

EFFECT OF SULPHUR DIOXIDE ON PRECIPITATION  
AND ON THE SULPHUR CONTENT AND  
ACIDITY OF SOILS IN  
ALBERTA, CANADA

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ABSTRACT

Rain and snow in Alberta are seldom acid. The S content of snow is so low that the snow pack gives a deposition of less than 1 kg S/ha, even downwind from large SO<sub>2</sub> emission sources. Rainfall contributes at the most 4 kg S/ha yearly near SO<sub>2</sub> sources, and only about 1 kg S/ha in clean areas. However, rain intercepted by forest trees exposed to SO<sub>2</sub> emission becomes acid (pH 3.5 to 4.5) and has a S content of 3 to 4 times greater than rain. Soils absorb large amounts of S from emissions (up to 50 kg S/ha annually) but much of the S is found in non-sulphate form. Soils are slowly acidified by the SO<sub>2</sub> at a rate estimated at 1 pH unit in 10 to 20 years. Water surfaces will absorb SO<sub>2</sub> emissions at a rate of about 4 to 15 kg S/ha annually. Particulates deposit 3 to 4 times as much S as is deposited by rainfall.

INTRODUCTION

Sulphur gas emission from natural gas processing and oil sand extraction annually contributes about 225,000 tonnes of sulphur (S) to the atmosphere in Alberta. The S content of rain and snow was measured in Central Alberta more than five years ago and showed only 2 to 4 kg S per ha annual deposition (Walker, 1969). Central Alberta contains half of the S gas emissions in the province, and deposition of 2 to 4 kg S per ha yearly indicates a wide dispersion of S gas in Alberta and beyond.

Our work during the last two years has shown that the S content in dry fallout is often greater than ten times the S content in wet fallout,

in non-forested areas. Wet fallout intercepted by a forest canopy was found to contain up to four times the S content of free wet fallout. In both forested and agricultural areas the cumulative S contribution of wet fallout and dry fallout was sufficient to cause soil acidification. The approximate rate of acidification was estimated at 1 pH unit reduction per 10 to 20 years of emission.

#### METHODS AND MATERIALS

Ninety-three fallout monitoring stations (Figure 1) were installed in Alberta and Western Saskatchewan. Site locations were based on source distributions and prevailing winds.

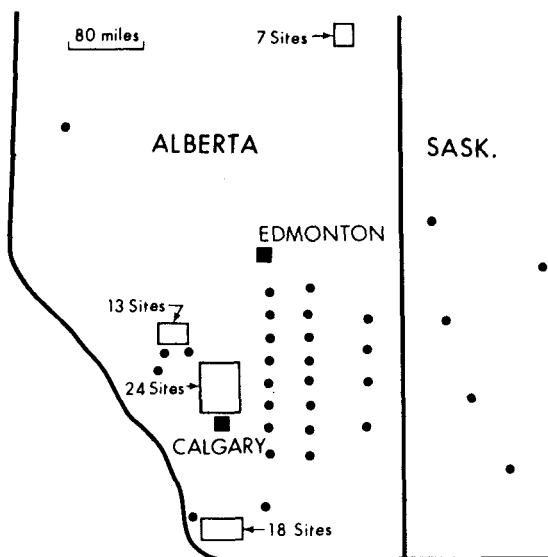


Figure 1. Location of sulphur monitoring stations in Alberta

Rain was collected weekly at each site over a four month period during the summers of 1973 and 1974. Snow was sampled at selected stations during late winter. Two types of intercepted wet fallout (throughfall and stemflow) were measured at eight selected sites in 1973 and at 18 sites in 1974. Wet fallout samples were analyzed to determine pH and  $\text{SO}_4\text{-S}$ .

Particulate fallout was measured at 11 selected stations from July to October, 1974 using a modified Nipher gauge. Particulates were analyzed for  $\text{SO}_4\text{-S}$  content.

In addition at all stations the rate of  $\text{SO}_2$  absorption by soils and resultant pH depression were determined. Replicated samples of three soil types common to all stations were used for this study.

One-litre containers of soil were placed under a solid roof (closed canopy) at each station so that they received no wet fallout but were exposed to free air movement (wind) under the roof. All containers were watered, up to field capacity, weekly. As well, at selected stations, similar soil containers were placed in the open, subjected to all fallout. The latter containers were of two types, with plants (barley, alfalfa, bromegrass) and without plants. The vertical pH gradient and  $\text{SO}_4\text{-S}$  gradient over the 12 cm soil depth was determined in each soil container.

