

Isotopic evidence for the origin of sulphate in coastal rain

By M. A. WADLEIGH^{1*}, H. P. SCHWARCZ² and J. R. KRAMER², ¹*Department of Earth Sciences, Memorial University of Newfoundland, St. John's, Newfoundland, Canada, A1B 3X5*; ²*Department of Geology, McMaster University, Hamilton, Ontario, Canada, L8S 4M1*

(Manuscript received 15 July 1994; in final form 1 March 1995)

ABSTRACT

Stable sulphur and oxygen isotopic analyses were combined with chemistry, air mass back trajectories and factor analysis on 39 rainfall events collected at Shelburne, Nova Scotia, Canada in an attempt to identify the sources of sulphate in precipitation falling in this coastal area. Sulphate in the Shelburne rain samples can be described by two-endmember mixing between continental and oceanic sources. The continental endmember is characterized by $\delta^{34}\text{S} \approx 4\text{‰}$ and $\delta^{18}\text{O} \approx 11\text{‰}$ and is interpreted as representing the average value for continentally-derived, long range transported sulphate. The marine endmember has $\delta^{34}\text{S} \approx 21\text{‰}$ and $\delta^{18}\text{O} \approx 9.5\text{‰}$ corresponding to the composition of oceanic dissolved sulphate which entered the rain as sea spray. Significant components of putative marine, DMS-derived sulphate were not observed in any of the rain samples.

1. Introduction

Emissions of reduced sulphur compounds from vegetation, wetlands, soils and the ocean total $\approx 65 \text{ Tg S y}^{-1}$ (range 30 to 100 Tg S y^{-1}) and represent the largest natural contributors of sulphur to the atmosphere apart from sea spray (Brimblecombe et al., 1989). They include hydrogen sulphide (H_2S), dimethyl sulphide (DMS), carbon disulphide (CS_2) and carbonyl sulphide (COS) (Ryaboshapko, 1983; Steudler and Peterson, 1984; Aneja and Cooper, 1989). DMS is the most important of these compounds in the marine environment accounting for $\approx 35 \text{ Tg S y}^{-1}$ (range 20 to 50 Tg S y^{-1} ; Saltzman and Cooper, 1989; Whelpdale, 1992). Concentrations of DMS in seawater in most ecological zones are broadly correlated to levels of marine primary production (Andreae and Barnard, 1984) and oxidation of DMS leads to sulphate formation in the troposphere. The potential environmental impact of this biogenic sulphate aerosol in terms of rainfall acidity, climate (Bates et al., 1987; Charlson et al.,

1987; Shaw, 1983) and the extreme sensitivity of remote regions to perturbations makes it essential that this source of sulphur to the atmosphere be characterized.

Direct information about sources of atmospheric sulphur compounds cannot be obtained by concentration measurements alone. However, large differences in the sulphur and oxygen isotopic composition between various reservoirs have prompted the application of stable isotopes to quantify specific contributions to the atmospheric load.

Precipitation is the main removal mechanism for sulphate. The isotopic composition of sulphate dissolved in precipitation is controlled by the nature and composition of the source, whether or not it has undergone chemical transformation, its temperature of formation and how it was incorporated into the rain. Sulphate is incorporated into precipitation through nucleation scavenging during cloud formation (Scott, 1978), in-solution formation of sulphate from absorbed sulphur dioxide (Scott and Hobbs, 1967) and below cloud scavenging of sulphate particles by rain (Hobbs, 1979; Scott, 1981). In general, in-solution production contributes the largest percentage of sulphate

* Corresponding author.

in industrial regions while nucleation scavenging is most important in remote regions. Both sulphur and oxygen isotopes are sensitive to these relative inclusion pathways. If the isotopic compositions of the sources are sufficiently different from one another and if the changes that accompany subsequent chemical and physical transformations are understood, the stable isotopes of oxygen and sulphur have great potential as source tracers.

The path travelled by an air mass prior to a rain event can be modelled using three dimensional air mass back trajectory analysis. By relating this transport information to the chemistry of the associated precipitation event it becomes possible to hypothesize concerning sources and estimate the extent to which air mass back trajectories can predict air and subsequent precipitation quality. This application is somewhat different from the more traditional approach of using trajectories to screen air masses for sampling.

2. Goals of this study

A coastal location was proposed as the site for collection of precipitation samples. In this environment both sea spray, with its well established sulphur and oxygen isotopic compositions, and continental sulphate should be strongly represented. By using the air mass back trajectories of storm events we hoped to be able to separate the influence of these two source regions. The Atmospheric Environment Service (AES) Upper Air Station at Shelburne, Nova Scotia was chosen as the specific sampling site. Shelburne is located on the Atlantic coast approximately 200 km southwest of Halifax (Fig. 1). This location, near a zone of high productivity, was also suitable for evaluating the potential contribution of DMS. Using a combination of chemical and stable isotopic analyses of the rains, we further proposed to quantify the contribution of the marine com-

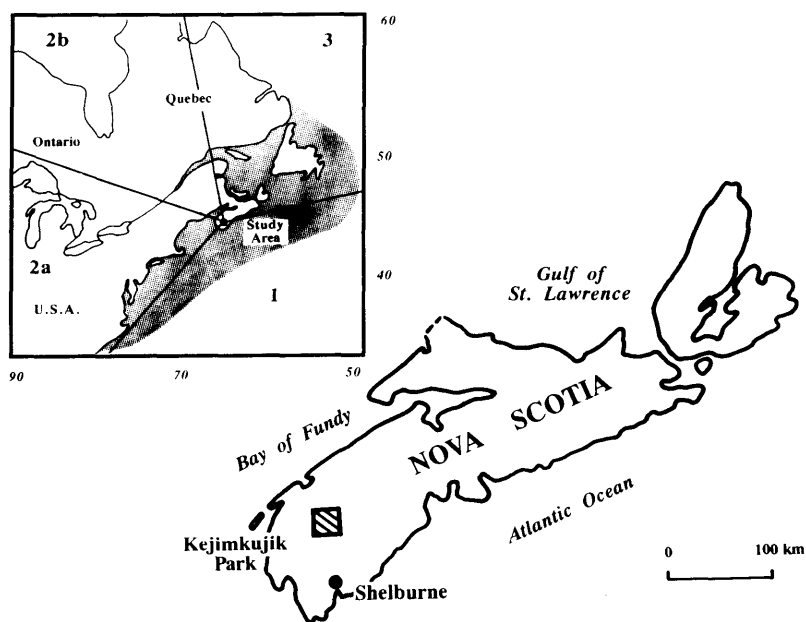


Fig. 1. A high volume precipitation collector was located at the Atmospheric Environment Service upper air station in Shelburne, Nova Scotia, Canada. Air mass back trajectories were computed from Kejimikujik Park. Inset shows position of study area relative to the rest of eastern North America. Air mass back trajectory sectors are also identified on the inset. Sector 1 represents samples of marine origin (azimuth ≈ 080 to 220). Sector 2 represents samples of continental origin and is subdivided into 2a Great Lakes and south (azimuth ≈ 220 to 280) and 2b north of the Great Lakes (azimuth ≈ 280 to 350). Sector 3 includes samples of mixed marine and continental origin (azimuth ≈ 350 to 080). Stippled pattern identifies zone of high biological productivity.

ponent and to allocate it to DMS and sea spray sulphur sub-components.

Such a coastal site stands at the boundary between 2 regions in which the sulphur and oxygen isotopic patterns in precipitation are known to be quite different. By choosing this location therefore, we would be able to use the inter-regional isotopic (as well as chemical) contrast to sort out the effects of these two source regions. Only a few other studies have applied the combination of oxygen and sulphur isotopes in precipitation to elucidate sources, mechanisms of sulphate formation and transport phenomena. Furthermore, these studies have either been based entirely within the continent (Caron et al., 1986; Van Stempvoort et al., 1992; Holt and Kumar, 1991; Norman, 1991) or on the shore of a smaller landmass where the full effect of continental sources may not be felt (Mizutani and Rafter, 1969; Cortecchi and Longinelli, 1970; Norman, 1991).

3. Stable isotopes

The isotopic composition of a substance (A) is expressed as deviations (δ) in parts per thousand (permil, ‰) from a universal standard according to the following equation

$$\delta_A = [(R_A/R_{\text{standard}}) - 1] \times 10^3,$$

where R denotes the ratio of the minor isotope to the major isotope, i.e., $^{18}\text{O}/^{16}\text{O}$ or $^{34}\text{S}/^{32}\text{S}$. The standard for comparison of sulphur isotope compositions is troilite (FeS) from the Canyon Diablo meteorite (CDT). For oxygen it is Standard Mean Ocean Water (V-SMOW).

3.1. Sulphur

Fig. 2a illustrates sulphur isotopic compositions of species relevant to the atmosphere. The various contributions can be broadly subdivided into marine and continental source regions.

