 | 0.6 | 10.9 | 1.9 | 1.2 | 0.7 | 5.6 | 1.1 | 1.2 | 0.9 | 5.3 | 1.0 | 1.7 | 1.0 | 8.2 | 1.9 | 2.1 | 1.4 | 8.0 | 1.6 | 0.0 | 0.0 | 0.0 | 0.0 | 1.5 | 0.9 | 7.6 | 1.5 |
| | > 100 km | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 13 | Algar | 1.4 | 1.0 | 9.2 | 2.0 | 1.8 | 1.3 | 10.8 | 2.3 | 1.7 | 1.6 | 8.1 | 2.2 | 1.6 | 1.8 | 8.7 | 1.8 | 1.4 | 1.4 | 6.9 | 1.8 | 1.6 | 2.1 | 7.4 | 1.6 | 1.6 | 1.5 | 8.5 | 1.9 |
| 14 | May | 1.3 | 1.0 | 6.5 | 1.6 | 1.6 | 1.2 | 6.9 | 1.5 | 0.4 | 1.0 | 2.4 | 0.6 | 1.5 | 1.5 | 3.4 | 1.2 | 1.4 | 1.5 | 6.4 | 1.5 | 1.3 | 1.1 | 6.9 | 1.8 | 1.2 | 1.2 | 5.4 | 1.4 |
| | Mean | | | | | | | | | | | | | | | | | | | | | | | | | 1.4 | 1.3 | 6.9 | 1.6 |

[a] Geometric means weighted by the leachate volume.

[b] Mean value excludes values for Supertest Hill, because of road dust contamination.

## 8.11 ANALYSIS OF PERMANENT PLOT SOILS

At the 15 sites, located at distances of 4 to 173 km from the emitter (Table 1, Figure 1), which were used for obtaining rain samples, and to expose soils in containers, permanent plots were set out in 1976. These replicated small plots (Figure 5) were soil sampled in 1976 and 1978.

The values were compared for 1976 and 1978 for soil content of soluble sulphate-S (Table 64), soil content of total S (Table 65), and soil pH (Table 66). During two years, one would not expect much change in natural soils, but there was a trend to an increase in soil pH in the organic layers from 1976 to 1978 and an increase in total S content in the mineral layers. In addition, there was little change in the soluble sulphate-S content in the soils, and this is to be expected considering the mobility of sulphate. However, these differences between 1976 and 1978 are best not over-emphasized because two years is a short span of time. These results will become more useful as soil sampling is made in the future.

Table 64. Sulphate Cotent of Top Layers of Soils in "Permanent Plot" Samples in Separate Years.

| Site No. | Site Name | Distance from $SO_2$ Source (km) | Year | Sulphate-S Content (ppm) Live Moss | Fresh Litter | L-F-H Layers | Mineral Layer (0 to 15 cm) |
|---|---|---|---|---|---|---|---|
| 6 | Steepbank 2 | 4 | 1976 | | 116 | 88 | 3.5 |
| | | | 1978 | | 62 | 120 | 1.5 |
| 8 | Muskeg Mountain[a] | 38 | 1976 | | 64 | 22 | 2.1 |
| | | | 1978 | | 44 | 23 | 1.7 |
| 13 | Algar | 101 | 1976 | 375 | 112 | 41 | 1.1 |
| | | | 1978 | 337 | 62 | 56 | 1.2 |
| 14 | May | 173 | 1976 | 346 | 90 | 35 | 2.7 |
| | | | 1978 | 244 | 84 | 75 | 2.1 |

[a] Plot under jack pine.

