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SULFATE YIELDS AND ISOTOPIC RATIOS OF SULFATE SULFUR IN RIVERS OF THE NORTHWEST TERRITORIES

by

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EXECUTIVE SUMMARY

Recent concern over haze in the arctic has led to the realization that anthropogenic emissions of pollutants to the atmosphere in industrialized areas of the world may be transported great distances, even to remote regions once considered to be beyond the reach of human activities. Monitoring of softwater rivers in the Northwest Territories by Water Quality Branch of Environment Canada was commenced in the 1960s and 1970s, and the data are stored in NAQUADAT, Canada's national water quality data storage system. From these data it has been calculated that sulfate yields of such rivers, draining the Canadian Shield, are to now quite low, ranging from 3 to 6 meq m^{-2} yr^{-1} (1.4 to 2.9 kg ha^{-1}).

This paper presents the results of isotopic analyses of sulfate sulfur from large volume samples from ten of these rivers. The samples were collected with the cooperation of the Chief, Western & Northern Region, NWRI, by staff of Water Resources Branch, Yellowknife, in the late summer of 1984. The isotopic ratios obtained for these rivers

are similar to results obtained for surface waters at lower latitudes. The results suggest that the data for these northwest territory rivers represent true 'background' levels of atmospheric deposition of anthropogenic pollutants.

ABSTRACT

Rivers in the Northwest Territories draining the Canadian Shield in the zone of continuous permafrost have sulfate yields ranging from 3 to 6 meq $m^{-2}yr^{-1}$. Stable isotope ratios of sulfate sulfur from these rivers range from -0.91 to +7.01 per mil. The negative value obtained for the Quoich River may indicate the presence of reduced sulfur compounds in its watershed. Results for the Tree, Ellice and Back Rivers may have been influenced by seasalt. Results for the other rivers are very similar to those obtained for surface waters at lower latitudes (47°N), indicating that the processes affecting the isotopic ratios of sulfate sulfur in surface waters operate similarly at 65°N and at 47°N.

RÉSUMÉ

Dans les Territoires du Nord-Ouest, les rivières qui sillonnent le bouclier canadien dans la zone de pergélisol permanent produisent un taux de sulfate allant de 3 à 6 mé m^{-2} an^{-1}. Les ratios d'isotopes stables dans le soufre sous forme de sulfates que l'on retrouve dans ces rivières s'échelonnent de -0,91 à +7,01 par mil. La valeur négative obtenue de la rivière Quoich peut indiquer la présence de composés soufrés désoxygénés dans son bassin hydrographique. Les résultats des rivières Tree, Ellice et Back ont pu être influencés par le sel marin. Pour les autres cours d'eau, les résultats sont fort semblables à ceux que l'on a obtenus dans les eaux de surface aux latitudes inférieures (47° N.), ce qui indique que les processus qui influent sur les ratios isotopiques du soufre sous forme de sulfates dans les eaux de surface fonctionnent de façon semblable à 65° N. et à 47° N.

INTRODUCTION

In 1985 Thompson and Hutton presented data on sulfate yields of lakes from ELA (Experimental Lakes Area, near Kenora, Ontario) in western Ontario across eastern Canada to Labrador. Sulfate yields ranged from 12 meq m^{-2} yr^{-1} at ELA to a maximum of 115 meq m^{-2} yr^{-1} from Lac Laflamme in the High Laurentians of Quebec, and decreased to 20 meq m^{-2} yr^{-1} in Labrador. Rivers in the Northwest Territories, on the Canadian Shield, in the zone of continuous permafrost, have even lower sulfate yields than waters in the remote regions of ELA and Labrador, ranging from 3 to 7 meq m^{-2} yr^{-1}. Because these river yields of sulfate are so very low, it is likely that the sulfate they carry is "background" sulfate that is part of the natural hydrological cycle. We were interested, therefore, to learn if the stable isotopes of S in the sulfate in these rivers would provide data to aid in the understanding of the natural sulfur cycle.

Samples 20 L in size because of the low sulfate concentrations were collected between August 27 and September 12, 1984, were shipped to Burlington and taken to McMaster University for the isotopic analyses.

Figure 1 is a generalized map of the Northwest Territories showing the approximate western extent of the outcrop of Precambrian rocks, the approximate southern boundary of the zone of continuous permafrost, the rivers of interest, and the sampling locations. The rivers, the latitude and longitude of the sampling points, the drainage areas, mean annual runoffs, and mean sulfate yields are listed in Table 1.

Chemical data for these rivers and some discharge data (to 1978) are stored in NAQUADAT, Canada's national water quality data storage system (Demayo, 1970). Discharge data are also available from annual and summary publications of the Water Survey of Canada, or by application to the Director, Water Resources Branch, Department of the Environment, Ottawa K1A 0E7.