Marine emissions: sea spray is derived from the well-mixed reservoir of oceanic sulphate which has a constant sulphur isotopic composition of $+21\text{‰}$ (Rees et al., 1978). No major fractionation is involved in the formation of spray from dissolved oceanic sulphate (Luecke and Nielsen, 1972). Therefore its $\delta^{34}\text{S}$ should be $\approx +21\text{‰}$.

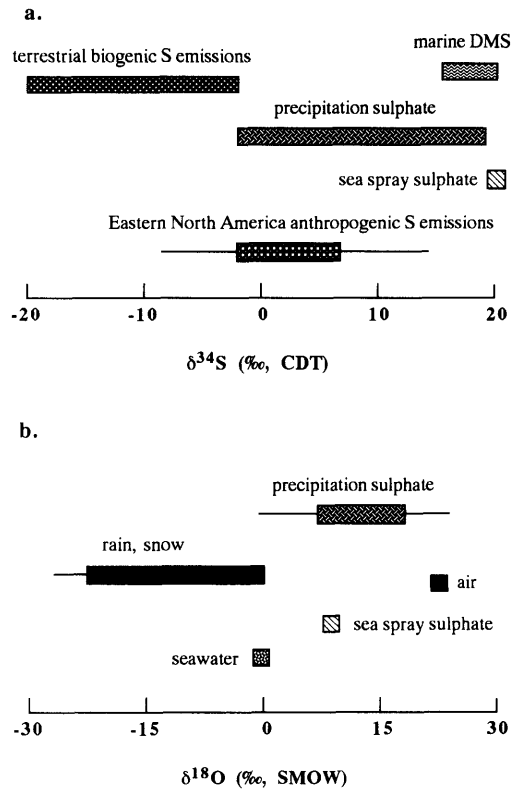


Fig. 2. (a) Range of sulphur isotopic compositions of species relevant to the atmosphere. (b) Range of oxygen isotopic composition of species relevant to the atmosphere.

There appears to be little or no fractionation of sulphur during its incorporation into marine plant tissue, but a slight fractionation of -1 to -4‰ when volatile sulphides are produced from amino acid sulphur through bacterially mediated processes. Marine DMS is produced as a by-product of protein synthesis by phytoplankton (Andreae, 1980) and under these circumstances is not likely to be depleted in ^{34}S relative to seawater sulphate by more than 4‰ (Hitchcock and Black, 1984; Calhoun and Bates, 1989). A few sulphur isotope measurements of submicrometer aerosol sulphates consistent with a marine DMS origin have been made over remote parts of the south Pacific Ocean (Calhoun et al., 1991). The mean $\delta^{34}\text{S}$ value was $+15.6 \pm 3.1\text{‰}$.

Sulphides produced by mixed bacterial cultures in estuarine sediments (Nakai and Jensen, 1964) or

marine sediments (Kaplan, 1975; Carlson and Forrest, 1982) are depleted in ^{34}S by 20 to 30‰ relative to the sulphate substrate. Therefore H_2S produced by bacterial sulphate reducers from a seawater sulphate substrate (+21‰) should have $\delta^{34}\text{S}$ between -9 and +1‰. In more restricted environments such as salt marshes and tidal flats where seawater may have been depleted in ^{32}S by prior bacterial action, resultant sulphide may be also depleted in ^{32}S slightly extending the expected range of values (Hitchcock and Black, 1984).

Continental emissions: Continental emissions include biogenic and anthropogenic components. The primary sulphur precursor for continental biogenic emissions is dissolved sulphate, derived from rainwater or groundwater. In particular, groundwater sulphate is obtained from oxidized sedimentary or igneous sulphides and leached evaporites, sources with sulphur isotopic compositions that vary widely. However, if the sulphate has not been subject to bacterial reduction in the soil it is observed to average between 0 and +1.5‰ (Nielsen, 1974; Newman et al., 1991). No major isotopic fractionation is involved in the uptake of sulphur by plants (Mekhtiyeva and Pankina, 1968) so this estimate would extend to biogenic emissions by plants to the atmosphere. Bacterial reduction would preferentially consume the lighter isotope according to the fractionation described above. This would enrich the groundwater reservoir in ^{34}S and correspondingly enrich emissions by vegetation to the atmosphere. Using sulphur isotopic data collected in a four year study of remote areas of Canada, Nriagu et al. (1987) determined that the seasonal variations ($\delta^{34}\text{S} \approx 2$ to 3‰ higher in winter than summer) were best explained by an increased release of biogenic sulphur during the summer. They estimated the composition of the biogenic sulphur component to be -2.4‰.

Anthropogenic emissions consist of compounds generated by industrial processing of native sulphur and H_2S , sulphide ores, coal and petroleum. $\delta^{34}\text{S}$ values show a wide range depending on the exact nature of the source, from ≈ -3 ‰ in Italy (Corceci and Longinelli, 1970) to +2‰ in Sudbury (McMaster University unpublished data) to $> +20$ ‰ for the sour gas wells in Alberta (Krouse, 1980).

Sulphur from all of these sources can be incor-

porated into continental rain. Commonly quoted average values for aerosols and rain in central and eastern North America fall between +3‰ and +6‰ (Caron et al., 1986; Nriagu et al., 1991; Barrie et al., 1992). Sulphur in Canadian Arctic haze is slightly heavier than this ranging from a minimum monthly value of 5.5‰ in March/April to a maximum of 9.5‰ in August (Nriagu et al., 1991). The biogenic component of this sulphur is estimated to comprise between 14 and 30% of the total with the higher percentage corresponding to summer measurements (Li and Barrie, 1993).

3.2. Oxygen

Fig. 2b summarizes oxygen isotopic compositions relevant to atmospheric sulphates. Marine and continental components can be recognized as well as the compositions of different oxidants. Measurements of oceanic dissolved sulphate indicate a constant oxygen isotopic composition averaging ≈ 9.5 ‰ (Lloyd, 1968). It is assumed that this value is retained in sea spray as is the case for $\delta^{34}\text{S}$.

Dansgaard (1964) demonstrated that the $\delta^{18}\text{O}$ value of average annual meteoric precipitation decreases by 0.7‰ per °C decrease in average annual air temperature. The oxygen isotopic composition of precipitation also depends on factors such as degree of rainout, but temperature and associated variables such as latitude and altitude are the most important parameters. This produces strong seasonal variations in isotopic composition of rain and snow with minimum values occurring in winter. In North America, precipitation $\delta^{18}\text{O}$ values typically range from ≈ -5 ‰ in the south to -20 ‰ in northern regions. Much is known about the oxygen isotopic composition of the atmosphere and the factors affecting the composition of water vapour such as geographical location, season, plant transpiration, etc. Atmospheric oxygen is strongly enriched in ^{18}O and has a constant isotopic composition of +23‰ (Dole et al., 1954; Kroopnick and Craig, 1972). But comparatively little information is available on the ^{18}O contents of atmospheric oxidants such as O_3 , H_2O_2 , and NO_2 or free radicals such as OH and HO_2 .

Several field studies of atmospheric sulphates have reported $\delta^{18}\text{O}$ values. Precipitation sulphates in the Chicago area of the American midwest range from +4 to +20‰ (Holt and Kumar, 1991);

in Gracefield, New Zealand they range from +7 to +14‰ (Mizutani and Rafter, 1969); in Pisa, Italy from +6 to +17‰ (Cortecci and Longinelli, 1970); in La Jolla, California from +8 to +11‰ (Kroopnick, 1977); in Quebec, Canada from +9 to +14‰ (Caron et al., 1986); in Alberta from -3 to +15‰ (Norman, 1991; Krouse, 1980) and in Bermuda from +7 to +12‰ (Norman, 1991). While these values seem quite variable the oxygen isotopic compositions of the non-seasalt component (or excess sulphate) are actually quite similar in average.

3.3. Oxidation

Sulphur isotopes can be fractionated by many natural geochemical processes including oxidation. Oxidation of SO₂ can proceed in both the aqueous and gaseous phases by a variety of reaction mechanisms and with different oxidants, and is characterized by a small kinetic isotope effect (e.g., $\alpha = 0.996$ @ 25°C for the step involving oxidation of HSO₃⁻ by dissolved O₂; Saltzman et al., 1983). The result is a product sulphate with $\delta^{34}\text{S}$ a few ‰ lower than the precursor SO₂. Aqueous phase oxidation is also accompanied by a large equilibrium isotope effect ($\alpha = 1.011$ to 1.0165 @ 25°C; Eriksen, 1972; Egiazarov, 1971) which occurs during dissociation of SO₂·H₂O to HSO₃⁻ and H⁺. Therefore, gas phase (homogeneous) oxidation mechanisms would produce sulphate which is isotopically lighter than the precursor SO₂ while aqueous phase (heterogeneous) oxidation mechanisms would produce sulphate that is isotopically heavier. For example, sulphate derived from homogeneous oxidation of SO₂ emitted with $\delta^{34}\text{S} = +6$ ‰ would have a sulphur isotopic composition of +2‰ due to the kinetic isotope effect, while sulphate derived from heterogeneous oxidation of the same SO₂ would have $\delta^{34}\text{S} = +13$ to +18.5‰ because of the additional equilibrium isotope effect. An additional complication is the fact that the equilibrium isotope effect is temperature dependent. There is some disagreement with respect to the magnitude of the change but not the direction; α increases with decreasing temperature. A seasonal decrease in temperature would increase $\delta^{34}\text{S}$ of the product sulphate by 0.08 to 0.145‰ per °C. It has also been observed that homogeneous reactions are more important during

warmer months while heterogeneous reactions dominate during cooler months (Saltzman et al., 1983).

