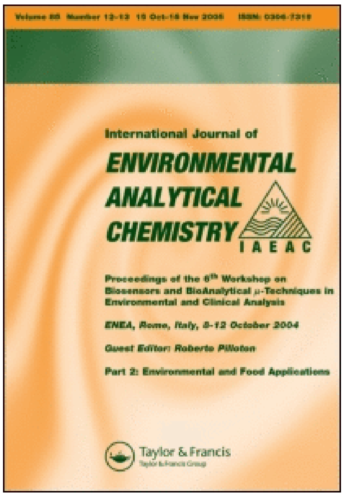

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Characterization of Trace Elemental Pollutants in Urban Snow Using Proton Induced X-ray Emission and Instrumental Neutron Activation Analysis

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To cite this Article Landsberger, S. , Jervis, R. E. , Kajrys, G. and Monaro, S.(1983) 'Characterization of Trace Elemental Pollutants in Urban Snow Using Proton Induced X-ray Emission and Instrumental Neutron Activation Analysis', International Journal of Environmental Analytical Chemistry, 16: 2, 95 — 130

To link to this Article: DOI: 10.1080/03067318308078354

URL: http://dx.doi.org/10.1080/03067318308078354

Intern. J. Environ. Anal. Chem., 1983, Vol. 16, pp. 95–130
0306-7319/83/1602-0095 $18.50/0

Printed in Great Britain

Characterization of Trace Elemental Pollutants in Urban Snow Using Proton Induced X-ray Emission and Instrumental Neutron Activation Analysis†

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(*Received March 4, 1983, in final form June 10, 1983*)

Proton-induced X-ray emission (PIXE) and instrumental neutron activation analysis (INAA) methods have been employed to determine trace elemental pollutants in urban snow collected mostly from the island of Montreal and some from Toronto. The use of small pore filters, 0.40 μm, enabled a distinction to be made between soluble and insoluble particulate fractions. Results for those elements, including heavy metals, that filtered through the 0.40 μm pore filters gave an indication of their bioavailability and potentially toxic actions.

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A total of twenty-five trace elements (Na, Mg, Al, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Cd and Pb) were obtained in the soluble snow portion with detection limits between 0.2 ng/g and 147 ng/g. Twenty-eight elements (Na, Mg, Al, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Cd, Sb, La, Sm and Pb) were analyzed with detection limits between 3 μg/g and 720 μg/g in the insoluble particulate matter. INAA proved to be an extremely valuable complement to PIXE in determining Al, Mn and V with very good precision and accuracy. These elements were then used as internal standards for PIXE analysis of the particulate matter. In particular Al was used as a normalizing element for enrichment factor evaluations.

Comparison of S, V, Ni, Zn, Se, Cd and Pb in the soluble and insoluble fractions revealed that all these elements exhibited high solubilities along with very high enrichment factors. These results suggested the anthropogenic nature and potential toxic actions of these elements. Enrichment factor calculations done for the particulate matter also showed that S, Cr, Co, Ni, Cu, Zn, Br, Sb and Pb were anthropogenic. In general comparisons of urban snow particulate matter and published aerosol enrichment factors showed comparable results. Finally, a comparison of enrichment factors in both the soluble and insoluble portions of urban snow with those in coal, considered as a typical combustion source of airborne particulates, showed a strong correlation.

1. INTRODUCTION

Among recent environmental studies the measurement of trace elements, in fine particulates and in wet atmospheric depositions, has received increased attention because of their potential toxic effects.[1-11]

A recent comprehensive paper has effectively reviewed and assessed the atmospheric deposition of trace elements.[12] The demand for fossil fuels for transportation, various industries and temperature controlled commercial and residential buildings has led to an ever-increasing and undesirable release of many trace elements into the atmosphere. This is further compounded by emissions from remote metal smelters, urban waste incinerators and petrochemical plants. In particular, sulphur has recently received a significant amount of attention since it is one of the main precursors of acid precipitation and has potential environmental and health consequences.[13] However, the "co-contaminants" of acid rain and snow are also important since elements such as vanadium, manganese, nickel, copper, zinc, arsenic and selenium which can be emitted together with sulphur, are potentially toxic, even at quite low concentrations.[14]

The present investigation concerns the use of PIXE and INAA to characterize trace elements in both the soluble and particulate portions of urban snow. In general, the use of both nuclear analytical methods, gave comprehensive results on trace elements in wet atmospheric deposition which could be used in investigating atmospheric scavenging processes, assessing the environmental impact of the precipitation of these elements into various ecosystems and in initiating environmental and epidemiological studies. Although the multi-elemental content of urban aerosols has been explored fairly systematically, such techniques have by and large been neglected for wet atmospheric precipitation samples. The present study can be considered as our modest effort to fill this gap.

2. EXPERIMENTAL METHODS AND DEVELOPMENT OF ANALYTICAL TECHNIQUES

2.1 Environmental sampling and sample treatment

In this study snow samples were collected from the ground late in the winter season at thirty-four equidistant locations (4–5 km) around the island of Montréal in February 1979. Approximately 100 g of frozen snow were removed from the sample bag, allowed to melt in a Millipore Swinex water filtration apparatus and drawn through a preweighed 0.40 μm Nuclepore filter which was pre-rinsed three times with distilled and deionized water. These thin 0.4 μm Nuclepore filters were well-suited as backing material for the determination of the composition of particulate matter by PIXE.

All containers and materials which came in contact with the melted snow were left at least 24 hours in a 20% solution of nitric acid and rinsed seven times with distilled and deionized water. This greatly minimized any possible contamination. A more detailed discussion of the methodology of sample collection and laboratory pre-treatment can be found elsewhere.[1-3]

2.2 Meteorological (wind and temperature) influences

Daily wind and temperature data for the island of Montréal were obtained by Atmospheric Service Department of the Environment—Canada.

Wind velocities and directions during the winter months of December through February (1978–1979) remained fairly constant. Prevailing wind direction for these months was westerly with a mean velocity between 16–19 km/h. The temperatures for the same period remained under 0°C about 85% of the time. Under such conditions snow melting may have occurred, but not in any appreciable amount.

2.3 Target preparation and experimental set-up for PIXE analysis

Targets for the PIXE analysis were prepared according to a procedure reported in previous studies.[1,2] The targets were bombarded with 1.6 MeV and 3.0 MeV proton beams obtained from the Université de Montréal Van de Graaff accelerator. A quantity of 200 μL of the preconcentrated snow sample was doped with 200 μL of cobalt used as an internal standard (300 μg/g for the samples and 30 μg/g for the blanks). For the 3.0 MeV protons bombardment, molybdenum (100 μg/g for the samples and blanks) was chosen. Both cobalt and molybdenum were adopted as the internal standards since they were not detectable in any of the samples and their position in the spectra did not interfere with any neighbouring X-ray peaks.

A quality of 25 μL of the well-stirred doped solution, was deposited on a 0.1 μm or 0.2 μm Nuclepore filter and quickly placed in a vacuum chamber and freeze-dried for about two hours. This freeze-drying technique generated microcrystalline structures, ensuring a uniform distribution of elements throughout the target.[15] The complete experimental PIXE set-up method of analysis and reproducibility experiments have been fully described in previous works.[1,2,15,16,17,19]

2.4 X-ray absorption matrix effects

A possible complication in X-ray analysis is the self-absorption of emitted X-rays by the matrix of the sample itself. Calculations using tabulated absorption coefficients[18] showed negligible X-ray absorption losses for the targets prepared using the snow soluble portion. For the particulate matter targets, losses were also negligible when the target thickness was less than $600\,\mu g/cm^2$. In the present study the target thickness was always kept below this value. A comparison of the results obtained through graphite furnace atomic absorption spectrometry and PIXE analysis for the snow soluble portion showed a good agreement.[19] As well, INAA of the particulate matter agreed within ±15% with the concentrations determined by PIXE.

