Sulphur Isotope Fractionation

in Smelter Emission Streams and Precipitation

Sudbury, Ontario.

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ABSTRACT

International Nickel Company's 1250 ft. stack located in Sudbury, Ontario emits an estimated 3,000 tons of sulphur oxide daily. The purpose of this study is to investigate the use of stable sulphur isotopes as a means of tracing the movement of these sulphur oxide emissions. Sulphur isotope analysis were done for lakewater, rainwater and sediment samples taken from the Sudbury-Timagami district and also for particulate and gas samples taken from the 600 ft. level of the International Nickel Company's 1250 ft. stack.

The δS^{34} values of lake surface samples showed a decrease related directly to the increase of the logarithm of the distance from Sudbury. The maximum δS^{34} value for the lakewater samples was + 8.49 p.p.t. at a distance of 7 miles from Sudbury. The minimum δS^{34} value for lakewater samples was +2.97 p.p.t. at a distance of 55 miles from Sudbury.

The rainwater δS^{34} values vary from + 4.85 p.p.t. recorded for a station 5 miles north of Sudbury to + 2.07 p.p.t. for a station 60 miles east north east of Sudbury.

The increase in δS^{34} values in the lakewater relative to rainwater strongly suggest that the oxidation of $SO_{2(g)}$ to SO_4^{2-} is occurring in the lakes in the Sudbury-Timagami district.

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INTRODUCTION

Statement of Problem

The fate of particulate and sulphur oxide emitted by Sudbury's metal ore smelting industry is a major environmental concern. The degree and spatial extent of environmental damage as a result of International Nickel Company's 1250 ft. stack is a subject of much debate. The exact process of sulphur oxide removal and the quantity removed in the locality are not clearly understood. The intent of this research is to use stable sulphur isotopes as a means to assess the role of sulphur oxide emissions in the Sudbury district.

Setting

The Sudbury area has encountered environmental problems as a result of the emission of particulate and gaseous pollutants by the metal ore smelting industry. Sudbury particulate emissions have been estimated at 3.4×10^4 tons for the year 1972 (Ministry of Environment, 1972). The effect of the erection of the International Nickel Company's 1250 ft. stack on previously outlying area is a subject of continuing concern. The lakes of the Sudbury region are relatively deep, acid shield lakes, due to the sulphate loading by precipitation. It has been shown (Conroy, Jeffries, Kramer, 1973, unpublished) that the pH of lakes under heavy sulphate loading is determined by the availability of calcium ions to the lake water. The Lorrain quartzite lakes have a pH less than 5; while, lakes with portions of their drainage basin covered with glacial till have pH

of approximately 7. The dominant lithologies of the Sudbury-Timagami district are shown in Figure 1. The six major drainage basins are shown in Figure 2.

Approach to Problem

The use of stable sulphur isotopes as an environmental research tool in the Sudbury district is favoured by the following facts:-

1) Sudbury is a large sulphur oxide emitting source, surrounded by hundreds of square miles of relatively non industrialized land.

2) The many hundreds of lakes in the area enable lake-water sulphur isotope samples to be taken at various distances and orientations from Sudbury.

3) The dominance of the International Nickel Company's 1250 ft. stack over other Sudbury sulphur oxide emitters enable the use of the sulphur oxide of this stack to be used as a tracer.

The measurements of the pH, Eh, metal concentration, sulphate concentration and other physical parameters in air, rainwater, lakewater, lake sediment and soil samples will give an estimate of emissions removal. However, through the use of stable sulphur isotopes it is possible to trace the $SO_{2(g)}$ movement in the environment. An understanding of the net sulphate contamination and its effect on the environment must be known to deal constructively

Figure (1)   Sketch Map of Geology of Sudbury-Timagami Region

SUDBURY - TIMAGAMI
REGION

SCALE 1:250,000

TIMAGAMI

47°00'

LAKE
WANAPITEI

SUDBURY

Legion

S   Keweenan
O   Gowganda
X   Lorrain
// Archean
Unconsolidated Sediments
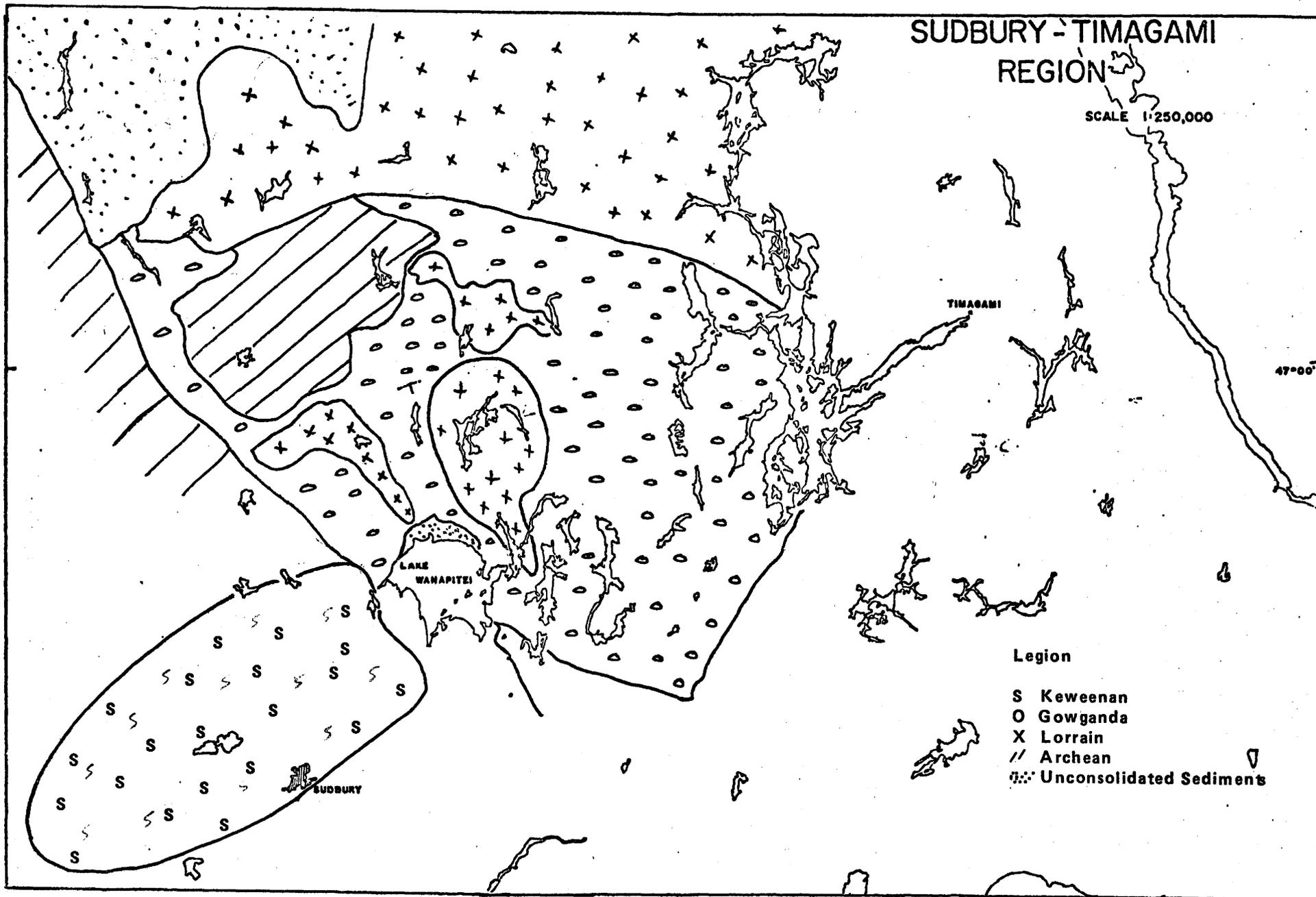
Figure (2)   Sketch Map of Drainage Basins of Sudbury-Timagami Region

SUDBURY - TIMAGAMI REGION

SCALE 1:250,000

Mattagami

Wanapitei

LAKE WANAPITEI

TIMAGAMI

47°00'

Ottawa

Sturgeon

Vermilion

SUDBURY

Veuve
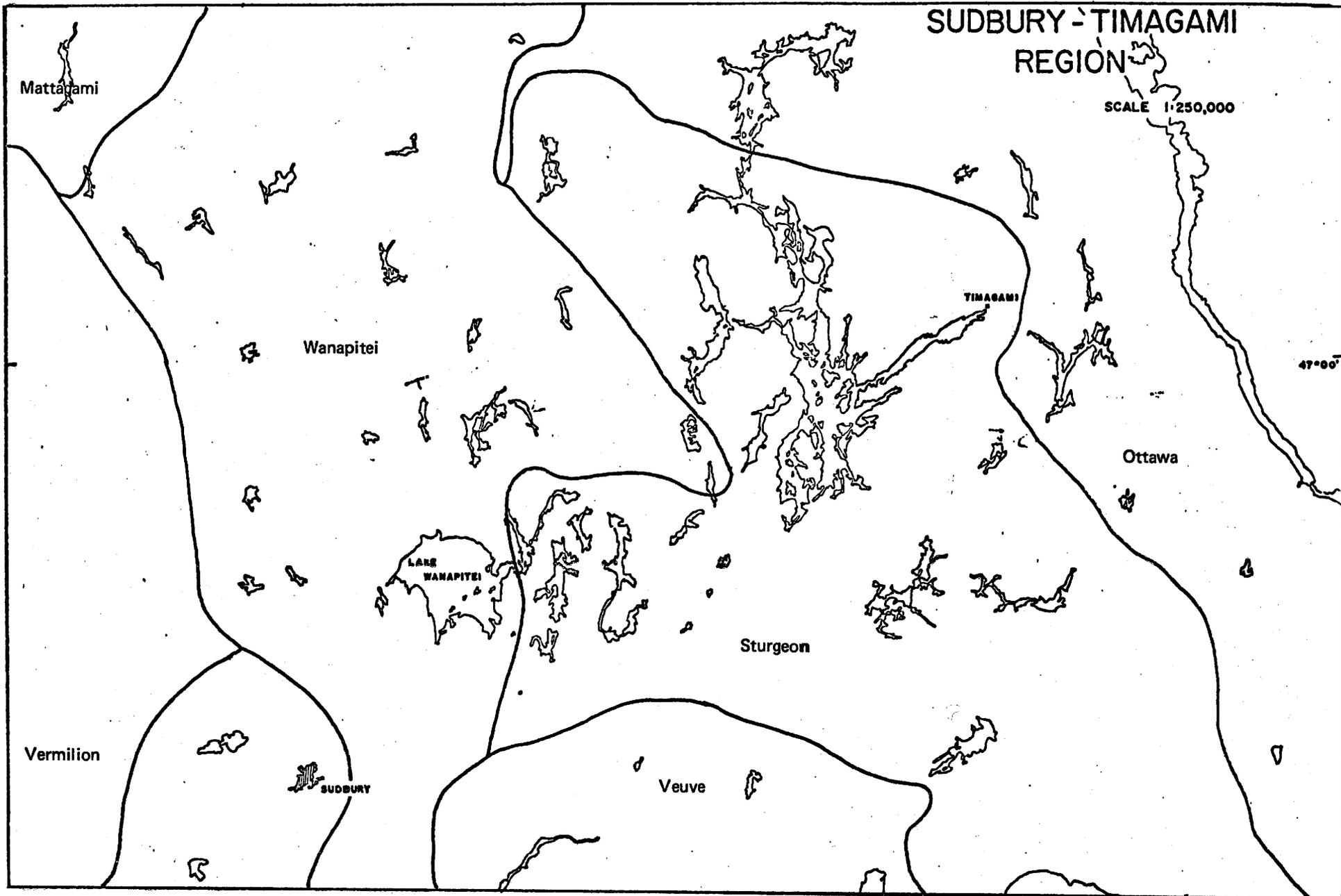
with the Sudbury sulphur problem. Also, the processes at work must be clearly understood.

