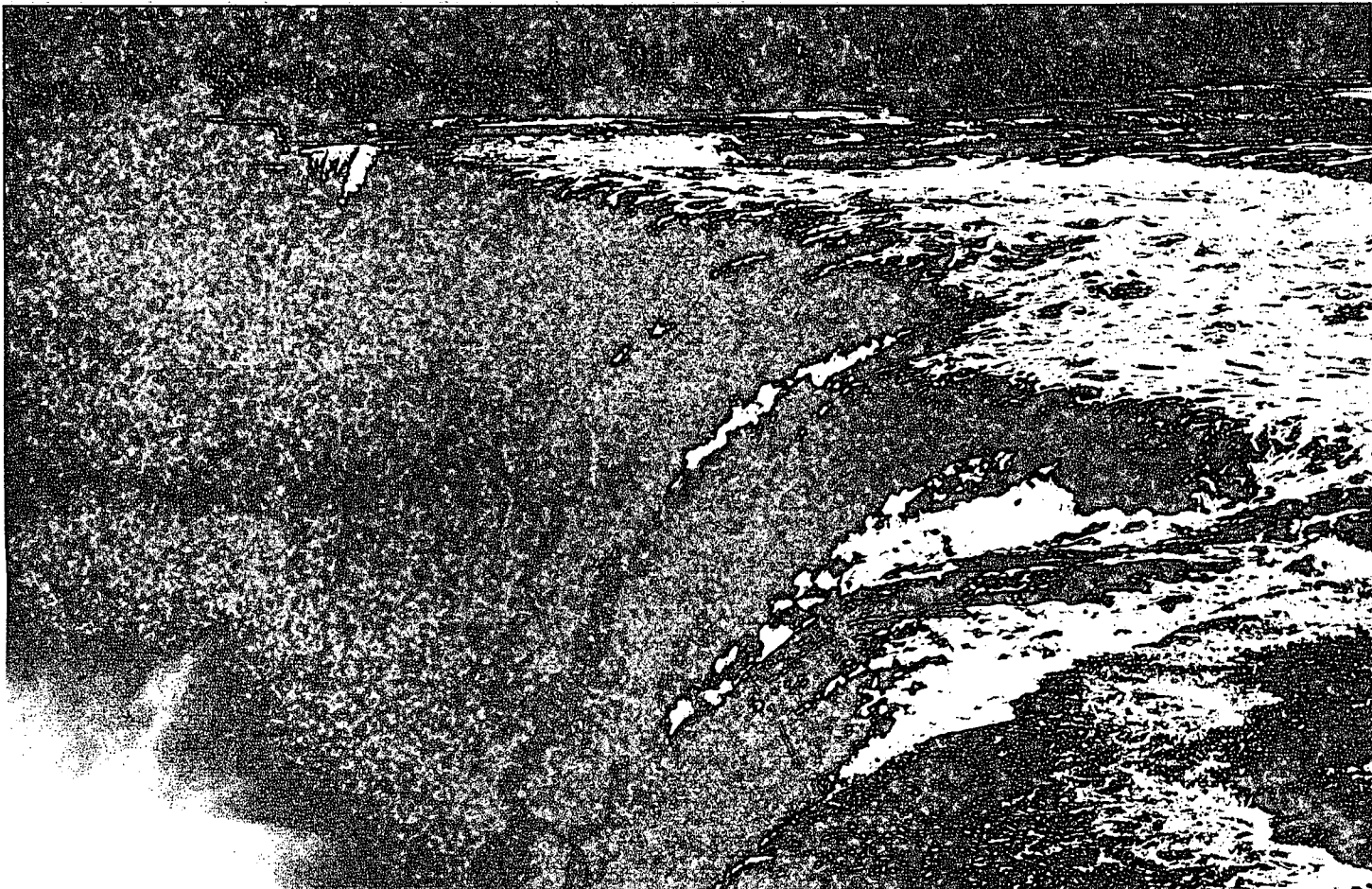


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Measurement of Lead, Cadmium, Arsenic and Mercury in Precipitation Events

M. C. Mehra



TECHNICAL BULLETIN NO. 127

INLAND WATERS DIRECTORATE
ATLANTIC REGION
WATER QUALITY BRANCH
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M. C. Mehra

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Abstract

This study describes concentrations of lead, cadmium, arsenic and mercury in wet precipitation samples collected at Moncton, New Brunswick. The sampling and analyses were done in the period June through November 1981. The volume-weighted averages for Pb, Cd and As were found to be 5.28, 0.77 and 0.028 $\mu\text{g/L}$, respectively. Mercury, however, was not detected in the samples. The data show that with increasing Pb levels, Cd and As levels also increase, and that Pb levels remain roughly 7 and 188 times greater than those of Cd and As.