At each station, the absorption of  $\text{SO}_2$  by a free water surface under a closed canopy (roof) was also measured. In addition, at six stations standard soil containers, using a 5 cm surface layer of live sphagnum peat moss as the upper soil layer, were exposed to wet and dry fallout.

The  $\text{SO}_4\text{-S}$  was determined by a modification of the method of Dean (1966). The  $\text{SO}_4\text{-S}$  in rain and snow was taken as being total S after it was found the S in rain and snow was in  $\text{SO}_4\text{-S}$  form. The total S of soils and plants was determined by digesting in nitric and perchloric acids and the  $\text{SO}_4\text{-S}$  was measured on the digests.

## RESULTS AND DISCUSSION

### 1. pH AND $\text{SO}_4\text{-S}$ IN WET FALLOUT

The results of  $\text{SO}_4\text{-S}$  and pH determinations in snow at stations surrounding an oil sand extraction plant in a forested area are shown in Table 1. Below the hatched line in the table are results from a site in Northern Saskatchewan located 450 km away from any S emission sources.

The daily gaseous emission of S from the plant shown in Table 1 exceeds 150 tonnes. The total winter accumulation of S in the snow pack five km from the plant was less than 1 kg/ha, only slightly greater than accumulation 450 km distant. Noting that 150 tonnes/day could represent the deposition of 1 g of S per day on a land area of 150,000 ha, it is apparent that the contribution of  $\text{SO}_4\text{-S}$  in snowfall during the winter months is insignificant. Similar results were found in the vicinity of a gas processing plant in a forested area emitting 84 tonnes of gaseous S per day with  $\text{SO}_4\text{-S}$  content of 0.15 to 0.82 kg/ha in the snow pack. Similarly, the pH of snow pack adjacent to S emission sources was nearly the same value as the pH of the snow pack in remote Western Canada sites (approximately pH 5 to 6).

Table 1. The soluble sulphur and pH of snow near an oil sand plant in the Spring of 1974

Distance and Direction from Plant	Date	S in Snow (kg SO <sub>4</sub> -S per ha)	pH of Snow
3 km N.W.	February 22	0.18	4.7
3 km N.W. (on river)	February 22	0.60	5.2
5 km South	February 22	0.15	5.2
10 km South	February 22	0.48	4.8
55 km S.W.	February 22	0.33	5.2
2.5 km S.E.	April 10	0.20	5.0
4 km S.E.	April 10	0.21	5.4
24 km S.W.	April 10	0.25	5.2
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Northern Sask.	February 8	0.10	5.0

Table 2 gives results of pH and SO<sub>4</sub>-S determinations in rain

Table 2. Characteristics of rain during a 3-month period in the summer of 1973 in Alberta

Location	Number of Stations	Average pH	Average SO <sub>4</sub> -S Content (ppm)	S Brought Down by Rain (kg/ha/3 months)
Remote Station	4	6.3	0.7	0.5
Exposed Station				
Southern Plant	4	6.3	2.7	1.5
Calgary-Olds Area	24	6.7	1.6	1.5
West Central Forest	6	5.5	1.5	1.9
Northern Forest	2	6.2	1.4	1.5

collected in the vicinity of four S emission areas and in remote stations during the summer of 1973. As is shown rain is approximately five times higher in S concentration than snowfall. This is true both for remote stations and stations close to S sources. Notice that even though the SO<sub>4</sub>-S concentration is high enough to indicate a pH of 3 to 4 in pure water, most rains in this region are rich in cations, resulting in near-neutral pH readings. It must be noted that, once again, the S concentration in rainfall is insignificant in terms of the total daily emissions of gaseous S in Alberta. The results in Table 2 are for June, July and August, the months which get the majority of rainfall, and as shown those three months get the most S emission in the rainfall. Considering both rain and snow, deposition of S in precipitation is at most 4 to 5 kg/ha annually near emission sources, and at least 1 to 2 kg/ha in areas remote from sources.

Rain became strongly acid when intercepted by forest trees exposed to S emissions (Baker, Hocking and Nyborg, 1973). The increased acidity of the intercepted rain in exposed areas was accompanied by increased  $\text{SO}_4\text{-S}$  content (Nyborg, et al., 1975). Table 3 shows the

Table 3. Sulphur deposition by rain and by spruce throughfall

Location	Sulphur Deposition (kg/ha/Month)	
	Rain	Throughfall
Controls (2 sites)	0.1	0.2
*Exposed (3 sites)	0.7	2.6

\*Within 8 km of oil sand extraction plant.

deposition of S in both rain and throughfall at controls and exposed sites. Deposition of S in throughfall was only 0.2 kg/ha/month at remote controls, but was 2.6 kg/ha/month at exposed sites. Apparently S gases were absorbed on trees and then washed off by intercepted rain and this is one of the main ways S is deposited in Alberta forests.