Table 65. Total Sulphur of Top Layers of Soils in "Permanent Plots" Sampled in Separate Years.

| Site No. | Site Name | Distance from $SO_2$ Source (km) | Year | Total S Content (ppm) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Live Moss | Fresh Litter | L-F-H Layers | Mineral Layer (0 to 15 cm) |
| 1 | AOSERP Camp | 11 | 1976 | | 925 | 380 | 28 |
| | | | 1978 | | 840 | 300 | 45 |
| 2 | MacKay River | 21 | 1976 | 1575 | 1590 | 1230 | 90 |
| | | | 1978 | 1650 | 1020 | 1310 | 73 |
| 3 | Supertest Hill | 7 | 1976 | | 1835 | 1630 | 36 |
| | | | 1978 | | 1345 | 1530 | 57 |
| 4 | Steepbank A | 32 | 1976 | 1200 | 1415 | 1170 | 44 |
| | | | 1978 | 1390 | 1052 | 901 | 73 |
| 5 | Steepbank 1 | 17 | 1976 | 480 | 1335 | 1210 | |
| | | | 1978 | 730 | 780 | 1301 | |
| 6 | Steepbank 2 | 4 | 1976 | | 1720 | 1130 | 67 |
| | | | 1978 | | 1190 | 685 | 76 |
| 7 | Thickwood Hills | 31 | 1976 | 1210 | 1975 | 1090 | 58 |
| | | | 1978 | 1365 | 1435 | 1120 | 76 |
| 8 | Muskeg Mountain[a] | 38 | 1976 | | 840 | 255 | 42 |
| | | | 1978 | | 850 | 295 | 40 |

continued ...

Table 65. Continued.

| Site No. | Site Name | Distance from $SO_2$ Source (km) | Year | Total S Content (ppm) |  |  |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | Live Moss | Fresh Litter | L-F-H Layers | Mineral Layer (0 to 15 cm) |
|  | Muskeg Mountain[b] | 38 | 1976 | 1550 | 1880 | 1047 |  |
|  |  |  | 1978 | 1780 | 1595 | 1000 |  |
| 9 | Bitumount | 39 | 1976 | 1365 | 1395 | 715 | 29 |
|  |  |  | 1978 | 1481 | 1145 | 422 | 54 |
| 10 | Gordon Lake[a] | 75 | 1976 |  | 960 | 260 | 16 |
|  |  |  | 1978 |  | 705 | 250 | 18 |
|  | Gordon Lake[c] | 75 | 1976 |  | 1800 | 1370 | 36 |
|  |  |  | 1978 |  | 1205 | 525 | 62 |
| 11 | Birch Mountain | 79 | 1976 |  | 915 | 355 | 46 |
|  |  |  | 1978 |  | 770 | 290 | 62 |
| 12 | Richardson | 102 | 1976 |  | 690 | 190 | 19 |
|  |  |  | 1978 |  | 760 | 235 | 20 |
| 13 | Algar | 101 | 1976 | 1270 | 1310 | 520 | 48 |
|  |  |  | 1978 | 1210 | 1250 | 730 | 70 |
| 14 | May | 173 | 1976 | 1415 | 1280 | 1255 | 53 |
|  |  |  | 1978 | 1050 | 870 | 1200 | 72 |

continued ...

Table 65. Concluded.

| Site No. | Site Name | Distance from $SO_2$ Source (km) | Year | Total S Content (ppm) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Live Moss | Fresh Litter | L-F-H Layers | Mineral Layer (0 to 15 cm) |
| 15 | Hangingstone River | 67 | 1976 | | 1930 | 1845 | 69 |
| | | | 1978 | | 1435 | 1367 | 64 |

[a] Plot under jack pine.

[b] Plot under black spruce.

[c] Plot under aspen.

Table 66. Soil pH of Top Layers of Soils in "Permanent Plots" Sampled in Separate Years.

| Site No. | Site Name | Distance from $SO_2$ Source (km) | Year | Live Moss | L-F-H Layers | Mineral Layer (0 to 15 cm) |
|---|---|---|---|---|---|---|
| 1 | AOSERP Camp | 11 | 1976 | | 4.93 | 5.73 |
| | | | 1978 | | 5.41 | 5.80 |
| 2 | MacKay River | 21 | 1976 | 4.48 | 4.73 | 4.20 |
| | | | 1978 | 4.66 | 4.81 | 4.08 |
| 3 | Supertest Hill | 7 | 1976 | | 5.75 | 5.41 |
| | | | 1978 | | 6.35 | 5.63 |
| 4 | Steepbank A | 32 | 1976 | 5.02 | 5.10 | 4.87 |
| | | | 1978 | 5.59 | 5.21 | 4.95 |
| 5 | Steepbank 1 | 17 | 1976 | 4.29 | 3.90 | |
| | | | 1978 | 4.45 | 5.01 | |
| 6 | Steepbank 2 | 4 | 1976 | 5.96 | 5.87 | 6.22 |
| | | | 1978 | | 5.97 | 6.36 |
| 7 | Thickwood Hills | 31 | 1976 | 5.40 | 5.28 | 4.83 |
| | | | 1978 | 5.70 | 5.32 | 4.87 |
| 8 | Muskeg Mountain[a] | 38 | 1976 | | 4.47 | 4.69 |
| | | | 1978 | | 4.35 | 4.64 |
| | Muskeg Mountain[b] | 38 | 1976 | 5.32 | | 6.45 |
| | | | 1978 | 6.04 | | 6.90 |