Removal of sulphur dioxide from the atmosphere by rainfall will fractionate the sulphur isotopes. The heavy isotopes will be enriched in the more highly oxidized SO_4^{2-} molecules. As a result, the plume $SO_{2(g)}$ will become depleted with respect to the heavy isotopes with distance from the source. Sulphur isotope analysis of plume samples, or rainwater samples, taken at various distances would show a change in $\leqslant S^{34}$ related to the rate of removal.

BACKGROUND SULPHUR ISOTOPE THEORY

Isotopes are defined as atoms whose nuclei contain the same number of protons but differing number of neutrons. Stable isotopes, such as those of sulphur, have a decay rate lower than the present day detection limits. The fractionation of isotopes in nature is due to the physical and chemical diffences between the isotopes. For two isotopes of the same element, the lighter isotope will have the larger zero point energy due to its higher vibrational energy. Thus, bonds formed by the lighter isotope will be weaker and preferentially destroyed in chemical reactions. In general, the heavier isotope will concentrate in the reactions and the lighter isotope in the products.

Fractionation may be due to kinetic effects such as one isotopic species diffusing faster than another or by isotopic exchange reactions between substances, phases or molecules. However, most natural fractionation processes are a combination of the two and may be considered physio-chemical effects. Example of processes involving isotopic fractionation are condensation, crystallization, evapouration, melting, absorption, desorption and diffusion.

Sulphur has four stable isotopes with the following average abundance (Namara and Thode, 1950) in percents:- S^{32} - 95.02, S^{33} - 0.75, S^{34} - 4.21 and S^{36} - 0.02. The isotope S^{35} is radioactive and is not found in nature.

For atmospheric fractionation of sulphur isotopes, liquid to gas phase changes and possible diffusion effects would be suspect mechanism. For sediment sulphur isotope fractionation desorption, adsorption, and chemical processes aided by bacterial activity would be major contributors. In the case of lakewater, isotopic fractionation of sulphur would be limited to phase changes.

Sulphur from the Canyon Diablo meteorite is used as a standard for most sulphur isotope work. The ratio of S^{32}/S^{34} of the Canyon Diablo sulphur is 22.210 and deviations of samples from this value are expressed in terms of a "del S^{34} value" as given in the following expression.

$$\delta S^{34} = \frac{S^{32}/S^{34} \text{ (standard)} - 1}{S^{32}/S^{34} \text{ (sample)}} \times 1000$$

The δS^{34} value for a field sample will be a result of a weighted average of all contributing sources. The "del S^{34} value" will be changed by physio-chemical processes and will be a strong tool in assessing effectiveness of physio-chemical activities on SO_2.

In general, the oxidation of a substance result in an increase in δS^{34} value in the products and a decrease in the reactants.

PREVIOUS WORK

Sulphur Oxide Processes

Fractionation of sulphur isotopes may occur during incomplete combustion of metal sulphides during the smeltering processes. Further oxidation of $SO_{2(g)}$ may occur in the stack according to the following reaction.

$$SO_2 + \tfrac{1}{2} O_2 \xrightarrow{K} SO_3 \tag{1}$$

The reaction rate is very fast at high temperatures but the equilibrium yield is very low. Flue gases have been found to contain 25 p.p.m. SO_3 relative to 1000 p.p.m. SO_2 (Equation (1)). The ratio of oxidation of SO_2 may be aided by catalysts such as nitrogen dioxide. This catalytic effect is limited by the dominance of nitrogen monoxide over nitrogen dioxide in the stack and by extreme slow rate of reaction in the atmosphere:

$$2NO + O_2 \longrightarrow 2NO_2 \tag{2}$$

In general, fractionation in the stack is limited by low yields of products at high temperatures.

In the atmosphere sunlight may aid the reaction:

$$SO_2 + \tfrac{1}{2} O_2 \longrightarrow SO_3 \tag{3}$$

The reaction of sulphur dioxide and $\tfrac{1}{2} O_2$ to produce SO_3. If one

considers the amount of ozone in the atmosphere relative to water content, reactions with water in the plume will be dominant.

The oxidation of $SO_{2(g)}$ by water may proceed by two methods.

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad (4)$$

or

$$SO_2 + H_2O + \tfrac{1}{2} O_2 \rightarrow H_2SO_4 \qquad (5)$$
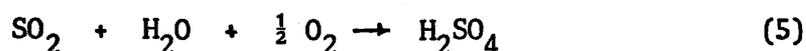
The effect of reaction (4) will be limited by low solubility of SO_2 in water. Reaction (5) will be aided by metal ion or any strong oxidizing agent. It has been shown (Yamamoto and Ohtake, 1955) that large particles act as condensation nuclei:

	radius (um)				
Size Distribution	0.1-0.2	0.2-0.4	0.4-0.6	0.6-1.0	1.020
Percentage acting as Condensation nuclei	0.4	2	17	60	100

Since mixing with ambient air in the plume will offset the effects of fractionation by diffusion, the fractionation during the reaction of $SO_{2(g)}$ with $H_2O(1)$ has been the subject of much investigation (Hales, Thorp and Wolf, 1970). They investigated the effect of the acidity of condensation droplets on the solubility of $SO_{2(g)}$.

The solubility of $SO_{2(g)}$ in low concentrations decreases with decreasing pH of condensate. The lowering of the pH of the condensate by reactions other than the oxidation of $SO_{2(g)}$ effectively reduces the amount of dissolved $SO_{2(g)}$ in the water droplet.

Figure (3)   Dependency of Solubility of $SO_{2(g)}$ on Excess Acidity of Precipitation, (Hales, Thorp and Wolf).
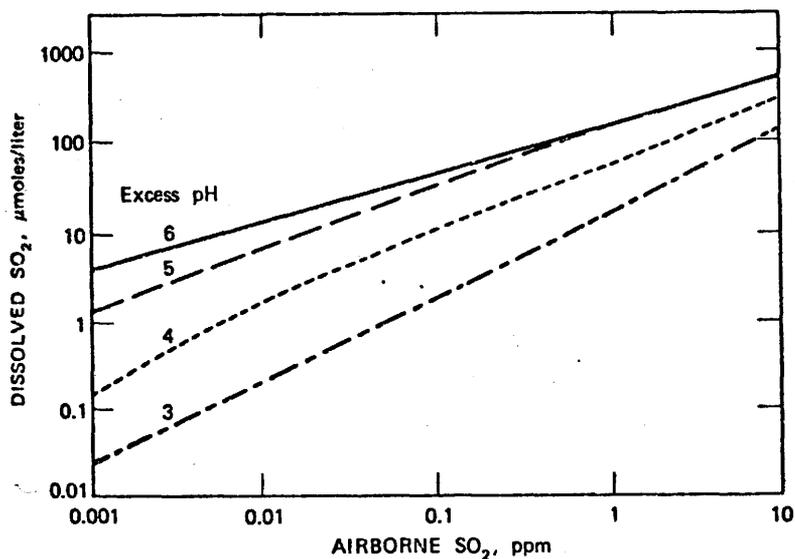
The $SO_{2(g)}$ adsorbed during condensation may be desorbed during the subsequent fall through the cleaner air under the plume. The absorption/desorption process has been illustrated by Hale, Thorpe and Wolf and is given in Figure (4).

Figure (4)   Concentration of $SO_{2(g)}$ as a function of droplet fall

distance.
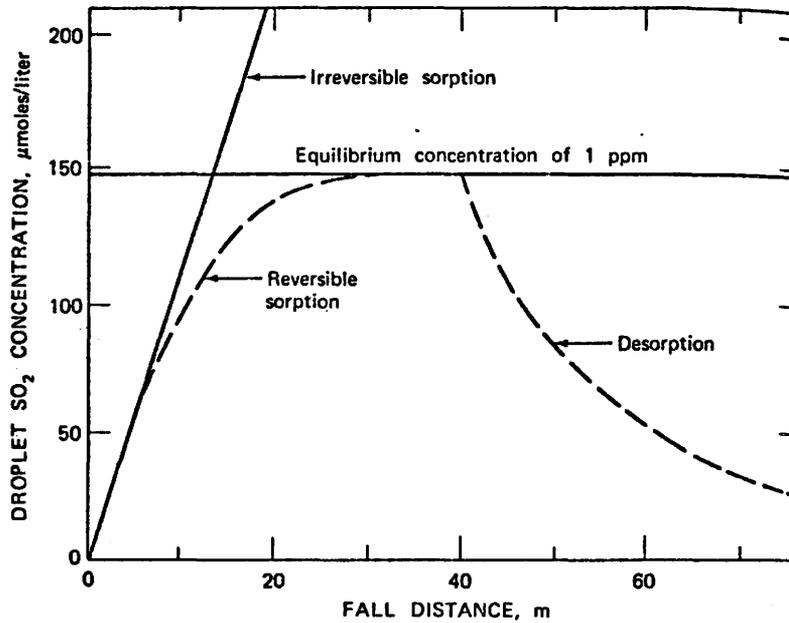
In absence of a catalyst the oxidation of $SO_{2(g)}$ to SO_4^{2-} is quite small. (Junge 1969) predicts the concentration of $SO_{2(g)}$ in the concentration of $SO_{2(g)}$ in the cloud water may be calculated by the formula:

$$K = \frac{Ec}{L}$$

where: c = concentration of $SO_{2(g)}$

L = liquid content of cloud

E = rainout efficiency

Washout of $SO_{2(g)}$ has been discredited as an important mechanism since in recent studies $SO_{(g)}$ concentrations have been found to increase near ground with time during rainfall. It may be possible that an absorption of $SO_{2(g)}$ in the cloud during droplet condensation combined with a washout of $SO_{2(g)}$ directly under the cloud and a desorption with increase in fall velocity are the mechanisms at work. Thus, the increase in $SO_{2(g)}$ concentration at ground level during periods of precipitation may be due to the effectiveness of the desorption process rather than the absence of a washout process. The net effect of this cyclic process during rainfalls of several hours duration would be the removal of a large percentage of $SO_{2(g)}$ present in the plume.

In summary, the oxidation of $SO_{2(g)}$ to SO_4^{2-} is aided by high concentrations of $SO_{2(g)}$, high concentrations of water vapour, the buffering of the droplet pH by other constituents in the plume. The removal of $SO_{2(g)}$ in the gas phase will be aided by unbuffered pH of water droplet and high concentration of $SO_{2(g)}$ in the plume.

Stable Sulphur Isotope as Tracers

The stable isotopes of sulphur have been used to trace sulphur compound movements in the atmosphere, lakewater and groundwater. It has been shown (Brookhaven Report, 1969) that emissions from a point source could be traced in an area of many sources such as New York City. The procedure was to burn a fuel oil of known isotopic ratio in a power plant. A fuel oil with a heavy sulphur isotopic enrichment that was distinctive from the backgroud sulphur isotope ratios was chosen. Samples of $SO_{2(g)}$ were then taken at various distances from the power plant and the sulphur isotopes analysed. The stable sulphur isotope ratio of the sample taken would be a result of the background sulphur and the power plant emissions. By this method the influence of the plant under study could be assessed for various air sampling stations around the source. The Brookhaven Report also showed that by choosing a plant which was isolated from other emission centres, the stable sulphur isotope method enabled the study to access the oxidation of $SO_{2(g)}$ occurring in the plume.

The study (Holt et al, 1971) showed that the stable isotopes of sulphur could be used to trace water from deep wells, through the sewage process, and identify them as sewage effluents in small streams. The success of this study was due to the high enrichment of the heavy sulphur isotope in deep well water relative to surface creek water. In multiple source studies, the greater the heavy isotope enrichment difference between sources, the more effective stable sulphur isotopes will be as a tracer.

