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Isotopic composition of sulfur in precipitation within the Great Lakes Basin

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ABSTRACT

By monitoring both the isotope ratio variations and the concentrations of sulfur in bulk precipitation samples, the seasonal changes in the relative contributions of airborne sulfur from bacteriogenic and anthropogenic sources have been assessed. Although the $\delta^{34}S$ values during the winter months are generally higher than those of the summer months by about 4‰, there is no corresponding seasonal variability in sulfur concentrations. In general, the average SO_2 concentrations at urban stations are also higher during the winter months. Precipitation samples at urban sites usually have higher sulfur contents and are enriched in ^{34}S compared to samples at rural and remote locations. On the basis of these observations, it is suggested that the bacteriogenic sulfur emissions within the basin may account for 10–30% of all the sulfur emitted in the basin. The data suggest that the biogenic release of sulfur from land areas may be smaller than the figures employed in many models of the global sulfur cycle.

1. Introduction

Isotope ratio measurements have provided important clues on the sources and sinks of sulfur in the atmosphere (e.g., see Östlund, 1959; Nakai and Jensen, 1967; Mizutani and Rafter, 1969; Cortecci and Longinelli, 1970; Grey and Jensen, 1972; Newman et al., 1975a; 1975b; Hitchcock, 1976; Ludwig, 1976). We have monitored the isotopic compositions and concentrations of sulfur in bulk precipitation (rainfall plus dry fallout) samples collected from October 1973 through June 1975 at 37 stations in the Great Lakes Basin. The results of the large-scale, regional survey are summarized in the present report.

The area under study, which is restricted to the Canadian side of the Great Lakes Basin, covers about 3.2×10^5 km^2. Within this region, it is estimated that 3×10^9 kg of SO_2 is released annually into the atmosphere. A substantial quantity of atmospheric sulfur is also imported from the United States side of the Basin (see Kramer, 1975). Anthropogenic and bacteriogenic sources account for most of the annual sulfur emission; less than 10% of the airborne sulfur cycled through the basin comes from sea-salt spray and volcanogenic effluvia (Nriagu, 1975).

2. Methodology

The distribution of the sampling stations is shown in Fig. 1. Monthly bulk precipitation samples were collected using the samplers described by Shiomi and Kuntz (1973). No bacteriocide was added to the samples which were stored under aerobic condition. If biological growth occurred in the samples, it was definitely minor. To our knowledge, the fractionation of sulfur isotopes resulting from biological assimilation of sulfate in aerobic solutions is generally quite small (e.g., see Ishii, 1953). After filtering through 0.45 μm Millipore membrane, each sample was treated with two drops of bromine and boiled down to 200–400 ml. The sulfate in the sample was then determined gravimetrically as barium sulfate.

The barium sulfate was thermally decomposed to release SO_2 by the method of Holt and Engelkemeir (1970). The $^{34}S:^{32}S$ ratios of the SO_2 samples were measured on a dual-collector, isotope