2.5 Typical spectra from the soluble portion of snow samples using PIXE

Figures 1 and 2 show typical spectra of 100 ml of freeze-dried soluble snow bombarded with 1.6 and 3.0 MeV protons, respectively. It should be noted that sodium and chlorine, often prevalent in wet precipitation samples do not significantly appear in the X-ray spectra at 1.6 MeV. This is due to the relatively low efficiency for sodium and to the evaporation of the chlorine from the heat generated by the proton beam.

Previous studies on the analytical blanks have shown that some trace element contaminations arose from the Nuclepore filters.[2] However, these filter contributions were small, remained fairly constant and could be reliably evaluated and subtracted from the final results.

2.6 Typical spectra from the particulate portion of snow samples using PIXE

Snow samples (5–10 liters) were left melted in a large Pyrex beaker. To the unfiltered snow water, Ultrex nitric acid was added to it to a content of 1%. The resulting solution was then stirred by a glass rod and about 150 mL was filtered. The particulate matter (1 mg to 4 mg) remaining on the Nuclepore filter was then found to be evenly distributed. Subsequently, the filter was dried in air overnight and used for PIXE analysis. Several tests conducted on the particulate matter with 0.1 N hydrochloric acid and 1% Ultrex nitric acid showed negligible loss.

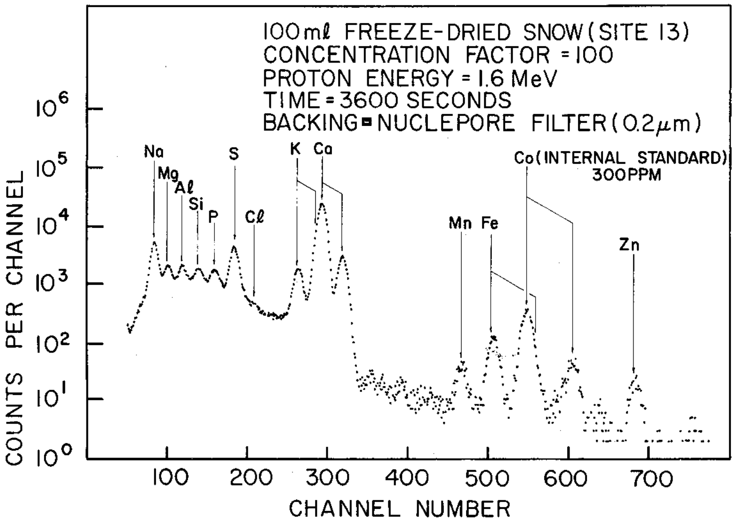

FIGURE 1 Characteristic X-ray spectrum from a preconcentrated filtered snow sample bombarded with 1.6 MeV protons.

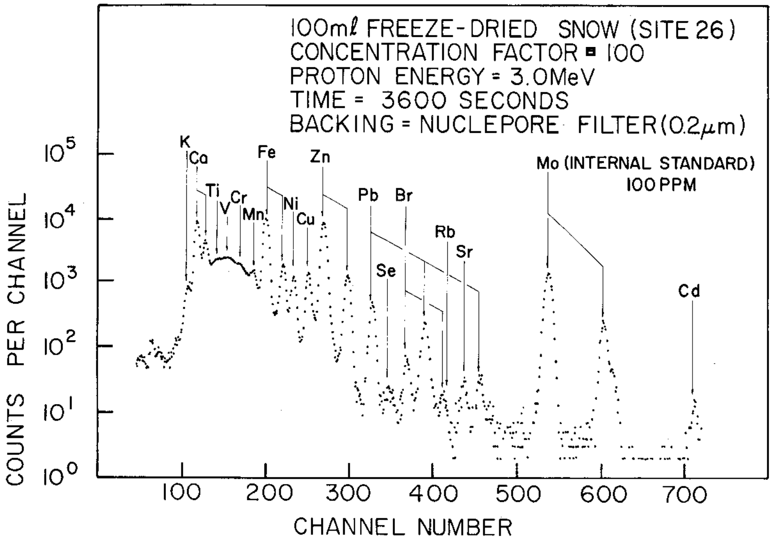

FIGURE 2 Characteristic X-ray spectrum from a preconcentrated filtered snow sample bombarded with 3.0 MeV protons.

Typical X-ray spectra of the snow particulate matter bombarded with the 1.6 MeV and 3.0 MeV proton beams are shown in Figures 3 and 4, respectively. One of the most obvious differences found in bombardment of the particulate matter, was a significant increase in counting statistics. In particular, the elements Mg and Al at 1.6 MeV and Ti, V and Cr at 3.0 MeV which were difficult to detect in the soluble portion, appear to stand out very clearly in the insoluble portion. Thus, analysis of these peaks was far more reliable in the particulate matter.

To determine the elemental concentrations in the particulate matter, the addition of an internal standard was not possible. However, the concentrations of aluminum, vanadium and manganese all possessing excellent sensitivities with INAA, were used as internal standards to determine the concentrations of remaining trace components detected by PIXE. Trace elemental concentrations from the filters were totally negligible.

2.7 Instrumental neutron activation analysis set-up

The source of neutrons used in these experiments was the SLOWPOKE-2 research reactor at the University of Toronto. Neutron fluxes of 2.5×10^{11} n.cm^{-2}.s^{-1} and 1×10^{12} n.cm^{-2}.s^{-1} (maximum), respectively, were used for irradiation of standards, soluble portions and particulate matter of the snow samples.

All the radionuclide gamma-ray spectra were obtained using a 24% efficient germanium lithium drifted, Ge(Li), detector having a resolution of 1.9 keV full width at half maximum (FWHM) for the 1332 keV cobalt peak. This was used in conjunction with a 4096 channel Canberra Series 80 analyzer. The concentrations of the elements which had yielded the observed radionuclides on activation were derived from their net peak areas using a semi-absolute method previously described.[20]

2.8 Typical spectra from the soluble portion of snow samples using INAA

Measurements were performed on unconcentrated and concentrated filtered snow samples. The snow samples were placed in acid-cleaned

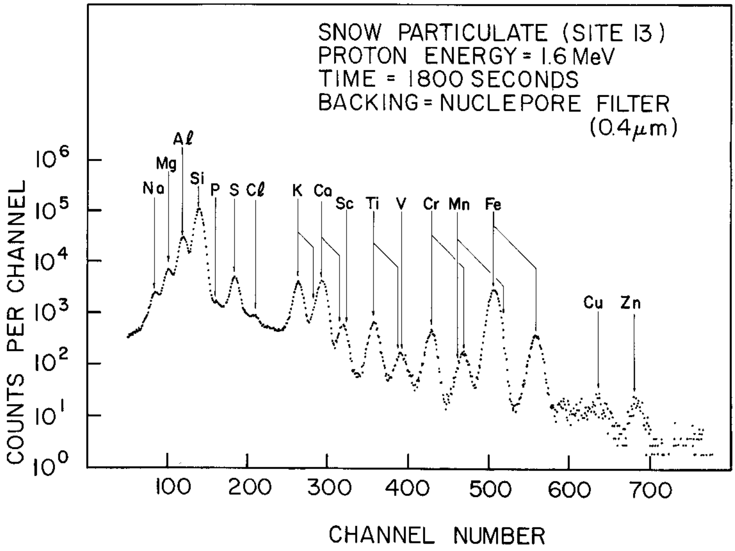

FIGURE 3 Characteristic X-ray spectrum from snow particulate matter sample bombarded with 1.6 MeV protons.