ANALYTICAL TECHNIQUES

The Sudbury sulphur oxide emissions were estimated by the
Department of Environment, Government of Canada, to be 3.4×10^6 tons
for the year 1972. The particulate emissions for Sudbury were
estimated to be 3.4×10^4 tons for the year 1972. The emissions of
carbon monoxide, hydrocarbons, and oxides of nitrogen were relatively
minor. Thus, Sudbury is unique in the dominance of sulphur oxides
over all other emissions. This high emission of sulphur oxides will
result in high $SO_{2(g)}$ concentration in the plumes.

The relationship of stack $SO_{2(g)}$ emissions, rainfall, lakewater
and lake sediment is shown in Figure 5.

Rainwater samples were collected for the three week shutdown
period of the International Nickel Company's 1250 ft. stack from
July 23rd to August 13th, 1973. Rainwater samples were collected for
the month before and after the shutdown period in order to assess the
effect of the International Nickel Company's 1250 ft. stack emissions
on sulphate and δS^{34} values for area rainfall.

The lakewater and lake sediment samples were taken from the
centre of the lake to avoid any local input effects on sulphate and
δS^{34} values. The lake pattern of the Sudbury-Timagami region is
thought to be controlled by glacial striation trends. The bedrock
is impermeable Canadian shield rocks, Precambrian in age. Due to
the limited glacial till cover and impermeable nature of the bedrock
the lakes will be considered as simple "catch" basins for the

Figure (5)   Schematic Representation of $SO_{2(g)}$ Removal From Atmosphere and Resulting Fractionation

Depletion of heavy isotope

high $SO_{2(g)}$ concentration

low $SO_{2(g)}$ concentration

large particulate water film
$SO_{2(g)} + SO_4^{2-}$ enriched in heavy isotope

rainfall
$SO_{2(g)} + SO_4^{2-}$ enriched in heavy isotope

rainfall
$SO_{2(g)} + SO_4^{2-}$ enriched in heavy isotope

Stack

degassing of $SO_{2(g)}$ depleted in heavy isotope

degassing of $SO_{2(g)}$ depleted in heavy isotope

$SO_{2(g)}$ $\xrightarrow[\text{of heavy isotope}]{\text{enrichment}}$ SO_4^{2-}

$SO_{2(g)}$ $\xrightarrow[\text{of heavy isotope}]{\text{enrichment}}$ SO_4^{2-}

Lake

sediment

Lake

sediment

rainwater. The lakes are of the north temperate classification and are moderately to strongly stratified during the summer months. Since the lake is temperature stratified in the summer, ion transfer across the metalimnion will be small and physical mixing processes limited. Therefore, the surface lakewater δS^{34} values will be a result of the input during the summer. The input into the lakes will be a result of precipitation in the drainage basin. Thus, the sulphate in the lakes will be derived from atmospheric $SO_{2(g)}$. The δS^{34} of rainwater and lakewater sulphate will be identical if all $SO_{2(g)}$ oxidizing to SO_4^{2-} is occurring in the atmosphere. An increase in the heavy isotope in the lakewater relative to the rainwater will indicate oxidation of $SO_{2(g)}$ to SO_4^{2-} is occurring in the lakes.

The lakes sampled lie to the north east of Sudbury and were chosen on the basis of five criteria:-

1) Distance and orientation from Sudbury

2) Size

3) Depth

4) Drainage basin

5) Lithology

Lakes of varying distance and orientation from Sudbury were chosen in order to give the study a large enough scope to allow resolution of large scale removal processes. The larger lakes in the area were preferentially sampled since they are thought to have a greater volume to input ratio. The large volume to input ratio would mean an increase in the storage capacity and the sulphur

species would represent the accumulation of at least several months of inflow. The deeper lakes were choosen for two reasons. The deeper lakes are not subject to the high biological activity as a result of a complex water-sediment interface (Conroy, 1972). The deeper lakes also experienced a stronger temperature stratification than most shallow lakes. The temperature stratification prevents ion transfer between the hypolimnion and epilimnion (Stuiver, 1972). Thus, for the large deep lakes the surface water will reflect the input δS^{34} values independent of sediment-water interface reduction reactions.

The drainage basins of the Sudbury-Timagami district are shown in Figure 2. Samples were taken from various drainage basins to assess the dependence of δS^{34} values on drainage pattern. The lithology of the Sudbury area may be divided into three types:-

1) Lorrain quartzite

2) Igneous and metamorphic

3) Glacial till surficial deposits

The unconsolidated sediments of this region have been shown (Conroy, Jeffries and Kramer, 1973, unpublished) to be a very important variable in the ability of Sudbury area lakes to buffer the pH while under heavy sulphate loading.

The lakewater and sediment samples were collected during a three week intensive lake study in the Sudbury-Timagami district. The majority of the area is not accessible by road and float equipped light aircraft are extremely useful. The field work consisted of a

compact airborne lab and sampling set-up used in conjunction with a more complex labratory located at Lakeland Airways office in Timagami. Lakewater surface isotope samples were taken 0.5 meters below the surface of the lake. Lakewater bottom isotope samples were acquired by using a Van Dorn sampling device. The pH dissolved oxygen and secchi disk readings were taken within ten minutes after sample was removed from lake. The sediment samples were taken by using an Eckman sediment dredge. The top three inches were removed from the surface of the total sediment sample and sealed in small plastic bags. The sediment samples were then immedicately placed in a cooler.

The rainwater samplers used were a modification by McMaster University of those designed by the United States Geological Survey (Conroy, Jeffries and Kramer, 1973, unpublished). A small number of rainwater stations near Sudbury were chosen from the Northern Ontario network maintained by McMaster University.

Sulphur isotope analysis were carried out at Canada Centre for Inland Waters using the procedures listed in Appendix I. The water leachable sediment sulphur isotope analysis were also done at Canada Centre for Inland Waters using the procedures listed in Appendix I.

The International Nickel Company's 1250 ft. stack samples were taken at the 600 ft. level by the Ministry of the Environment, Air Management's stack sampling project. Wind Direction analysis was based on the daily reports of Sudbury Climatological Station for the periods designated.

EXPERIMENTAL RESULTS

Climatological Data

The results of rainfall and wind direction analysis are given
in Tables 1 and 2, respectively. The dominance of moisture
bearing south west winds is shown clearly in Figure 6. The wind
direction for the Sudbury area shows a tendency to blow to the
north east. As shown in Figure 7, for the periods - September 30th,
1972 to September 30th, 1973, and June 1st, 1970 to June 1st, 1971;
the wind pattern changes very little.

TABLE 1

RAINFALL ANALYSIS TABLE FOR SUDBURY CLIMATOLOGICAL STATION

Wind Direction	Wind Direction in Degrees	Amount of Rainfall for Period Sept 72 - Sept 73	Number of Rainfalls for Period Sept. 72 - Sept 73	Amount of Rainfall for Period Jan. 70 - Jan. 71
West	0	0.56	2	1.17
West South West		2.26	10	1.57
South West		5.29	21	2.20
South South West		3.25	10	2.13
South	90	1.06	5	0.92
South South East		3.20	13	3.33
South East		2.72	9	3.15
East South East		1.83	4	1.77
East	180	0.84	4	4.07
East North East		3.73	9	1.96
North East		2.26	11	3.26
North North East		1.79	8	1.35
North	270	0.76	6	1.27
North North West		1.90	11	1.6l
North West		0.65	3	0.40
West North West		0.61	2	0.61
West	0.360	0.56	2	1.17

Figure (6)   Number of Rainfalls versus Wind Direction

(for period Sept. 30,1972 to Sept. 30, 1973)
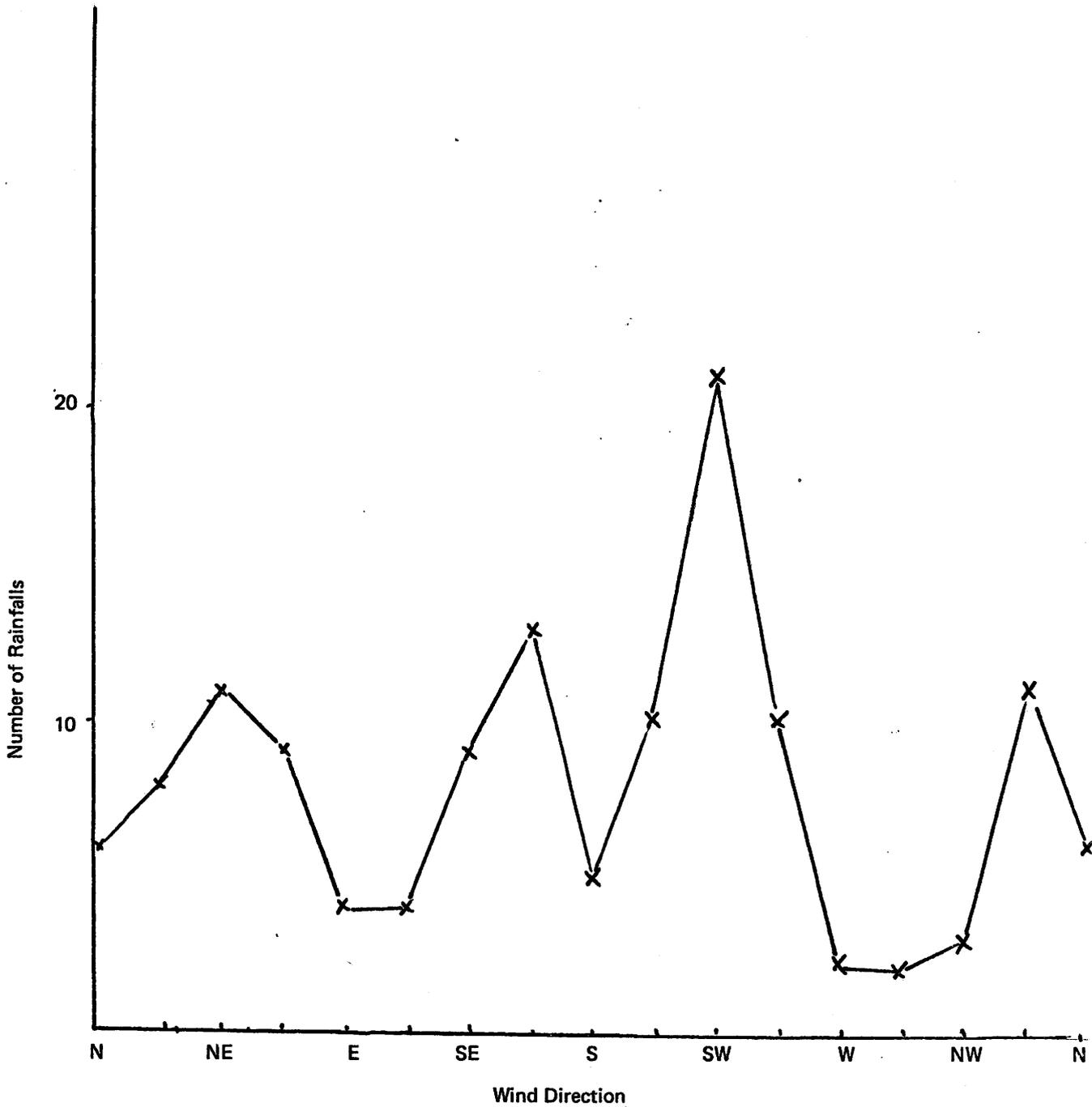
TABLE 2

WIND DIRECTION FREQUENCY FOR SUDBURY CLIMATOLOGICAL STATION

Wind Direction	Jan. 1 1971 to Jan. 1 1972 (hours/year)	Sept. 30 1972 to Sept. 30 1973 (hours/year)
West	505	415
West South West	474	375
South West	427	418
South South West	539	587
South	677	545
South South East	678	700
South East	575	646
East South East	357	437
East	286	330
East North East	264	316
North East	325	372
North North East	446	524
North	564	568
North North West	752	722
North West	903	747
West North West	781	714
West	505	415