Résumé

Cette étude décrit les concentrations de plomb, de cadmium, d'arsenic et de mercure dosées dans des échantillons de précipitations humides prélevés à Moncton (N.-B.). L'échantillonnage et les analyses ont été effectués de juin à novembre 1981. La concentration moyenne, pondérée selon le volume, était de 5.28, 0.77 et 0.028 $\mu\text{g/L}$, respectivement pour Pb, Cd et As; on n'a décelé aucune trace de mercure. Les résultats montrent que les concentrations de Cd et de As augmentent en proportion de celle de Pb, et que celle-ci demeure environ 7 et 188 fois plus élevée que celles de Cd et de As, respectivement.

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INTRODUCTION

The term "acid rain" generates immediate public interest. During the last decade there has been increasing public awareness that the atmospheric dispersion of industrial pollutants renders precipitation acidic. The substances derived from oxides of sulphur and nitrogen resulting from the combustion of fossil fuels in stationary or mobile sources are the primary agents causing the acidity in the atmosphere and hence are of major environmental concern (1, 2). Acidification and associated chemical, physical and biological changes are clearly evident in aquatic ecosystems. Scientific studies and research completed in recent years show that water resources, fish, soil, crops, vegetation and other biological species are suffering the ill effects of acid precipitation (3-11). Thus the surveillance of acid precipitation has become a priority over the last decade.

Acid precipitation has far-reaching effects. Emissions of the gaseous acidic pollutants from power plants, smelters, industries and automobiles can be transported hundreds or even thousands of kilometres away from their sources, to eventually be deposited as components of precipitation. To appreciate the environmental effects of these pollutants in precipitation, a clear understanding of the mechanisms involved in the long-range transport of air pollutants is necessary. Very often these emitted materials undergo chemical and physical transformation before being returned to the earth's surface. Because acidic and acidifying substances may be transported over long distances through the atmosphere, sensitive receptor areas at considerable distances from sources of emissions are at risk (11).

In recent years attention has been focused on the surveillance and environmental impact of the acidic components in precipitation occurring in the eastern United States and Atlantic Canada (5-7). However, high temperature processes such as fossil fuels combustion can also release many trace elements, which like the acid-forming components, may become part of rain and snow and subsequently be deposited in streams, lakes and other terrestrial zones of importance (12-15). Moreover, such anthropogenically released trace metals may undergo long-range transport and follow a dispersion pattern similar to that observed for gaseous pollutants. In such an event, there

would be a potentially deleterious impact on the receptors that would not be limited to the geologically acid-sensitive areas.

Heavy metal contamination of an ecosystem near a point source or far removed from it has been shown to result from industrial operations. Elevated levels of Cu and Ni in soils and vegetation have been observed up to 50 km from the metal smelting industry at Sudbury, Ontario (3, 4, 16, 17). Data have also been reported on the elevated concentrations of heavy metals in waters and in the lake sediments in areas distant from a point source (18). These observations readily suggest that metal inputs occur from the atmosphere through the long-range transport and deposition process. Lantzy and Mackenzie (19) have estimated that on a global basis, elements such as Pb, Cd, Cu and Zn are distributed primarily via the atmosphere. These nonvolatile elements in the atmosphere remain associated as enriched aerosols of fine particle size ($<1 \mu\text{m}$), which is strongly indicative of their atmospheric introduction by a high temperature process, natural or anthropogenic.