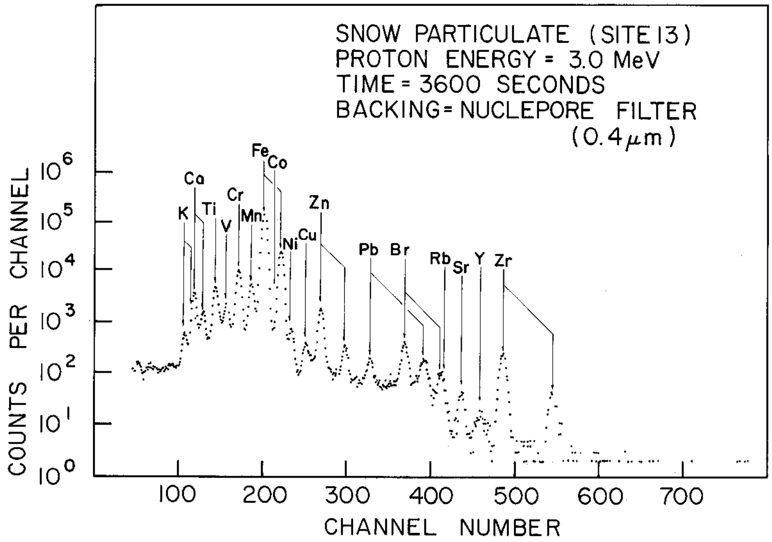

FIGURE 4 Characteristic X-ray spectrum from snow particulate matter sample bombarded with 3.0 MeV protons.

plastic vials which were heat-sealed and then thermal neutron-activated in the SLOWPOKE-2 reactor. After neutron bombardment, the liquids were transferred to pre-weighed unirradiated vials to avoid any contribution from impurities contained in the original vials themselves.

A typical gamma spectrum for an unconcentrated filtered snow sample (1 mL), is shown in Figure 5. As can be seen only the peaks belonging to Br, Mn, Na, V, Al and Cl are clearly visible. The use of a preconcentrated sample gave no benefit in the detection of any other element. Both Na and Cl, so highly soluble and prevalent in precipitation samples, contributed high background levels and high deadtimes and prevented achieving good sensitivities for the other elements. A complete comparative analytical study for the snow soluble portion between INAA, PIXE and atomic absorption spectrometry can be found elsewhere.[19]

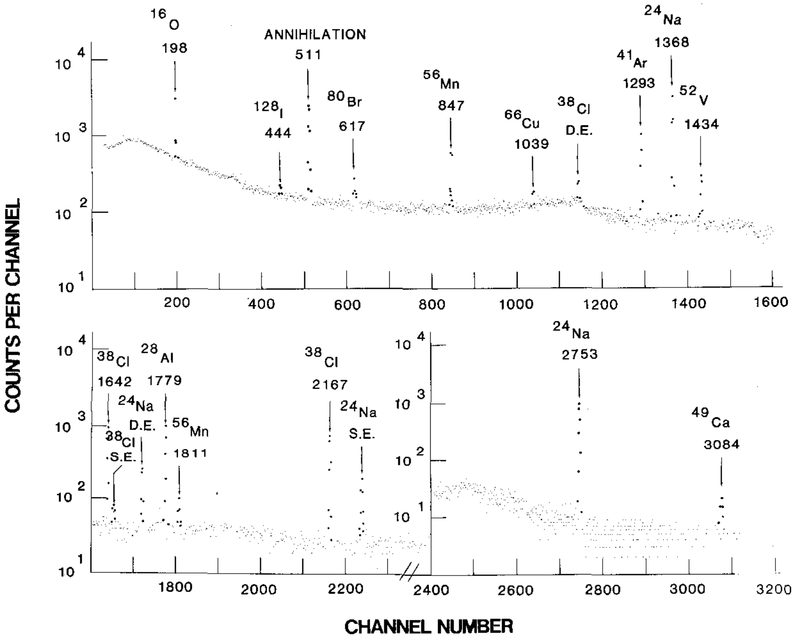

FIGURE 5 Typical spectrum from an unconcentrated filtered snow sample bombarded with thermal neutrons: $\text{flux} = 1.0 \times \mathrm{lo}^{12}\,\mathrm{n.cm}^{-2}\,\mathrm{sec}^{-1}$; $t_i = 10$ min: $t_d = 90$ sec; $t_c = 10$ min.

2.9 Determination of the particulate matter of snow samples using INAA

The use of INAA for the determination of trace elements in the particulate matter was more successful than for the soluble portion. To maximize sensitivities for short-lived nuclides the filters were irradiated for 5 minutes at a flux of 1×10^{12} n.cm^{-2} sec^{-1}. However, the presence of aluminum in a high abundance (18,000 μg/g–45,000 μg/g) together with its high activation cross-section necessitated a longer delay time of 15 minutes. This was to reduce the very high deadtime and background caused by excessive ^{28}Al. Elements such as titanium, copper and calcium were hard or impossible to achieve. A counting time of 10 minutes, (as in the soluble portion) was used.

For the medium and long-lived nuclides, a flux of 1.5×10^{11} n/cm^2-sec for 16 hours was used, with a delay time of 3 days and 18–21 days, respectively. The appearance of ^{82}Br with its many peaks considerably hindered the detection of several elements. As in the case for sodium in the soluble portion, the particulate samples could be counted only after a period of three days when the background effect of the ^{82}Br peaks ($t_{\frac{1}{2}} = 35.3$ h) was reduced. The long-lived nuclides of iron, zinc, cobalt and scandium were seen and their concentrations measured. Trace element contaminants from the filters were negligible in the INAA measurements. The results on detection and determination limits for trace elements in soluble and particulate matter, yielded by PIXE and INAA, are shown in Tables I and II.

3. RESULTS AND DISCUSSION

3.1 Trace element composition of snow, concentration variation from site to site and snow depth profile

The results for 25 elements found in the melted snow water and 28 elements in the particulate matter are given in Tables III and IV. Evaluated enrichment factors for the individual elements are also shown. There is a wide range of concentrations for the elements for both the melted snow and particulate matter.

To examine concentration variations from site to site a graph of the total deposition of 16 elements varying with eight sample sites is

TABLE I

Detection and determination limits of soluble portion for PIXE and INAA

Element	Detection limit[a] (ng/g) PIXE	Detection limit[a] (ng/g) INAA[b]	Determination limit[a] (ng/g) PIXE	Determination limit[a] (ng/g) INAA
Na	127	10	420	32
Mg	45	75	150	250
Al	38	1	125	4
P	26	—	86	—
S	19	—	63	—
Cl	18	13	60	44
K	12	300	40	1000
Ca	11	60	36	200
Ti	4	11	13	35
V	3	0.06	10	0.2
Cr	2	5	7	16
Mn	1	0.2	3	0.5
Fe	0.9	485	3	1600
Co	0.5	1.5	2	4
Ni	0.3	44	1	145
Cu	0.2	4.5	0.7	15
Zn	0.2	34	0.7	115
As	0.2	0.6	0.7	2
Br	0.2	0.6	0.7	2
Sr	0.2	10	0.7	33
Cd	2	18	7	60
Pb	0.5	—	1.7	—

[a] Calculated according to Currie, reference 59.

[b] INAA not applicable to P, S and Pb.