Figure (7) Wind Direction Frequency for Sudbury
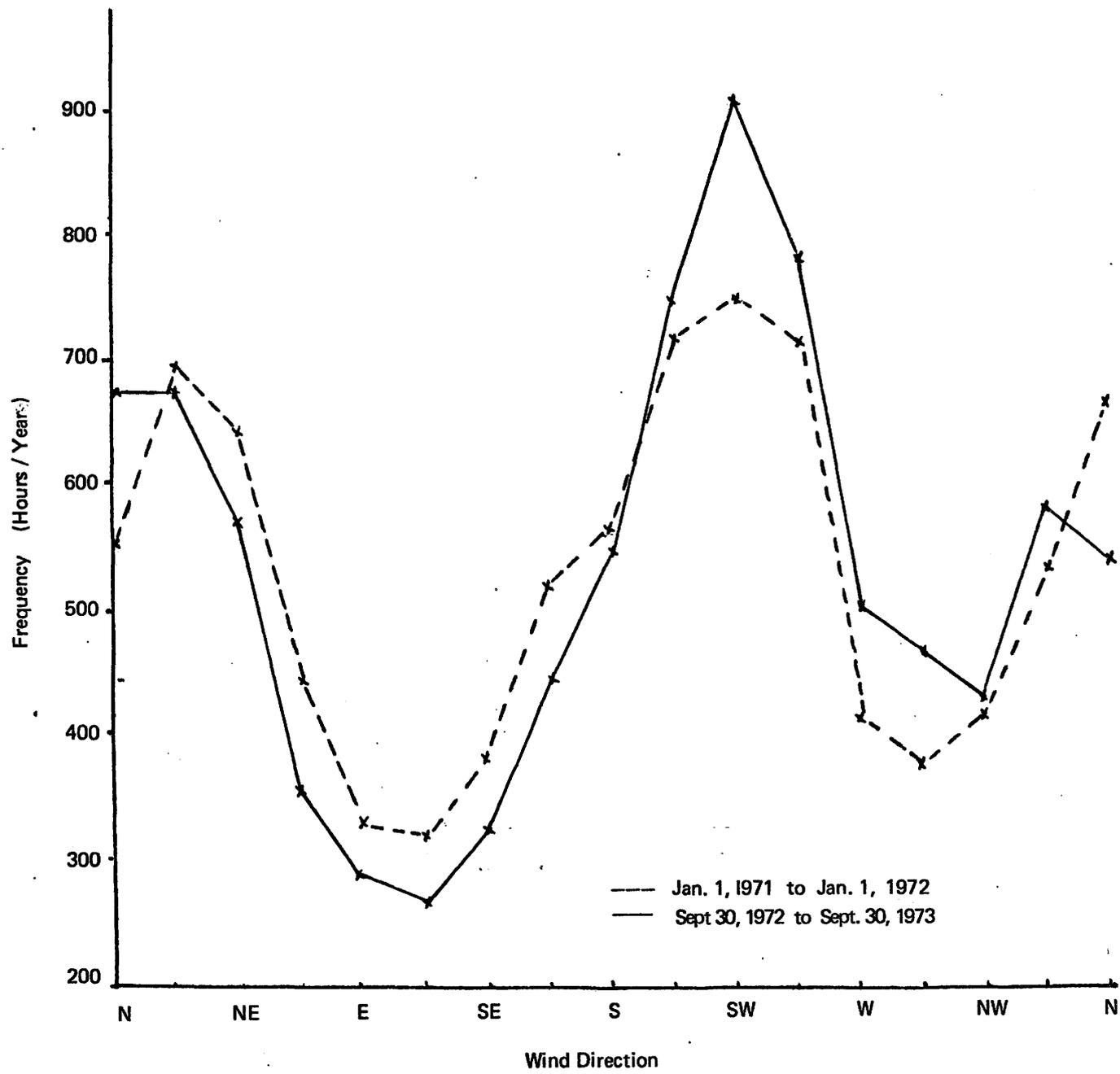
RESULTS

Rainwater Data

The locations of the rainwater sample stations are shown in

Figure 8. The samples were collected on July 23rd, 1973 for the

month prior to shutdown of the International Nickel Company's

1250 ft. stack. Samples for several stations were collected for

the shutdown period, July 23rd, 1973 to August 13th, 1973. Samples

were also collected for the month following August 13th, 1973. The

results of sulphate and sulphur isotope analysis for rainwater in

the Sudbury region are shown in Table 3. Analytical procedures

are given in Appendix I.

Figure 9 and 10 show sulphate and δ S^{34} contours (respectively)

for rainwater samples in Sudbury region for the month previous to

the International Nickel Company's ·1250 ft. stack shutdown.

Figure (9)   Sketch Contour Map of Rainwater Sulphate (mg./1.) for

Sudbury-Timagami Area.
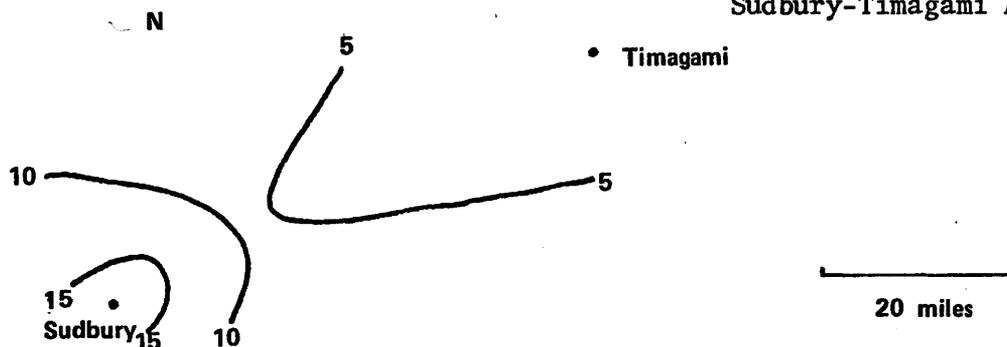
The sulphate·value is extremely high (16.8 mg./1.) at Sudbury

North station and apparent high lobes extend to the east.

- 25 -

Figure (8)   Lake and Rainwater Station Locations
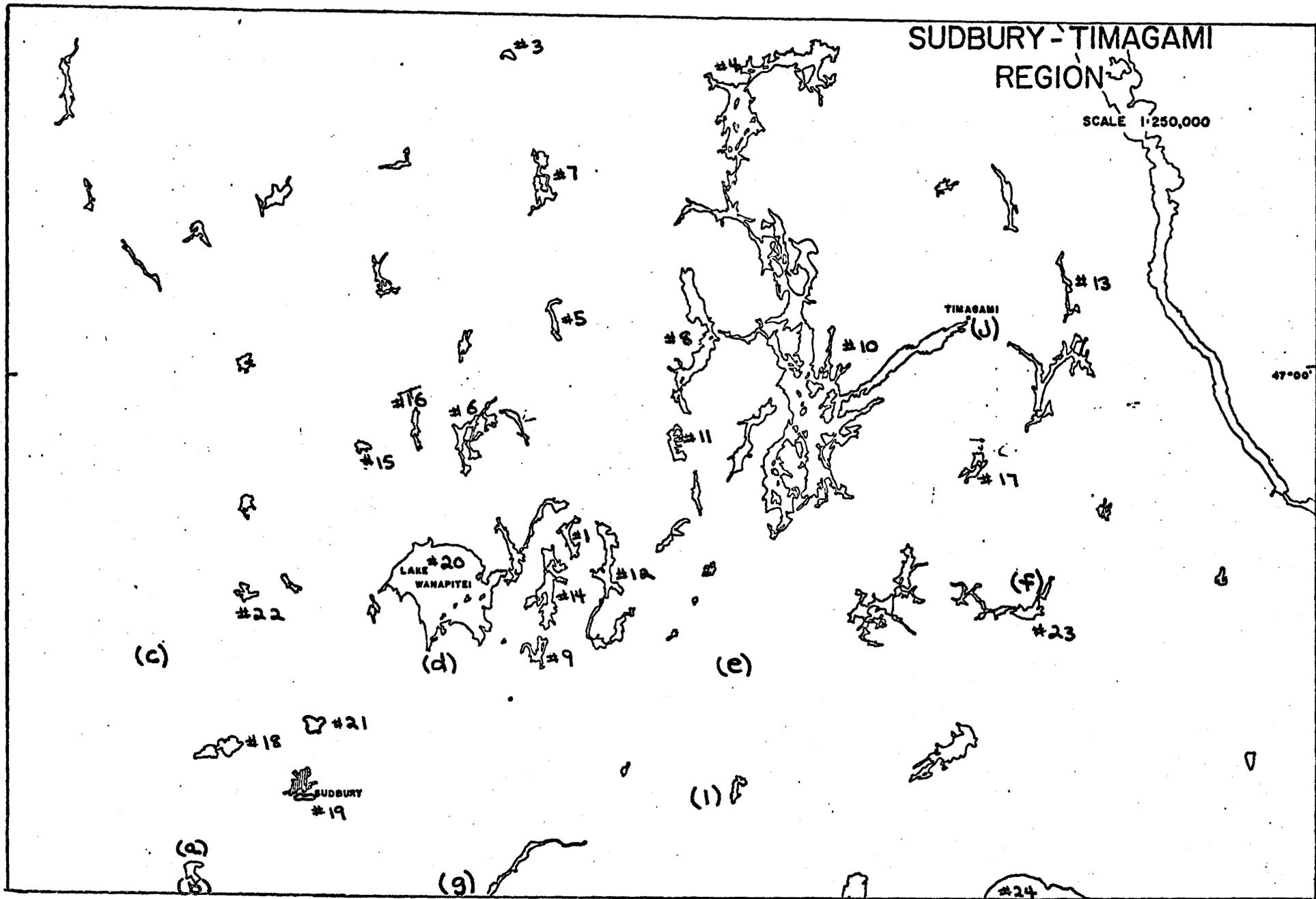
TABLE 3
SULPHATE AND δS^{34} VALUES FOR SUDBURY AREA RAINWATER

Station	Before Inco Shutdown		During Inco Shutdown		After Inco Shutdown	
	Sulphate mg/liter	δS^{34} p.p.t.	Sulphate mg/liter	δS^{34} p.p.t.	Sulphate mg/liter	δS^{34} p.p.t.
a) Sudbury North	16.8	+ 4.85	4.7	+ 3.42	8.0	+ 4.16
b) Sudbury South	15.1		2.1		3.3	
c) Windy Lake	10.1		0.3	+ 3.05	10.9	
d) Skead	11.5	+ 2.84	3.2	+ 4.21	4.7	+ 2.86
e) River Valley	5.6	+ 2.07	1.2	+ 2.90	6.9	+ 3.21
f) Marten River	5.6	+ 3.72	3.2	+ 2.98	5.7	
g) Jamot	3.5		0.3		5.7	
h) Powassan	3.2		4.3		5.0	
i) Verner	5.6		4.4	+ 2.21	9.3	+ 3.37
j) Temagami	4.3	+ 3.17			5.9	

Figure (10) Sketch Contour Map of Rainwater $\mathcal{S}$ S^{34} p.p.t. for

Sudbury-Timagami Area.

N   • Timagami

3,0
    3.0

20 miles

4.0
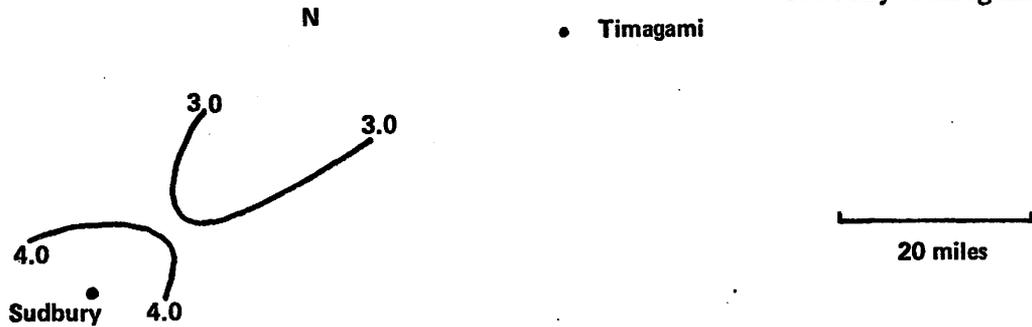
Sudbury   4.0

The S^{34} value is also highest at Sudbury North station with an apparent low lobe stretching east north east of Sudbury.