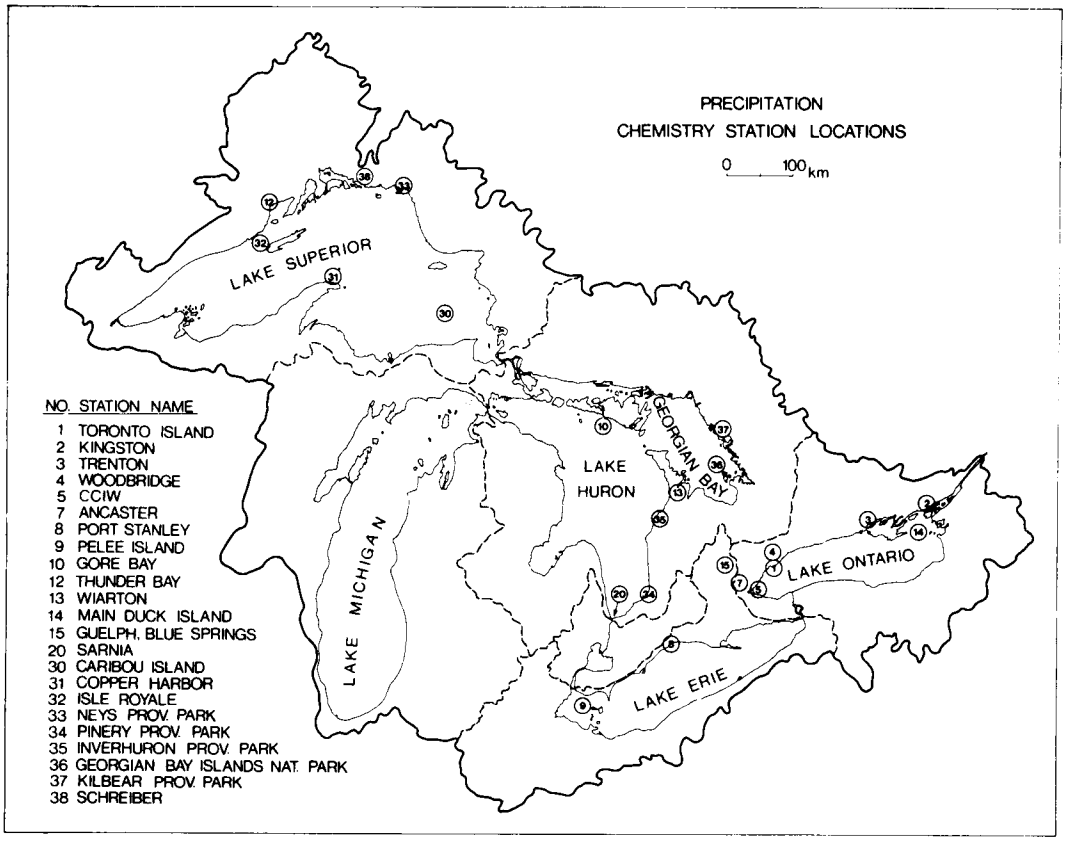

Fig. 1. Great Lakes Basin showing approximate locations of precipitation samplers.

ratio mass spectrometer (VG Micromass, 602C). The isotope ratio results are reported in the usual units of per mil (‰) deviations of the $^{34}S : ^{32}S$ ratios (R) of samples from that of the standard Canyon Diablo troilite:

$$\delta^{34}S = 100\,(R_x/R_{std} - 1)$$

where the subscripts x and std refer to sample and standard respectively. The reported isotope results have an overall precision of ±0.2‰.

3. Results and discussion

The isotopic compositions of sulfur in bulk precipitation collected during 1973 through 1975 are given in Table 1; the corresponding sulfate concentrations in the samples are shown in Table 2. The average $\delta^{34}S$ data for representative urban (Toronto and Hamilton), rural (Trenton and Kingston) and remote (Inverhuron, Kilbear and Neys) stations are shown in Fig. 2, whereas the corresponding sulfate concentrations are shown in Fig. 3. The mean data for all stations in the study area are also shown (as inserts) in Figs. 2 and 3.

The most striking feature of the $\delta^{34}S$ data is the marked seasonal variation, with the samples in the winter months being much heavier than those of the summer months. For all the stations, the mean difference in $\delta^{34}S$ between the winter and summer months is about 4‰. The disparities in $\delta^{34}S$ values between the urban and rural as well as remote stations are also quite pronounced. In general, the remote stations are lighter than the urban stations by about 2‰. In contrast to the $\delta^{34}S$ data, seasonal variations in sulfate concentrations are either not apparent or are very subdued (see Fig. 3). Notice also that the sulfur concentrations at remote locations are less than those of urban stations (Table 1).

Table 1. *Stable isotope ratios (per mil) in bulk precipitation collected at stations in the Great Lakes Basin*

Sample location	Oct. 1973	Nov. 1973	Dec. 1973	Jan. 1974	Feb. 1974	Mar. 1974	Apr. 1974	May 1974	June 1974	July 1974	Aug. 1974	Oct. 1974	Nov. 1974	Dec. 1974	Jan. 1975	Feb. 1975	Mar. 1975	Apr. 1975	May 1975	June 1975
Toronto Is.	+5.58	+7.55	+9.29			+7.51		+5.02	+4.28	+4.04	+4.04	+6.46	+8.60			+8.92		+5.95		+4.38
Kingston				+6.13	+5.45	+4.52	+3.77	+4.25	+3.60				+5.57	+6.83	+6.23	+6.15			+4.70	
Trenton				+6.10				+3.52	+3.47	+2.97	+2.98	+4.29			+6.51	+6.06	+5.22		+4.70	
Woodbridge	+4.90	+7.04	+6.41	+8.20		+6.06	+4.81	+4.46	+4.24	+3.09		+5.83	+8.09	+8.16	+8.80	+6.75				+4.48
C.C.I.W.	+5.37		+7.24	+8.54	+8.30	+7.91	+6.12	+5.12	+4.38		+5.36	+5.75	+6.41	+7.20	+8.10	+8.16	+7.28		+4.94	+5.07
Ancaster								+5.02	+3.59											
Port Stanley				+6.43	+5.53	+4.42	+3.47	+3.48	+2.77	+3.43	+3.30	+3.56	+6.10		+8.24		+6.27		+4.76	+1.15
Pelee Is.			+5.83				+4.01	+3.93	+2.23				+7.19	+4.78						
Gore Bay				+5.90				+3.11	+2.09	+1.66	+2.02	+3.78		+5.17						
Thunder Bay	+3.43	+6.17		+6.11			+4.24	+5.13	+5.32	+6.05	+2.79	+5.22			+7.22			+4.57		+5.94
Wiarton				+5.73	+4.26	+3.77	+3.50	+3.30	+2.74	+2.98	+2.98	+3.40		+6.03		+5.37		+5.54	+3.59	
Sarnia				+6.81	+6.24	+5.63	+4.70	+4.18	+4.01	+3.84		+4.96	+5.11		+6.70	+6.18	+5.76	+5.09	+5.27	+4.24
Copper Harb.	+3.78			+6.46	+4.91			+3.49	+3.23	+4.19		+3.26		+6.14				+3.99	+2.53	
Isle Royale				+5.67	+5.42				+2.87	+3.04		+4.71								
Neys Pk.			+6.51					+2.57	+3.83	+2.72	+1.92	+4.50		+5.31	+8.18		+4.69			+3.84
Pinery Pk.		+5.97		+7.42	+5.61	+5.18	+4.48	+4.25	+3.78		+3.10	+3.83	+5.02							
Inverhuron Pk.		+3.69		+5.15	+5.59	+4.88	+3.85	+3.25	+2.94		+2.19	+4.29	+5.69	+6.15	+7.85	+4.82	+5.37			
Geo. Bay Is. Pk.				+5.43					+2.29	+2.77	+2.21	+3.93		+6.79						
Kilbear Pk.		+6.34	+5.00	+5.73	+5.68	+4.60	+3.69	+3.29	+2.78		+2.09	+4.15		+5.70	+6.55	+4.65	+5.20	+3.93	+3.78	+3.74