TABLE II

Detection and determination limits of snow particulate matter for PIXE and INAA

	Detection limit[a] (μg/g)		Determination limit[a] (μg/g)	
Element	PIXE	INAA[b]	PIXE	INAA
Na	720	1,400	2,370	4,600
Mg	270	3,250	890	10.700
Al	200	160	660	530
P	130	—	430	—
S	120	—	400	—
Cl	100	300	330	1,000
K	82	1,050	270	3,500
Ca	72	1,700	240	5,600
Ti	65	1,350	215	4,500
V	44	8	145	26
Cr	26	115	86	380
Mn	11	3	36	10
Fe	20	8,000	66	26,500
Co	12	13	40	45
Ni	9	6,000	30	20,000
Cu	8	350	26	115
Zn	8	450	26	1,500
As	8	5	26	17
Br	14	8	46	27
Sr	15	1,600	50	5,300
Cd	20	150	66	500
Pb	35	—	115	—

[a] Calculated according to Currie, reference 59.

[b] INAA not applicable to P, S and Pb.

TABLE III

Range of concentrations and enrichment factors in the snow melted portion[a]

Element	Range (ng/g)	Average E.F.
Al	25–750	=1
Na	2,000–21,000	336
Mg	27–650	20
P	85–2,500	640
S	310–3,500	7,000
Cl	2,500–30,000	30,000
K	100–8,000	80
Ca	1,000–7,500	170
Ti	2–55	7
V	1–21	54
Cr	<7	<300
Mn	3–170	27
Fe	1–750	3
Co	<1	<55
Ni	2–300	1,300
Cu	1–140	1,900
Zn	5–300	3,700
As	<1	<1,800
Se	<1–3	15,000
Br	1–30	5,500
Rb	<1–4	13
Sr	3–80	50
Mo	<1	<3,000
Cd	1–75	220,000
Pb	1–300	2,900

[a] Average enrichment factors based on values computed for individual samples.

TABLE IV

Range of concentrations and enrichment factors in the snow particulate portion

Element	Range (μg/g)	Average E.F.
Al	18,000–45,000	=1
Na	1,500–8,500	0.7
Mg	850–6,000	0.6
P	<150	<1
S	4,000–12,000	62
Cl	2,500–15,000	60
K	5,000–12,000	0.8
Ca	2,000–25,000	0.6
Sc	1–10	1
Ti	2,000–15,000	1.6
V	100–500	9
Cr	100–3,500	32
Mn	150–600	1.5
Fe	15,000–65,000	3
Co	40–150	18
Ni	100–500	15
Cu	100–500	30
Zn	200–20,000	170
As	<5	<10
Se	<11	<400
Br	2,000–10,000	4,500
Rb	14–65	1.5
Sr	85–200	1.5
Cd	<30	<2,500
Sb	4–145	330
La	15–110	1.5
Sm	2–16	1.5
Pb	250–950	90

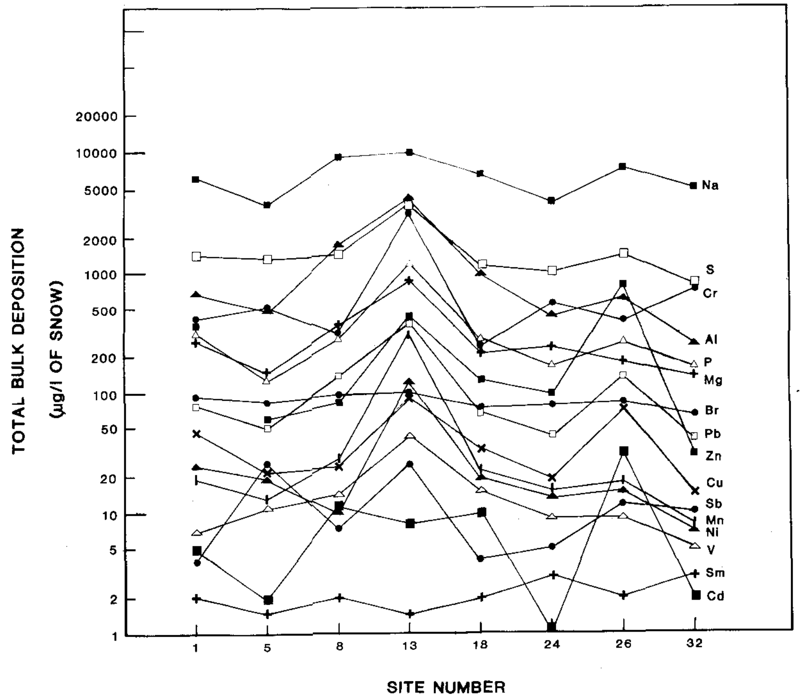

FIGURE 6 Variation of total snow deposition with Montreal sample sites.

shown in Figure 6. These results represent the filtration of 5 to 10 litres of snow from each site. With the exception of site 13 and to a lesser extent site 26 the fluctuations in concentrations for total deposition are not highly significant. One possible reason that all the concentrations appear to peak at site 13 is that this site is situated close to several refineries. In coroboration of this finding, a recent study, published during this work, on sulphur dioxide has shown that one of the highest concentrations of SO_2 was at a sample site close to site 13.[21]

To investigate the extent of possible concentration variations in snow samples near any single sampling location eight inner-city Toronto samples were chosen in equidistant locations on the perimeter of a circle with a 10 metre radius. The elements Na, Cl, V, Mn, Br and Al were analyzed in the filtered melted snow. The variation of these trace element concentrations within the sites was small having an average standard deviation of ±15%. It would therefore appear that snow collected at one sample site can be considered to be fairly representative of a local mode.

To examine the extent of variation, if any, among a group of different elements with snow depth, three snow samples were individually quartered vertically and 100 g aliquots from each were analyzed both for the filtered snow water and particulate matter fractions.

The measured concentrations showed no significant trend in increase or decrease in either the soluble or insoluble parts of the snow even between sampling sites 5 km apart. However, when evaluations of enrichment factors (EF) (a measure of the degree to which an element seems enriched over natural sources) were done there was a definite trend toward the increase of EF values in the melted snow portions with an increase in snow depth. No such increases were seen for the particulate matter. This would seem to indicate that during the snow season soluble elements, including sulphur and toxic heavy metals, filtered downward in the snow pack. Evaporation due to solar radiation and melting during the warm days most probably accounted for this phenomenon. This has been substantiated in laboratory and field tests where 50%–80% of the pollutants in snow were released in the first 30% of melted snow water.[22] There is particular concern that during the spring meltdown, any short term increase in acid concentration or heavy metal deposition may cause physiological stress to fish and aquatic organisms[23,24] as well as polluting drinking water supplies and agricultural areas.[4]

3.3 Solubility of trace elements in melted snow

From the point of view of toxicity a knowledge of water soluble–insoluble fractions are desirable.[25] The filtration techniques used in this study have enabled a distinction to be made between soluble and insoluble parts of melted snow. This is of major importance since it is known that metals seldom interface with biological systems in elemental form. Instead they appear as discrete compounds which may be lipid-soluble and pass through biological membranes with varying degrees of ease. These elements, in the form of soluble salts readily dissociate themselves, become free ions and are able to interact in biota according to their ability to bind with organic ligands.