## 2. ACIDIFICATION OF SOIL AND AMOUNT OF SULPHUR DEPOSITION BY DRY FALLOUT

The pH of soils after being kept in containers under closed canopies is shown in Figure 2. In an area of more than 1,000 square km

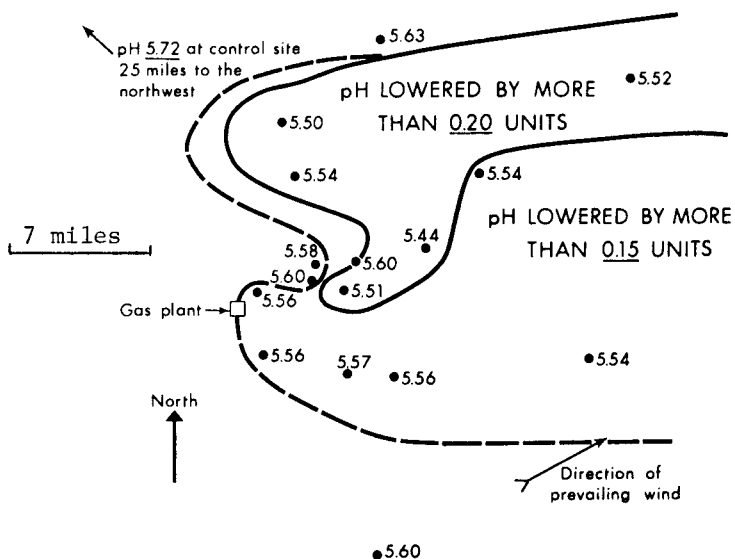


Figure 2. The pH of two soils (0-12 cm depth) under closed canopies for three months in southern Alberta. Control pH = 5.72

downwind from a gas processing plant in Southern Alberta, the pH was depressed by at least 0.15 units in a period of three months. Figure 3

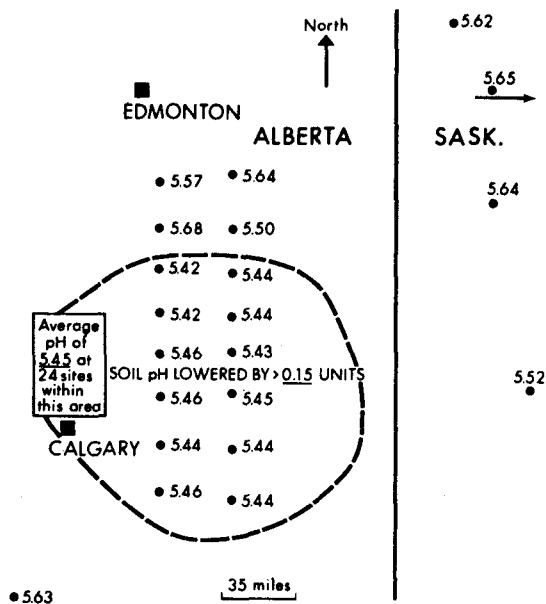


Figure 3. Average pH of top 5 cm of two soils under closed canopies for three months in 1973, in central Alberta and Saskatchewan

gives results of pH depression of soils under closed canopies for the central region of Alberta for the same three month period. Within an area of 25,000 square km the pH was depressed on approximately 0.15 units. One-half of the S emissions in Alberta are emitted upwind from this study area.

Table 4 gives results of pH determination on soil containers under

Table 4. The pH of two soils exposed to the atmosphere for 3 months in 1973 at stations from different areas of Alberta and Saskatchewan

Location	Major Vegetation	Number of Stations	Size of Area in Which Stations Located (Km <sup>2</sup> )	Average pH of Soil	
				0-1 cm	0-5 cm
Remote Controls	Prairie & Forest	4	--	5.50	5.64
<u>Exposed Sites</u>					
Waterton Plant	Prairie	18	1,200	5.43	5.46
Central Alberta	Prairie	36	25,000	5.40	5.45
Ram River Plant	Forest	8	500	5.26	5.55
Oil Sand Plant	Forest	2	--	5.17	5.54

closed canopies after three month exposures in prairie and forested areas. It is seen that pH depression in the forested sites is only half as great as that in prairie sites. Nevertheless, considering the cumulative pH depression over a period of several years, soil forests may be seriously acidified. Our technique was setting bare soils in containers that were on a shelf 0.5 m above the ground and the experimental soils were therefore probably more exposed to SO<sub>2</sub> than were natural soils. However, this experiment demonstrates that soils will be acidified by SO<sub>2</sub> emission, regardless of the exact rate in natural soils.