Figure 11 and 12 show sulphate and $\mathcal{S}$ S^{34} contours (respectively) for the three week period of the International Nickel Company's 1250 ft. stack shutdown.

Figure (11) Sketch Contour Map of Rainwater Sulphate (mg./l.) for

Sudbury-Timagami Area

N

• Timagami

3.0
                        3.0

                        3.0

3.0   •Sudbury

3.0   20 miles
      3.0   3.0
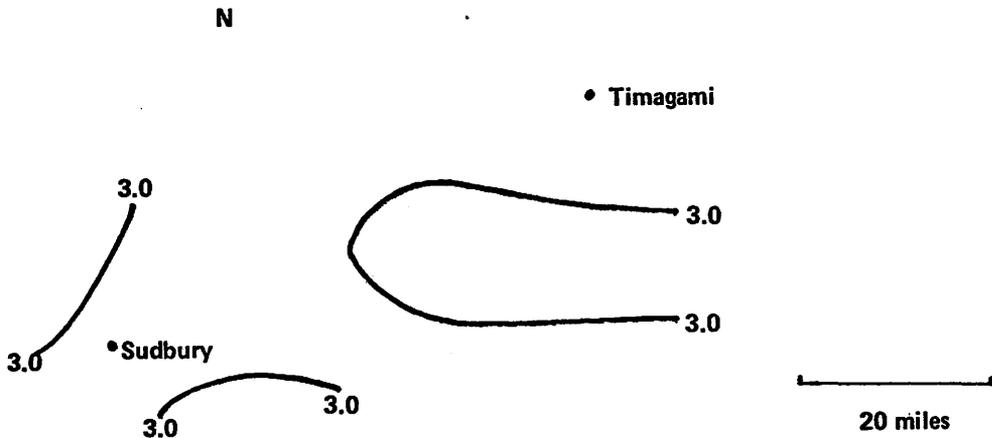
The sulphate values recorded for this shutdown period dropped to below 5.0 mg./l. for the entire area. Sudbury remains the centre of high sulphate values (4.7 mg./l.).

Figure (12) Sketch Contour Map of Rainwater δS^{34} p.p.t. for

Sudbury-Timagami Area

N

• Timagami

4.0

4.0

3.0

Sudbury

3.0

20 miles
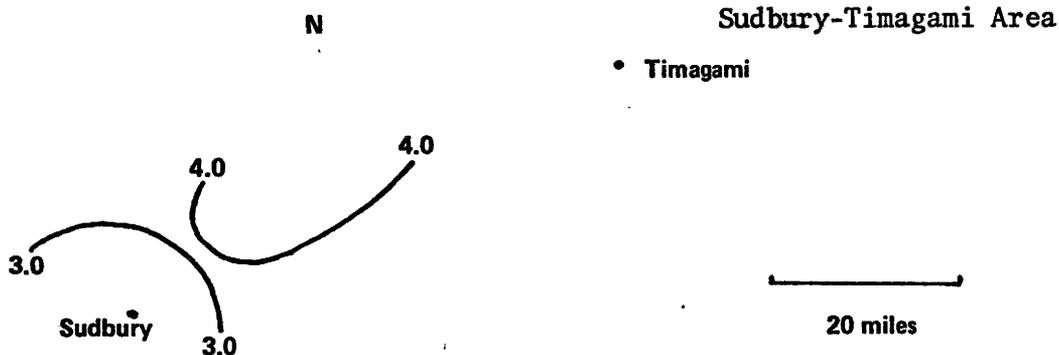
The δS^{34} decreased from + 4.85 p.p.t. at the Sudbury North station before shutdown to + 3.42 p.p.t. during shutdown. The δS^{34} increased at the Skead station from + 2.84 p.p.t. before shutdown to + 4.21 during shutdown.

Figure 13 and 14 show the sulphate and δS^{34} contours (respectively) for the month following the International Nickel Company's 1250 ft. stack shutdown.

Figure (13) Sketch Contour Map of Rainwater Sulphate (mg./l.) for

Sudbury-Timagami Area

N

• Timagami

10

5   5

10

5   Sudbury

5

20 miles
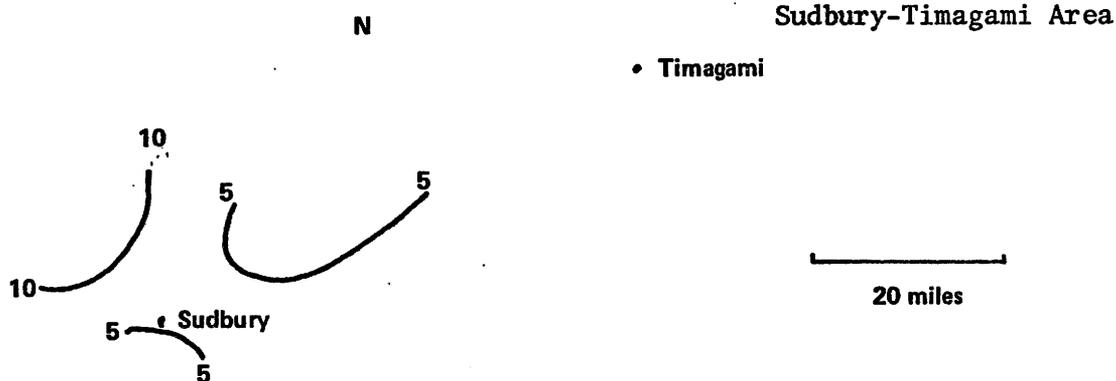
Lobes of low sulphate values are found to the north east and south west of Sudbury.

Figure (14)   Sketch Contour Map of Rainwater δ S^{34} p.p.t. for

Sudbury-Timagami Area

N

3.0

3.0

4.0

• Sudbury

4.0

• Timagami

20 miles

Sudbury is the centre of high δ S^{34} values for the period

following the International Nickel Company's 1250 ft. stack shutdown.

Interpretation of results is somewhat restricted due to a lack

of sampling stations to the north and north east of Sudbury.

However, the following generalities may be stated for the sulphate

and δ S^{34} rainwater values.

1)   When the International Nickel Company's 1250 ft. stack is

in operation the sulphate and δ S^{34} values rise.   The

Sudbury North station rainwater has a sulphate value of

16.8 mg./1. and a δ S^{34} value of + 4.85 p.p.t. before

shutdown.   The month during shutdown the rainwater values for

sulphate and δ S^{34} are 4.7 mg./1. and + 3.42 p.p.t. respec-

tively.   The month after shutdown the rainwater values for

sulphate and δ S^{34} are 8.0 mg./1. and + 4.16 p.p.t. respec-

tively.

2)   When the International Nickel Company's 1250 ft. stack is

in operation the region to the east north east of Sudbury

experience high sulphate and δS^{34} values. Sulphate values are greater than 5.0 mg./l. and δS^{34} values are greater than + 3.0 p.p.t. in this region.

3) Low δS^{34} values are found to be less than + 3.0 p.p.t. from the Skead station to just south of Timagami during International Nickel Company's 1250 ft. stack operation.

Lakewater Data

Figures 15 and 16 show the distribution of lakewater sulphate and δS^{34} values respectively, for the Sudbury-Timagami region. Both contour maps show Sudbury to be the centre of the high values. The major difference between the two maps is in the area to the north-east of Sudbury where sulphate values greater then 20 mg./l. and correspond with low δS^{34} (+ 4.00). The contour maps have been constructed from the data listed in Table 4.

Figures 17 and 18 show lakewater sulphate and δS^{34} values as a function of the logarithm of the distance from Sudbury. As shown in Figures 17 and 18 there is a direct relationship between both sulphate and δS^{34} and the logarithm of the distance from Sudbury. The rainwater values have been plotted on Figure 17 and 18 for comparision purposes. The sulphate values for the lakewaters are about twice the concentration of the rainwater samples at all distances from Sudbury. The δS^{34} values of the lakewaters are also about twice the value of rainwater δS^{34} values.

The slope of the lakewater sulphate versus logarithm of the distance from Sudbury is steeper than that of the rainwater. The slope of the lakewater δS^{34} versus logarithm of distance from Sudbury also has a steeper slope than the similar rainwater curve.

The 1250 ft. International Nickel Company's stack sulphur dioxide sample has a δS^{34} value of + 7.39. This value is lower than the δS^{34} value for lakes within 10 miles of Sudbury and much higher than

TABLE 4   SUDBURY AREA SURFACE & BOTTOM LAKEWATER DATA

LAKE WATER   DATA TABLE

Surface Water	Direction	Distance (miles)	Log Distance	Sulphate (mg./l.)	Composite pH	δS^{34} p.p.t.
1. Donald	048°	31.35	1.4962	17.45	4.20	3.94
2. Laura	030°	36.67	1.5643	17.70	5.15	5.33
3. Sunny Water	015° 30'	65.71	1.8177	9.57	4.30	3.15
4. Lady Evelyn	033° 30'	61.43	1.7884	12.35	6.02	4.08
5. Yortson	028°	45.87	1.6616	16.21	5.50 est	5.10
6. Chiniguchi	024° 30'	33.57	1.5260	16.07	4.20	5.15
7. Florence	022°	55.16	1.7416	14.01	4.40	2.97
8. Obabika	043°	50.79	1.7058	14.92	6.55	4.60
9. Ashigami	0.62°	23.17	1.3650	17.50	6.50	6.72
10. Temagami	054° 30'	62.14	1.7934	19.20	6.80	3.27
11. Emerald	047° 30'	43.65	1.6400	20.00	6.40	3.94
12. Maskinonge	055°	32.94	1.5177	18.82	5.40	3.39
13. Lorrain	056° 30'	78.97	1.8975	11.05	7.03	3.78
14. Kukagami	052°	27.14	1.4337	19.20	5.25	5.17
15. Fraleck	010° 30'	29.60	1.4713	11.57	5.00	5.11
16. Telfer	018°	32.14	1.5071	18.01	4.26	4.57
17. Jumping Caribou	065°	64.29	1.8081	17.33	6.10	5.26
18. Whitewater	292°	7.38	0.8681	32.00	7.50	8.49
19. Ramsey	116°	19.29	1.2852			8.13
20. Wanapitei	0.36°	42.06	1.6239		7.10	4.49
21. Whitson	010°	6.75	0.8290	26.06		7.95
22. Nelson	344° 15'	16.75	1.2239		4.50	5.86
23. Marten	076°	64.52	1.8097		6.40	5.20
24. Nipissing						5.05

BOTTOM WATER

1. Sunny Water	015° 30'	65.71	1.8177	10.99		3.12
2. Donald	048°	31.35	1.4962	19.74		4.65
3. Chiniguchi	024° 30'	33.57	1.5260	20.17		4.47
4. Lorrain	056° 30'	78.97	1.8975	12.89		4.39
5. Temagami	054° 30'	62.14	1.7934	23.54		3.46

