

ABNORMALLY ENRICHED ELEMENTAL CONCENTRATIONS IN URBAN SNOW

J.J. Drake and S.J. Vermette
Department of Geography
McMaster University
Hamilton, Ontario
Canada L8S 4M1

and

S. Landsberger and A. Simsons
Nuclear Reactor
McMaster University
Hamilton, Ontario
Canada L8S 4K1

ABSTRACT

Using two multi-elemental techniques (instrumental neutron activation analysis and inductively coupled plasma-atomic emission spectroscopy) we have been able to characterize upwards to eighteen trace elements in the soluble fraction of urban snow. Quality control was achieved by using an NBS certified water standard. Enrichment factor calculations have shown that many trace elements show abnormally high values which can be attributed to short and long-range transportation of either polluted or naturally occurring aerosol composition. In particular we have shown that elemental analysis of urban snow can act as a very good environmental monitor.

INTRODUCTION

Investigation of trace elemental contaminants in snow has not received a great deal of attention for the obvious reason that snowfall does not occur often enough in many places to warrant useful environmental studies. However, investigations of snow composition can be just as informative as that from rainfall. In the last decade several groups throughout the world Struempfer (1976), Thornton et al. (1981), Schrimpff et al. (1979), Forland and Gjessing (1975), including several in Canada, Landsberger et al. (1983), Concord Scientific Corporation (1981), Barrie and Walmsley (1978) have studied the elemental composition of snow. Many other scientists have studied polar snows in great detail Boutron and Patterson (1983), Ng and Patterson (1981) and Boutron (1982). In general little has been done in studying trace elemental pollutants in urban snowfall (Landsberger et al., 1983).

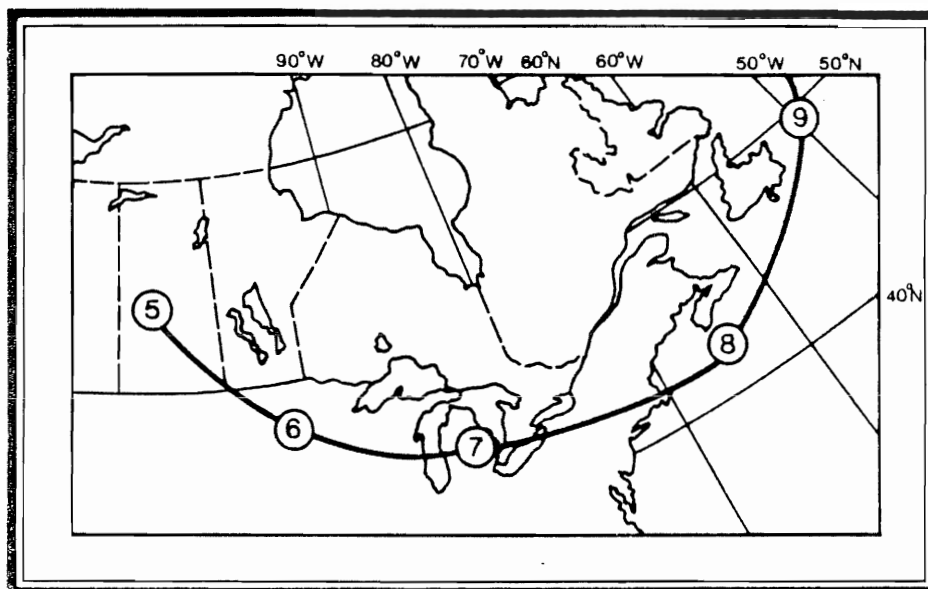
We would like to report on the analytical results as well as environmental interpretations of snow collected in an industrialized city (Hamilton, Ontario) on 8 January 1985. In particular, we clearly demonstrate how instrumental neutron activation analysis (INAA) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) have proved to be very complimentary multi-elemental methods in such an environmental program. Both methods have unique advantages.

The preliminary results of this urban snow study is part of a greater on-going investigation of trace elemental pollutants in precipitation (both rain and snow) in a city wide network.

A. Winter Storm of 7 January 1985

The snow in Hamilton originated from a low that developed over Saskatchewan on 5 January 1985. The low pressure system tracked eastward across the northern United States and was centered over southwest Michigan and Detroit on 7 January 1985. (Figure 1). The low drew air from the American Midwest to the Hamilton area.

Figure 1: Track of Storm of 7 January 1985, over Hamilton, Ontario



The precipitation began at 0600 hours on 7 January 1985 and persisted through out the day dissipating in the early morning hours of 8 January 1985. Initially the precipitation was a trace of freezing drizzle which developed into snow soon after it began. The 24 hour record at Hamilton's weather office indicates that from 0100 of 7 January 1985 to 0100 8 January 1985 11 cm of snow fell.

The average wind speed was 19.3 km/hr which resulted in some drifting of snow. The prevailing wind direction was from the NE and thus off Lake Ontario. A portion of the snow accumulation could be attributed to lake effects. After 1800 on 7 January 1985 there was shifts in wind direction from the NW and SW but winds from the NE dominated all day.