Table 2 shows the number of samples from each river for which data are stored in NAQUADAT, the range of discharge values for the sampling dates, the range of conductance, chloride, and sulfate values, the chloride and sulfate values for the samples discussed in this report, and the δ^{34}/S ^{o}/oo results obtained on these samples.

Sulfur Content and Isotope Ratio Measurements

Standard methods (Thode *et al.*, 1961) were used to determine the sulfur content and isotope ratios of these river water samples, but, because the samples were so dilute, they were allowed to concentrate by evaporation from 8 litres to one litre before analysis. Each river sample was analysed in duplicate. No precipitates were visible in the samples after evaporation, although several of these samples exhibited a slight brownish coloration. The sulfate in the evaporated samples was precipitated as $BaSO_4$, reduced to H_2S with HI-H_3PO_2-HCl mixture and converted to Ag_2S and finally to SO_2 gas. The sulfate content was measured gravimetrically as Ag_2S and isotopic analysis of the SO_2 gas was determined using a high precision mass isotope ratio mass spectrometer described by Thode _et al_. (1961) and modified by Beaver (1973). Sulfur isotope ratios are expressed in the notation:

$$\delta^{34}S\ ^{o}/oo = \left[\frac{(^{34}S/^{32}S)_{sample}}{(^{34}S/^{32}S)_{standard}} - 1\right] \times 1000$$

The standard ratio is that of troilite sulfur of the Canyon Diablo meteorite.

DISCUSSION

Because of their northern locations and the presence of permafrost, the greater part of the flows of these rivers occurs during the summer months. It is not known to what extent the summer flow represents snowmelt, but according to Barry and Hare (1974), most of the precipitation in the Canadian arctic falls during July to

September, and snowfall, which reaches its maximum in October - November, represents 30 to 40% of the total annual precipitation.

According to Barrie et al. (1981), arctic haze which reaches its maximum during the winter, is a product of human activities, mainly fossil fuel consumption, and about 30% of the aerosol mass is sulfates. The winter maximum in haze is partly due to minimal pollutant removal processes, i.e., cloud formation and wet precipitation. Barrie et al. (1981) also state that several indicators point to Siberia and North America as the main sources of arctic haze aerosols. We infer from these discussions that the sulfate in these rivers is mainly atmospheric in origin, chiefly carried down by wet precipitation during the summer, and that the sources of the aerosol that provided the sulfate are distant. Sulfate in surface waters, of course, represents an integration of sulfates from a series of aerosols and perhaps some sulfate derived from minerals in the watershed. The low sulfate yields of these rivers are in accord with the understanding that the sources of sulfate are distant and that atmospheric scavenging processes are inefficient.

The stable isotope values for sulfate sulfur in these rivers (Table 2) are similar to results obtained for rain or surface waters at lower latitudes. Holt et al. (1972) report isotopic ratios of sulfur in rainstorms near Chicago ranging from +3 to +8 per mil. Nriagu and Coker (1978) reported isotopic ratios of sulfate sulfur in bulk precipitation samples in the Great Lakes Basin ranging from +1.9

to +9.3 per mil, with a pronounced seasonal variation, the heaviest values being observed in the winter. Lakes north of Sault Ste. Marie, Ontario, sampled in June 1983, gave results for sulfate sulfur ranging from +3.3 to +7.2 per mil with a mean of +4.5 per mil (15 lakes) (H.G. Thode, unpublished data).

The results obtained for sulfate sulfur in rivers in the Northwest Territories range from −0.92 to +7.01 per mil. The rivers are not thought to receive much seasalt because the Cl^- concentrations in these samples are generally low (Table 2). However, as can be seen on Figure 1, two of the rivers, the Tree and the Ellice, are sampled only about 16 km from the coast, and that may explain the somewhat higher del values obtained for those rivers. The chemical data stored in NAQUADAT have been examined for internal evidence as to whether the CL^- is of marine origin. Table 3 shows the number of samples, the correlation coefficient obtained for linear regression between Na^+ and Cl^-, and the mean Na^+/Cl^-. The seawater ratio of Na^+ to Cl^- in weight units is 0.556 (truncated from Connors and Kester, 1974). For most of these rivers the mean ratio of Na^+ to Cl^- is very different from that of seawater, but the data for the Tree, the Ellice, and the Back Rivers suggst that some part of the Cl^- in those rivers is from seasalt.

There cannot be very much marine sulfate, however, because Arctic Ocean sulfate sulfur is so heavy - +20.1 per mil (Thode _et al._, 1961). The negative value of −0.91 per mil obtained for the Quoich

River may point to the presence of reduced sulfur compounds somewhere in its watershed.