The elements Pb and Cd have received special attention with respect to environmental contamination. Lead emissions result principally from combustion, e.g., antiknock Pb compounds in automobiles or burning of fossil fuels. The Canadian emissions alone from these two sources amount to about 14 300 tons annually, which accounts for nearly 67% of all the lead emissions from other sources (20). Evidence of the presence of Pb aerosols in the stratospheric region of the atmosphere has been presented by Jaworowski and Kowanacka (21). This is important because this stratospheric Pb provides a route for its efficient long-range transport as well as a route for its incorporation into precipitation. Lead has been observed in precipitation in amounts that vary depending on whether the area is industrialized-urban or rural. Some recent Canadian data for bulk precipitation events from an industrialized-urban area show Pb levels of $180 \mu\text{g/L}$ compared with $12 \mu\text{g/L}$ found in a rural zone in central Ontario (16). In Manitoba-Saskatchewan industrialized-urban and rural areas (15), the levels observed were $30.7 \mu\text{g/L}$ and $4.3 \mu\text{g/L}$, respectively. In the rural zone of the Atlantic area (New Brunswick), the Pb level was much lower at $2.77 \mu\text{g/L}$ (22).

The information available on Cd emissions in this respect is limited. Nevertheless, it is estimated that in Canada nearly 0.5 ton per year of Cd is discharged into the atmosphere from motor vehicle emissions alone (tires and oils) (23). These emissions are much lower than those of Pb and are reflected in the reduced Cd levels in bulk precipitation events. In industrialized-urban and rural areas of central Ontario, the Cd values observed were 4.7 and 0.6 $\mu\text{g/L}$, respectively (16). In Manitoba-Saskatchewan industrialized-urban and rural areas (15), the Cd levels found were 2.8 and 0.3 $\mu\text{g/L}$, respectively. In the rural zone of the Atlantic Provinces, Cd concentration was only 0.57 $\mu\text{g/L}$ (22).

Besides the nonvolatile elements there are other elements that exist in volatile form (Hg, As), which if released into the atmosphere, disperse and are transported over long distances from the point sources by wind and dust. Joensuu (24) has calculated an annual global dispersion of nearly 3000 tons of Hg through the combustion of coal. The Canadian emissions in this respect have been estimated to be around 22 tons/year of which nearly 90% becomes airborne on release (25). Mercury levels in rainfall samples collected in the summer of 1978 in Ontario were found to vary from 0.03 to 0.11 $\mu\text{g/L}$, depending upon the quantity of the accumulation (26).

Global emissions for the element As are of the order of 700 tons/year from industrial sources, as reported by Bertine and Goldberg (27). The Canadian contribution in this case has been estimated at about 38 tons/year (28). The precipitation distribution data are limited for As, but some recent studies show a low of 0.01 $\mu\text{g/L}$ to a high of 13.9 $\mu\text{g/L}$, with a mean in a range from 0.65 to 1.44 $\mu\text{g/L}$ (28).

The previous observations indicate the importance of the study of the trace metal components of precipitation. In this report, the trace metal elements Pb, Cd, As and Hg in wet precipitation are discussed; these elements have been identified as priority pollutants by Environment Canada.

Precipitation samples were collected at Moncton, New Brunswick, during the summer of 1981. In the period June through August, the samples collected were analyzed for Pb, Cd and As, and in the period August through November, the samples collected were analyzed for Hg.

SAMPLING STATION AND SAMPLING PROCEDURE

The selection of a sampling station is critical. Sampling stations should be some distance from the local traffic density or an industrial area and at the same time

should be easily accessible. In this study, the sampling station was set up at the Université de Moncton on the open roof of an administrative complex (Édifice Taillon), which is six stories high.