The extent of soluble forms of the elements (less than 0.40 μm) in melted snow detected in this study is presented in Table V. The very high water solubility percentages of many of the elements: Na(98%), Mg(70%), P(100%), S(87%), Cl(98%), K(78%), V(57%), Mn(69%), Ni(77%), Cu(83%), Zn(77%), Sr(77%), Cd(100%) and Pb(85%) clearly suggest the importance of studying precipitation chemistry in both its soluble and insoluble forms. Furthermore it can be seen that the majority of the pollutants in the snow appear in the soluble form and subsequently can be more toxicologically significant. The

TABLE V

Percentage of element in filtered snow water compared to *total elemental concentration*

Element	Average total concentration of eight samples (μg/L)	% element in filtered snow
Na	6,600	98%
Mg	350	70%
Al	1,150	18%
P	300	100%
S	1,500	87%
Cl	8,200	98%
K	1,130	78%
Ca	8,200	97%
Ti	100	19%
V	14	57%
Mn	53	69%
Fe	1,500	23%
Ni	30	77%
Cu	40	83%
Zn	1,100	77%
Br	80	5%
Sr	25	77%
Sb	0.4	<1%
Cd	13	100%
La	0.6	<1%
Sm	0.05	<1%
Pb	116	85%

elements which are known to mainly originate from the earth's crust or soil by the action of various erosion phenomena exhibited low solubilities in melted snow. These include: Al, Fe, Ti, La and Sm.

3.3 Enrichment factors

In order to distinguish naturally-occurring elements in precipitation or aerosols from those arising from various types of pollution. Gordon, Zoller and Gladney[26] proposed the use of elemental enrichment factors (EF). An element's enrichment factor is defined as follows:

$$\mathrm{EF}=\frac{(X/C)_{\text{atmosphere}}}{(X/C)_{\text{earth's crust}}}$$

where X and C are the concentrations of the element of interest and a reference element, respectively. An EF value greater than unity would suggest that the element arises predominantly from one or more anthropogenic sources.

Ideally-suited reference elements for the purpose of computing EF values, are those which are high in crustal abundance, are found at significant concentrations in most places, have a well-known crustal composition, are not themselves enriched by local anthropogenic contributions and are reliably analyzed at atmospheric concentration levels. The most commonly used crustal reference material for EF evaluations is globally-averaged crustal rock and were obtained from Weldpohl.[27] Reference elements used in previous studies have been aluminum,[28] scandium,[29] sodium[30] and manganese.[31] It was decided to use aluminum as the normalizing element in both the melted snow and particulate portions. Aluminum is easily analyzed with excellent precision using activation analysis and it has been already proposed by Rahn[32] as a "universal" reference element.

Even though crustal abundances were not available for the Montreal region it has been pointed out that local variations of aluminum and other elements in rocks and soils do not differ more than a factor of two.[32] Therefore EF values below ten may not be especially significant. However EF values above ten should be highly significant and indicative of local or long-ranged contributions to the concentration of the element.

3.4 Enrichment factors in snow and inter-city comparisons

The enrichment factors evaluated for the melted snow and particulate matter parts are given in Tables III and IV while inter-city comparisons of EF values for soluble and insoluble parts are shown in Tables V and VI. In an attempt to obtain more representative results, EF values were computed from the concentration data of each individual sample rather than using values averaged among all the sites. All inter-city enrichment factors were calculated by the present authors.

TABLE VI

Inter-city comparison of enrichment factors for the snow melted portion[a]

	Enrichment factors							
Element	Montreal	Toronto[b]	Across Canada[c]	Tallahasse[d] (Florida)	Northern Minnesota[e]	Hiyoshi[f] (Japan)	Ghent[g] (Belgium)	Northern Alberta[h]
Al	=1	=1	=1	—	=1	—	=1	=1
Na	336	248	80	—	—	—	23	—
Mg	20	—	66	—	13	—	14	—
S	7,000	—	—	4,900	—	—	—	—
Cl	30,000	34,000	110	—	—	—	2,900	—
K	80	—	34	16	—	—	—	—
Ca	170	34	140	33	18	—	50	—
Ti	7	—	—	—	—	—	5	—
V	54	32	40	—	—	—	25	2,500
Mn	27	12	75	6	6	2	45	—
Fe	3	—	—	=1	1	=1	1.5	3
Ni	1,300	—	—	200	26	24	100	8,500
Cu	1,900	2,300	1,300	1,100	54	90	300	—
Zn	3,700	—	880	1,184	1,250	300	550	—
Se	15,000	—	—	—	—	—	—	—
Br	5,500	4,700	13,000	—	—	—	5,200	—
Sr	50	—	—	—	—	—	66	—
Cd	220,000	—	—	—	1,500	—	—	—
Pb	2,900	—	—	5,500	290	400	—	—

[a] All these results represent precipitation filtered through 0.40 μm pore sizes.
[b] Snow collected at one inner-city sample site by the authors (1982).
[c] Hamilton and Chatt (1981) Average of 23 sample sites across Canada. (ref. 8)
[d] Shigeru, Darzi and Winchester (1982). Enrichment factor calculated with respect to iron. (ref. 5)
[e] Thornton et al., (1981). (ref. 6)
[f] Hashimoto et al., (1981). Enrichment factor calculated with respect to iron. (ref. 38)
[g] Schutyser, Maenhaut and Dams (1978)' (ref. 37)
[h] Barrie, (1979). (ref. 36)

A. Soluble portion

Differences are evident from the EF results for the snow melted components compared to the particulate matter in that much higher values were found for the soluble elements. Except for Mg, Ti, Mn, Fe and Sr whose values ranged from 3–54, the remaining EF values ranged from 80 for K up to an extremely high value of 220,000 for cadmium. On the other hand, EF values very close to unity were found for many elements in the particulate matter. Potentially toxic elements such as S, Ni, Cu, Se, Cd and Pb exhibited very high EF values both in Montreal and in other cities. In particular sulphur was found to have an EF value of 7,000 in Montreal indicating a strong anthropogenic contribution. Studies of sulphur compounds in the atmosphere have now been well documented.[13]

Bromine and lead, considered by some authors to originate from automobile exhausts,[33–35] consistently exhibited high EF values, 5,500 and 2,900 respectively. The EF value of vanadium was found to be 54 which is not as high as first expected considering that the main source of vanadium is from the burning of fossil fuels. The enrichment factor of 13 for rubidium remains an anomaly.

The inter-city comparison for the snow melted portion is given in Table V. Data obtained from examined more elements than in other published works and some significant trends seem evident. The EF values for iron always fell between 1.5–3 for all the cities including snow collected near an oil extraction plant in Northern Alberta.[36] Titanium EF values were found to be low for precipitation samples in Montreal (EF = 5) and Ghent, Belgium[37] (EF = 7). Sodium and chlorine EF values varied between 80–336 and 110–34,000, respectively. These large variations could be expected since marine aerosols of Na and Cl can influence their trace concentrations and subsequent EF values. Sulphur in Tallahasse rainwater[5] had an EF value of 4,900 comparable to the result of 7,000 found in Montreal snow. These two results may indicate the extent of anthropogenic sulphur in precipitation in the eastern seaboard of North America.

EF values for vanadium varied little among the compared cities ranging from 25–52. A noted exception was the result from the snow collected in the vicinity in Northern Alberta oil extraction plant (EF = 2,500). Manganese, as well, seemed to exhibit EF values with few fluctuations (EF = 2–27). Both bromine and lead have high EF values ranging from 4,700–13,000 and 290–5,500, respectively, when compared among the cities. Similar trends were found for Ni, Cu and Zn. However, Montreal's snow had the highest EF values for copper and zinc. The highest EF value for nickel (EF = 8,500) was found in snow collected around the oil extraction plant in Alberta.

It is interesting to note that snow collected in the "isolated" Lake Itasca State Park, (northern Minnesota)[6] still had large EF values for zinc, cadmium and lead, and to a certain degree nickel and vanadium. This lends credibility to the view that many pollutants undergo long-range transportation. This conclusion may also explain the high elemental concentrations and subsequent large EF values in Montreal and Toronto snow.