continued ...

Table 66. Concluded.

| Site No. | Site Name | Distance from $SO_2$ Source (km) | Year | Live Moss | L-F-H Layers | Mineral Layers (0 to 15 cm) |
|---|---|---|---|---|---|---|
| 9 | Bitumount | 39 | 1976 | 5.17 | 5.40 | 5.93 |
| | | | 1978 | 5.64 | 5.70 | 6.02 |
| 10 | Gordon Lake[a] | 75 | 1976 | | 4.92 | 4.71 |
| | | | 1978 | | 5.01 | 4.64 |
| | Gordon Lake[c] | 75 | 1976 | | 5.08 | 4.80 |
| | | | 1978 | | 5.21 | 4.75 |
| 11 | Birch Mountain | 79 | 1976 | | 3.89 | 4.94 |
| | | | 1978 | | 3.79 | 5.07 |
| 12 | Richardson | 102 | 1976 | | 4.48 | 5.38 |
| | | | 1978 | | 4.67 | 5.39 |
| 13 | Algar | 101 | 1976 | 5.11 | 4.03 | 4.11 |
| | | | 1978 | 4.89 | 4.10 | 4.32 |
| 14 | May | 173 | 1976 | 4.84 | 4.16 | 4.47 |
| | | | 1978 | 4.80 | 4.30 | 4.70 |
| 15 | Hangingstone River | 67 | 1976 | | 6.11 | 4.82 |
| | | | 1978 | | 6.14 | 4.84 |

[a] Plot under jack pine.

[b] Plot under black spruce.

[c] Plot under aspen.

## 9. LIST OF AOSERP RESEARCH REPORTS

1. AOSERP first annual report, 1975.
2. Walleye and goldeye fisheries investigations in the Peace-Athabasca Delta--1975.
3. Structure of a traditional baseline data system. 1976.
4. A preliminary vegetation survey of the AOSERP study area. 1976.
5. The evaluation of wastewaters from an oil sand extraction plant. 1976.
6. Housing for the north--the stackwall system; construction report--Mildred Lake tank and pump house. 1976.
7. A synopsis of the physical and biological limnology and fishery programs within the Alberta oil sands area. 1977.
8. The impact of saline waters upon freshwater biota (a literature review and bibliography). 1977.
9. A preliminary investigation into the magnitude of fog occurrence and associated problems in the oil sands area. 1977.
10. Development of a research design related to archaeological studies in the Athabasca oil sands area. 1977.
11. Life cycles of some common aquatic insects of the Athabasca River, Alberta. 1977.
12. Very high solution meteorological satellite study of oil sands weather: "a feasibility study". 1977.
13. Plume dispersion measurements from an oil sands extraction plant, March 1976.
14. None published.
15. A climatology of low-level air trajectories in the Alberta oil sands area. 1977.
16. The feasibility of a weather radar near Fort McMurray, Alberta. 1977.
17. A survey of baseline levels of contaminants in aquatic biota of the AOSERP study area. 1977.