B. Snow Collection And Preparation For Analysis

The frozen state of snow allowed us to use a simple and flexible method where snow could be collected insitu. Samples were collected from six predetermined sites. These sites were chosen because of their proximity to summer rain collection sites (representing a cross-section of the study area), distance from immediate sources of pollution and in areas with minimum horizontal snow movement. Using a plastic scoop, sheathed in a clear polyethylene bag, the first few centimeters of snow were removed and underlying snow was placed into a 29 cm x 34 cm clear polyethylene bag. Extreme caution was used to collect snow as to avoid contamination. Cross-contamination between sites was minimized by replacing, after collection, the clear polyethylene bag in which the plastic scoop was wrapped.

The samples were kept frozen prior to filtering. The filter housing, consisting of a Millipore Swinex water filtration apparatus and Erlenmeyer flasks were washed with soap and distilled water, rinsed thoroughly with distilled water, left soaking in an acid bath of 5% HNO₃, rinsed with deionized-distilled water and dried in an oven. The snow to be filtered was removed from the centre of the collected snow sample and thus was not contaminated by the sides of the polyethylene bag and subsequently packed into the filter housing by a plastic scoop. The snow was allowed to melt passively through a pre-cleaned 0.4 µm. Nuclepore filter paper into an Erlenmeyer flask. The liquid sample was then acidified with one mL of ultrapure nitric acid (Ultrex) and stored prior to irradiation. Approximately 100 mL was collected.

C. INAA

An aliquot of about 5 mL of filtered snow was placed in an acid washed vial, closed, placed in a "rabbit carrier" and then thermally neutron activated at the Neutron Activation Facility at the McMaster Nuclear Reactor. Once the "rabbit" returned the liquid sample was transferred to a pre-weighed acid washed vials and presented to a hyperpure germanium detector for counting. The resolution of the counting system, including a 21% efficient APTEC detector coupled to Canberra 2020 amplifier and thence a Series 90 Canberra analyzer, was 2.2 KeV full width half-maximum at the 1332 KeV cobalt peak.

Typically a 5 minute irradiation at a flux of $\sim 5 \times 10^{12} \text{ n} \cdot \text{cm}^2 \cdot \text{sec}^{-1}$, a 2 minute delay time and a 5 minute counting time was sufficient to get good precision. Ten elements (Al, Br, Ca, Cl, Cu, I, Mg, Mn, Na, and V) were readily determined. After the counting period was over the vial was weighed again to determine the exact weight transferred. Synthetic standards were used to calibrate the procedure while quality control was ensured by analysing a NBS certified water reference standard (Table 1).

Determination of the concentrations was done by using an in-house versatile program employing strict statistical parameters.

D. ICP-AES

The remainder of the snow samples were then analyzed using an ARL 34000 at ICP-AES system at the Institute of Environmental Sciences at the University of Toronto. A complete description of the system including typical detection limits have been previously published (Landsberger et al. (1985)). Concentrations for eight elements including B, Ba, Cr, Co, Fe, Ni, S and Zn were determined.

RESULTS AND INTERPRETATIONS

The concentration values for eighteen elements from six different sampling sites are presented in Table 2. Mean concentrations, typical detection limits and precision of the methods used are also shown. As can be seen several of the elements, notably aluminum, calcium, chlorine, magnesium and sodium have a relatively wide range of reported

concentrations. Most of the other elements exhibited much less of a variation. Concentrations were highest in east Hamilton where most of the city's steel industry is located.

Table 1: Results for NBS 1643b Certified Water Standard

<u>Element</u>	<u>INAA¹</u> (ppb)	<u>ICP-AES¹</u> (ppb)	<u>NBS Value²</u> (ppb)
Al	18±3	--	--
B	--	93±1	(94)
Ba	--	43±1	--
Br	13±2	--	--
Ca	35.2±1.4 (ppm)	37±1 (ppm)	(35) ppm
Cl	4.8±0.3 (ppm)	--	--
Cr	--	--	--
Co	--	28±1	26±1
Cu	19±3	24±3	21.9±0.4
Fe	--	104±1	99±8
I	1.7±0.1	--	--
Mg	9.3±0.5 (ppm)	9.9±0.2 (ppm)	(15) ppm
Mn	30±2	30±1	28±2
Na	8.0±0.4 (ppm)	--	(8) ppm
Ni	--	49±4	49±3
S	--	390±14	--
V	44±3	47±1	45.2±0.4
Zn	--	64±1	66±2

1. All results represent on average value of 5 replicates and standard deviation.
2. All NBS values certified except those in parenthesis. Several other elements have no provided values.

Table 2: Range of Concentrations, Mean Values and Detection Limits in the Snow Soluble Portion.