$\delta^{18}\text{O}$ values of sulphates depend on those of the water, oxidants and mechanisms involved in their formation. Mechanisms can be broadly subdivided into: (i) aqueous systems and (ii) systems with no liquid water. Holt et al. (1981) studied aqueous mechanisms of oxidation of SO₂ using oxygen isotopes. They observed that the $\delta^{18}\text{O}(\text{SO}_4)$ varied with the $\delta^{18}\text{O}(\text{H}_2\text{O})$ according to regression equations of the general form

$$\delta^{18}\text{O}(\text{SO}_4) = \approx \frac{3}{4} \delta^{18}\text{O}(\text{H}_2\text{O}) + C$$

suggesting that three of the four oxygen atoms in the sulphate are isotopically controlled by the water. In similar studies of SO₂-air-water vapour mixtures in which the water vapour is in large excess the same result was obtained. Under both sets of circumstances oxygen isotopes in SO₂ equilibrate rapidly with those in either the water in which it is dissolved or the water vapour with which it is associated (Pryor and Tonnelato, 1967). Therefore, the oxygen isotopic composition of the product sulphate should always be $\frac{3}{4}$ controlled by this water.

Sulphur trioxide (SO₃) is formed during high temperature oxidation of SO₂ such as occurs in exhaust gases from smelters or power plants. While the same rapid equilibration of oxygen isotopes with water takes place, the isotopic composition of the water is much higher to begin with, making the product sulphate higher also. This so-called "primary" sulphate (formed within combustion sources before emission to the atmosphere) may be recognized by its higher oxygen isotopic composition ($\approx +40$ ‰).

The rate of approach to oxygen isotope equilibrium between SO₄²⁻ and H₂O ($\frac{1}{4}\text{S}^{18}\text{O}_4^{2-} + \text{H}_2^{16}\text{O} \rightleftharpoons \frac{1}{4}\text{S}^{16}\text{O}_4^{2-} + \text{H}_2^{18}\text{O}$) increases with increasing temperature and decreasing pH but is negligible at earth surface conditions. At pH ≈ 4 , the half-life of oxygen isotope exchange between sulphate and water is of the order of 10³ years. Therefore, once formed, sulphates are extremely stable with respect to oxygen isotope exchange with water (Lloyd, 1968).

4. Analytical procedures

A high volume rain sampler was constructed to yield enough sulphate for sulphur and oxygen isotope analyses from individual events. An inclined V-shaped trough design was adapted with an effective sampling area of 1.3 m². The sampler was made of pressure treated cedar, lined with 4 mil linear polyethylene sheeting and was covered between sampled events to minimize dry deposition. Rainwater was collected by AES personnel into clean, 23-l capacity cubitainers which were then shipped to McMaster University for processing and analysis. Samples were received within 1 to 2 weeks. 39 precipitation events were obtained between August, 1983 and July, 1985 representing a variety of precipitation amounts, intensities and seasonal conditions. Rainfall amounts were from 1 to 38 mm and durations ranged from 1 to 24 h. Air mass back trajectory information for each sampled event was supplied by the AES.

Table 1 lists analytical methods, detection limits and errors on replicate analyses of laboratory standards. pH was determined upon sample arrival. Samples were then filtered through a 0.45 µm Nuclepore system and a 500 ml aliquot was removed for determinations of Na⁺, K⁺, Ca²⁺, Mg²⁺, NH₄⁺, Cl⁻, SO₄²⁻, NO₃⁻ and a repeat of pH. Sulphate was concentrated by ion exchange chromatography using hydrous zir-

conium oxide (Mizutani and Rafter, 1969) and was precipitated as barium sulphate (BaSO₄). BaSO₄ was combusted under vacuum with an excess of graphite (C) at 1000°C to quantitatively remove oxygen as CO₂ for oxygen isotope analysis. The BaS (+C) residue from this procedure was placed on Whatman #41 filter paper and quickly washed with deionized water such that the soluble BaS dripped through the filter into a solution of silver nitrate (AgNO₃) immediately precipitating silver sulphide (Ag₂S). The Ag₂S was washed free of nitrate, dried and then combusted under vacuum with an excess of cupric oxide (CuO) at 950°C to quantitatively remove sulphur as SO₂ for sulphur isotope analysis. Five times throughout the sampling period a field "blank" sample was requested in order to maintain quality control. Blanks were collected in the same manner as samples, but substituting deionized water. Concentrations were at or below detection limit in most cases (NO₃, SO₄, Mg, K), and above detection limit in Ca, Na, Cl. Only in the case of Ca were the blanks considered significant. Concentrations were constant from blank to blank and average values were subtracted from the measured sample values. Further technical details can be found in Wadleigh (1989). All chemical and isotope analyses were carried out at McMaster University. Tables 2 and 3 contain chemical (corrected for blanks) and isotopic data for the sampled rain events.

Table 1. *Analytical methods*

Element	Technique	Detection limit	Error*
Ca, K, Na, Mg	atomic absorption spectroscopy	0.05 ppm	±0.03 ppm
pH	pH and reference electrodes		±0.01 pH units
NH ₄	colorimetry	0.03 ppm	
Cl, SO ₄ , NO ₃	ion chromatography	0.05 ppm	±0.02 ppm
SO ₄ extraction	ion exchange	98–100% recovery	
δ ³⁴ S(SO ₄)	mass spectrometry		±0.2‰
δ ¹⁸ O(SO ₄)	mass spectrometry		±0.3‰
δ ¹⁸ O(H ₂ O)	mass spectrometry		±0.1‰

* Error refers to the standard deviation of replicate analyses of standards of known composition. It includes all stages in the sample preparation.

Table 2. *Chemical data for Shelburne rainfall events*

Sample	Amt (mm)	pH	Cond (μ S)	Ca	Mg	K	Na (ppm)	NH ₄	Cl	NO ₃	SO ₄
12/8/83	37.2	4.72	23	0.50	0.06	0.05	0.60	0.08	1.46	0.41	1.45
22/8/83	1.0	3.56	113	0.21	0.06	0.88	1.21	1.10	1.56	3.05	15.0
29/8/83	2.3	3.57	158	0.05	0.05	0.48	0.95	0.99	2.06	6.85	14.0
31/8/83	30.7	4.27	31	0.06	0.10	0.32	1.56	n/d	2.86	1.05	2.55
17/9/83	6.0	5.61	36	0.05	0.36	0.20	5.36	n/d	7.49	0.25	2.45
22/9/83	10.9	5.82	n/a	0.05	0.15	0.32	2.78	n/d	3.90	0.25	1.62
24/9/83	1.8	3.41	86	0.06	0.05	0.20	0.95	0.55	1.51	3.25	14.5
3/10/83	18.4	5.20	2.6	0.05	0.05	0.05	0.51	n/d	1.01	0.25	0.45
6/10/83	10.4	5.48	28	0.05	0.66	1.12	1.67	0.05	2.04	3.75	1.74
13/10/83	19.0	5.73	21	0.05	0.24	0.44	2.09	n/d	3.60	0.25	0.75
19/10/83	5.0	4.09	26	0.05	0.18	0.54	0.83	n/d	0.98	1.51	2.73
24/10/83	28.7	5.21	1.0	0.05	0.07	0.29	0.29	n/d	0.37	0.25	0.25
5/11/83	23.2	6.05	84	0.26	0.88	0.50	7.34	n/d	14.6	0.25	2.92
3/12/83	7.2	6.61	54	0.17	0.51	0.47	7.34	n/d	10.1	2.77	3.13
6/1/84	6.8	6.75	25	0.17	0.08	0.34	2.92	n/d	2.06	1.83	2.77
5/2/84	19.2	6.45	16	0.05	0.10	0.14	1.80	n/d	1.86	0.25	0.55
6/4/84	20.0	6.65	36	0.12	0.30	0.28	5.03	n/d	5.44	0.25	1.82
1/5/84	7.2	5.50	9.8	0.07	0.05	0.15	0.77	n/d	0.58	0.43	1.15
19/6/84	6.0	6.48	26	0.18	0.36	0.18	2.63	n/d	4.65	0.44	1.15
8/7/84	1.3	6.69	101	0.54	1.46	0.67	10.9	n/d	31.4	0.25	6.21
8/8/84	2.4	3.89	45	0.18	0.06	0.10	0.56	n/d	0.88	3.92	3.38
5/9/84	2.7	5.77	1.7	0.05	0.05	0.05	0.55	n/d	0.57	0.25	0.76
26/9/84	4.7	3.80	84	0.34	0.12	0.39	1.95	n/d	1.47	5.57	8.64
23/10/84	14.8	4.31	23	0.05	0.05	0.05	0.38	n/d	0.61	0.52	2.31
19/11/84	1.4	3.89	84	0.33	0.53	0.10	3.97	n/d	7.82	5.48	4.53
3/12/84	9.0	5.20	30	0.09	0.44	0.14	2.56	n/d	6.00	0.25	1.72
6/12/84	17.6	6.09	1.0	0.25	1.04	0.35	7.75	n/d	11.5	0.25	2.34
19/12/84	1.4	5.75	1.0	0.21	0.80	0.29	5.16	n/d	9.81	0.25	2.75
24/12/84	11.2	5.03	18	0.07	0.17	0.08	1.17	n/d	2.70	0.38	1.39
28/12/84	n/a	4.62	35	0.09	0.49	0.20	3.10	n/d	6.91	0.25	2.28
29/11/84	n/a	4.08	32	0.10	0.21	0.13	1.45	n/d	3.54	1.19	2.11
5/6/85	15.0	4.09	25	0.05	0.05	0.05	0.05	0.21	0.70	2.35	2.35
16/6/85	4.0	4.48	1.8	0.05	0.05	0.05	0.05	n/d	0.40	0.25	0.88
12/6/85	7.2	3.92	23	0.05	0.05	0.10	0.05	0.22	0.56	4.55	2.15
24/6/85	7.9	3.78	45	0.20	0.17	0.11	0.84	0.07	1.38	2.07	4.25
27/6/85	n/a	4.16	24	0.19	0.32	0.19	2.04	0.08	3.06	3.95	1.15
11/7/85	n/a	3.66	36	0.05	0.05	0.05	0.41	0.43	0.73	1.39	3.65
16/7/85	38.4	4.27	1.8	0.05	0.05	0.05	0.05	0.03	0.25	0.25	0.63
26/7/85	13.2	3.79	30	0.13	0.05	0.06	0.26	0.08	0.54	1.25	2.88