18. Interim compilation of stream gauging data to December 1976 for AOSERP. 1977.

19. Calculations of annual averaged sulphur dioxide concentrations at ground level in the AOSERP study area. 1977.

20. Characterization of organic constituents in waters and wastewaters of the Athabasca oil sands mining area. 1978.

21. AOSERP second annual report, 1976-77.

22. AOSERP interim report covering the period April 1975 to November 1978.

23. Acute lethality of mine depressurization water to trout-perch and rainbow trout: Volume 1. 1979.

24. Air system winter field study in the AOSERP study area, February 1977.

25. Review of pollutant transformation process relevant to the Alberta oil sands area. 1977.

26. Interim report on an intensive study of the fish fauna of the Muskeg River watershed of northeastern Alberta. 1977.

27. Meteorology and air quality winter field study in the AOSERP study area, March 1976.

28. Interim report on a soils inventory in the Athabasca oil sands area. 1978.

29. An inventory system for atmospheric emissions in the AOSERP study area. 1978.

30. Ambient air quality in the AOSERP study area. 1977.

31. Ecological habitat mapping of the AOSERP study area: Phase 1. 1978.

32. AOSERP third annual report, 1977-78.

33. Relationships between habitats, forages, and carrying capacity of moose range in northern Alberta. Part 1: moose preferences for habitat strata and forages. 1978.

34. Heavy metals in bottom sediments of the mainstem Athabasca River upstream of Fort McMurray: Volume 1. 1978.

35. The effects of sedimentation on the aquatic biota. 1978.

36. Fall fisheries investigations in the Athabasca and Clearwater rivers upstream of Fort McMurray: Volume 1. 1978.

37. Community studies: Fort McMurray, Anzac, and Fort MacKay. 1978.

38. Techniques for the control of small mammal damage to plants: a review. 1979.

39. The climatology of the AOSERP study area. 1979.

40. Mixing characteristics of the Athabasca River below Fort McMurray --winter conditions. 1979.

41. Acute and chronic toxicity of vanadium to fish. 1978.

42. Analysis of fur production records for registered traplines in the AOSERP study area, 1970-1975.

43. A socio-economic evaluation of the recreational use of fish and wildlife resources in Alberta, with particular reference to the AOSERP study area. Vol. 1: summary and conclusions. 1979.

44. Interim report on symptomology and threshold levels of air pollutant injury to vegetation, 1975 to 1978.

45. Interim report on physiology and mechanisms of air-borne pollutant injury to vegetation, 1975 to 1978.

46. Interim report on ecological benchmarking and biomonitoring for detection of air-borne pollutant effects on vegetation and soils, 1975 to 1978.

47. A visibility bias model for aerial surveys of moose in the AOSERP study area. 1979.

48. Interim report on a hydrogeological investigation of the Muskeg River basin, Alberta. 1979.

49. The ecology of macrobenthic invertebrate communities in Harley Creek, northeastern Alberta.

50. Literature review on pollution deposition processes. 1979.

51. Interim compilation of 1976 suspended sediment data for the AOSERP study area. 1979.

52. Plume dispersion measurements from an oil sands extraction plant, June 1977.

53. Baseline states of organic constituents in the Athabasca River system upstream of Fort McMurray. 1979.

54. A preliminary study of chemical and microbial characteristics of the Athabasca River in the Athabasca oil sands area of northeastern Alberta. 1979.

55. Microbial populations in the Athabasca River. 1979.

56. The acute toxicity of saline groundwater and of vanadium to fish and aquatic invertebrates. 1979.

57. Ecological habitat mapping of the AOSERP study area (supplement): Phase I. 1979.

58. Interim report on ecological studies on the lower trophic levels of Muskeg rivers within the AOSERP study area. 1979.

59. Semi-aquatic mammals: annotated bibliography. 1979.

60. Synthesis of surface water hydrology. 1979.

61. An intensive study of the fish fauna of the Steepbank river watershed of northeastern Alberta. 1979.

62. Amphibians and reptiles in the AOSERP study area. 1979.

63. Analysis of AOSERP plume sigma data. 1979.

64. A review and assessment of the baseline data relevant to the impacts of oil sands developments on large mammals in the AOSERP study area. 1979.

65. A review and assessment of the baseline data relevant to the impacts of oil sands development on black bear in the AOSERP study area. 1979.