Excluding the data from the Tree, the Ellice, and the Quoich Rivers, the mean of seven values is +4.6 per mil, which is very near the mean of +4.5 per mil found for 15 lakes north of Sault Ste. Marie. The atmospheric processes or sources that tend to cause a shift in the isotopic ratio of sulfate sulfur must be similar in the arctic to those in lower latitudes.

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TABLES

Table 1 The rivers in the Northwest Territories, the latitude and longitude of the sampling sites, their drainage areas, mean annual runoff, and mean sulfate yields.

Table 2 The number of samples available for rivers in the Northwest Territories, the range of discharge values for the various sampling dates, and the range of conductance, chloride and sulfate values; the chloride concentrations, the sulfate concentrations, and stable isotopic ratios of sulfate sulfur for the samples of August - September, 1984.

Table 3 The number of samples for each river, the correlation coefficient for the linear regression between Na^+ and Cl^-, and the mean Na^+/Cl^- (in weight units).

FIGURES

Figure 1 A generalized map of part of the Northwest Territories showing the rivers sampled and the locations of the sampling sites.

TABLE 1. The rivers in the Northwest Territories, the latitude and longitude of the sampling sites, their drainage areas, mean annual runoff, and mean sulfate yields.

River	Location of Sampling Site		Drainage Area	Mean Runoff	Mean Sulfate Yield
	Latitude	Longitude	km^2	$m\ yr^{-1}$	$meq\ m^{-2}\ yr^{-1}$
Hanbury	63-35-30 N	105-09-00 W	5 810	0.179*	6.3
Thelon	64-32-10 N	101-23-50 W	65 300	0.102	2.6
Dubawnt	64-16-01 N	99-35-47 W	67 600	0.150	3.4
Kazan	63-39-00 N	95-51-15 W	72 300	0.187*	4.6
Quoich	64-27-30 N	94-07-10 W	28 700	0.162*	5.0
Lockhart	62-53-20 N	108-28-20 W	26 700	0.126	3.4
Coppermine	65-25-00 N	114-00-30 W	20 300	0.141	4.3
Tree	67-38-10 N	111-53-30 W	5 960	0.177*	6.0
Ellice	67-42-30 N	104-08-30 W	16 900	0.124**	6.1
Back	66-05-00 N	96-30-00 W	96 200	0.145*	4.4

* Discharge is very low in winter.

** Discharge is zero during winter.

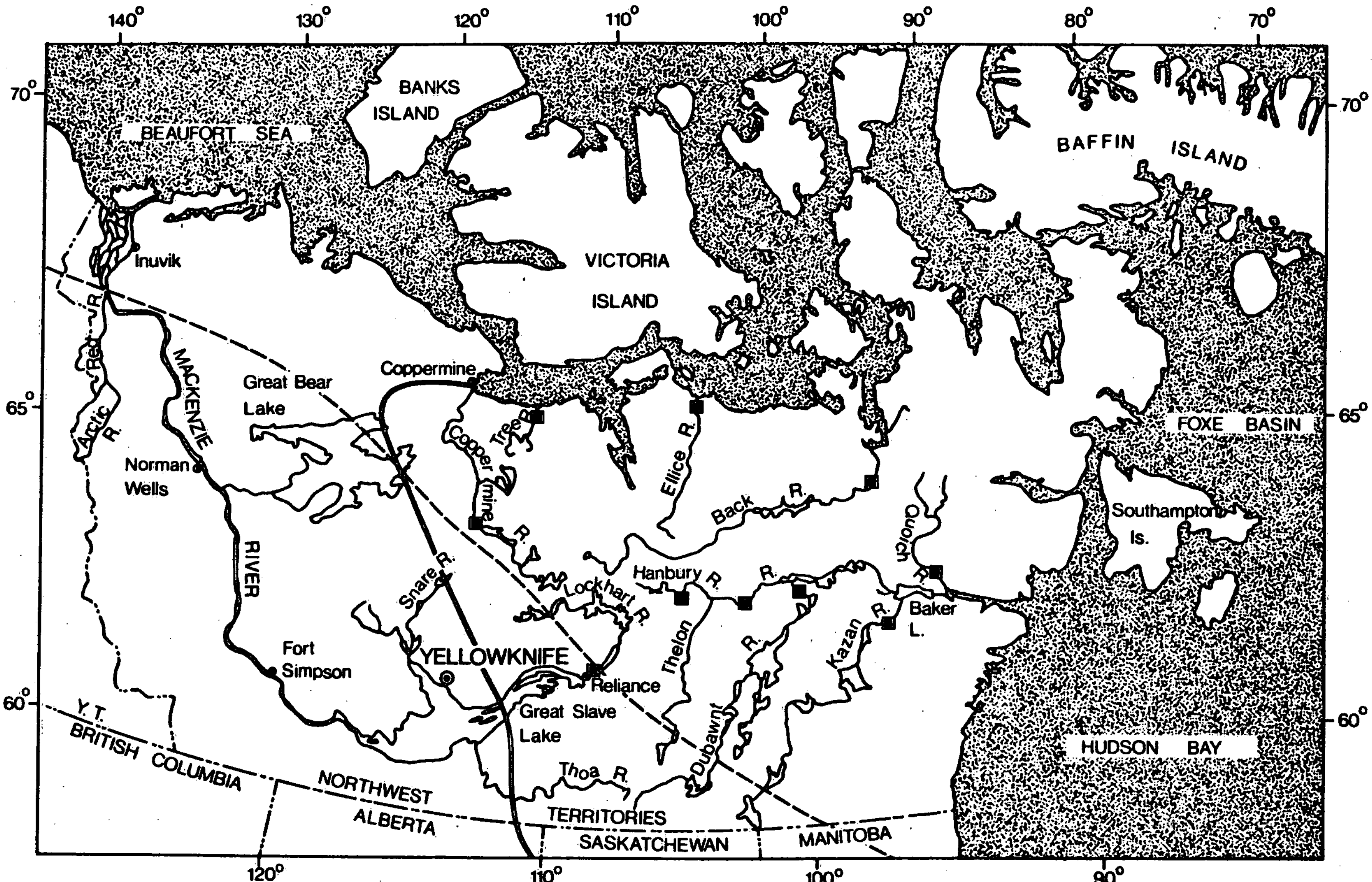
TABLE 2. **The number of samples available for rivers in the Northwest Territories, the range of discharge values for the various sampling dates, and the range of conductance, chloride and sulfate values; the chloride concentrations, the sulfate concentrations, and stable isotopic ratios of sulfate sulfur for the samples of August - September, 1984**