n/a: not measured.

n/d: below detection limit.

5. Results

5.1. Calculation of seaspray component

Percent sea spray (PSS) values were calculated for each sample using the measured sulphate to chloride ratio compared to the seawater ratio (0.14) following the example of Mizutani and

Rafter (1969) and confirmed for this area by Wadleigh (1989), Wadleigh et al. (1994).

$$\text{PSS} = 0.14 / (\text{SO}_4 / \text{Cl}) \times 100\%$$

These values are listed in Table 3. Fig. 3 shows a plot of PSS values versus the sulphur isotopic

Table 3. Additional data for Shelbourne rain samples

Sample	SO ₄ /Cl	PSS	δ ³⁴ S(SO ₄)	δ ¹⁸ O(SO ₄)	δ ¹⁸ O(H ₂ O)
12/8/83	1.0	14	7.1	10.3	-7.8
22/8/83	9.6	1.5	2.0	11.2	-4.0
29/8/83	6.8	2.1	4.2	13.1	-3.4
31/8/83	0.89	16	5.7	12.6	-7.8
17/9/83	0.33	42	11.7	n/a	-3.5
22/9/83	0.42	33	11.7	8.9	-7.1
24/9/83	9.6	1.5	2.5	9.5	-4.0
3/10/83	0.45	31	7.3	n/a	-8.3
6/10/83	0.85	16	4.8	11.1	-4.8
13/10/83	0.21	67	13.4	7.9	-3.8
19/10/83	2.8	5.0	4.2	9.6	-9.6
24/10/83	0.68	21	6.1	6.5	-14.4
5/11/83	0.20	70	n/a	8.0	-17.6
3/12/83	0.31	45	11.0	6.2	-15.5
6/1/84	1.3	10	5.9	8.9	-9.1
5/2/84	0.30	47	9.3	7.9	-8.7
6/4/84	0.33	41	10.3	10.6	-4.0
1/5/84	2.0	7.0	6.0	13.0	-4.3
19/6/84	0.25	56	11.5	9.1	-1.1
8/7/84	0.20	71	11.4	9.3	-1.9
8/8/84	3.8	3.6	4.7	11.9	n/a
5/9/84	1.3	11	5.1	6.3	-7.3
26/9/84	5.9	2.4	3.6	12.6	n/a
23/10/84	3.8	3.7	6.2	12.8	-1.9
19/11/84	0.58	24	9.9	11.8	-8.3
3/12/84	0.29	49	12.6	9.0	-2.6
6/12/84	0.20	69	16.2	5.7	-6.9
19/12/84	0.28	50	14.9	13.8	-5.9
24/12/84	0.51	27	7.9	8.2	-1.7
28/12/84	0.33	42	12.5	9.8	-7.7
29/11/84	0.60	23	8.0	10.4	-1.6
5/6/85	3.4	4.2	4.4	11.4	-6.7
16/6/85	2.2	6.4	4.4	7.8	-3.6
12/6/85	3.8	3.6	4.2	11.4	-6.3
24/6/85	3.1	4.5	4.3	8.2	-4.4
27/6/85	0.38	37	12.2	8.7	-4.6
11/7/85	5.0	2.8	4.2	10.2	-4.9
16/7/85	2.5	5.6	5.4	11.5	-5.1
26/7/85	5.3	2.6	3.7	9.9	-6.3

n/a: not analyzed due to insufficient sample.

composition of the sulphate extracted from each sample. Ordinary linear regression of δ³⁴S on PSS yields the equation

$$\delta^{34}\text{S}(\text{SO}_4) = 0.16 \pm 0.02 \times (\text{PSS}) + 3.8 \pm 0.7\text{‰}$$

with a correlation coefficient of 0.924. At 100 PSS the line extrapolates to a δ³⁴S value of +19.9 ± 1.8‰, indistinguishable from the sulphur isotopic composition of dissolved sulphate in seawater. The

95% confidence limit on the regression equation has been included on the diagram.

Fig. 4 shows the oxygen isotopic composition of sulphate plotted against PSS. The regression equation is

$$\delta^{18}\text{O}(\text{SO}_4) = -0.04 \times (\text{PSS}) + 10.9\text{‰}$$

but the correlation coefficient is not significant (0.435). The 95% confidence interval includes the

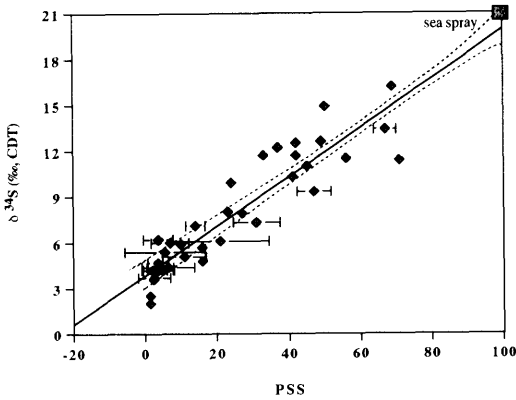


Fig. 3. Sulphur isotopic composition of dissolved sulphate for each rain event plotted against the corresponding sea salt component (PSS) using Cl as the conservative tracer. Solid line represents the equation determined by ordinary linear regression. Dashed lines enclose 95% confidence interval on the regression equation. Error bars represent relative errors calculated according to Abramowitz and Segun (1968). Where error bars are not evident they are smaller than the symbol.

value for dissolved seawater sulphate ($+9.45\text{‰}$). At $\text{PSS} = 0$, $\delta^{18}\text{O}(\text{SO}_4) = +10.9\text{‰}$. No doubt the poor correlation with PSS is due at least in part to this similarity in isotopic compositions (if they were equal then the correlation would be absent altogether, i.e., $r = 0$).

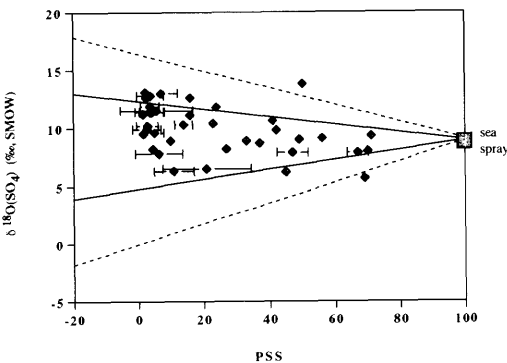


Fig. 4. Oxygen isotopic composition of dissolved sulphate for each rain event plotted against PSS. The dashed lines define an envelope containing all samples which converges at the sea spray $\delta^{18}\text{O}(\text{SO}_4)$ value at 100 PSS. At 0 PSS the isotopic compositions are $+18\text{‰}$ and -2‰ . The solid lines define a narrower envelope which contains all but two of the data points. It too converges at the sea spray $\delta^{18}\text{O}(\text{SO}_4)$ value at 100 PSS. At 0 PSS the isotopic compositions are $+13\text{‰}$ and $+4\text{‰}$. Error bars are as in Fig. 3.