Two all-glass WITKOM samplers were installed for the duration of the study. They had been designed specifically for this work by the Water Quality Branch Laboratory of the Inland Waters Directorate in Moncton. The essential features of the WITKOM sampler are illustrated in Figure 1. The sampler is a Pyrex assembly fitted with standard B 24/40 joints. The 65-cm central column has five angular side openings which plug into 250-mL jointed (B 24/40) Erlenmeyer flasks. Each flask in turn is fitted with an adjusted long-stemmed (10-mm diameter) cup valve so that a flask is cut off the system whenever just over 200 mL of the precipitation is collected. An opening toward the top of the

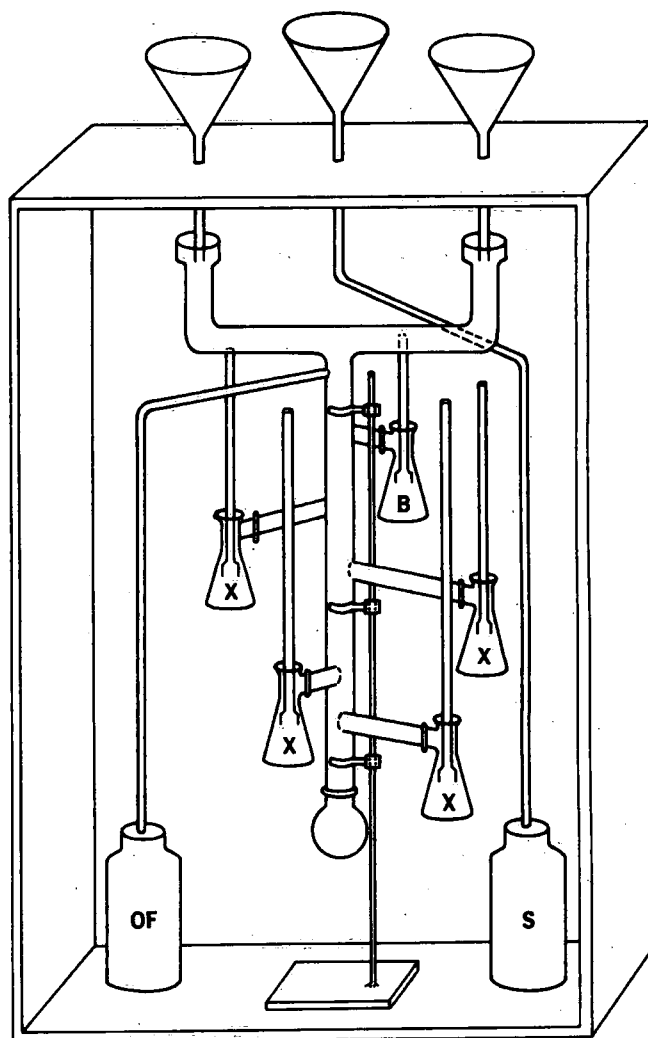


Figure 1. WITKOM sampler: X—sample flask, B—filled blank flask, OF—overflow reservoir, S—stock reservoir for the entire event.

central column functions as an overflow pass and transfers any surplus to a plastic reservoir. Two cup-shaped funnels connected to a U-tube sit on top of the central column to receive the precipitation sample. The sample is actually delivered through two (30-cm diameter) plastic funnels mounted on top of a wooden box in which the entire sampler is housed, secured by metallic clamps. In addition, another similar plastic funnel is installed alongside and is connected directly to a large plastic container to receive the entire sample directly.

As the WITKOM sampler employed in this study was an all-glass assembly, it could easily be installed and cleaned whenever necessary. Yet there were some limitations. First, the cup valve joint used to cut off sampling in a sequential flask is rather fragile and breaks easily under mild pressure, particularly during the dislodging of a sample flask. This makes it unsuitable in its present form for mobile or field use. Secondly, the sampler design rejects the first 50 to 60 mL of the sample, which is a constraint if a correlation is sought between the collected fractions and the total sample. Thirdly, the sampler can accommodate only four sequential samples, which in its present design are obtained with about 750 mL of the precipitation. Our observations show that twice or even more than this amount can be collected in a particular event. The design and the performance characteristics of the sampler can be improved to overcome these constraints if continuous sampling is sought in the future.

A standard rain gauge and a tipping-bucket gauge (operated on a 7.5-V dry cell battery) procured from the Atmospheric Environment Service were installed alongside the sampler to retrieve information on the total precipitation and its time-based distribution in a particular event. The standard rain gauge directly measures the total quantity of rain in millimetres. Dips and elevations are recorded on a calibrated chart coupled with the tipping-bucket gauge. Each dip or elevation on the chart represents a time interval related to a fixed quantity of rain sample, thus permitting a time-based observation regarding a precipitation event.

