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Trace Elements in Frobisher Bay Rainwater

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ABSTRACT. Using short-decay instrumental neutron activation analysis, concentrations of the trace elements Al, Br, Ca, Cl, Cu, I, Mg, Mn, Na, and V were determined in rainfall sampled from Frobisher Bay, N.W.T., during three weeks in the summer of 1984. Detectable concentrations were reported for all ten elements. Enrichment factors revealed that concentrations generally represent either crustal or oceanic natural backgound levels.

Key words: trace elements, precipitation, Arctic, Frobisher Bay

RÉSUMÉ. A l'aide de l'analyse par activation neutronique à décroissance courte, des concentrations des oligo-éléments Al, Br, Ca, Cl, Cu, I, Mg, Mn, Na et V furent décernés dans des échantillons d'eau de pluie à Frobisher Bay, aux T. N.-O., pendant trois semaines durant l'été de 1984. Ces dix éléments furent chacun représentés par des concentrations décelables. Des facteurs d'enrichissement signalèrent que les concentrations proviennent en général de sources naturelles océaniques ou de croûte terrestre.

Mots clés: oligo-éléments, précipitation, Arctique, Frobisher Bay

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INTRODUCTION

The chemistry of atmospheric precipitation is of growing scientific concern. Aside from the elements that contribute to acid rain, there are numerous co-contaminants in precipitation, the concentrations and sources of which are not well understood.

Deposition by precipitation is a primary route by which atmospheric aerosols reach ground or water surfaces to interact with the ecosystem (Royal Society of Canada, 1985), yet there has been limited study of elemental composition of arctic precipitation (L.A. Barrie, pers. comm. 1985).

Precipitation is somewhat insensitive to the detection of atmospheric pollution as it generally discriminates against the fine particles containing the greatest pollution signal. The measurement of elemental concentrations in precipitation, however, is useful for the modeling of aerosol washout near the surface and the determination of elemental loadings to the environment during the arctic summer.

The sampling of atmospheric pollution has previously been confined to the filtering of aerosols and the sampling of snowpacks and ice cores (L.A. Barrie, pers. comm. 1985). Arctic aerosol studies confirm the existence of the polluting "arctic haze" in the winter and early spring months, while the summer months have generally been found to be unpolluted (Kerr, 1981; Barrie *et al.*, 1981).

Concentrations during the summer months found to represent natural background levels serve as useful precursors to more detailed study and as useful comparisons to concentrations found during months of higher pollution levels.

The present research documents the concentrations and possible sources of ten trace elements in summer rains from Frobisher Bay, N.W.T. Precipitation was monitored for approximately three weeks 11 July-5 August 1984, and samples were collected during ten rain events. The very low detection limits and the precision of neutron activation analysis allowed determination of natural or anthropogenic (man-made) sources for elemental concentrations in rain samples.

METHODOLOGY

Due to the remoteness of the arctic study location, the use of either a bulk precipitation sampler, as described by Gambell and Fisher (1966), or a Sangamo wet-only precipitation sampler was impractical. The intent was to remove the collector between precipitation events and thus sample only wet deposition. The precipitation sampler had to be easily transportable, non-mechanical and of simple but durable construction. To meet these requirements a modified bulk sampler was developed (Fig. 1).

Each bulk sampler consisted of a 500 ml Nalgene polyethylene container inside a 1000 ml container of similar composition. The large outer container had the upper portion cut off to allow positioning of the inner container. A 15 cm polyethylene funnel was positioned with the spout inside the mouth of the inner container. To avoid the necessity of washing the funnel and inner container following each collection, both were lined with replaceable polyethylene bags.

In order to avoid contaminating samples in the field, contact with the polyethylene bags and bottles was restricted to the outside surfaces only. All containers were sealed immediately upon removal from the sampler, and samples were transferred directly from the polyethylene bags to tightly capped storage containers immediately following the rain event. No bags were reused and all bottles were thoroughly cleaned, as prescribed by the Inland Waters Directorate (1983). Each storage bottle was preacidified with 2% nitric acid to limit the absorption of elements of interest to the walls of the storage bottle. Blanks with known concentrations of elements were stored 24 h in the polyethylene bags, and no significant contamination or absorption was found (Table 1). Precipitation samples stored in polyethylene bottles by the Great Lakes Institute have shown no decrease in elemental concentrations between subsequent analyses spaced several months apart (P. McQuarrie, pers. comm. 1984). Samples employed in this study were stored a few months prior to analysis, and caution was employed at all stages to avoid contamination (Bingham, 1984).