B. Particulate matter

The EF results for many of the elements found in the particulate matter as Na, Mg, P, Cl, K, Ca, Sc, Ti, Mn, Fe, Sr, La and Sm were close to unity (ranging from 0.6–3) suggesting that they originated from natural sources. Another group of elements: V, Cr, Co, Ni and Cu had EF values lying between 9–32 suggesting that these elements may possibly originate from pollution sources. These low EF values coupled with insolubility of these elements in water, suggest that they are not an immediate major concern of pollution (as they are in the soluble portion).

The relatively high EF results for sulphur, lead, zinc and antimony in the particulate matter (90, 170, 330 and 4,500, respectively) suggest that much of their occurrence in the particulate matter arise from local and non-local anthropogenic sources. Sources for sulphur, lead and bromine have been previously discussed. Zinc, of which 25% of the total concentration was found in the particulate matter, can be produced by the abrasion of rubber tires, smelting and automotive exhausts.[39] Antimony which was found exclusively in the particulate matter is commonly used as a hardening agent in lead refineries and may also arise from refuse incinerators, burning of fossil fuels and the abrasion of synthetic rubber.

Few studies have been carried out to determine trace elements in the particulate matter contained in snow or rain. Forland and Gjessing[40] investigated the deposition of air pollutants in Bergen, Western Norway, and measured sulphate, magnesium and calcium concentrations as well as pH values and conductivity. However, the melted snow water was only coarsely filtered and some of their interpretations may have been misleading. Similar work was also done in Norway.[41] Deposition velocities for airborne lead and sulphur to a snow surface were estimated but no filtration procedures were used to distinguish the soluble and insoluble fractions. A comparison of the EF values for trace elements in particulate matter determined in Montreal urban snow and other various cities is shown in Table VII.

TABLE VII

Inter-city comparison of enrichment factors for the snow particulate portion

	Enrichment factors				
Element	Montreal	Across Canada[a]	Ghent[b] (Belgium)	Hiyoshi[c] (Japan)	Alberta[d]
Al	=1	=1	=1	—	=1
Na	0.7	0.8	0.4	—	—
Mg	0.6	3	1	—	—
Cl	60	30	2	—	—
K	0.8	1	0.9	0.8	—
Ca	0.6	0.8	0.4	0.2	—
Sc	1	1.2	—	—	—
Ti	1.6	1.6	1.4	1	2.8
V	9	2.4	4	—	112
Mn	1.5	3.6	3	0.6	0.9
Fe	3	2.6	3	=1	—
Cu	30	0.17	—	4	—
Ni	15	—	37	3	—
Zn	170	19	15	6	—
As	10	23,000	62	—	—
Br	4,500	—	23	—	—
Sb	330	1,162	176	—	—
La	1.5	14	2	—	—
Sm	1.5	2	2	—	—

[a] Hamilton and Chatt (1982). (ref. 8)
[b] Schutyser, Maenhaut and Dams (1978). (ref. 37)
[c] Hashimoto et al., (1981); normalized to Fe = 1. (ref. 38)
[d] Barrie (1979). (ref. 36)

One interesting aspect of the data is the consistent trends among the EF values of some chemically related elements. Insoluble elements as Sc, Ti and Fe all have EF values very close to unity. The elements of Na, Mg, K, Cu, Ca, La and Sm also have EF values close to one. These results suggest that such elements are mainly soil- or crustal-derived. Antimony EF values ranged from 176–1,162. The higher value of 1,162 is comparable to average Sb EF values of 1,880 found in aerosols of twenty-nine cities throughout the world.[32] The Montreal value of about 330 is six times lower than the EF value of 1,880 but approximately six times greater than a measured EF value of 53 for Toronto aerosols sampled near a metal refinery plant.[35]

Zinc had an EF value of 170 in Montreal snow. This value is comparable to those determined from urban aerosols EF = 320[42] but three times smaller than the average value found by Rahn.[32] Particulate vanadium had an EF value of 9 comparable to samples taken in Ghent and across Canada, but ten times less than EF values (EF = 112) for snow sampled around the oil extraction plant in Northern Alberta. Zinc and bromine had values of 170 and 4,500 respectively, larger than those found in Canada and Ghent. Interesting data was the extremely high EF value for arsenic of 23,000 in the precipitation samples collected across Canada.

3.5 Enrichment factors in coal compared to enrichment factors in snow

In order to consider the possible influence of fossil fuel burning on the relative concentrations and enrichment factors in urban atmosphere Rahn[32] proposed a comparison of enrichment factors in coal (having a similar definition as previously given) and urban aerosols. A similar comparison can be made for snow and is shown in Figure 7. The EF values obtained for coal used here were taken from an average of six trace element concentrations of different coals previously compiled.[32]

The trend in Figure 7 shows a significant degree of correlation between EF values for melted snow and particulate parts with the EF values for coal. In general the correlation gives direct evidence of the extent to which trace elements, many of which are potentially toxic and originate from the burning of various fossil fuels, have enriched the urban atmosphere and have added to the atmospheric burden and have subsequently fallen as wet precipitation (snow or rain). It is also important to point out that potentially toxic elements S, Se, Cd, Pb, Zn, Ni and Cu are not only enriched in coal but also mainly enriched in the melted snow portion.

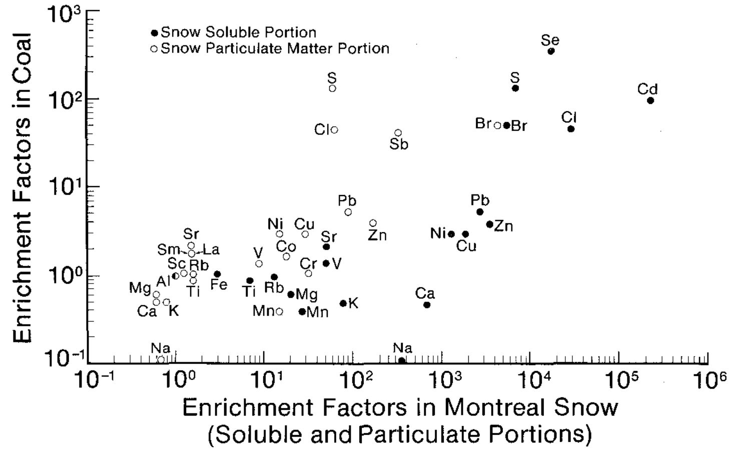

FIGURE 7 Enrichment factors in coal as compared with enrichment factors in Montreal snow.

3.6 Elemental pair correlations and multi-elemental analysis

In an attempt to elucidate relative contributions among multiple local and distant sources, elemental pair correlations (EPC) and multi-elemental clusters (or grouping of certain elements) in atmospheric deposition could be useful. Postulation of atmospheric particulate sources using chemical balances for coal, oil, refuse combustion, soil, dust, motor-vehicle, limestone and marine aerosols have already been attempted.[43]

Elemental pair correlations among the elements found in snow determined in this work were done in five different sets of pairs. These results were determined by using individual concentrations of pairs of elements at each site.

They represent: case (a) correlations based on the concentrations for both soluble and insoluble portions added together; case (b) correlations based on the concentrations for both the soluble and insoluble portions as well as the insoluble portion; case (c) correlations based on the insoluble portion only; case (d) correlations based on the soluble portion only; case (e) correlations based on the concentrations of the soluble and insoluble concentrations as well as the soluble portions. To have more meaningful results only correlation coefficients of $r = 0.80$ with a 1% significance or better, ($P \leq 0.01$) were accepted.