Figure (15) Contour of Lakewater Sulphate Values (mg./l.)
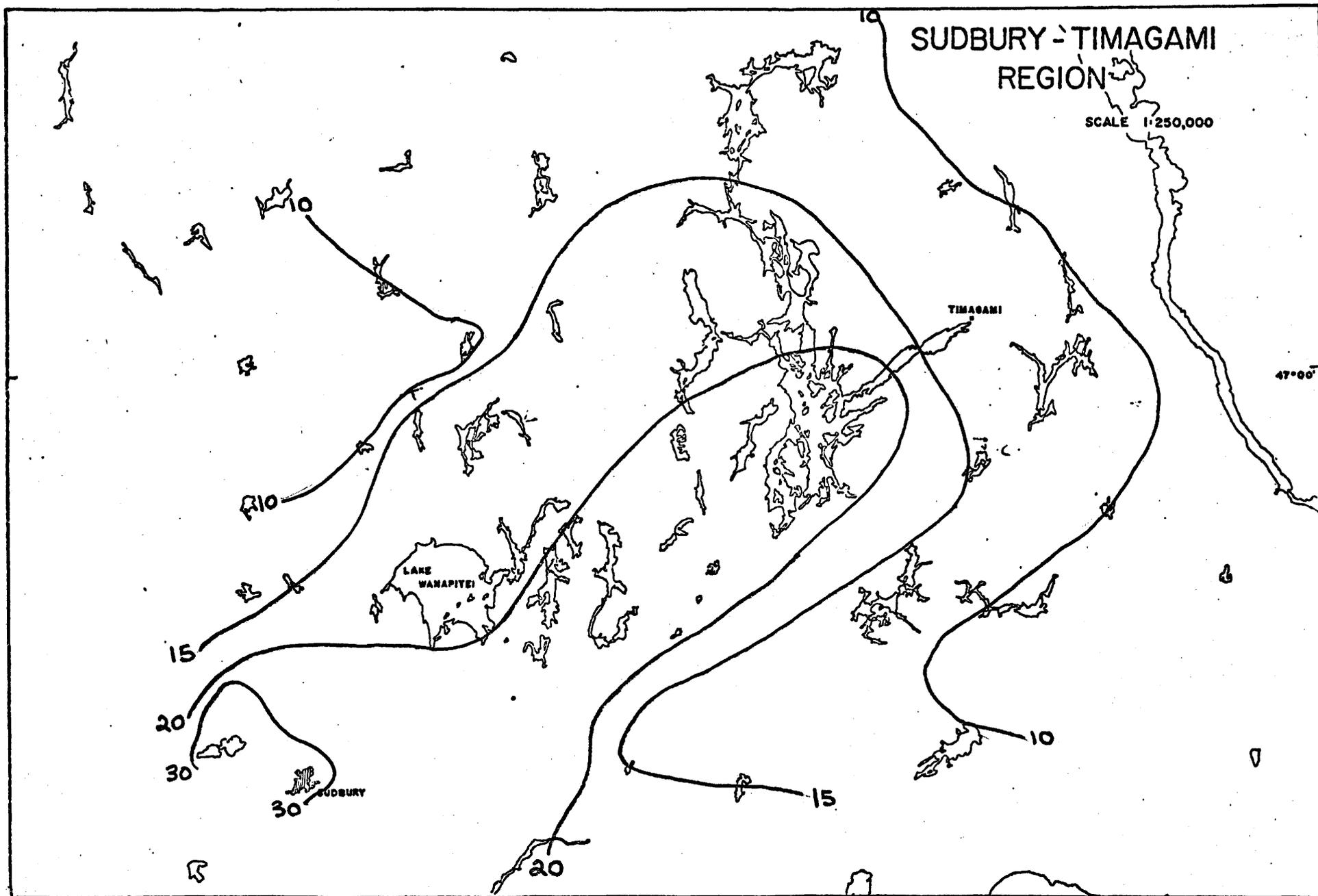
Figure (16) Contour of δS^{34} Values (p.p.t.)
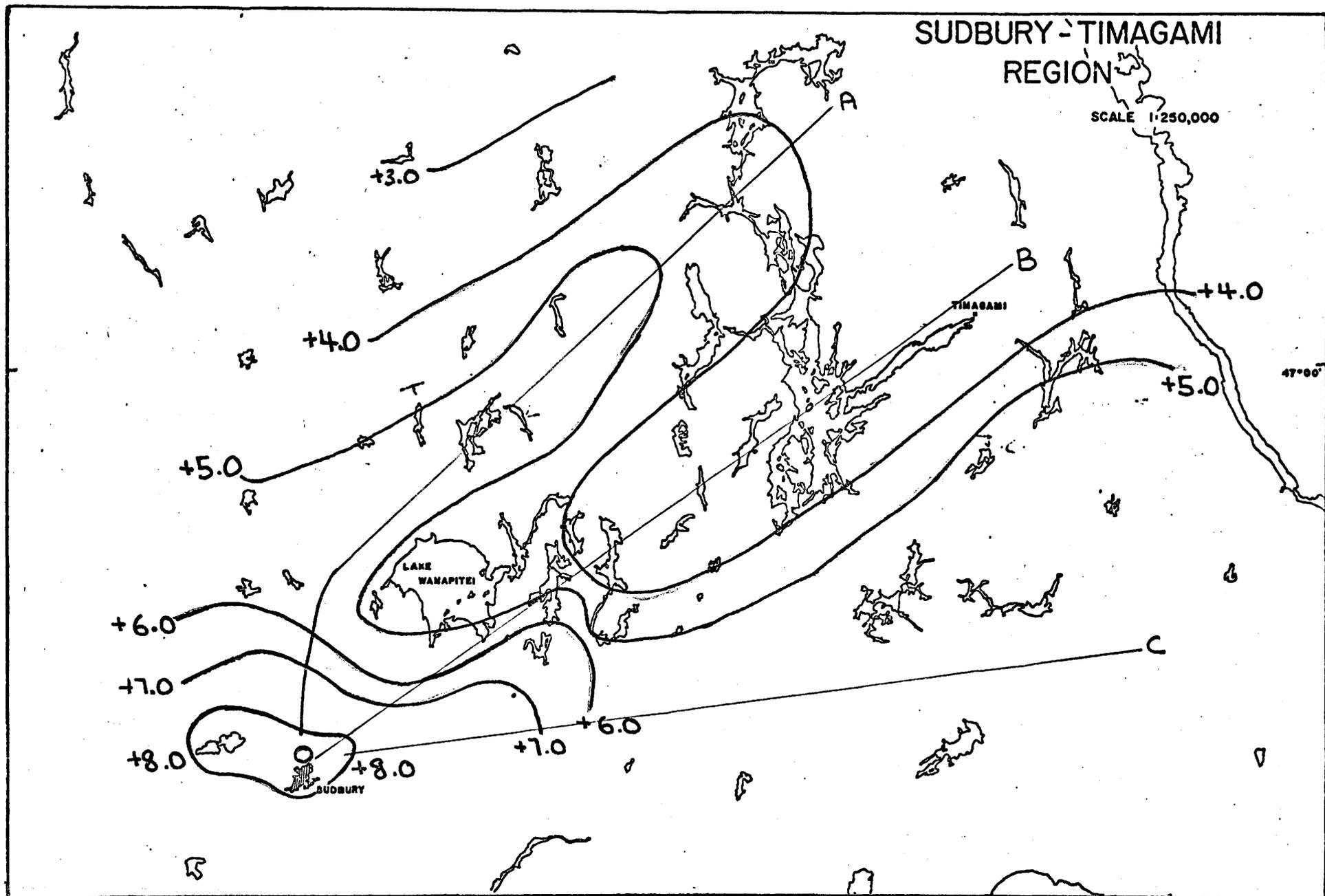
Figure (17) Sudbury-Timagami Area Lakewater and Rainwater Sulphate Values versus Log. of the Distance from Sudbury
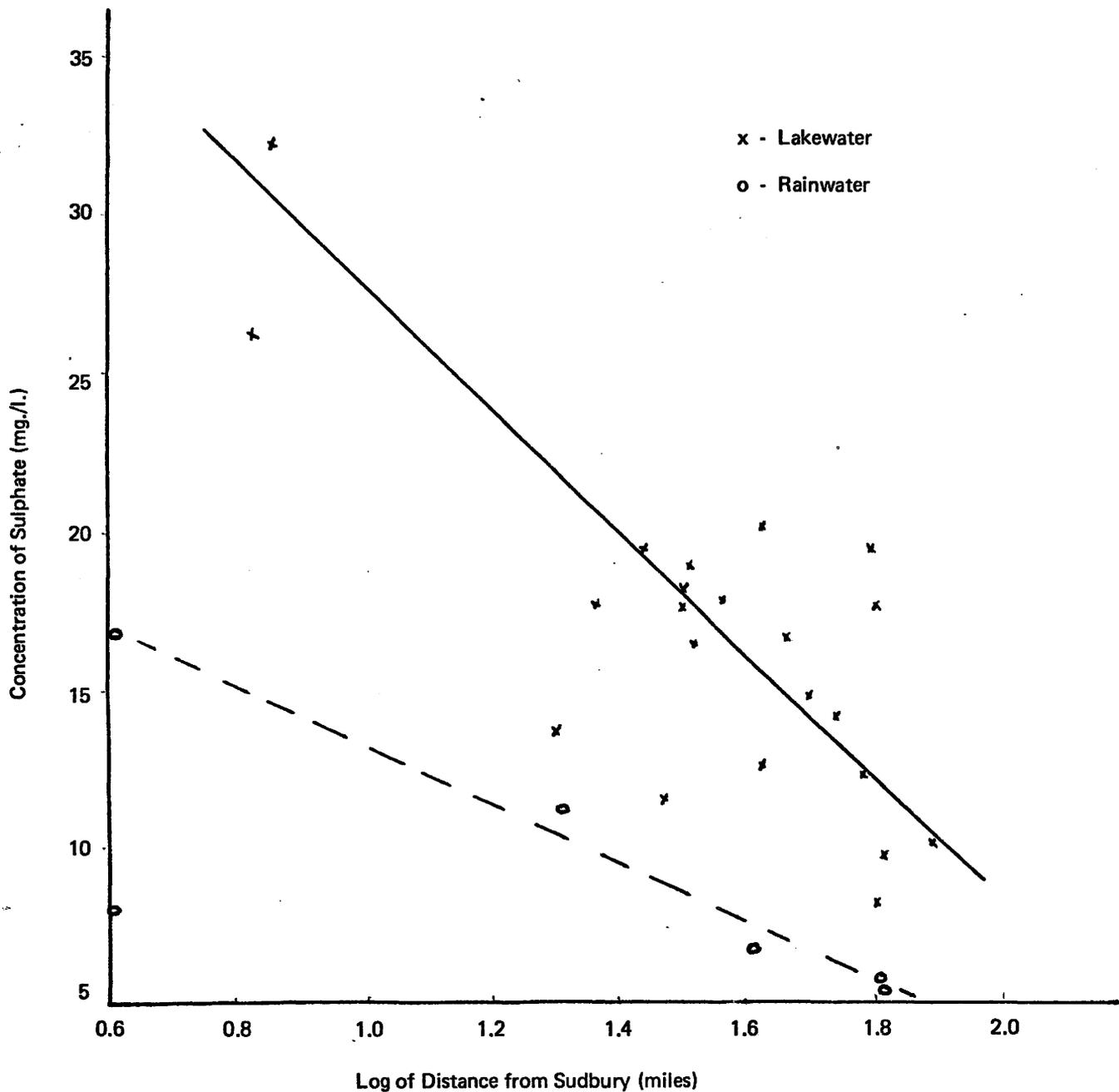
Figure (18) δ S^{34} Values of Lakewater and Rainwater versus the Log. of the Distance from Sudbury

x - Lakewater

o - Rainwater

- Rainwater during Inco shutdown

δ S^{34} (p.p.t.)