No correlation is apparent between sulphate and water oxygen isotopic compositions for the Shelburne samples.

5.2. Air mass back trajectories

Air mass back trajectories are relevant to air pollution studies since they should be indicative of the emission areas over which the air parcel travelled. Three-dimensional, isobaric air mass back trajectory analysis was performed for the sampled rain events. This produced a reconstruction of the path travelled by the air mass of interest over the previous 4 to 120 h. Wind fields at 3 pressure levels (1000, 925 and 850 mbar) were analyzed and trajectories were computed every 6 h. Details of the method are in Olson et al. (1978). Trajectories were found to represent a variety of source regions and presumably air qualities and have been grouped into sectors ranging from (1) totally marine (\approx azimuth 080° to 220°) to (2) continental ($\approx 220^\circ$ to 350°) to (3) mixed continental/marine ($\approx 350^\circ$ to 080°). The continental sector is further subdivided into (2a) Great Lakes and south and (2b) north of the Great Lakes (Fig. 1). The 850-mbar level is usually recognized as being representative of the transport level at which many air pollutants are carried (OECD, 1977). Azimuths for this level at 24, 48 and 120 h are listed in Table 4.

Very little difference is observed in source region distribution based on the 850 mbar level 24 and 48 hour back trajectories (Fig. 5). The majority of source regions are in sectors 1 and 2a. At 120 h, some of the trajectories trace back to sector 2b as a result of curvature in their path. A single 850 mb trajectory originated in sector 3 and was primarily marine in path.

In a general way the provenance of the air mass could be related to the chemistry of sampled rain events. Samples with $\text{PSS} < 20$ had 24, 48 and 120 hour back trajectories which were continental in origin with paths crossing remote (sector 2b) as well as industrialized (sector 2a) regions. Higher PSS samples ($\text{PSS} > 40$) were more frequent in the winter months and did not at first appear to originate solely in the marine environment. For these samples only the 24 hour back trajectory corresponded with the marine origin indicated by the chemistry. Samples that still did not have a purely marine back trajectory recorded over this

Table 4. Azimuths for 850 mb level air mass back trajectories

Sample	24-h	48-h	120-h
12/8/83	272	305	320
22/8/83	320	325	300
29/8/83	305	312	295
31/8/83	310	310	316
17/9/83	171	020	310
22/9/83	205	203	258
24/9/83	290	283	258
3/10/83	225	210	199
6/10/83	228	240	258
13/10/83	173	149	155
19/10/83	280	287	310
24/10/83	253	255	320
5/11/83	074	200	229
3/12/83	264	270	323
6/1/84	210	227	290
5/2/84	218	220	220
6/4/84	173	170	275
1/5/84	237	245	260
19/6/84	228	246	270
8/7/84	195	178	165
8/8/84	n/a	n/a	n/a
5/9/84	250	260	267
26/9/84	244	253	243
23/10/84	270	258	240
19/11/84	277	275	280
3/12/84	207	252	295
6/12/84	192	253	295
19/12/84	276	267	260
24/12/84	240	255	283
28/12/84	268	257	275
29/11/84	198	150	280
5/6/85	281	295	000
16/6/85	236	252	310
12/6/85	257	292	323
24/6/85	238	252	315
27/6/85	149	182	175
11/7/85	228	250	270
16/7/85	246	250	245
26/7/85	229	220	223

n/a: trajectory not available.

time interval could still be explained since their most recent trajectory (i.e., 6 to 12 h before arrival in Shelburne) passed over the Bay of Fundy which is expected to be similar in character to the ocean. These observations suggest that the last 24 hours of an air mass trajectory are the most important for accumulation of seasalt and possibly even for indicating the most likely source of sulphate.

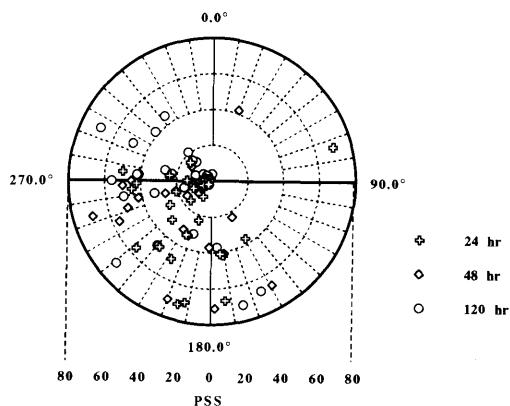


Fig. 5. 24, 48 and 120-h, 850 mbar level, air mass back trajectories for all samples plotted as a function of PSS. Angle measurements are azimuth degrees; radius measurements are PSS in percent.

5.3. Factor analysis

Table 5 shows a varimax rotated principal factor solution for variables measured on the suite of Shelburne rain samples. Three factors were extracted accounting for 75 % of the original variance. Using the Burt-Banks Formula (Burt and Banks, 1947) it was determined that loadings greater than 0.31 are significant on all factors at the 95 % confidence level. Variables with high

Table 5. Factor analysis solution for Shelburne rain events

Variable	Factor			Communality
	1	2	3	
log Ca	0.54	0.02	0.34	0.41
log Mg	0.93	0.14	-0.05	0.89
log K	0.35	0.78	-0.40	0.89
log Na	0.96	0.06	-0.03	0.92
log NH ₄	-0.27	0.73	0.40	0.77
pH	0.64	-0.32	-0.47	0.74
log Cl	0.93	0.09	0.15	0.89
log NO ₃	-0.22	0.72	0.28	0.65
log SO ₄	-0.03	0.78	0.46	0.83
PSS	0.87	-0.28	-0.17	0.87
δ ³⁴ S(SO ₄)	0.79	-0.40	-0.10	0.80
δ ¹⁸ O(SO ₄)	-0.21	0.29	0.44	0.32
δ ¹⁸ O(H ₂ O)	0.06	0.04	0.53	0.29

Factor loadings in bold type are calculated to be significant at the 95 % confidence level. Communality is an indication of the amount of variance explained by the combination of factor loadings for each variable.

positive loadings on Factor 1 include Mg^{2+} , Na^+ , pH , Cl^- , PSS and $\delta^{34}\text{S}$. Air mass back trajectories for samples with high concentrations of these species are not entirely marine in origin but are all associated with "marine" environments (i.e., Bay of Fundy) and since these elements are among the major constituents of seawater, this factor is interpreted as the "marine" component. Factor 2 consists of the positively loading variables K^+ , NH_4^+ , SO_4^{2-} and NO_3^- . High concentrations of these species are associated with low PSS and do not behave sympathetically with the "marine" indicators. Air mass back trajectories for samples with high concentrations of these species are exclusively continental suggesting interpretation of this factor as "continental" (biogenic plus anthropogenic). Factor 3 contains moderate positive loadings for $\delta^{18}\text{O}(\text{SO}_4)$, $\delta^{18}\text{O}(\text{H}_2\text{O})$ and SO_4^{2-} plus a negative loading for pH . It has already been stated that no correlation exists between the oxygen isotopic compositions of sulphate and water so the interpretation of this factor is unclear. It should be noted however, that the oxygen isotopes are more "process" related (i.e., indicative of oxidation mechanism) while the other variables including the sulphur isotopes are more "source" related.

6. Interpretations

6.1. Sulphur isotopes

At PSS = 0, $\delta^{34}\text{S}$ of sulphate in Shelburne rain extrapolates to a value of $+3.8\text{‰}$. $\delta^{34}\text{S}$ of precipitation sulphate collected in remote sites within the Great Lakes region (Nriagu and Coker, 1978) averaged 4.5‰ . Holt et al. (1972) reported an average $\delta^{34}\text{S}$ for rain outside Chicago (Argonne) of 5‰ . An unpublished study by Thompson and Thode (H. G. Thode, personal communication) of the $\delta^{34}\text{S}$ of precipitation and lakewater in remote, unpolluted regions of Canada resulted in values of $\approx 4\text{‰}$ with little deviation. A study in southern Quebec (Caron et al., 1986) concluded that the sulphate in rainwater throughout the area of investigation had the same origin on the basis of the uniformity of their sulphur isotope values, which averaged 5‰ . These independent studies suggest that rainwater sulphate in rural to remote areas of central and eastern North America has a relatively constant sulphur isotopic

composition of $4\text{--}5\text{‰}$. Low PSS samples in this study may therefore represent the average composition of continental (North American) "background" or long range transported sulphate. The only other explanation for the constancy of this intercept in the current data set would be that the sulphate is derived from a single source. The fact that the air mass back trajectories for these samples scatter throughout most of eastern North America suggesting contributions from a variety of sources including natural and anthropogenic, makes this an unlikely alternative. At high PSS, recent (24-h) air mass back trajectories, chemistry and isotope compositions support a sea spray source for most of the sulphate. By definition at PSS = 100 the sulphate to chloride ratio of the sample is equivalent to that of bulk ocean water. The sulphur isotopic composition at this value is $+20\text{‰}$, close to the expected value of $+21\text{‰}$.