At the McMaster University swimming pool-type reactor, short-decay instrumental neutron activation analysis employing gamma spectroscopy was used on the precipitation samples for the simultaneous analysis of Al, Br, Ca, Cl, Cu, I, Mg, Mn, Na, and V. A wet sample was irradiated in a thermal neutron flux of 5×10^{12} n cm^2 sec^{-1} for 10 min. The irradiated sample was transferred to an inert vial and analyzed on a hyper-pure

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germanium counter. An average delay time of 90 s and a count time of 10 min gave optimum precision. Quality control was maintained with synthetic standards and the analysis of the National Bureau of Standards water standard (NBS 1643-a) with the rain samples.

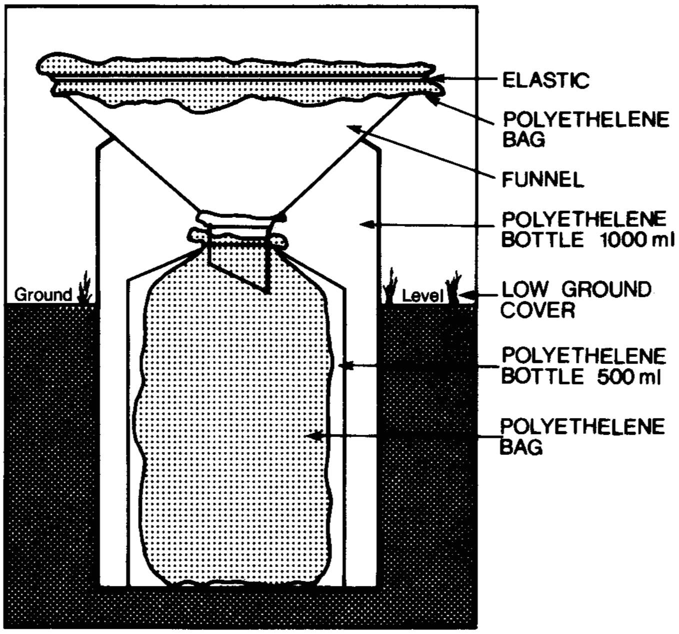

FIG. 1. Modified bulk sampler.

TABLE 1. Test results of contamination or absorption from polyethylene bags (ppb)

Element	NBS 1643-b (determined value)[1]	NBS 1643-b (24 h in polyethylene bag)[1]
Al	19 +- 2	14 +- 2
Br	<4	<4
Ca	39224 +- 2972	40702 +- 2058
Cl	5114 +- 229	5422 +- 243
Cu	20 +- 6	22 +- 6
I	<3	<3
Mg	8293 +- 732	8547 +- 759
Mn	32 +- 1	33 +- 2
Na	8844 +- 398	9196 +- 414
V	48 +- 1	50 +- 1

[1] Averages and errors based on three determinations.

ANALYSIS AND DISCUSSION

The concentrations of the trace elements for each precipitation event and average concentrations for the study period are shown in Table 2. Concentrations of Ca, Cl, Mg, and Na are recorded by the Canadian Network for Sampling Precipitation (CANSAP) at selected arctic locations, and the concentrations reported here are in general agreement with 1977-81 arctic CANSAP data. The Frobisher Bay data most closely resemble data from Fort Chimo, which is the nearest arctic CANSAP site.

To differentiate between natural and anthropogenic (man-made) sources of trace elements, enrichment factors (EF) were calculated as follows:

$$\text{EF (crust or ocean)} = \frac{\text{(E1/RE1) in precipitation}}{\text{(E2/RE2) in crust or ocean}}$$

The enrichment factors were normalized to Al for crustal sources and to Na for ocean sources. The ratio between the concentration of an element (E1) in rainfall and that of one of the two reference elements (RE1 - Al or Na) in rainfall was compared to the concentration ratio between the same elements in the crust or ocean (E2/RE2). If the ratios are the same, they give an enrichment factor of one, and this is referred to as unity. Values close to unity for the crustal enrichment factor indicate a probable crustal source, and similarly values close to unity for the ocean enrichment factor indicate a probable ocean source. Enrichment factors greater than one and that cannot be explained by either of the natural sources are a general indication of anthropogenic sources (Rahn, 1976).

As shown in Table 3, crustal enrichment factors for Ca, Mg, Mn, and V approach unity and are supportive of crustal weathering as a source. This hypothesis is further supported by strong to moderate correlation coefficients between Al and Mg, Mn, and V (0.94, 0.88, and 0.63 respectively), which suggest a common source for these elements. Ocean enrichment factors for Br and Cl approach unity (Table 4) and indicate a possible ocean source. Correlation coefficients between Na and Br and between Na and Cl (0.90 and 0.98) are also indicative of a common source for these elements. The element Ca, although not enriched and appearing to be derived from crustal weathering, is correlated quite strongly with Na (0.83) and the other elements hypothesized as being from ocean sources.