Log of Distance from Sudbury (miles)
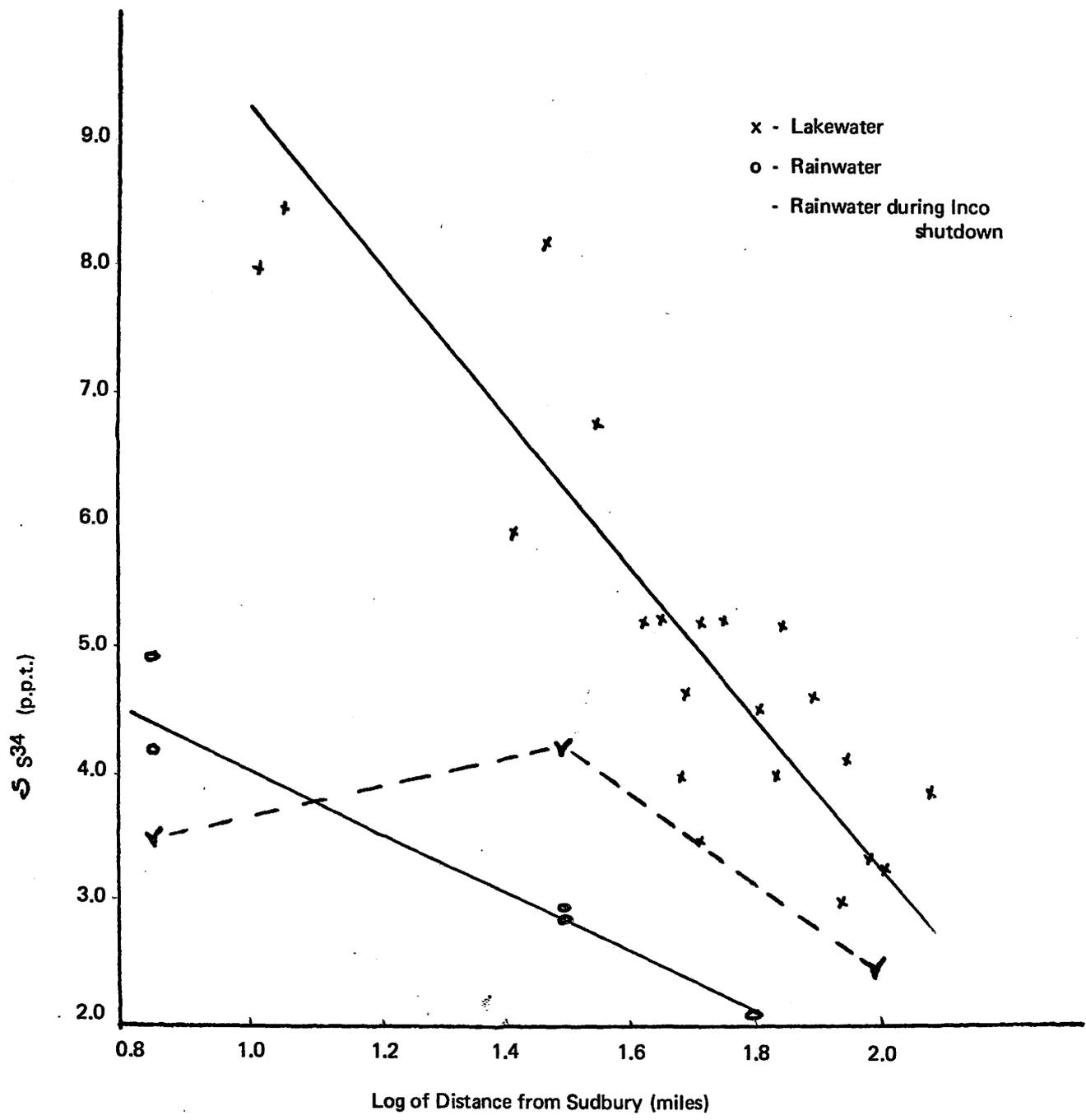
the δ S^{34} value of the Sudbury North precipitation station before and after the International Nickel Company's 1250 ft. stack shutdown. The Sudbury North station is 5 miles from the International Nickel Company's 1250 ft. stack.

Lake Sediment Data

The amount of water leachable sulphur and δ S^{34} values for Sudbury area lake are shown on Table 4. The amount of water leachable sulphur varied from 0.69 mg. sulphur/gr. dry sediment to 3.75 mg. sulphur/gr. dry sediment. The δ S^{34} values ranged from + 12.42 p.p.t. to - 13.04 p.p.t. In the absence of non water leachable sulphur amounts and δ S^{34} values interpretation is a best speculative.

TABLE 5

WATER LEACHABLE SULPHUR AND δS^{34} DATA FOR SUDBURY AREA LAKE SEDIMENTS

Lake	Sulphur (mg. elemental S) (gr. Sediment)	δS^{34} p.p.t.	
Chiniguchi	0.859		
Marten	2.598	+ 0.86	
Telfer	2.404	+12.42	
Donald	1.493	−11.01	
Lorrain	0.974	+ 2.96	
Shoofly	0.729		
Kukagami	2.289	− 7.79	
Maskinonge	0.691	−13.04	
Sunny Water	1.287	+ 2.86	
Laura	0.428	+ 4.24	
Nelson	2.232	+ 4.80	∞
Ashigami	1.051	− 6.33	
Wanapitei	0.398	+ 3.07	
Obabika	0.442	− 3.15	
Joe (contaminated)	3.754	+11.71	
Jumping Caribou	1.451	+ 4.05	
Florence			

Discussion

It appears that the $SO_{2(g)}$ in the International Nickel Company's
1250 ft. stack having a δS^{34} value of + 7.39 p.p.t. undergoes severe
fractionation between the time it leaves the stack and is removed
as SO_4^{2-} having a δS^{34} of less than + 5.0 p.p.t. at the Sudbury
North sample station. This high fractionation within the first five
miles of the 1250 ft. stack is in agreement with the Brookhaven
Report which found critical fractionation within two miles of the
source. Data (Junge, 1963) relating particle size to frequency of
water vapour condensation indicates that the largest particulates
are the first to incur condensation. These large particles upon
cooling act as condensation nuclei for the 3 - 4% water vapour
found in the emission gases, after leaving the stack. The water
film on the large particulates would give the water a very large
reactive surface aiding the efficiency of this liquid at scavenging
$SO_{2(g)}$. The metal ions on the surface of the particulate would act
as a catalyst for the oxidation of $SO_{2(g)}$ to SO_4^{2-}. As the
particulates burdened with a water film became to heavy to be
supported by the plume eddies, they would experience a downward
acceleration which (Hales, Thorp and Wolf, 1967) would reach
a critical velocity and begin to desorb $SO_{2(g)}$. Since the gas
trapped in the water film was in the process of being oxidized from
$SO_{2(g)}$ to SO_4^{2-}, fractionation between sulphur isotopes in gas and
liquid stages would be occurring. By this mechanism the desorbed
gas would be of lower δS^{34} than the δS^{34} of the original $SO_{2(g)}$
emitted from the stack. The International Nickel Company's 1250 ft.
stack is 450 feet higher than that studied by Hales, Thorp and Wolf,
with considerably greater tonnage of $SO_{2(g)}$ emissions. At this

greater height the desorption process would be of greater importance
in the movement of $SO_{2(g)}$ both in the plume and below it. Thus,
removal of the large particulate within five miles of the stack is
the probable cause of the lowering of δS^{34} of $SO_{2(g)}$ in the plume
over the Sudbury North station. It is assumed here that the δS^{34}
of the SO_4^{2-} in the rain sample is at least slightly higher than the
$SO_{2(g)}$ from which it originated. During periods of increased humidity
or rainfall this process would be of greater efficiency.

At distances greater than three to four miles from the emission
source, the effect of the large particulate condensation process
would diminish. In these regions effective removal of $SO_{2(g)}$ would
occur only during periods of precipitation. The Sudbury area being
relatively free of ions such as NH_4^- to buffer the pH and allow
continuing oxidation of $SO_{2(g)}$ to SO_4^{2-} is unique in this feature.
If the SO_4^{2-} present in the lakewater is a result of sulphur species
introduced by area rainfall and the δS^{34} is related to fractionation
occurring in the rainfall and lakewater, the following conclusions
are plausible. The increase in δS^{34} in the lakewater and the
parallel increase in SO_4^{2-} concentration must be due to $SO_{2(g)}$
oxidizing to SO_4^{2-} occurring in the rivers, streams and lakes. The
effect of the degassing process on the δS^{34} of the lakes will be
proportional to the amount of $SO_{2(g)}$ loading received by the lake.
The concentration of $SO_{2(g)}$ in the plume will decrease with distance
from Sudbury due to mixing with ambient air. As a result, the lakes
further from Sudbury will show less enrichment in the heavy isotope.

Three distinct patterns are illustrated by the δ S^{34} contours as shown in Figure 16. The centre of each contour pattern is marked with a dashed line and are labelled O - A, O - B and O - C. The signifigance of each lobe will be interpreted in accordance with previously discussed theory in the following paragraphs.

The high δ S^{34} lobe bisected by the line O - A is the general direction from Sudbury which receives the most rainfall by winds carrying Sudbury emissions. As stated this wind direction is strongly associated with thunderstorms in the region and the resultant δ S^{34} contours should reflect the $SO_{2(g)}$ density during these rainfalls. The centre of the high lobe would coincide with the direction of the greatest number of rainstorm winds carrying Sudbury emissions. Areas to either side of line O - A. would be subject to less frequent Sudbury emission removal and would have less $SO_{2(g)}$ influx into the lakewater. The high δ S^{34} values near Sudbury are a result of the high density of $SO_{2(g)}$ in the plume during almost all periods of rainfall. It appears that the pattern centered by line O - A is a zone subject to high intensity loading of $SO_{2(g)}$ rainwater at frequent intervals.

The line labelled O - C on Figure 16 represents the centre of a large lobe of δ S^{34} values which remain greater than + 5.0 p.p.t. at distances of greater than 40 miles from Sudbury. The sulphate values of lakes in this lobe are less than would be expected due to their distance from Sudbury. The existence of this area of high δ S^{34} values may be interpreted in terms of the wind patterns in the Sudbury region. A review of the spring and summer wind

directions existing prior to periods of precipitation reveals

that west south west winds are in the majority of instances

followed by rainfall. It is possible that during stabilized west

south west wind conditions the sulphur dioxide tends to build-up

in an area centered by line O - C. This build-up may be a result

of the trapping of $SO_{2(g)}$ on the large airborne particulates.

These particles and dust would be of such a size that a thin

film of water would not give them sufficient mass to result in

a net downward velocity. The process will be aided by an increase

in humidity and low wind velocities. It has been shown

(Brookhaven Report, 1969 and Hales, Thorp and Wolf, 1970) that on

occasions the concentration of $SO_{s(g)}$ in the plume decreased in

the first few miles and then remained constant or slightly increased

to distances up to 14 miles. During the period of high $SO_{2(g)}$ and

fine particulate build-up, the water films on the particulate would be

in contact with highly concentrated $SO_{2(g)}$ for time periods which could

exceed several hours. The oxidation of $SO_{2(g)}$ to SO_4^{2-} would lower the

pH of the condensate to the critical value within the first few miles

from the source. Once the pH has passed the critical value of 4,

the oxidation of $SO_{2(g)}$ to SO_4^{2-} in the water film on the particulate

becomes negligable and the absorption of $SO_{2(g)}$ as a result of

collision would be of increasing signifigance. Termination of this

low velocity west south west wind by a thunderstorm moving in any direction would result in large quantities of dissolved $SO_{2(g)}$ being added to rivers and lakes in this locality. This process is probably active in all directions about Sudbury but is most frequent to the east north east of Sudbury. The degassing of this high concentration $SO_{2(g)}$ rainfall would result in high δS^{34} values as found in these lakes. Due to the infrequency of this mechanism the sulphate would be diluted by numerous rainfalls containing only background sulphate concentrations.

The lobe of the δS^{34} values bisected by the line O - B in Figure 15 is the area effected by both modes of sulphur dioxide removal described above. This area is at the fringes of both modes of $SO_{2(g)}$ removal and due to the mixing of ambient air with the outer edges of the plume will receive lower inputs of $SO_{2(g)}$ and SO_4^{2-} with each rainfall. The zone centered by line O - B will be subject to low dissolved $SO_{2(g)}$ concentration in the rainwater but the loading of $SO_{2(g)}$ into the area lakes will be relatively constant.