Most studies that have utilized sulphur isotopes to distinguish sources of atmospheric sulphur have relied heavily on the seasonality of the data to support their interpretations (Nriagu et al., 1987 for example). The isotopic composition of precipitation sulphates from Shelburne, weighted according to sulphate concentration and sample volume is much heavier in winter ($+13.6\text{‰}$) than summer ($+4.9\text{‰}$). This is a direct reflection of higher concentrations of seasalt in the atmosphere during the boreal winter; a well documented observation (Erickson et al., 1986). It is possible to mathematically subtract the seasalt component in each rain sample by comparing measured SO_4/Cl ratios with the ratio for bulk ocean water in a manner analogous to the PSS calculation (Wadleigh et al., 1994). The remaining sulphate is termed "excess". Once the proportion of excess sulphate is known, its isotopic composition can be determined using this value and the sulphur isotopic composition of seasalt sulphate in a simple, two-component mixing equation. When the seasalt component is removed the seasonal trend reverses and becomes less pronounced. The weighted mean $\delta^{34}\text{S}$ of winter "excess" sulphate is $+1.7\text{‰}$ while for summer it is $+2.9\text{‰}$. This trend is opposite to that observed by Nriagu and Coker (1978), Caron et al. (1986) and Nriagu et al. (1987) but is similar to that found by Saltzman et al. (1983) and Nriagu et al. (1991). The temperature dependence of fractionation accompanying oxidation of a relatively uniform reservoir of atmospheric SO_2 to

HSO_3^- would produce heavier winter values since α increases with decreasing temperature, so this mechanism cannot account for the observed seasonality. The trend must therefore indicate a non-uniform atmospheric reservoir of SO_2 . This could be created by one of: (i) a change in the isotopic composition of a single source of emitted sulphur affecting the region, (ii) a change in the isotopic character of the sulphur burden due to different sources dominating in different seasons or (iii) sampling of different source regions in different seasons due to changing meteorological conditions. The third possibility, that of sampling different source regions to explain the seasonal sulphur isotopic trend is supported by air mass back trajectories. Six of the eleven summer samples had 850 mb 120-h back trajectories from sector 2b tracing back to northeastern Ontario and northwestern Quebec whereas winter samples did not have any particular trajectory in common. Nriagu et al. (1991) have shown that the sulphur isotopic composition of Canadian Arctic haze reaches a maximum of $\approx +9\text{‰}$ in the summer, significantly higher than the summer average at Shelburne. Perhaps a higher component of this sulphur is being sampled by the air masses reaching Shelburne in the summer months.

6.2. Oxygen isotopes

The poor correlation of $\delta^{18}\text{O}(\text{SO}_4)$ with PSS is not unexpected considering the variety of mechanisms potentially contributing to sulphate formation and the small difference in $\delta^{18}\text{O}$ expected between the continental and marine sources of sulphate. However, as mentioned above average $\delta^{18}\text{O}$ values of sulphates from several studies using samples with low calculated sea spray components ($<20\%$) are remarkably constant between $+11$ and $+12\text{‰}$. Using the same reasoning here as for sulphur, 11‰ may be proposed as an estimate of the average $\delta^{18}\text{O}(\text{SO}_4)$ of continental (North American) rain.

At PSS = 100 we expect the data to converge to the known seawater $\delta^{18}\text{O}(\text{SO}_4)$ value of $+9.5\text{‰}$. The data can be contained in a three endmember envelope consisting of the oxygen isotopic composition of sea spray sulphate ($+9.5\text{‰}$ at PSS = 100), $\delta^{18}\text{O}(\text{SO}_4) = +18\text{‰}$ and $\delta^{18}\text{O}(\text{SO}_4) = -2\text{‰}$ at PSS = 0 (Fig. 4). High temperature homogeneous oxidation of SO_2 likely to occur at a stack point source produces ^{18}O -enriched

“primary” sulphate ($\delta^{18}\text{O} \approx +40\text{‰}$) while low temperature oxidation mechanisms produce sulphate whose $\delta^{18}\text{O}$ tracks the composition of the associated water (Holt et al., 1982). Therefore, these endmember compositions for continental sources of sulphate are not unreasonable considering the variety of seasonal conditions and potential combinations of oxidation mechanisms represented by the suite of samples.

A correlation would be expected between the oxygen isotopic composition of sulphate and its associated rainwater only if oxygen from the rainwater or water vapour was utilized in the formation of the sulphate (i.e., within the transporting air mass). The lack of correlation between these variables in the current data set suggests that this is not the case here. But the relationship could be masked by large amounts of sea spray sulphate, whose oxygen would not be able to equilibrate with local water. This is easily checked (in a manner analogous to sulphur as discussed above) and no trend is revealed when $\delta^{18}\text{O}$ values are corrected for their sea spray component. Other possibilities are that this sulphate consists totally of long range transported sulphate not related to local water, or that it reflects mixing between this aged sulphate and one or both of local sources dependent on ambient $\delta^{18}\text{O}(\text{H}_2\text{O})$ and marine sulphate.

Fig. 6 shows the data from this study plotted

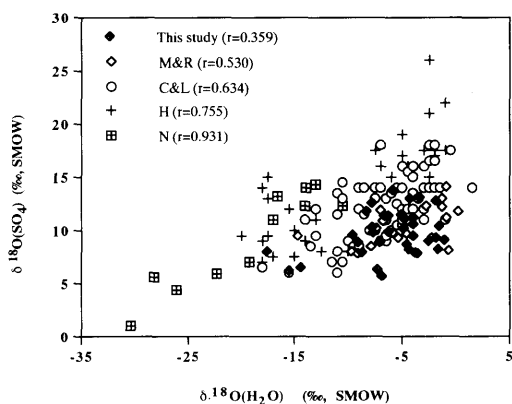


Fig. 6. $\delta^{18}\text{O}(\text{SO}_4)$ versus $\delta^{18}\text{O}(\text{H}_2\text{O})$ for the Shelburne data compared to the data of Mizutani and Rafter (1969) (M & R), Cortecchi and Longinelli (1970) (C & L), Holt et al. (1979) (H) and Norman (1991) (N). Correlation coefficients (r) decrease with decreasing industrial influence on the sampling site.

with the data of Mizutani and Rafter (1969), Cortecchi and Longinelli (1970), Holt et al. (1981) and Norman (1991). Linear regression coefficients were found to decrease as proximity of the sampling site to industrial influence decreased: Calgary, Alberta (0.93) > Argonne, Illinois (0.75) > Pisa, Italy (0.63) > Gracefield, New Zealand (0.53) > Shelburne, Nova Scotia (0.36) with each site presumably having lower percentages of local pollutant sulphate and correspondingly higher percentages of long range transported and/or seasalt sulphate.

The sulphate in Shelburne rain most likely consists of a mixture of sea spray sulphate and long range transported sulphate, both with $\delta^{18}\text{O}$ independent of local atmospheric water.

7. Discussion

7.1. Anthropogenic sulphate

Comparison of previous work with this study suggests that the closer the region of sampling to industrial sources of SO_2 , the better the correlation between $\delta^{18}\text{O}(\text{SO}_4)$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ and the higher the $\delta^{18}\text{O}(\text{SO}_4)$ for a given $\delta^{18}\text{O}$ of associated rainwater. These observations have important implications for the origins of precipitation sulphate. First of all they suggest a higher proportion of "primary" sulphate with high $\delta^{18}\text{O}$ in industrial areas (Norman, 1991; Holt et al., 1982). Secondly they support the predominance of different sulphate sources in industrial versus remote areas (Hegg, 1983). In-solution sulphate production, thought to dominate in industrial areas results in a correlation between sulphate and water $\delta^{18}\text{O}$. Condensation of water vapour onto existing sulphate-containing nuclei, thought to be the major process in more remote regions, would not yield such a correlation since local water is not involved in formation of the sulphate.

Additional information relating to anthropogenic sulphate is obtained from air mass back trajectories. PSS values do not extend past 70 even when the corresponding trajectories appear totally marine, confirming the long range transport of sulphate of continental origin over the ocean. Approximately 30% of the sulphate over the North Atlantic is derived in this way. Based on the budget of Brimblecombe et al. (1989) it could be

estimated that at least 75% of this continentally derived sulphate is of anthropogenic origin.