Table 5 shows the amount of SO<sub>4</sub>-S gained by bare uncovered soil.

Table 5. Sulphur brought down in rain and gained by bare soil from June 1 to September 1 at stations near a gas processing plant

Location of Station		SO <sub>4</sub> -S (km/ha)	
Direction	Distance From Plant (km)	In Rain	Gained by Soil
Directly Downwind	2	2.0	20.1
	6	1.5	12.1
	10	1.3	10.3
Not Directly Downwind	5	1.8	8.0
	11	1.0	5.4
	11	1.4	3.8

This amount is up to ten times as much detected in rainfall. At the six stations located 11 km or less from a gas plant, the soils gained from 3.8 to 20.1 kg/ha of SO<sub>4</sub>-S. However, some soils store little or no SO<sub>4</sub>-S from S emission, but instead they convert SO<sub>4</sub>-S to forms that can be found in analysis for total S. An example is shown in Table 6 from four stations. Calculating from the S content of crop and the SO<sub>4</sub>-S content of the soil, the soil and crop apparently gained from 15 to -2 kg/ha of S emissions. However, using the same calculation but using total S rather than SO<sub>4</sub>-S, the gain of the soil was 53 to 13 kg/ha. On this soil most of the S emissions do not remain as SO<sub>4</sub>-S. Further, crops grown on the soil took up only 1 to 2 kg/ha of S when fertilized with 22 kg/ha of S which was not recovered as SO<sub>4</sub>-S in the soil.

An experiment was conducted with a controlled chamber containing an atmosphere with 24 parts per billion (ppb) of SO<sub>2</sub> (Table 7). This laboratory experiment verifies field results on the absorption of SO<sub>2</sub> by soils and the consequent depression of pH. After 30 days of

Table 6. The  $\text{SO}_4\text{-S}$  and total S in a cropped soil kept in containers 3 months at stations near a gas processing plant

Distance from gas plant (Km)	Crop uptake of S (kg/ha)		Change in $\text{SO}_4\text{-S}$ of soil during cropping (kg/ha)	Gain in total S by non-S fertilized soil and plants (kg/ha)
	NPK*	NPKS*		
2	11	13	+3	47
6	8	9	-2	12
16	8	9	+1	37
37	**	**	+15	53

\* The NPK treatment received nitrogen, phosphorus, and potassium fertilizers. The NPKS treatment received in addition sulphur at a rate of 22kg S/ha in form of  $\text{Na}_2\text{SO}_4$ .

\*\* Plants were not grown in containers at this station.

Table 7. Effect of exposed to 24 ppb of  $\text{SO}_2$  for 30 days on soils, spruce bark, forest litter, and water (Temperature 20°C, relative humidity, 40%)

Material	Soluble $\text{SO}_4\text{-S}$ (ppm)		Total S (ppm)		pH	
	Control	Change on Exposure	Control	Change on Exposure	Control	Change on Exposure
<u>Soils</u>						
Chernozemic	3.2	+ 8.0	187	+16	6.04	-0.13
Luvisolic	3.0	+ 9.0	174	+18	5.86	-0.10
Luvisolic + 5% $\text{CaCO}_3$	7.4	+14.5	182	+30	0.21	-1.23
<u>Spruce Bark</u>	54.2	+30.0	--	--	--	--
<u>Forest Litter</u>	46.7	+35.6	--	--	--	--

exposure to 24 ppb of  $\text{SO}_2$ , two soils which were kept in 1-cm deep in open containers increased their  $\text{SO}_4\text{-S}$  content by 8 or 9 ppm. However, the total S of the soils had increased by twice as much, demonstrating that soils can convert  $\text{SO}_2$  into a non-sulphate form. Also, the pH of soils decreased by approximately 0.1 units. Bark and forest litter exposed at the same time gained about 30 ppm of  $\text{SO}_4\text{-S}$ . This experiment shows that  $\text{SO}_2$ , at concentrations not much above those found downwind from emissions, is absorbed by soils at a surprisingly high rate.

A preliminary experiment on absorption of  $\text{SO}_2$  by live sphagnum was conducted in the field. The sphagnum was obtained from an area remote from  $\text{SO}_2$  emissions, placed in pots and set out at six sites.



Table 8. The soluble sulphate content of the top 2.5 cm of live sphagnum moss set out for 8 weeks at 4 stations near an oil sand plant and at 2 control stations

Distance and Direction of Stations from Plant	Soluble SO <sub>4</sub> -S (ppm) of Top 2.5 cm of Moss
<u>Exposed Sites</u>	
2 km East	96
4 km East	100
8 km East	98
8 km South	122
<u>Control Sites</u>	
24 km SW	46
54 km SW	43

After eight weeks moss gained about 50 ppm of soluble SO<sub>4</sub>-S at sites near a SO<sub>2</sub> emission source as compared to control sites.