Table 2. *Sulfate concentrations (p.p.m.) in bulk precipitation in the Great Lakes Basin*

Sample location	Dec. 1973	Jan. 1974	Feb. 1974	Mar. 1974	Apr. 1974	May 1974	June 1974	July 1974	Aug. 1974	Oct. 1974	Nov. 1974	Dec. 1974	Jan. 1975	Feb. 1975	Mar. 1975	Apr. 1975	May 1975	June 1975
Toronto Is.	1.2			6.4		5.8	7.4	11.9	11.9	15.9	6.3			9.0		7.4		5.8
Kingston		1.3	3.9	4.3	9.0	7.4	8.8			17.7	4.6	2.2	4.4	5.4			10.5	3.1
Trenton		8.2				5.4	7.7	16.9	7.5	9.5	6.7	1.0	5.9	5.7	7.2		8.3	5.5
Woodbridge	4.1	4.6	7.9	6.6	4.0	4.6	5.5	12.5		8.3		7.9	2.3	3.7	9.0			7.4
C.C.I.W.	6.8	10.2	13.3	10.6	7.6	8.6	8.7		12.8	14.3		15.2	10.8	9.0	6.6		16.8	11.8
Ancaster						5.3	9.5											
Port Stanley		3.7	1.5	7.0	11.3	8.6	8.2	7.2	7.4	12.8		1.2	3.9		4.9		8.5	8.7
Pelee Is.	11.1				10.4	7.5					7.0	8.3						
Gore Bay		2.6				3.8	6.1	4.4	3.7	4.0		3.4						
Thunder Bay	3.7	2.4			4.3	4.5	3.3	4.5	3.9	4.3			1.8			6.0		3.2
Wiarton		1.9	4.5	3.6	3.7	4.6	5.6	9.1	9.1	4.0		3.4		4.7		4.8	9.8	
Sarnia		5.1	6.1	2.8	11.1	6.2	10.9	9.8	9.8	16.6	6.2		8.4	7.8	8.1	3.3	14.8	6.7
Copper Harb.		1.2	2.4			5.7	3.9	4.2		2.5		1.9				2.8	2.5	
Isle Royale		1.9	1.6				3.0	2.3	2.4	3.1								
Neys Pk.	2.2					3.2	1.9	1.5	3.3	2.2		2.7	1.8		2.6			2.4
Pinery Pk.		4.1		3.5	6.4	4.2	9.3		6.1	5.8	2.2							
Inverhuron Pk.		3.2	4.5	4.4	3.1	5.8	7.3		8.2			3.9	1.5	3.2	1.1			5.5
Geo. Bay Is. Pk.		4.5					3.9	6.3	7.5	4.2		3.0						
Kilbear Pk.	4.1	2.5	3.1	1.8	3.9	4.2	7.5		5.8	4.9		2.6	2.1	2.1	2.4	3.5	6.6	7.0