As a result of this constant $SO_{2(g)}$ loading, this district exhibits sulphate values greater than 20 mg./1.

Mass Balance of International Nickel Company's 1250 ft. Stack Sulphur

Emissions and Sudbury-Timagami District Lakewaters

Using S^{34} Fractionation

The sulphur mass balance is based on the conservation of the stable sulphur isotopes S^{32} and S^{34} and assumes only transformation of $SO_{2(g)}$ to SO_4^{2-}.

(δS^{34} of emission sulphur)(Mass of emission sulphur) =

(δS^{34} of sulphur of specific environment)(Mass of sulphur of

specific environment)

The mass balance is carried out for the Sudbury-Timagami quadrant by making the following assumptions:

1) Evapouration of rainfall is small relative to total amount of precipitation.

2) All sulphate in the lake waters is derived from atmospheric $SO_{2(g)}$ originating from International Nickel Company's 1250 ft. stack.

3) The Sudbury area receives 35 inches of precipitation in one year.

The method used for computation of the sulphur mass balance is given below:

1) The average distance of each contour shown in Figure 16 from Sudbury was estimated.

2) The area between each contour for the Sudbury-Timagami

quadrant was calculated.

3) The average sulphate concentration for the area between each contour was estimated and multiplied by area between the same two contours.

4) The δS^{34} was then multiplied by the product of the amount of rainfall received in one year times the product calculated in step 3.

5) The sum of calculations based on steps 1 to 4 for each contour will give the mass enrichment of S^{34} in the Sudbury-Timagami area precipitation in one year.

6) The total sulphur oxide emissions for one year of the International Nickel Company's 1250 ft. stack was multiplied by the δS^{34} of + 7.39 for the emission sample analysis.

Calculations

δS^{34} contour	Area (cm^2)	Volume (cm^3)	(δS^{34} p.p.t.)(mass gr.)
- 8.0	5.0×10^{11}	444.5×10^{11}	107.2×10^{11}
- 7.0	11.2×10^{11}	551.2×10^{11}	77.0×10^{11}
- 6.0	31.2×10^{11}	177.8×10^{12}	213.6×10^{11}
- 5.0	244.6×10^{11}	1892.6×10^{12}	1420.0×10^{11}
- 4.0	604.0×10^{11}	3195.0×10^{12}	1298.0×10^{11}

Total of $(\delta S^{34}$ p.p.t.)(mass) for all contours standardized in terms of $SO_{2(g)}$ = 2.056×10^8 (p.p.t.)(kg.)

International Nickel Company's 1250 ft. stack emissions for one

year (Conroy, Jeffries, Kramer, 1973) times δS^{34} of $+$ 7.39 p.p.t.

= 3000 ton/day x (365) x (7.39 p.p.t.)

= 8.2 x 10^9 (p.p.t.)(kg.)

Percentage of emissions removed within 65 miles of Sudbury in

one year = $\dfrac{2.056 \times 10^8 \text{ (p.p.t.)(kg.)}}{8.2 \times 10^9 \text{ (p.p.t.)(kg.)}}$ x 100 = 2.5

CONCLUSIONS

The use of stable sulphur isotopes in northern lake districts to trace plumes containing sulphur oxides is feasible. The δS^{34} values for surface lakewaters were apparently not effected by the drainage basin of the lake or the rock type found in the drainage basin. However, the δS^{34} values for surface lakewaters were directly related to the logarithm of the distance from Sudbury. The high δS^{34} of the lakewater relative to rainwater samples suggests that large amounts of sulphur dioxide are flushed into the lake in a gaseous state. This process appears active at distances of at least 65 miles from Sudbury. A mass balance for sulphur for the Sudbury area using S^{34} fractionation that indicates 2.5 of the International Nickel Company's 1250 ft. stack, sulphur oxide emission are removed in the Sudbury-Timagami quadrant within 65 miles of Sudbury.

The sharp difference in δS^{34} of the International Nickel Company's sulphur oxide emission and the rainwater sulphate at the Sudbury North station indicates a high percentage of $SO_{2(g)}$ is oxidized within the first few miles of the stack. The role of particulates in this oxidation may be critical.

The rainwater δS^{34} decreased with the distance from Sudbury was probably the result of a preferential removal of the heavy isotopes by rain droplets. This process leaves the $SO_{2(g)}$ remaining in the plume relatively depleted in the heavy isotope.

FUTURE RECOMMENDATIONS

The most feasible method to approach an intensive study of an area such as Sudbury would be as follows:-

1) Set up a skeleton network of $SO_{2(g)}$ and rainfall stations within a 100 miles of source.

2) Monitor a few lakes of average size and depth for a few months to assess the effect of precipitation on isotopic ratio of lakes.

3) An intensive sulphur isotope sampling of surface lakewater during the late summer before the breakdown of temperature stratification.

4) Co-ordination of metal and sulphur species data for rainwater, lakewater and air should enable a good evaluation of sulphur oxide movement in the area.

The wind direction seems to control the amount of removal of sulphur oxide which occurs. Areas to the south west and south east of Sudbury are probably also under heavy $SO_{2(g)}$ and SO_4^{2-} loading. A study conducted on another large sulphur oxide emitter such as Noranda, Quebec or Trail, British Columbia would be of considerable value as a check on the ability of the results of this study on Sudbury to be applied to other similar areas.

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APPENDIX   I

PROCEDURE FOR SULPHUR ISOTOPE ANALYSIS OF FRESH WATER SAMPLES

Percipitating $BaSO_4$

    1) Filter 1500 ml. of sample

    2) Place sample in 1800 ml. beaker and add two drops of bromine
       (under fume hood)

    3) Boil sample down to 500 ml. using hot plate (under fume hood)

    4) While still boiling add an excess of saturated $BaCl_2$ (about
       10 ml.)

    5) Allow sample to cool and filter to remove percipitated $BaSO_4$

Preparation of $BaSO_4$ for Burning

    1) Heat metal crucible to drive off water

    2) Weigh crucible

    3) Fold filter paper containing $BaSO_4$ and press into the bottom
       of crucible

    4) Heat crucible and $BaSO_4$ until only pure white $BaSO_4$ percipitate
       remains (5 minutes)

    5) Allow to cool and weigh crucible and $BaSO_4$ percipitate

    6) Weigh small glass receptacle

    7) Place 30-40 m.gr. of powdered $BaSO_4$ in small glass receptacle
       and weigh

    8) Place an equal amount of quartz chips on top of $BaSO_4$ and
       compress with glass rod to remove air pockets (do not weigh
       quartz chips)

    9) Compress a small amount of glass wool on top of quartz chips

10) Place small glass receptacle in larger glass receptacle and again place glass wool in tube opening

PROCEDURE FOR SULPHUR ISOTOPE ANALYSIS OF FRESH WATER SAMPLES

Special Note

1) Filter paper used was .45 u

2) Addition of bromine prevents oxidation in sample during boiling

3) $BaCl_2$ must be added in excess to assure all $BaSO_4$ will percipitate

4) Crucible must be kept in dehydration chamber except when in use to prevent inflation of weights

5) When burning filter paper all dark spots (organic debris) must be completly oxidized before heating is discontinued to assure only $BaSO_4$ remains

PROCEDURE FOR SUDBURY STACK SAMPLES - SULPHUR ISOTOPE ANALYSIS

Impinger washed with KOH

1) Add Nitric Acid until pH 2-3

2) 100 ml. heated to boil

3) Excess $BaCl_2$ added

4) $BaSO_4$ percipitated filtered out

Condensate Sample

1) 97 ml. boiled away

2) Residue weighed

3) Residue mixed with EshKa mixture

4) Burned for ten minutes

5) Dissolved in Nitric Acid

6) Boiled and excess $BaCl_2$ added

7) $BaSO_4$ percipitate filtered out

Particulate Sample

1) Fuse with EshKa mixture

2) Dissolve residue in .1N Nitric Acid

3) Boil and add $BaCl_2$ excess

4) $BaSO_4$ percipitate filtered out

PROCEDURE FOR SEDIMENT PREPARTION FOR SULPHUR ISOTOPE ANALYSIS

Removal of water leachable Sulphate

1) 3-4 gms. of sediment (oven dried) was added to 200 ml. of deionized water

2) 1 ml. of hydrogen peroxide was added to the sediment and the slurry was boiled for five minutes

3) The slurry was filtered through 45 u filters paper and the filtate processed the same water sample

Removal of Total Sulphur for Sulphur Isotope Preparation

1) 3-4 grams of sediment sample dried in oven at 90°- 100° C.

2) 1-2 grams of dry sediment mixed with an equal amount of escKa

3) Fused for five to ten minutes in intense flame

4) Fused product dissolved in .1 Normal nitric acid and same process as for water samples followed

CONVERSION OF $BaSO_4$ TO SO_2

1) Attach the quartz envelope (containing sample of barium sulfate) to the collection line via the vacuum-tight Cajon union.

2) Turn on the mechanical pump and close Tap T12. Open Taps T8, T9 and T1 to T6. All other taps must remain closed.

3) Turn on the cold water tap and observe a steady flow of water through the cooling coil of the diffusion pump. Fill the cooling trap D with liquid nitrogen. (Some liquid nitrogen must be maintained in this trap for as long as the diffusion pump is on). Switch on the diffusion pump heater.

4) When the pressure on the guage falls below 0.01 torr, close T8 and open T9. Continue evacuating the system till the pressure falls below 10^{-3} torr.

5) Immerse traps A and B in liquid nitrogen and after 2 mns. close T2, T6 and T7. Open T8.

6) Flame the sample tube as described in Holt and Engelkemier (Anal. Chem., 44 (1970), 1451 - 1453). At the end of the thermal decomposition process, close T1, and continue to pump till the pressure again falls below 10^{-3} torr. Use the diffusion pump by closing T8 and opening T7.

7) Remove the liquid nitrogen from trap A only and thaw with a heat gun. After 2 minutes, close T3 and T4, and then warm trap B with the heat gun. When dry, immerse trap B in dry ice-acetone bath and wait for 5 minutes to allow water to freeze.

8) Place liquid nitrogen on trap C. Close T5. Open T4 and T6 and distil the gases into Trap C (5 minutes). Close T6 and exchange

the liquid nitrogen on trap C for pentane (-125° C.).

9) Replace the dry ice-acetone mixture on B with liquid nitrogen. After distilling off the CO_2 impurity (see note below), close T6 and then trap C. Measure the gas volume.

10) Place a collection tube on line and evacuate. Open T6 and freeze the sample into the collection tube with liquid nitrogen. Seal and remove.

11) While the sample is being transferred to the collection tube, open T2 and remove the liquid nitrogen container from B (and dry this trap with the heat gun). Place a new sample on line and start to evacuate with the mechanical pump. Taps T4 and T5 must remain closed during these operations.

12) Shut down procedure. Close T7 and open T8. Switch off the diffusion pump heater. After 10 minutes, close T8 and T9. Switch off the mechanical pump and open T12. Turn off the cold water tap.

Note: Distilling CO_2 impurity from the gas mixture in trap C. About 5 minutes after replacing the liquid nitrogen on trap C with pentane, tap T6 is carefully opened. The pressure rises and then rapidly drops to less than 10^{-2} torr. As soon as the pressure drops, T6 is shut immediately. If T6 is left open too long, SO_2 starts distilling over. The distillation process takes only a few seconds.

Calculations:

Theoretical volume of SO_2 (cc)

$$= \frac{mg\ BaSO_4}{233.4} \times 22.4 = mg\ BaSO_4 \times 0.096\ ccs$$

Sulphur Isotope Analysis

All stable sulphur isotope analysis were done on a double beam mass spectrometer.

BaSO$_4$ to SO$_{2(g)}$ Conversion Apparatus

Pirani Gauge

T11

Sample port

T5

T6

T7

T2

T10

T3

Cajon union

T1

Sample

A

B

C

D

T9

T8

Heater

To mechanical pump

T4