7.2. Biogenic sulphate

DMS: There are no records of DMS measurements in the ocean or atmosphere in the zone of high productivity off the coast of Nova Scotia, but extrapolation from other studies suggests that it is present in twice average (open ocean) concentrations, and its influence should therefore be detectable. To search for DMS, Fig. 3 has been redrawn in the form of a three component mixing diagram showing the triangular field in which samples containing a component of DMS-derived sulphate would plot (Fig. 7). All samples are assumed to consist only of mixtures of DMS-sulphate, sea spray and the homogenized terrestrial component. The lowermost boundary of the field is defined by the two component mixing line between continental sulphate ($+4\text{‰}$) and sea spray ($+21\text{‰}$). The other boundaries are delineated using the coordinates of a "pure" DMS signal for which

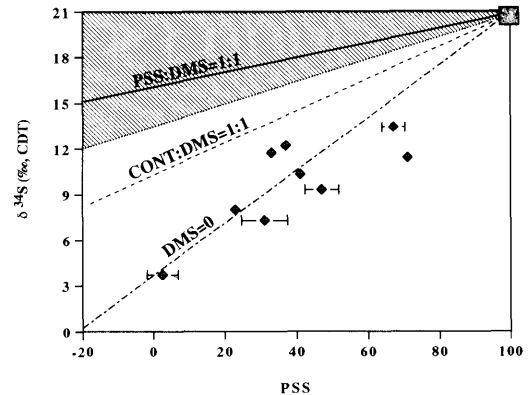


Fig. 7. Sulphur isotopic composition of sulphate versus PSS for a three-component model consisting of continental ($\delta^{34}\text{S} \approx +4\text{‰}$), sea spray ($\delta^{34}\text{S} \approx +21\text{‰}$) and DMS-derived excess sulphate ($\delta^{34}\text{S} \approx +16\text{‰}$). Dot-dashed line represents line of true mixing between continental and sea spray sulphate, i.e., no DMS component. Dashed line represents three-component mixing between continental, sea spray and DMS-derived sulphate with the continental and DMS components in a ratio of 1:1. Solid line represents two-component mixing between sea spray and DMS-derived sulphate. The 9 Shelburne samples with purely marine trajectories are shown as well as the field corresponding to the McArdle and Liss (1992) data set (shaded).

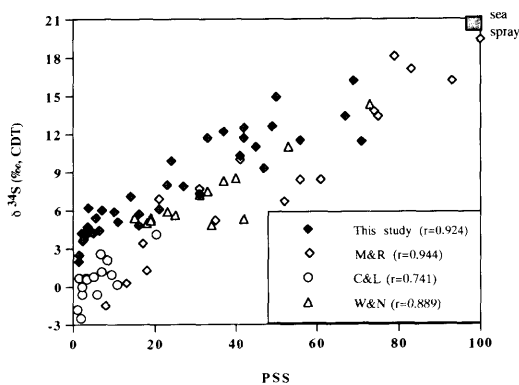


Fig. 8. Sulphur isotopic composition of sulphate versus PSS for this study compared with data from Mizutani and Rafter (1969) (M & R), Cortecchi and Longinelli (1970) (C & L) and Wakshal and Neilsen (1982) (W & N). Correlation coefficients (r) ranging from 0.741 to 0.944 all suggest two-component mixing between continental/terrestrial (anthropogenic or natural) and marine (sea spray) sources.

the most recent isotopic estimate is $\delta^{34}\text{S} = +15.6 \pm 3.1\text{‰}$ (at PSS = 0). Inspection of Fig. 7 reveals that DMS is a small component in the Shelburne rains.

The New Zealand, Italian and Israeli rains plot in a manner similar to that of the Shelburne data (Fig. 8). None of these marine influenced sites show large contributions from DMS. However, summer aerosol samples from Mace Head, a remote site on the west coast of Eire apparently do plot in the triangular field described above (McArdle and Liss, 1992) demonstrating that this technique can distinguish DMS-derived sulphate. To the best of our knowledge this is the only data set reported containing points in this triangular region. The lack of points in this region for the current and other data sets is strong evidence that DMS is not a significant source of sulphate in precipitation in Shelburne and those other locations. Possible explanations for the absence of DMS include: (i) the suggestion that DMS production is a "dry season phenomenon" only,

making it detectable in aerosols but not rains or (ii) that there is not as much DMS in the coastal atmosphere as has been estimated through extrapolation from existing open ocean data sets.

8. Conclusions

Chemical, isotopic and air mass back trajectory analyses have been combined with factor analysis on 39 coastal rain events from Shelburne, Nova Scotia in an attempt to obtain specific sulphate source information. Application of sulphur and oxygen isotopes in combination allows us to identify sources on both regional and local scales. The data set as a whole is dominated by two-component mixing between continental and oceanic sources with the continental signature representing the sulphur and oxygen isotopic compositions of homogenized, long-range transported, "aged" sulphate and the marine signature representing the isotopic compositions of dissolved oceanic sulphate. The inference of terrestrial signatures and associated transport phenomena is supported by air mass back trajectory analysis. Previous studies have utilized back trajectories as part of a sampling protocol, to ensure that samples of purely marine rains or aerosols are obtained. Here, a variety of source regions were sampled intentionally and the air mass back trajectories were used to help define isotopic character. Finally, we see no evidence for a DMS component at Shelburne, even in the most marine rains. Analysis of data for measurements made in New Zealand, Italy and Israel also fails to reveal a significant DMS component.

9. Acknowledgements

This research was supported by NSERC grants to HPS and JRK. We wish to thank the AES personnel at the Upper Air Station in Shelburne for sample collection and M. Knyf and J. Gleed for laboratory assistance.

REFERENCES

- Abramowitz, M. and Seguin, I. 1968. *Handbook of mathematical functions*, p.14. Dover Publications, New York.
- Andreae, M. O. 1980. Dimethyl sulphoxide in marine and freshwaters. *Limnol. Oceanogr.* **25**, 1054–1063.
- Andreae, M. O. and Barnard, W. R. 1984. The marine chemistry of dimethyl sulphide. *Marine Chem.* **14**, 267–279.
- Aneja, V. P. and Cooper, W. J. 1989. Biogenic sulphur emissions: a review. In: *Biogenic sulphur in the environ-*