River	Number of Samples	Range of Discharge for Sampling Dates $m^3\ s^{-1}$	Range of Conductance $\mu S\ cm^{-1}$	Range of Chloride $mg\ L^{-1}$	Chloride this Report $mg\ L^{-1}$	Range of Sulfate $mg\ L^{-1}$	Sulfate this Report $mg\ L^{-1}$	$\delta^{34}S\ ^0/_{00}$
Hanbury	7	2.73 - 104.0	15 - 28	0.3 - 1.7	0.29	L1.0 - 3.4	1.55	4.10
Thelon	29	10.2 - 940.0	26 - 90	2.2 -12.0	2.66	L1.0 - 2.2	0.75	4.96
Dubawnt	11	177.0 - 566.0	16 - 34	L0.1 - 2.0	0.52	L1.0 - 2.1	0.68	5.16
Kazan	35	22.8 - 1310.0	18 - 48	0.4 - 3.1	0.42	L1.0 - 2.2	0.88	4.72
Quoich	30	0.681 - 1160.0	5 - 33	0.5 - 2.5	1.32	L1.0 - 2.8	0.94	-0.91
Lockhart	34	65.4 - 165.0	11 - 30	0.2 - 0.5	0.33	L1.0 - 2.0	1.37	3.95
Coppermine	42	33.1 - 253.0	7 - 28	0.2 - 1.6	0.28	L1.0 - 4.5	1.32	4.36
Tree	45	2.77 - 151.0	29 -111	0.9 - 3.4	1.81	L1.0 - 3.6	1.47	7.01
Ellice	29	26.6 - 530.0	17 - 70	1.5 - 9.9	3.56	1.0 - 6.0	1.81	6.30
Back	34	22.5 - 2780.0	12 - 43	0.5 - 2.6	0.71	L1.0 - 2.6	0.94	4.90

L means less than, or below, detection limit.

TABLE 3. **The number of samples for each river, the correlation coefficient for the linear regression between Na^+ and Cl^-, and the mean Na^+/Cl^- (in weight units).**

River	Number of Samples	Correlation Coefficient	Mean Na^+/Cl^-
Hanbury	7	0.92	0.82
Thelon	29	0.93	0.22
Dubawnt	11	0.51	0.78
Kazan	34	0.56	1.15
Quoich	30	0.59	0.80
Lockhart	34	nil	1.45
Coppermine	42	0.02	1.74
Tree	45	0.91	0.59
Ellice	26	0.84	0.60
Back	34	0.81	0.67



Approximate Western extent of outcrop of Canadian Shield rocks

Approximate Southern boundary of zone of continuous Permafrost

Sample stations