<u>Element</u>	<u>Range of Concentrations</u> (ppb)	<u>Mean</u> (ppb)	<u>Detection Limit</u> (ppb)	<u>Precision</u> (%)
Al	20-95	48	2 (INAA)	5
B	15-44	20	14 (ICP)	1
Ba	4-6	5	1 (ICP)	2
Br	4-26	12	2 (INAA)	10
Ca	511-4676	1374	85 (INAA)	8
Cl	837-2407	1360	20 (INAA)	3
Cr	6-8	7	7 (ICP)	10
Co	<10	<10	10 (ICP)	5
Cu	<5-46	19	6 (INAA)	20
Fe	18-36	30	4 (ICP)	1
I	2-6	4	0.7 (INAA)	5
Mg	<140-424	196	140 (INAA)	15
Mn	6-29	15	1 (INAA)	5
Na	309-2306	1022	15 (INAA)	3
Ni	8-13	11	5 (ICP)	8
S	683-1042	723	40 (ICP)	4
V	0.6-1.4	0.8	0.1 (INAA)	4
Zn	12-51	25	12 (ICP)	2

To help distinguish naturally-occurring elements in precipitation or aerosols from those arising from various types of pollution elemental enrichment factors (EF) can be employed. An element's enrichment factor is defined as follows:

$$EF = \frac{(X/C) \text{ atmosphere}}{(X/C) \text{ reference material}}$$

where X and C are the concentrations of the elements of interest and reference element, respectively. An EF value greater than unity would suggest that the element arises predominantly from one or more anthropogenic or natural sources. Anthropogenic sources include both long-range transport and local emissions, while natural sources include lithospheric dust from the crust, marine aerosols formed from the bursting of air bubbles at the sea surface, and possibly from lake waters. Average EF values are shown in Table 3. Concentrations for the earth's crust are taken from Taylor (1964) for seawater from Bowen (1966) and for Lake Ontario from Allen (1977) and Bell (1980) with aluminum, sodium and calcium as the reference elements, respectively.

Table 3: Crustal, Oceanic, and Lake Ontario Enrichment Factors for the Snow Soluble Portion.

Element	Ave. Crustal E.F. ¹ (normalized to Al)	Ave. Seawater E.F. ² (normalized to Na)	Ave. L. Ontario E.F. ³ (normalized to Ca)
Al	=1	66000	21
B	7000	94	62
Ba	17	2500	10
Br	10000	2	13000
Ca	86	34	=1
Cl	11000	1	2
Cr	200	2800000	600
Co	<970	<380000	<3000
Cu	1400	43000	82
Fe	2	44000	28
I	19000	1000	58
Mg	28	2	1
Mn	56	110000	1300
Na	100	=1	3
Ni	540	33000	200
S	5500	13	--
V	20	6000	1200
Zn	770	36000	91

1. Taylor (1964)
2. Bowen (1966)
3. Allen (1977), Bell (1980)

One of the most revealing results is the very high crustal enrichment factors of boron, bromine, chlorine, iodine and sulphur. Sulphur's contribution to acid precipitation is now very well documented. Boron has been suggested to be a strong indication of fossil fuel burning (Gladney et al., 1978). Also very significant are the EF values for nickel, copper and zinc. Only iron has a value close to unity, while barium, calcium, magnesium, manganese, sodium and vanadium have values moderately enriched. All these values are comparable to those found in another major snow study done in Montreal (Landsberger et al., 1983).

Seawater EF values show generally reduced enrichment of the originally high crustal enriched elements. Seawater and Lake Ontario EF values near or at unity for chlorine, magnesium and sodium suggests a primarily marine or lake source. A seawater EF value near unity for bromine indicates a probable marine source.

Of particular importance is the significant EF values for chromium, cobalt, copper, manganese, nickel, vanadium and zinc. These elements may be associated with emissions from the steel industry and their enrichment may suggest a local anthropogenic source.

Ratios of certain elemental concentrations can also aid in "finger-printing" either anthropogenic or natural-occurring source emissions. Ratios for Cl/Na gave an average of 1.4 which is close to those found in marine environments of between 1.8-2.2. The Br/Cl ratios gave average values of 8.8×10^{-3} which is about of factor 2.6 times greater than found in sea-water of 3.42×10^{-3} . This can be attributed to the release of bromine from leaded gasolines. The halogen ratio of I/Cl had a value of 2.9×10^{-3} which is about 1,100 times higher than that found in sea-water of 2.63×10^{-6} . This result agrees well with the I/Cl ratio calculated in rainfall in Hawaii (Gladney et al., 1978). The high enrichment of the halogens on the atmosphere is a very complex phenomenon which is covered in a detailed review article by Ciercone (1981).

It is interesting to point out that INAA is unique in that Br, Cl, I can all be quantitatively determined. Other ratios including Mn/S, Mn/V and Cu/Zn are presently being investigated in a wider range of snow samples.

CONCLUSIONS

Upwards to eighteen elements have been determined with good precision and accuracy in urban snow. We have demonstrated in this pilot project that both instrumental neutron activation analysis and inductively coupled plasma-atomic emission spectroscopy offer a unique combination of determining many environmentally important elements in a totally non-destructive fashion. The one disadvantage is that both INAA and ICP-AES do not the capability of determining either lead or cadmium at the levels found in precipitation. Either a freezing technique employing ICP-AES or a graphite furnace atomic absorption spectrophotometry can be used to determine these two elements.

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