### 3. OTHER WAYS OF DEPOSITION OF SO<sub>2</sub> EMISSION

Absorption of S by a free water surface kept under a closed canopy was measured at each station in 1974. The absorption of S varied from 4 to 15 kg/ha per six months (the season of open water). In forested areas absorption by water was low in heavily treed sites and higher in open sites. These measurements would best be made over bodies of water so wind is restricted. Nevertheless, the crude measurements do indicate that over open waters there is more S deposited by absorption of SO<sub>2</sub> than there is deposition of S in rainfall.

Preliminary measurements were made in 1974 of the S fallout in dry particulates. In Central Alberta at six sites the S fallout averaged 0.28 pounds S/acre/week (equal to 0.32 kg S/ha/week), and little or none at sites remote from emissions in Saskatchewan (Figure 4). In Central Alberta and S fallout by dry particulates was 3.5 times the deposition of S by rainfall.

### GENERAL DISCUSSION

In Alberta rain and snow are usually not strongly acid, and deposit not more than 4 kg S/ha annually. When the ground is covered with snow (about five months of the year) the SO<sub>2</sub> emissions mostly drift out of Alberta because the snow pack contains only about 0.5 kg S/ha. However, for the rest of the year there are several ways other than rainfall in which SO<sub>2</sub> emissions are deposited--direct absorption

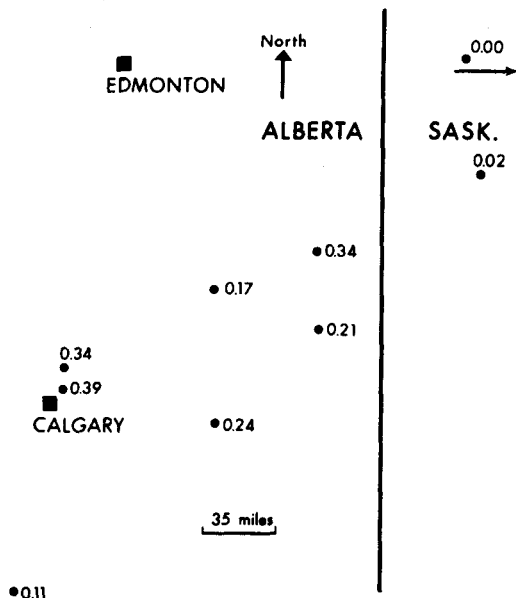


Figure 4. Apparent amount of sulphur deposited as particulates, in central Alberta and Saskatchewan (lb. S/acre/week)

by soils and water, intercepted rainfall by trees, and fallout of particulates containing S. Our estimate is that as much as 50 kg S/ha are deposited for 20 to 30 km downwind from large single emission sources. A small but measurable depression in soil pH accompanies the increase in S content of soils.

The acidification of soils is a long term effect of SO<sub>2</sub> emission. The acidification accumulates year after year, and soils remain acid even after SO<sub>2</sub> emissions have ceased. Soils can be returned to their pH only by application of lime.

Assume that in Alberta S from emissions is deposited mostly locally for 7 months of the year when the ground is free of snow. If the S was deposited on 2,000,000 ha it would average a rate of 50 kg S/ha. Considering the buffering ability of Alberta soils, the deposition of 50 kg S/ha annually would result in a drop in pH of 0.5 to 1.5 units in the top 15 cm of soils after a period of 10 to 20 years. Returning the soils to original pH would need about 2 tonnes of lime/ha. Agricultural soils are easily limed by spreading the lime and working in. It may not be practical to lime Alberta forest soils, because lime usually needs to be worked into soils under our conditions of low rainfall.

Unfortunately, the problem of acidification of soils in Alberta by SO<sub>2</sub> emissions is not all that simple (Nyborg et al., 1973; Hocking and Nyborg, 1974). We do not know what proportion of emitted S is deposited as H<sub>2</sub>SO<sub>4</sub> as compared to neutral salts. The amount of S gained by soils from SO<sub>2</sub> emissions can be determined only by total S

analysis which is a rather imprecise method. The depression in soil pH from exposure to SO<sub>2</sub> emissions for a year is at most 0.1 to 0.2 units, which is less than natural temporary shifts in soil pH with seasonal or yearly changes in biological activity. Consequently, results on rate of soil acidification by SO<sub>2</sub> emission are only approximate.

#### ACKNOWLEDGEMENTS

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