66. An assessment of the models LIRAQ and ADPIC for application to the Alberta oil sands area. 1979.

67. Aquatic biological investigations of the Muskeg River watershed. 1979.

68. Air system summer field study in the AOSERP study area, June 1977.

69. Native employment patterns in Alberta's Athabasca oil sands region. 1979.

70. An interim report on the insectivorous animals in the AOSERP study area.

71. Lake acidification potential in the AOSERP study area. 1979.

72. The ecology of five major species of small mammals in the AOSERP study area: a review. 1979.

73. Distribution, abundance, and habitat associations of beavers, muskrats, mink, and river otters in the AOSERP study area, northeastern Alberta. 1979.

74. Air quality modelling and user needs. 1979.

75. Interim report on a comparative study of benthic algal primary productivity in the AOSERP study area. 1979.

76. An intensive study of the fish fauna of the Muskeg River watershed of northeastern Alberta. 1979.

77. Overview of local economic development in the Athabasca oil sands region since 1976. 1979.

78. Habitat relationships and management of terrestrial birds in northeastern Alberta. 1979.

79. The multiple toxicity of vanadium, nickel, and phenol to fish. 1979.

80. History of the Athabasca oil sands region, 1890 to 1960's. Volume I: socio-economic developments. Volume II: oral history. 1980.

81. Species distribution and habitat relationships of waterfowl in northeastern Alberta. 1979.

82. Breeding distribution and behaviour of the White Pelican in the Athabasca oil sands area. 1979.

83. The distribution, foraging behaviour and allied activities of the White Pelican in the Athabasca oil sands area. 1979.

84. Investigations of the spring spawning fish populations in the Athabasca and Clearwater rivers upstream from Fort McMurray: Volume I. 1979.

85. An intensive surface water quality study of the Muskeg River watershed. Volume 1: water chemistry. 1979.

86. An observational study of fog in the AOSERP study area. 1979.

87. Hydrogeological investigation of Muskeg River basin, Alberta. 1980.

88. Ecological studies of the aquatic invertebrates of the AOSERP study area of northeastern Alberta. 1980.

89. Fishery resources of the Athabasca River downstream of Fort McMurray, Alberta: Volume 1. 1989.

90. A wintertime investigation of the deposition of pollutants around an isolated power plant in northern Alberta. 1980.

91. Characterization of stored peat in the Alberta oil sands area. 1980.

92. Fisheries and habitat investigations of tributary streams in the southern portion of the AOSERP study area. Volume 1: summary and conclusions. 1980.

93. Fisheries and aquatic habitat investigations in the MacKay River watershed of northeastern Alberta. 1980.

94. A fisheries and water quality survey of ten lakes in the Richardson Tower area, northeastern Alberta. Volume 1: methodology, summary, and discussion. 1980.

95. Evaluation of the effects of convection on plume behaviour in AOSERP study area. 1980.

96. Service delivery in the Athabasca oil sands region since 1961. 1980.

97. Differences in the composition of soils under open and canopy conditions at two sites close-in to the Great Canadian Oil Sands operation, Fort McMurray, Alberta. 1980.

98. Baseline condition of jack pine biomonitoring plots in the Athabasca oil sands area: 1976-1977.

99. Synecology and autecology of boreal forest vegetation in the AOSERP study area. 1980.

100. Baseline inventory of aquatic macrophyte species distributions in the AOSERP study area. 1980.

101. Woodland caribou populations dynamics in northeastern Alberta. 1980.

102. Wolf population dynamics and prey relationships in northeastern Alberta. 1980.

103. Analysis of the leisure delivery system 1972-1979, with projections for future servicing requirements.

104. Review of requirements for air quality simulation models. 1980.

105. Approaches to the design of a biomonitoring program using arthropods as bioindicators for the AOSERP study area. 1980.

106. Meteorological factors affecting ambient $SO_2$ concentrations near an oil sands extraction plant. 1980.

107. Small mammal populations of northeastern Alberta. Volume I: populations in natural habitats. 1980.

108. Small mammal populations of northeastern Alberta. Volume II: populations in reclamation areas. 1980.

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122. Soil inventory of the AOSERP study area.

123. Circulation of water and sediment in the Athabasca delta area. 1981.

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130. Climatological analysis of recent data from the Athabasca Oil Sands area. 1984.