The greatly enriched values of I are in agreement with the results of previous studies (Seto and Duce, 1972; Cicerone, 1981). This I enrichment is not hypothesized as anthropogenic but as preferential enrichment from the oceans. All study elements appear to represent natural background levels with the exception of Cu, which is enriched. A number of the Cu

TABLE 2. Concentration of select trace elements in Frobisher Bay rainwater (ppb)

Dates	Al	Br	Ca	Cl	Cu	I	Mg	Mn	Na	V
Jul 18-19/84	1300	10	1600	1300	24	14	800	25	1200	2
Jul 19-20/84	770	6	490	360	<12	30	300	13	400	1
Jul 21-22/84	690	4	570	220	13	36	340	10	280	1
Jul 27/84	1000	7	1200	840	<14	29	530	18	700	2
Jul 28-29/84	240	4	380	340	< 9	28	39	6	270	0.4
Jul 30-31/84	150	8	1400	1900	30	14	140	8	1300	0.4
Jul 31-Aug 1/84	1100	10	880	1100	18	29	450	15	1000	1
Aug 1-2/84	850	13	1900	3800	77	26	600	22	2400	3
Aug 3-4/84	1300	8	760	1300	<15	22	670	18	1000	1
Aug 4-5/84	250	7	600	1700	<11	30	66	7	1100	0.4
Average	760	8	970	1300	19	26	400	14	1000	1

TABLE 3. Crustal enrichment factors of Frobisher Bay rainwater normalized to aluminum (Wedepohl, 1971)

Dates	Al	Br	Ca	Cl	Cu	I	Mg	Mn	Na	V
Jul 18-19/84	= 1	210	3	240	48	1700	3	2	3	1
Jul 19-20/84	1	200	2	120	<13	6000	2	2	2	1
Jul 21-22/84	1	140	2	78	49	8300	3	2	1	1
Jul 27/84	1	190	3	200	<32	4400	3	2	2	1
Jul 28-29/84	1	400	4	350	<13	18000	1	3	4	1
Jul 30-31/84	1	1400	26	3200	530	15000	6	6	28	2
Jul 31-Aug 1/84	1	260	2	250	43	4200	2	2	3	1
Aug 1-2/84	1	410	6	1100	240	4700	4	3	9	3
Aug 3-4/84	1	170	2	240	<20	2700	3	2	3	1
Aug 4-5/84	1	770	7	1700	<47	19000	2	3	14	1
Average	1	280	3	410	65	5300	3	2	4	1

TABLE 4. Ocean enrichment factors of Frobisher Bay rainwater normalized to sodium (Bowen, 1966)

Dates	Al	Br	Ca	Cl	Cu	I	Mg	Mn	Na	V
Jul 18-19/84	1100000	1	33	1	69000	2000	5	110000	= 1	6800
Jul 19-20/84	2000000	2	31	1	<34000	13000	6	160000	1	10000
Jul 21-22/84	2500000	2	52	1	160000	22000	9	190000	1	22000
Jul 27/84	1500000	2	46	1	<64000	7200	6	130000	1	14000
Jul 28-29/84	930000	2	37	1	<16000	18000	1	120000	1	7800
Jul 30-31/84	120000	1	28	1	81000	1800	1	30000	1	1600
Jul 31-Aug 1/84	1100000	2	23	1	62000	5100	4	82000	1	7400
Aug 1-2/84	380000	1	21	1	110000	1900	2	48000	1	6400
Aug 3-4/84	1300000	1	19	1	<35000	3700	5	90000	1	6200
Aug 4-5/84	240000	1	14	1	<14000	4700	1	34000	1	1900
Average	830000	1	26	1	69000	4700	3	76000	1	5400

concentrations were below or near detection limits and thus are reported here with caution. However Zoller *et al.* (1974) have reported enriched Cu concentrations in Antarctic aerosols and hypothesized a correlation between high enrichment and high volatility.

Enrichments for individual elements vary from date to date, but Cu and I enrichment increases and Mg, Mn, and Ca become slightly enriched on particular dates, most notably 30-31 July 1984. These increases in enrichment appear to be related to the development of a deep stationary low over southern Baffin Island, which drew air from more southerly regions of North America. It is possible that this air mass carried enriched concentrations of these elements from southern industrial sources.

CONCLUSION

During the three weeks in which rainfall was sampled at Frobisher Bay, the ten targeted trace elements were detected with a wide range of concentrations between sampling dates. These concentrations have been determined to generally represent either natural crustal or oceanic background levels and therefore are not of anthropogenic origin.

Instrumental neutron activation analysis has been shown to be a useful method for determining extremely low elemental concentrations in arctic precipitation.

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