The majority of the correlations appeared when the total elemental concentrations were added [case (a)]. On the other hand, correlations for only the soluble concentrations, [case (d)], appeared for Na with Cl, Rb with Na, Cl and K, Mn with Ni, Mn with Ca, Cu with K, Sr with Ca, Pb with Ca and Mn with Sr. Few correlations appeared when only the insoluble portions were used. These included Ca with Mg, K with Al, Ti with K, Co with Cl and Zn with Cu. Some correlations such as Ni with V were expected and they did appear; case (a). However, strong correlations of Pb with Br did not. The crustal, non-enriched elements (see Table IV) Ti, Mg, Al and Fe were all correlated with each other, again as expected. Correlations of enriched S with non-enriched Mg and Al are anomalous as well as the correlation between Pb, an enriched element in the soluble and insoluble portions with the non-enriched elements Mg and Al.

It would appear that the use of correlation analysis of wet precipitation is far more complex than with aerosols. The varying solubilities of elements and their particular scavenging processes from the atmosphere and meteorological factors may hamper a good analysis of these correlations. Very few attempts have been achieved before this study utilizing elemental correlations in wet precipitation. Below are some of the more commonly used elemental ratios, and some used only recently in aerosols in which comparisons are made with the present results.

A. Na and Cl

Sodium and chlorine in the melted snow portion, gave a very strong correlation coefficient of $r = 0.97$. The overall ratio of Cl to Na was found to be 1.4 in Montreal and 1.8 in Toronto which compare well with Cl/Na ratios in marine environments (2.6[44] and 1.8[45]). However long-range transport of aerosols can play a significant role in the dispersion of marine sea-salt aerosols. From the ratios calculated it would appear that there could have existed a strong Cl/Na influence both in Montreal and Toronto precipitation. However this does not preclude the possibility that there may also have been contributions to atmospheric deposition from road salt or salt aerosols originating from crystals sprinkled on the winter roads.

B. Mn and V

In a recent paper, it has been suggested that Mn/V ratios in aerosols give a clear indication of sources of pollutants for aerosols occurring in the Arctic.[46] The conclusion was based on the finding that the Mn/V ratio in aerosol from Eurasia was greater than unity (viz. 2.0 ± 0.8) while a result less than unity (viz. 0.41 ± 0.09) was found for northeastern United States, a difference amounting to a factor of 5 ± 1. Calculations of Arctic aerosols for Mn/V could then be used to "fingerprint" the sources as either arising from North America or Eurasia.

Mn/V ratios computed from these results for Montreal snow gave qualified support to this hypothesis. While soluble portions gave a Mn/V ratio of 2.0, the insoluble portion ratio yielded a value of 0.5, and computations based on the total concentrations (soluble and insoluble portions) resulted in a ratio of 1.3. It would appear that the particulate matter in Montreal snow exhibited Mn/V ratios similar to those reported for northeastern U.S.A. aerosols. One interesting result found in this study was that Mn/V ratios for the snow soluble portion were greater than unity. Correlation coefficients for the soluble, insoluble and total concentrations for Mn and V were $r=0.85$, $P \leqq 0.02$, $r=0.35$, $P \leqq 0.40$ and $r=0.98$, $P \leqq 0.01$, respectively.

The source of vanadium is most probably oil, especially Venezuelan oil. This oil is usually rich in V and large quantities are combusted along the North American eastern seaboard.[47] Enrichment of manganese into the urban atmospheres has been suggested to originate mostly from heavy ferrous and nonferrous industries and automobile emissions.[46] It would appear therefore seem likely that Mn/V ratios and their respective enrichment factors at various locations may offer a good indication of whether there are appreciable local contributions of these elements.

C. Mn and sulphate ions

Correlations of Mn^{2+} and $SO_4{}^{2-}$ ions in rain have been studied by two groups of authors. Penkett *et al.*[48] have shown that where

Mn^{2+} concentrations were less than 1.1 micromolar the correlation with sulphate ions was low ($r=0.31$) but increased to $r=0.67$ when the Mn^{2+} concentrations increased. This value around 1.1 micromolar for Mn^{2+} concentrations was considered as a kind of "cutoff" point. On the other hand, Lindberg[49] has shown that the "cutoff" value for Mn^{2+} was 0.07 micromolar. Below this concentration value the correlation coefficient was $r=0.39$, $P \leqq 0.05$, while above this value the coefficient was $r=0.92$, $P \leqq 0.01$. It has been suggested that manganese in aerosols can act as a catalyst to accelerate the oxidation of SO_2 in the clouds.[50, 51] Furthermore it has been pointed out[49] that the Mn and sulphate relationships may be the results of post-depositional changes in rain chemistry.

Manganese and sulphur concentrations measured in this study were found to be mostly in the soluble form to the extent of 69% and 87%, respectively, with average enrichment factors of 27 and 7,000 respectively. It might be assumed that the soluble forms had the chemical compositions of Mn^{2+} and $SO_4{}^{2-}$ as usually exhibited in wet precipitation of these elements. In this study manganese concentrations were below 1.1 micromolar but greater than 0.07 micromolar. The correlation coefficient with sulphur was found to be $r=0.42$, $P \leqq 0.025$. This result is much closer to the one of $r=0.37$ reported by Penkett *et al.*,[48] giving supporting evidence that Mn^{2+} and $SO_4{}^{2-}$ are not strongly correlated above Mn^{2+} concentrations of 0.07 micromolar. This does not negate the findings of Lindberg[49] whose Mn^{2+} may have resulted from the long-range transport coming from sources such as the Indiana ferrous industries less than 100 km away.

Further investigations into the relationships of these two elements would be of interest not only in judging possible sources, but also in understanding better the catalytic effect of Mn^{2+} on the oxidation of SO_2 in the atmosphere.

D. V and Ni

Nickel and vanadium have been successfully used to "fingerprint" anthropogenic sources of these elements from crude oils. Breger and Zoller[52] plotted histograms of the V/Ni ratios of seventy-two different oils in which the results peaked at 0.25, 1.75 and 3.75. Other studies have shown V/Ni ratios to be 0.64 and 5.8.[43, 53] In this present study correlation coefficients for the soluble, insoluble and total deposition for nickel and vanadium in Montreal snow gave result of $r=0.10$, $r=0.40$ and $r=0.96$ respectively and corresponded to mean V/Ni ratios of 0.48, 1.1 and 0.62, respectively. The correlation between vanadium and nickel is strongest when the results for the total deposition in snow were used. Correlations done using only the insoluble or soluble fractions are probably insignificant. The difference in solubilities in melted snow (V=57% and Ni=77%) may account for these weak correlations.

E. Br and Pb

Strong correlations between Br and Pb in emissions from automobile exhausts have been reported by several authors.[42,44,54] The results found for Montreal snow did not yield the same significant trend. Curiously, while most of the Pb occurred in the soluble fraction (viz. 85%), Br was only soluble to the extent of 5%. A correlation coefficient based on total deposition was only $r=0.55$, $P \leq 0.15$. Although this was not as strong a correlation as findings in Toronto airborne particulate matter[44] of $r=0.93$, $r=0.81$ and $r=0.74$, at three different sampling sites, it nevertheless does give an indication of a similar relationship between these elements in urban environments. One possible reason for the less significant correlation in snow is that lead additives are being significantly reduced in automobile gasolines with time. For example, the Br/Pb ratio for the total deposition for 1978 was 1.2. This is about a factor of four greater than Br/Pb ratios measured earlier.[42,44,55,56] Any decrease in lead concentrations would tend to increase the Br/Pb ratio assuming there are other prominent sources of Br.