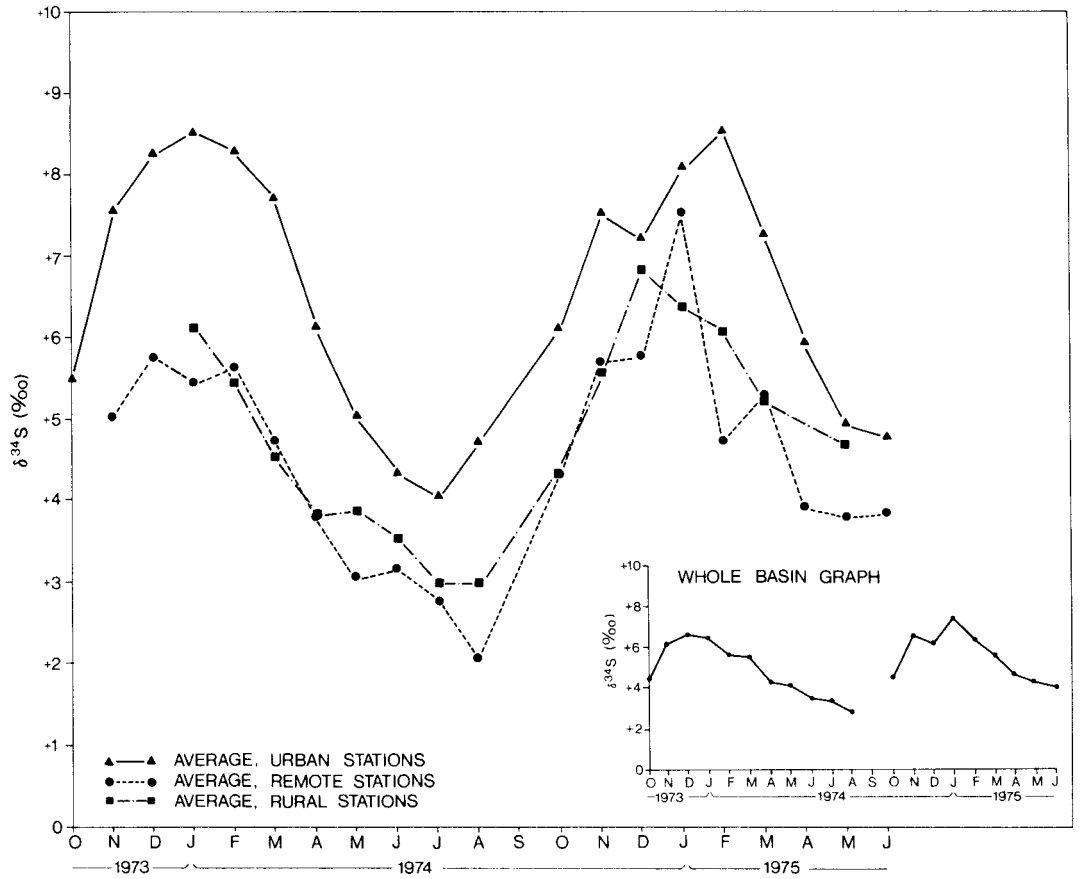

Fig. 2. Seasonal variations in averaged $\delta^{34}S$ data for urban, rural and remote stations. The graph for all stations is shown as an insert.

Several studies of temporal and spatial variations in isotopic composition of sulfur in precipitation have addressed the question of the origin of atmospheric sulfate and the washout mechanism. Mizutani and Rafter (1969) determined the isotopic compositions of both oxygen and sulfur in "rain only" samples collected at Gracefield, New Zealand, during only five months. Their data did not reveal a definite temporal trend, but did indicate that a large percentage of the sulfate in their rain water was derived from sea-salt sprays. Cortecci and Longinelli (1970) monitored the "precipitation only" samples at Pisa, Italy, from August 1968 to July 1969, and found the $\delta^{34}S$ values to be fairly constant throughout the year; their data ranged from −2.5 to 7.1‰. Holt et al. (1972) found large variations (of up to 5‰) in the isotopic compositions of sequential samples collected during two storms at Hinsdale (near Chicago), Illinois. Their results on composite samples from several storms, between March and June 1970, showed no temporal variability. It should be stressed that the studies above have used event only samples whereas bulk precipitation samples have exclusively been analyzed in the present study. A recent study (Kramer, 1975) shows that the deposition of sulfur in the Great Lakes Basin by rainfall is comparable to that from the dry fallout.

Östlund (1959) analyzed precipitation samples collected at several locations in North America and Scandinavia during 1957–58 and found no variation in $\delta^{34}S$ values with sample location. On the other hand, Jensen and his colleagues (Nakai and Jensen, 1967; Grey and Jensen, 1972) found large variations in the $\delta^{34}S$ values of rain and snow samples collected in Japan and the U.S.A. which