The standard chart of the tipping-bucket gauge was put in place normally in the morning (9:00 A.M.) and the sampler was left open for a 24-h period, whenever a rain-fall was announced by the local weather bureau. It remained fully covered at other times to protect it from dust, particularly if an extended dry period was anticipated. In the first few observations it became evident that a standard tipping-bucket chart simply records a straight line in the absence of any significant precipitation. Consequently, instead of a daily change, the chart was mounted only when a precipitation event was anticipated.

Samples collected per event basis in the period of June 5 through August 31, 1981, were analyzed for Pb, Cd and As content, and those obtained in the period August 24 through November 6 were analyzed exclusively for Hg content.

EXPERIMENTAL PROCEDURE

The designed capacity of the WITKOM sampler is limited to five samples, and each sample flask can accommodate 200 mL of sample. The fifth position was always reserved for an experimental blank for a particular precipitation event. The other four positions were used for sequential sample collection. A preservative was placed in each flask before its installation on the sampler.

Concentrated purified nitric acid (Supra pure) procured from the B.D.H. Company served as a general preservative for Pb, Cd and As. Ten drops (0.5 mL) were added to each sampling flask before collection. The blank was prepared by diluting the preservative (0.5 mL) to 200 mL with deionized doubly distilled water. Only complete samples were analyzed and considered in the data evaluation. The sample in each completely filled flask was divided into two parts upon retrieval. One aliquot (100 mL) was analyzed for the Pb and the Cd content, and the other (~50 mL) was reserved for the As analysis. The preservation procedures and the analytical methodologies given in the *Analytical Methods Manual* of the Inland Waters Directorate (29) were strictly followed.

The analysis for Pb and Cd involved the extraction of their ammonium pyrrolidine dithiocarbamate complexes into methyl isobutyl ketone. Their analytical concentrations were evaluated by comparison with their respective standards prepared in a similar manner using flame atomic absorption spectrophotometry. The standards in the required analytical range were prepared by diluting the certified atomic absorption solutions supplied by the Fisher Scientific Company. In this study data were recorded on the Perkin-Elmer model 5000 atomic absorption spectrophotometer in the air-acetylene mode.

The As analysis was completed using the flameless atomic absorption method. The element in a sample was chemically converted to volatile arsine (AsH_3), first by decomposition of organoarsenides with acidic persulphate, followed by reduction with a solution of KI and SnCl_2 and eventually generation of AsH_3 by treatment with NaBH_3 . The arsine vapours were passed through a heated open-ended furnace to obtain As in atomic form. The final concentration in a sample was obtained by comparison with As standards treated in the same manner. The experimental

data were recorded on the automated system already in operation at the Water Quality Branch Laboratory in Moncton.

The Hg analysis also employed the flameless atomic absorption method. The preservative used was 1 mL of 5% acidified (H_2SO_4) potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) solution per 100 mL of the sample. The chemical procedure involved oxidation of organic matter in the sample with H_2SO_4 , KMnO_4 and $\text{K}_2\text{S}_2\text{O}_8$, thereby ensuring that the Hg was in bivalent (Hg^{2+}) form. The use of stannous sulphate in hydroxylamine-sodium chloride solution then rendered it to elemental Hg. The Hg was sparged from solution with a stream of air and was passed through an absorption cell situated in the light path of a mercury lamp emitting radiation at 253.7 nm. The absorption of standards and the sample were observed under identical conditions and the Hg concentration was read from the data recorded graphically.