F. Cu and Zn

Recently, correlations between copper and zinc have been used in chemical element balances and as markers to suggest that these elements in the atmosphere can arise from refuse burning.[43,57] The results found in Montreal snow would tend to bear out this possibility. The Cu and Zn correlation coefficients were computed as $r=0.74$, $P \leq 0.02$, $r=0.99$, $P \leq 0.01$ and $r=0.51$, $P \leq 0.20$, for the soluble, insoluble and total depositions, respectively, while the Cu/Zn ratios were found to be 0.30, 0.17 and 0.26, respectively. Both Cu and Zn had similar solubilities in melted snow, 83% and 77% respectively and both had very high EF values in the soluble portions and moderately high EF values in the particulate fraction. Cu/Zn ratios in aerosols from St. Louis[58] were found to be 0.03, a factor five to ten times less than Cu/Zn ratios in Montreal snow.

It would therefore seem that Cu/Zn ratios, may be successfully used as a marker in determining incinerator and other sources of these elements. Further studies would be useful to provide a clearer verification of this hypothesis.

3.9 Cluster analysis

Multi-elemental cluster analysis is rapidly gaining recognition as a useful extension of elemental pair correlations. For use in environmental monitoring, the groupings or clustering of certain elements may give evidence of possible sources of pollution.

Results were available in this study for only thirty sets of samples in the soluble portion and eight samples in particulate and bulk portion. While the results for the particulate and bulk portion were inconclusive some interesting results for the soluble portion could be ascertained. Results are shown in Table VIII.

The elements Al, Fe, Mg, Zn, P, S, K and Ca did not appear to have any significant clustering with other elements. While Al, Fe and Mg were found not to be enriched in snow (see Tables III and IV), P, K and Ca were, but only in the soluble portion.

It appeared that V, Ti, Se, Rb, Br, Mn, Sr, Pb, Ni, Cu and Cd have some significant clustering. However it was previously shown that all elements but Ti had very high or relatively high EF factors as well. This would suggest that these elements may all come from some common sources. For example vanadium and nickel are known to be strongly correlated in crude oils. It is interesting to note that sulphur which also had a high EF in the soluble was not significantly clustered with any elements. This fact has also been confirmed for sulphur cluster analysis in aerosols.[60]

3.10 Environmental assessment and toxicological impact

Factors which influence elemental, and in particular heavy metal toxicity, include chemical composition and physical characteristics of

TABLE VIII

Cluster analysis of snow soluble portion

```
Number of   M    Z    T    V    S    R    B    M    S    P    N    C    C    F    A    P    S    K    C
Clusters    G    N    I         E    B    R    N    R    B    I    U    D    E    L                   A

19          *    *    *    *    *    *    *    *    *    *    *    *    *    *    *    *    *    *    *
18          *    *    *    *    ******    *    *    *    *    *    *    *    *    *    *    *    *    *
17          *    *    *    ***********    *    *    *    *    *    *    *    *    *    *    *    *    *
16          *    *    *    ****************    *    *    *    *    *    *    *    *    *    *    *    *
15          *    *    *    ****************    ******    *    *    *    *    *    *    *    *    *    *
14          *    *    *    **************************    *    *    *    *    *    *    *    *    *    *
13          *    *    *    **************************    *    ******    *    *    *    *    *    *    *
12          *    *    *******************************    *    ******    *    *    *    *    *    *    *
11          *    *    ************************************    ******    *    *    *    *    *    *    *
10          *    *    **********************************************    *    *    *    *    *    *    *
9           *    *    ***************************************************    *    *    *    *    *    *
8           ******    ***************************************************    *    *    *    *    *    *
7           ******    ********************************************************    *    *    *    *    *
6           ******************************************************************    *    *    *    *    *
5           ***********************************************************************    *    *    *    *
4           ****************************************************************************    *    *    *
3           *********************************************************************************    *    *
2           **************************************************************************************    *
1           *******************************************************************************************
```

the substances as they occur in a local atmosphere. It was not the intention of this study to determine the possible toxicological effects of atmospheric concentrations of metals in aerosols or precipitation. Such studies usually take many years to complete. However, atmospheric precipitation chemistry investigations, such as the present work, can give a general overall profile of the elements in the atmosphere which can be inhaled or which can enter the drinking water or food chains. An indication of the possible toxicity of elements in very low concentrations such as S, Se, V, Ni, Cu, Zn, Pb and Cd can indicate the importance of determining elements such as these in wet precipitation. The results of this present study have provided information of what particular elements are present in Montreal aerosols and which therefore can be possibly inhaled, especially the components which have dimensions of the respirable range of less than or equal to $0.40\,\mu$m.

From this present study we have estimated wet and dry deposition rates both for the soluble and insoluble fractions of snow as shown in Table IX. The total precipitation (rain and snow) was taken as the average over several previous years in Montreal. Results were extrapolated from this study to cover a one year period. Even though the scavenging processes for rain, snow and dry deposition are different, these broad averages can give a good estimation of bulk deposition rates.

Some elements of concern, especially the soluble ones in melted snow are the possibly toxic S, Ni, Cu, Z, V, P, Se, Cd and Pb. These elements had deposition rates ranging from $1\,\text{mg/m}^2/\text{yr}$ for Se to $1{,}300\,\text{mg/m}^2/\text{yr}$ for S. Special concern should be given to Pb and Cd which have been estimated to be 27 and $14\,\text{mg/m}^2/\text{yr}$, respectively. The dry deposition matter would not appear to be as hazardous due to its insolubility. However, this does not negate the possibility that these elements and others may indeed dissolve to a certain degree in the spring meltdown. This is especially true for the more soluble elements in acidic environments.

4. CONCLUSIONS

This study has shown the usefulness of nuclear analytical techniques, particularly proton-induced X-ray emission and instrumental

TABLE IX

Estimated total annual trace elemental deposition by wet and dry precipitation[a]

Element	Soluble portion[b] (mg/m^2/yr)	Insoluble particulate[c] matter (mg/m^2/yr)
Na	6,300	200
Mg	200	130
Al	100	640
P	700	4
S	1,500	200
Cl	12,000	17
K	2,200	200
Ca	4,800	150
Ti	15	65
V	4	6
Mn	8	4
Fe	60	810
Co	1	2
Ni	45	6
Cu	40	7
Zn	140	18
Se	1	1
Br	9	77
Rb	1	1
Sr	12	5
Cd	14	1
Sb	<1	0.5
Pb	27	4

[a] Due to the different scavenging process of snow, rain and dry deposition these averages only give an indication of total decomposition.

[b] Average of 30 samples based on the average annual rate of precipitation (rain and snow) of 100 cm.

[c] Average of 12 samples.

neutron activation analysis for the multi-elemental determination and characterization of both the soluble and insoluble fractions of snow. The techniques developed for filtration and preconcentration have provided a good basis for future routine analysis of atmospheric precipitation chemistry. Although the use of small pore filters to distinguish the soluble and insoluble portions of wet atmospheric deposition has been neglected by many researchers, this study has demonstrated the importance of such a separation step in assessing the relative bioavailability of toxic elements in terms of their solubilities and physical dimensions.

Certainly the last chapter on the analysis of atmospheric precipitation chemistry has not been written. One serious shortcoming is the apparent lack of standardized techniques employed by various research groups. These include sampling techniques, filtration procedures, comparison of techniques with other methods and standards and interpretation of data (e.g. EF values and environmental impact). Too often results are presented with no interpretations at all. Meteorological data is also often overlooked. In general, comparisons with other published work are difficult or impossible to achieve. Snow sampling techniques can be improved to include weekly or monthly collections. The combined use of aerosol and atmospheric precipitation analysis at the same sampling sites would give a much needed overall picture of the competing scavenging processes in the atmosphere. Finally, the use of elemental pair ratios and cluster analysis should be extended to cover a wider number of samples and sites to provide a better indication of groupings and sources of anthropogenic trace elements.

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