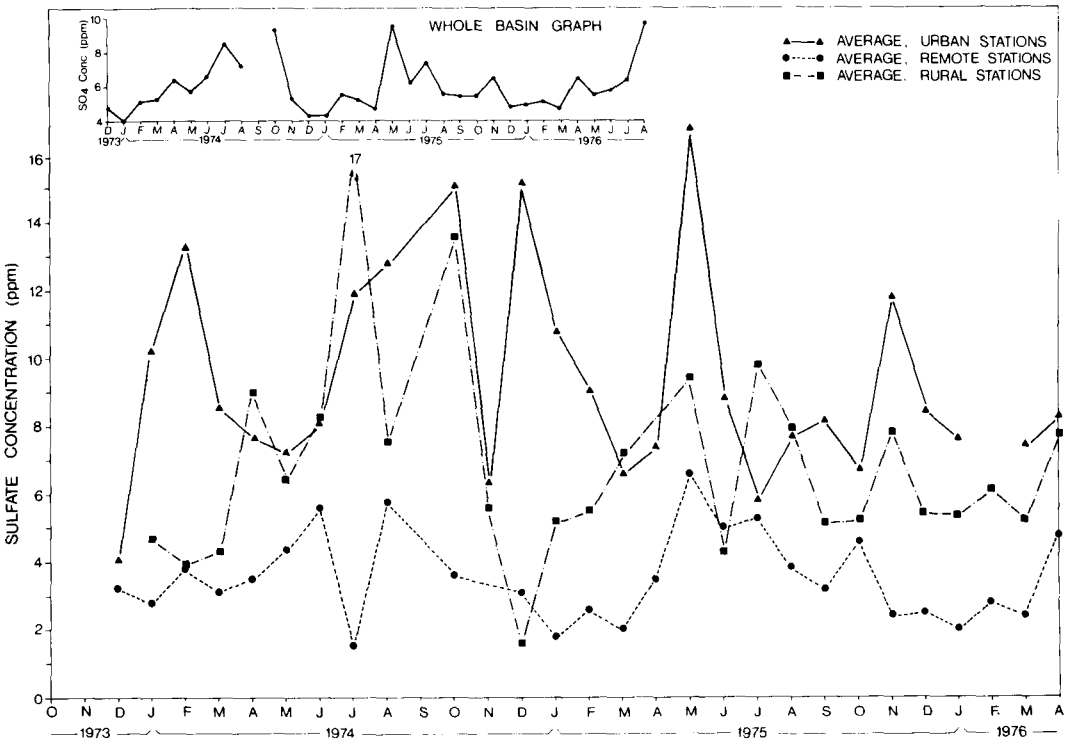

Fig. 3. Temporal variability in averaged sulfate contents of precipitation samples from urban, rural and remote stations. The mean data for all stations are shown as an insert.

were attributed to differences in the admixture of sulfur compounds from bacteriogenic and anthropogenic sources. They reported that the copper smelters near Salt Lake City were the dominant local sources of sulfur on a yearly basis, but that biogenic sources made a significant contribution during periods of peak activity. Ludwig (1976) recently reported that the $\delta^{34}S$ values of aerosol and cloud droplet samples collected in unpolluted marine air (San Francisco Bay area) were lower than those from the adjacent and more polluted urban areas. He concluded that the sulfur aerosols in the marine air were mostly derived from bacteriogenic sources. These studies thus generally show that the sulfur derived from seasalt sprays is not as great as one would expect, even in coastal areas, and that most of the airborne sulfur comes from pollutant and biogenic sources.

The processes responsible for the observed seasonality in the $\delta^{34}S$ values probably include: (a) seasonal variations in the contributions of the different sources to the atmospheric sulfur burden and (b) changes in mechanism of origin of the sulfur in precipitation, such as the fractionation of the isotopes during the removal of sulfur by rainfall compared to snowfall. The observed temporal trend in $\delta^{34}S$ values cannot be due to seasonal differences in the amount of sulfur removed from the atmosphere because the graphs of sulfur concentrations do not show a corresponding systematic variation. Indeed, Fig. 4 shows that the $\delta^{34}S$ values are independent of the sulfate concentrations in monthly bulk precipitation samples particularly at the urban stations. It is also significant that the $\delta^{34}S$ values are not strongly influenced by the precipitation intensity either during the summer or winter months (see Fig. 5); sequential sampling of storms likewise shows no systematic trend in the $\delta^{34}S$ values (see Holt et al., 1972).

Little is currently known about the fractionation of sulfur isotopes during the rainout versus snowout of sulfur compounds from the atmosphere. In an effort to get a handle on the problem, we are now monitoring the isotopic composition of sulfur in precipitation samples