- ment. ACS Symposium Series 393, (eds. E. J. Saltzman and W. J. Cooper), 2–13.
- Barrie, L. A., Ahier, B., Bottenheim, J., Niki, H. and Nriagu, J. 1992. Atmospheric methane and sulphur compounds at a remote central Canadian location. *Atmos. Env.* **26A**, 907–925.
- Bates, T. S., Cline, J. D., Gammon, R. H. and Kelly-Hansen, S. 1987. Regional and seasonal variations in the flux of oceanic dimethylsulphide to the atmosphere. *J. Geophys. Res.* **92**, 2930–2938.
- Brimblecombe, P., Hammer, C., Rodhe, H., Ryaboshapko, A. and Boutron, C. F. 1989. Human influence on the sulphur cycle. In: *Evolution of the global biogeochemical sulphur cycle*. SCOPE 39, (eds. P. Brimblecombe and A. Lein), John Wiley and Sons, 77–121.
- Burt, C. and Banks, C. 1947. A factor analysis of body measurements for British adult males. *Ann. Eugenics* **13**, 238.
- Calhoun, J. and Bates, T. 1989. Sulphur isotope ratios: tracers of non-seasalt sulphate in the remote atmosphere. In: *Biogenic sulphur in the environment*. ACS Symposium Series 393, E, (eds. E. J. Saltzman and W. J. Cooper). Washington, 367–379.
- Calhoun, J., Bates, T. and Charlson, R. 1991. Sulphur isotope measurements of submicrometer sulphate aerosol particles over the Pacific Ocean. *Geophys. Res. Lett.* **18**, 1877–1880.
- Carlson, P. R. and Forrest, J. 1982. Uptake of dissolved sulphide by spartina alterniflora: evidence from natural sulphur isotope abundance ratios. *Science* **216**, 633–635.
- Caron, F., Tessier, A., Kramer, J. R., Schwarcz, H. P. and Rees, C. E. 1986. Sulphur and oxygen isotopes of sulphate in precipitation and lakewater, Quebec. *Applied Geochem.* **1**, 601–606.
- Charlson, R. J., Lovelock, J. E., Andreae, M. O. and Warren, S. G. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* **326**, 655–661.
- Cortecci, G. and Longinelli, A. 1970. Isotopic composition of sulphate in rain water, Pisa, Italy. *Earth Planet. Sci. Lett.* **8**, 36–40.
- Dansgaard, W. 1964. Stable isotopes in precipitation. *Tellus* **16**, 436–468.
- Dole, M., Lange, G. A., Rudd, D. P. and Zaukelies, D. A. 1954. Isotopic composition of atmospheric oxygen and nitrogen. *Geochim. Cosmochim. Acta* **6**, 65–78.
- Egiazarov, A. S., Kaviladze, M., Kerner, M. N., Oziashvili, E. L., Ebraliidze, A. and Esakiya, K. E. 1971. Separation of sulphur isotopes by chemical exchange. *Isotopenpraxis* **7**, 379–383.
- Erickson, D. J., Merrill, J. T. and Duce, R. A. 1986. Seasonal estimates of global atmospheric sea salt distributions. *J. Geophys. Res.* **91**, 1067–1072.
- Eriksen, T. E. 1972. Sulphur isotope effects. 1. The isotopic exchange coefficient for the sulphur isotopes ^{34}S - ^{32}S in the system SO_{2g} - $\text{HSO}_3^-_{aq}$ at 25, 35 and 45°C. *Acta Chem. Scand.* **26**, 573–584.
- Hegg, D. 1983. The sources of sulphate in precipitation 1. Parameterization scheme and physical sensitivities. *J. Geophys. Res.* **88**, 1369–1374.
- Hitchcock, D. and Black, M. 1984. $^{34}\text{S}/^{32}\text{S}$ evidence of biogenic sulphur oxides in a salt marsh atmosphere. *Atm. Env.* **18**, 1–17.
- Hobbs, P. V. 1979. A reassessment of the mechanisms responsible for the sulphur content of acid rain. In: *Proc. Advisory Workshop to identify research needs on the formation of acid precipitation*. Electric Power Research Report EA-1074, 2–38.
- Holt, B. D. and Kumar, R. 1991. Oxygen isotope fractionation for understanding the sulphur cycle. In: *Stable isotopes: natural and anthropogenic sulphur in the environment*. SCOPE 43, (eds. H. R. Krouse and V. A. Grinenko), John Wiley and Sons Ltd., 27–41.
- Holt, B. D., Cunningham, P. T. and Kumar, R. 1981. Oxygen isotopy of atmospheric sulphates. *Env. Sci. Tech.* **15**, 804–808.
- Holt, B. D., Engelkemeir, A. and Venters, A. 1972. Variations in sulphur isotope ratios in samples of water and air near Chicago. *Env. Sci. Tech.* **6**, 338–341.
- Holt, B. D., Kumar, R. and Cunningham, P. T. 1982. Primary sulphates in atmospheric sulphates: estimation by oxygen isotopic ratio measurements. *Science* **217**, 51–53.
- Holt, B. D., Kumar, R., Cunningham, P. T., Bouchard, M., Engelkemeir, A., Johnson, S. A. and Neilsen, E. L. 1978. Regional oxygen-18 variations in particulate sulphate and water vapour at three sampling sites about 100 km apart. *Env. Sci. Tech.* **12**, 1394–1398.
- Kaplan, I. R. 1975. Stable isotopes as a guide to biogeochemical processes. *Proc. Royal Soc. London (Ser. B)* **189**, 183–211.
- Kroopnick, P. 1977. The $\text{SO}_4:\text{Cl}$ ratio in oceanic rainwater. *Pacific Sci.* **31**, 91–106.
- Kroopnick, P. and Craig, H. 1972. Atmospheric oxygen: isotopic composition and solubility fractionation. *Science* **175**, 54–55.
- Krouse, H. R. 1980. Sulphur isotopes in our environment. In: *Handbook of environmental isotope geochemistry (1). The terrestrial environment A* (eds. P. Fritz and J. Ch. Fontes). Elsevier Publishing Co., Amsterdam, 435–471.
- Li, S. M. and Barrie, L. A. 1993. Biogenic sulphur aerosols in the Arctic Troposphere: 1. Contributions to total sulphate. *J. Geophys. Res.* **98**, 613–622.
- Lloyd, M. R. 1968. Oxygen isotope behaviour in the sulphate-water system. *J. Geophys. Res.* **73**, 6099–6110.
- Luecke, W. and Nielsen, H. 1972. Isotopenfraktionierung des schwefels in blasenspruh. *Fortschr. Mineral.* **50**, Beiheft 3, 36–37.
- McArdle, N. C. and Liss, P. S. 1992. The use of stable sulphur isotopes to distinguish between natural and anthropogenic sulphur in the atmosphere. *EOS, Trans. Am. Geophys. Union/Supplement*, 88.
- Mekhtiyeva, V. L. and Pankina, G. R. 1968. Isotopic composition of sulphur in aquatic plants and dissolved sulphates. *Geochem.* **5**, 624–627.

- Mizutani, Y. and Rafter, T. A. 1969. Oxygen isotopic composition of sulphates, part 5, Isotopic composition of sulphate in rain water. Gracefield, New Zealand. *N.Z. J. Sci.* **12**, 69–80.
- Nakai, N. and Jensen, M. L. 1964. The kinetic isotope effect in the bacterial reduction and oxidation of sulphur. *Geochim. Cosmochim. Acta* **28**, 1893–1912.
- Newman, L., Krouse, H. R. and Grinenko, V. A. 1991. Sulphur isotope variations in the atmosphere. In: *Stable isotopes: natural and anthropogenic sulphur in the environment*. SCOPE 43, (eds. H. R. Krouse and V. A. Grinenko). John Wiley and Sons Ltd., 133–176.
- Nielsen, H. 1974. Isotope composition of the major contributors to atmospheric sulphur. *Tellus* **26**, 213–221.
- Norman, A. L. 1991. *Stable isotope studies of atmospheric sulphur: Comparison of Alberta, Canada and Bermuda*. M.Sc. thesis, Univ. Calgary, 162 p.
- Nriagu, J. O. and Coker, R. D. 1978. Isotopic composition of sulphur in precipitation within the Great Lakes basin. *Tellus* **30**, 365–375.
- Nriagu, J. O., Coker, R. D. and Barrie, L. A. 1991. Origin of sulphur in Canadian Arctic haze from isotope measurements. *Nature* **349**, 142–145.
- Nriagu, J. O., Holdway, D. A. and Coker, R. D. 1987. Biogenic sulphur and the acidity of rainfall in remote areas of Canada. *Science* **237**, 1189–1192.
- Olson, M. P., Oikawa, K. K. and MacAfee, A. W. 1978. *A trajectory model applied to the long-range transport of air pollutants: a technical description and some model intercomparisons*. LRTAP 78-4, AES, 24 p.
- Pryor, W. A. and Tonnelato, U. 1967. Nucleophilic displacements at sulphur III. The exchange of oxygen-18 between sodium thiosulphate-¹⁸O and water. *J. Am. Chem. Soc.* **89**, 3379–3386.
- Rees, C. E., Jenkins, W. J. and Monster, J. 1978. The sulphur isotopic composition of ocean water sulphate. *Geochim. Cosmochim. Acta* **42**, 377–381.
- Ryaboshapko, A. G. 1983. The atmospheric sulphur cycle. In: *The global biogeochemical sulphur cycle*. SCOPE 19, (eds. M. V. Ivanov and J. R. Freney), 203–296.
- Saltzman, E., Brass, G. and Price, D. 1983. The mechanism of sulphate aerosol formation: chemical and sulphur isotopic evidence. *Geophys. Res. Lett.* **10**, 513–516.
- Saltzman, E. and Cooper, D. J. 1989. Dimethyl sulphide and hydrogen sulphide in marine air. In: *Biogenic sulphur in the environment*. ACS Symposium Series 393, (eds. E. Saltzman and D. Cooper), 330–351.
- Scott, B. C. 1978. Parameterization of sulphate removal by precipitation. *J. Appl. Met.* **19**, 715–722.
- Scott, B. C. 1981. Sulphate washout ratios in winter storms. *J. Appl. Met.* **20**, 619–625.
- Scott, B. C. and Hobbs, P. V. 1967. The formation of sulphate in water droplets. *J. Atm. Sci.* **24**, 54–57.
- Shaw, G. E. 1983. Bio-controlled thermostasis involving the sulphur cycle. *Clim. Change* **5**, 297–303.
- Stuedler, P. A. and Peterson, B. J. 1984. Contribution of gaseous sulphur from salt marshes to the global sulphur cycle. *Nature* **311**, 455–457.
- Van Stempvoort, D. R., Fritz, P. and Reardon, J. 1992. Sulphate dynamics in upland forest soils, central and southern Ontario, Canada: stable isotope evidence. *Appl. Geochem.* **7**, 159–175.
- Wadleigh, M. A., Schwarcz, H. P. and Kramer, J. R. 1994. Sulphur isotope tests of seasalt correction factors in precipitation: Nova Scotia, Canada. *Wat. Air Soil Poll.* **77**, 1–16.
- Wadleigh, M. A. 1989. *Geochemical characterization of coastal precipitation: natural versus anthropogenic sources*. PhD thesis, McMaster University, 243 p.
- Wakshal, E. and Nielsen, H. 1982. Variations of $\delta^{34}\text{S}(\text{SO}_4)$, $\delta^{18}\text{O}(\text{H}_2\text{O})$ and Cl/SO_4 ratio in rainwater over northern Israel, from the Mediterranean Coast to Jordan Rift Valley and Golan Heights. *Earth Planet. Sci. Lett.* **61**, 272–282.
- Whelpdale, D. M. 1992. An overview of the atmospheric sulphur cycle. In: *Sulphur cycling on the continents. Wetlands, terrestrial ecosystems and associated water bodies*. SCOPE 48, (eds. R. W. Howarth, J. W. B. Stewart and M. V. Ivanov). John Wiley and Sons Ltd., 5–26.