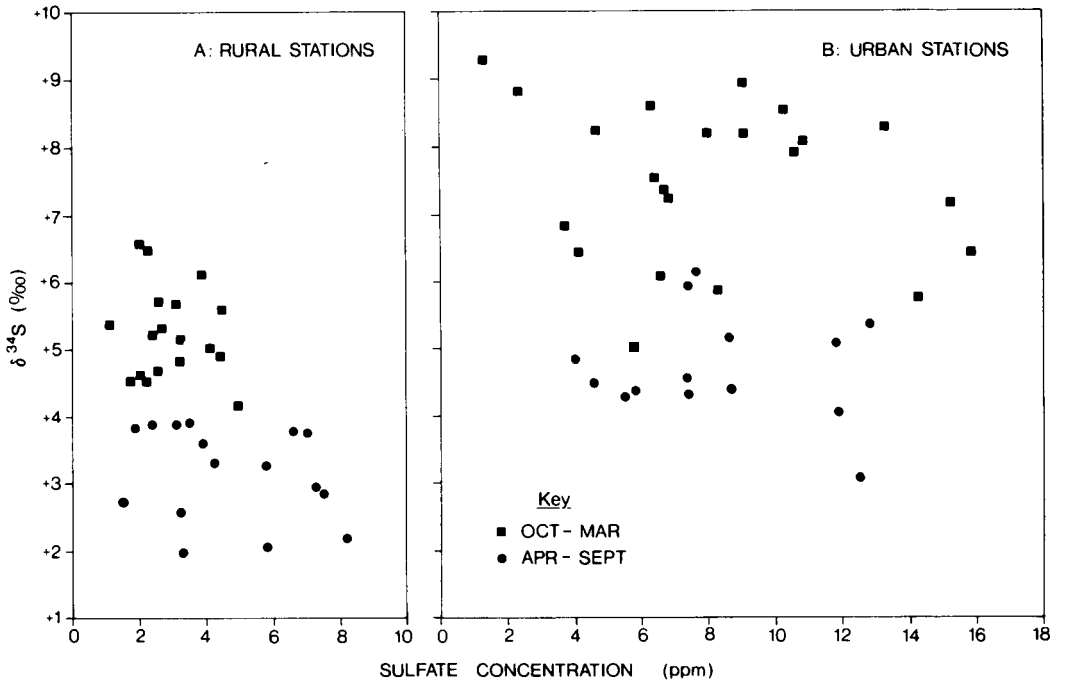

Fig. 4. Relationship between the $\delta^{34}S$ values and sulfate contents of bulk precipitation samples from remote (A) and urban (B) stations.

collected near the smelter stacks at Sudbury (Ontario), a source with relatively constant δ^{34} value. The preliminary data also show a seasonality in $\delta^{34}S$ values, implying that washout phenomena may contribute to the observed difference in the data for the summer and winter months. Around Sudbury, however, there is a significant correlation between $\delta^{34}S$ and the sulfate contents of the precipitation samples. The absence of a similar correlation in the present regional surveys suggests that the seasonal variability in $\delta^{34}S$ data cannot be attributed solely to the isotopic fractionation associated with the washout phenomena.

In order to ascertain exactly the isotopic effects of the precipitation processes, it would be necessary to determine the $\delta^{34}S$ values of the simultaneously collected SO_2, SO_4^{2-} and the rainfall or snowfall. It was not feasible to include all these measurements during the present study. We recognize that the sulfur content of the bulk precipitation samples is related in a complex fashion to the sulfur content of the ambient air (see Fisher, 1977). Table 3 shows the average monthly SO_2 levels at selected urban stations in the Great Lakes Basin; comparable measurements at non-urban locations are not available. Incidentally, the reduction in the SO_2 level at Sudbury is related to the installation of taller stacks at the smelters. Unfortunately, none of the air monitoring stations matches the rain monitoring station, making it impossible to assess the relationships between the

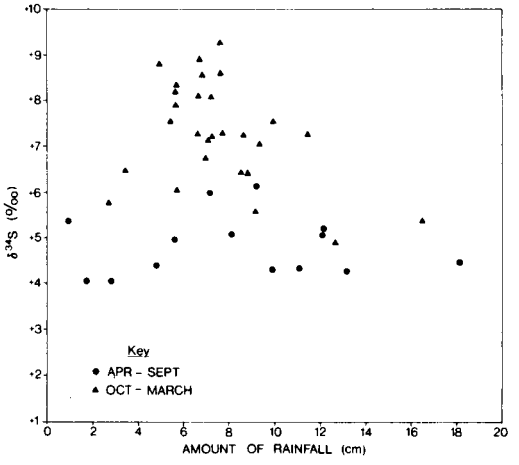

Fig. 5. Plot of mean rainfall (cm) versus $\delta^{34}S$ for urban stations.

Table 3. *Monthly average atmospheric sulfur dioxide concentrations at locations in the Great Lakes Basin*

	Time and SO_2 concentration (parts per hundred million)*											
	1974											
	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.
Windsor												
Norton Terminal Dock	1.8	3.4	1.9	1.7	2.1	1.6	1.9	2.4	2.0	3.7	2.3	1.8
471 University Ave.	5.5	3.5	1.6	3.5	2.5	2.8	4.0	3.2	2.6	3.6	3.1	3.8
Toronto												
67 College St.	2.4	2.0	1.2	1.7	0.9	0.8	0.7	1.1	0.8	0.4	0.9	1.8
Science Center, Don Mills	2.0	1.5	1.3	1.5	1.3	2.1	1.6	1.8	1.2	2.7	2.5	1.5
Evans and Arnold St.	2.2	2.1	1.5	1.8	1.9	1.7	1.5	0.9	0.7	1.3	1.2	1.5
Lawrence and Kennedy St.	0.6	0.6	0.5	0.7	0.6	0.7	0.6	1.2	1.1	1.3	0.7	0.9
Pharmacy and Hwy 401	1.0	0.9	1.1	1.1	0.9	1.1	0.6	0.6	0.3	0.2	0.4	0.6
Hamilton												
Barton and Sanford St.	2.0	3.3	2.3	2.1	2.7	2.0	1.3	1.5	1.3	2.8	1.9	2.6
North Park	5.7	1.5	1.6	1.8	1.0	1.2	1.3	1.2	2.1	1.8	1.4	2.0
Sudbury												
Ash St.	3.0	3.0	3.5	3.7	2.7	3.1	5.1	3.5	3.0	2.4	3.1	3.5
Sarnia												
156 Victoria St.	2.3	—	1.7	2.5	2.7	2.2	1.7	2.9	4.1	4.2	3.8	3.3
Average												
(Sudbury excluded)	2.6	2.1	1.5	1.8	1.7	1.6	1.5	1.7	1.6	2.2	1.8	2.0
	1975											
	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.
Windsor												
Norton Terminal Dock	—	4.2	2.4	2.8	3.1	3.0	3.2	2.3	1.0	0.7	1.0	1.4
471 University Ave.	4.3	4.0	2.1	2.4	2.9	2.1	3.3	2.7	2.4	1.8	2.1	2.8
Toronto												
67 College St.	1.3	1.5	2.0	1.4	1.6	1.9	1.1	0.7	0.9	1.9	1.6	1.9
Science Center, Don Mills	1.7	2.0	0.6	0.8	1.3	1.0	1.8	2.5	0.9	1.2	1.1	1.4
Evans and Arnold St.	1.8	1.8	1.2	1.2	1.1	0.8	0.6	0.3	0.5	0.8	1.2	1.5
Lawrence and Kennedy St.	0.9	0.9	0.6	0.9	1.0	2.0	1.4	0.9	1.3	1.8	1.5	1.7
Pharmacy and Hwy 401	1.1	0.9	0.9	0.9	1.5	1.4	0.9	0.3	0.6	1.6	0.9	1.2
Hamilton												
Barton and Sanford St.	2.1	2.0	2.2	2.3	2.2	2.0	1.1	1.8	1.5	2.4	2.1	2.6
North Park	2.0	1.7	1.0	0.6	0.9	0.5	1.2	1.4	1.1	1.3	2.0	1.9
Sudbury												
Ash St.	5.1	4.2	4.1	3.1	3.9	2.1	2.3	2.1	2.2	1.3	1.6	1.3
Sarnia												
156 Victoria St.	2.9	2.4	1.6	2.4	2.3	2.5	2.4	—	1.1	2.4	2.8	2.4
Average												
(Sudbury excluded)	2.0	2.1	1.5	1.6	1.8	1.7	1.7	1.4	1.1	1.6	1.6	1.9

* Compiled from data published by National Air Pollution Surveillance (1974/75).

sulfur isotopic composition and the ambient sulfur concentration. Table 3 does, however, emphasize the local origin of the atmospheric SO_2 at the urban stations. It is equally noteworthy that the average SO_2 concentrations at the urban locations are higher during the winter months than during the other times of the year (see below). Hitchcock (1976) also found the mean sulfate levels in urban sites in U.S.A. during winter and spring to be much higher than those of the other seasons.

The possibility that the seasonal variation in $\delta^{34}S$ may stem from differences in the extraregional contribution of sulfur by seasonally different prevailing winds should also be considered. Three major air mass types dominate the weather in the Great Lakes Basin: Arctic air, which moves in

from the north mostly in the winter time; Pacific air from the west coast, and the warm tropical air, which moves north from the Gulf of Mexico across the industrial regions of the eastern and mid-eastern U.S.A. The first two air masses should generally be clean, whereas the third air mass (which is responsible for much of the summer rainfall, often in the form of convective storms) should be heavily loaded with pollutant sulfur (Summers and Whelpdale, 1976). In terms of the prevailing winds, the sulfur contents of bulk precipitation samples and the mean monthly atmospheric SO_2 concentrations should be higher in summer compared to the winter time. Inspection of Table 2, however, reveals no significant seasonal differences in the observations made during 1974 and 1975; in fact, the opposite trend is found in urban stations (Table 3). Altschuller (1976) also reached the conclusion that climatological factors exercise only a minor influence on the regional distribution of sulfate in the U.S.A.

The foregoing suggests that the seasonal differences in $\delta^{34}S$ values are due, in part, to changes in the relative amounts of the atmospheric sulfur compounds derived from bacteriogenic and anthropogenic sources. It may be argued that in winter months, the increased use of fossil fuels to provide space heating increases appreciably the release of sulfur into the basin atmosphere (see Table 3). Recent studies by Goffin (1973) and Caulson (1973) suggest that the emission of SO_2 associated with space heating constitutes 10–30% of the total annual SO_2 emissions from anthropogenic sources. High SO_2 levels and high $\delta^{34}S$ values in winter times observed at the urban areas (see Fig. 2 and Table 3) are evidence that within the basin, the sulfur, due to space heating, apparently is enriched in ^{34}S relative to the background sulfur at the remote stations. In summer months, the space heating elements are inactive and the fact that the sulfur contents of the bulk precipitation remain unchanged (or show a marginal increase) can only indicate substantial bacteriogenic addition of sulfur to the atmospheric sulfur pool. The decrease in $\delta^{34}S$ values during the summer months strongly supports the argument; bacteriogenic sulfur released from soils and wetlands is characteristically depleted in ^{34}S (see Kemp and Thode, 1965; Grey and Jensen, 1972; Nriagu and Coker, 1976). By considering the isotopic effects of the washout phenomena to be minor, we can speculate that the maximum bacteriogenic contribution to the atmospheric sulfur burden is comparable to sulfur emissions associated with space heating, i.e., that the maximum contribution of sulfur from bacteriogenic sources is 10–30% of total sulfur emitted in the basin. Using other lines of evidence, Hitchcock (1976, 1977) essentially arrived at the conclusion that biogenic sources may give rise to local concentrations of particulate sulfur which are comparable to those observed in many cities in winter when pollutant sulfate sources are large.

There is the possibility that the sulfate at the remote stations represents anthropogenic background sulfate, whereas that at the urban sites includes both the common background sulfur and the specific contributions from local urban sources. In this case, it is doubtful whether the marked seasonality in $\delta^{34}S$ values would be observed unless the urban sources are putting out sulfur with seasonally varying isotopic composition. Even so, the differences between the $\delta^{34}S$ values of the winter and summer months should be much larger at the urban stations. Fig. 2, however, shows the amplitudes of the sinuous graphs for the urban and remote stations to be quite similar.

Our interpretation of the data needs to be confirmed by (a) the study of the time-dependent variation in $\delta^{34}S$ values of atmospheric sulfur in the basin, and (b) a detailed inventory of the sources and fluxes of sulfur in the basin. Indeed, it is our sincere hope that the present report will stimulate other studies on the cycling of sulfur in the Great Lakes Basin. The interpretation is consistent with the conclusion by Hitchcock (1976, 1977) that a large fraction of the summertime atmospheric sulfate, in many parts of the United States, is of local biogenic origin. This point was clearly demonstrated in the Monroe County (New York) sampling network, where she noted a strong correlation between SO_2 emissions and sulfate concentrations in the winter, but virtually no agreement in the summer, when the pattern was congruent with the distribution of wetlands.

Thus, by monitoring both the isotope ratio variations and the concentrations of sulfur in monthly bulk precipitation samples, it has been possible to ascertain the seasonality in the relative emissions of sulfur from anthropogenic and biogenic sources. The data implicate the summer time release of sulfur from soils and wetlands as an

important source of atmospheric sulfur compounds in the Great Lakes Basin. It seems reasonable to suggest that some of the bacteriogenic sulfur is derived from pollutant sulfur deposited on soils and wetlands in preceding years. Most models of the global sulfur cycle invoke such bacteriogenic emissions in order to balance the sulfur budget (see Robinson and Robbins, 1970; Moss; 1977). The present data, however, suggest that the biogenic release of sulfur from the land areas may be considerably smaller than the figures employed in many model calculations.

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ИЗОТОПНЫЙ СОСТАВ СЕРЫ В ОСАДКАХ В БАССЕЙНЕ ВЕЛИКИХ ОЗЕР

Путем мониторинга как вариаций отношений изотопов, так и концентрации серы в пробах осадков, определены сезонные изменения в относительных вкладах серы в воздухе от бактериогенных и антропогенных источников. Хотя величины $\delta^{34}S$ зимой обычно выше на 4‰, чем летом, нет соответствующей сезонной изменчивости в концентрациях серы. В общем средние концентрации SO_2 на городских станциях также выше в зимние месяцы. Пробы осадков в городских местах обычно имеют более высокие концентрации серы и обогащены ^{34}S по сравнению с пробами в сельских и отдаленных местностях. На основе этих наблюдений выяснено, что бактериогенные источники серы в бассейне Великих озер приблизительно эквивалентны по интенсивности источникам серы, связанным с использованием ископаемых топлив для обогрева, т.е. бактериогенные источники поставляют от 10 до 30% серы, выпускаемой в этой области.