The analytical precision for Cd and Pb analysis was evaluated by the successive analysis of at least eight standard solutions at a concentration in a range from 0 to 10 $\mu\text{g/L}$. The instrumental detection limit for Pb was observed to be 2 $\mu\text{g/L}$, while it was 0.5 $\mu\text{g/L}$ for Cd. The coefficients of variation on the mean absorbance data at these concentrations were $\pm 8.5\%$ and $\pm 10.3\%$, respectively. Two series of control samples (AAA and BBB) supplied by Environment Canada and each containing five samples were analyzed for Pb and Cd content. The mean concentrations for Pb (AAA = $2.38 \pm 0.30 \mu\text{g/L}$, BBB = $4.84 \pm 0.14 \mu\text{g/L}$) and Cd (AAA = $2.0 \pm 0.07 \mu\text{g/L}$, BBB = $5.34 \pm 0.09 \mu\text{g/L}$) showed statistical variations at these low concentrations in line with those observed with the standard samples. The As procedure had a working linear range of 0.1 to 50 $\mu\text{g/L}$. The detection limit was 0.1 $\mu\text{g/L}$ with a coefficient of variation of $\pm 4.8\%$ at 1.8 $\mu\text{g/L}$ concentration. The analytical range for the Hg method was 0.05-100 $\mu\text{g/L}$, with a detection limit of 0.01 $\mu\text{g/L}$. The coefficient of variation at 0.07 $\mu\text{g/L}$ concentration was $\pm 6\%$.

RESULTS

Ten analyzable events occurred in the first phase of the sampling period. The rainwater collection data are shown in Table 1, and the analytical data from the two samplers for Pb, Cd and As are summarized in Table 2.

In the majority of the cases for Pb and Cd, the absorbance data variations between the duplicate samples did not exceed 0.001 A and 0.005 A units, respectively, which correspond to concentrations below the detection limits.

But in a few instances, particularly for Pb, larger variations (up to a factor of 2) in the two results did occur. In summary, the reproducibility of the analytical data from the two samplers may be regarded as moderately successful. It should be noted that the blank values for sample No. 9 in Table 2 pertain to a control sample provided by Environment Canada and not to the blanks used in the other collections.

The data reveal that Pb does occur in the precipitation events. In this study concentrations ranging from 0 to 40 $\mu\text{g/L}$ were observed. The first flask in the sequential analysis generally contained higher amounts of Pb, which decreased progressively thereafter, although in a few cases this trend was reversed (cf. data for events 3 and 10, Table 2). This may be explained as the scavenging effect of rain on the suspended particulate matter in the atmosphere. The highest Pb level observed (40 $\mu\text{g/L}$), however, was lower than that noticed in other similar surveys in industrialized-urban areas, for example, in central Ontario (180 $\mu\text{g/L}$) (16). The volume-weighted average for Pb at 5.28 $\mu\text{g/L}$ (Table 3) in this respect remained close to that found in the earlier studies for the rural zones, ranging from 2.77 $\mu\text{g/L}$ in New Brunswick (22) to 12 $\mu\text{g/L}$ in central Ontario (16) and the Manitoba-Saskatchewan area (15).

The Cd concentrations were lower than those of Pb in conformity with their emissions described earlier. For this element the corresponding levels remained in a range from 0.10 to 5.10 $\mu\text{g/L}$. The volume-weighted average in this case at 0.77 $\mu\text{g/L}$ (Table 3) once again was close to values found for the rural zones in the range from 0.3 to 0.6 $\mu\text{g/L}$ (15, 16), although it was a little higher than the level of 0.57 $\mu\text{g/L}$, which had been found in an earlier survey for rural New Brunswick (22). Cadmium levels increase when there is an increase in Pb concentration. If the mean of the sequential collection data is compared with that of the stock data, a vague trend is manifested. In Table 3, ratios of Pb/Cd are compared. Although these data are too limited to draw any inference at this stage, generally one may interpret that Pb levels in wet precipitation are nearly seven times greater than those of Cd.

The occurrence of As in the precipitation events, on the other hand, was the least frequent of the three elements measured, since As concentrations only ranged from 0.00 to 0.438 $\mu\text{g/L}$, which are far lower than those of Pb or Cd. Some samples did not even show a detectable amount of As. However, an increase in As concentration occurs whenever there is an increase in Pb concentration (Table 3). The mean of the sequential samples and the stock sample average remain lower than 0.1 $\mu\text{g/L}$, which is well below the mean range of 0.65 to 1.44 $\mu\text{g/L}$ observed for some analyses in the United States and Canada (28).

As mentioned earlier, these observations do not establish a correlation in the distribution of these elements, but the experimental data tend to confirm the presence of Pb, Cd and As in the precipitation events. In general, it is seen that the blanks of the system either do not show any background levels or if noticed, they remain far below the sample data. Therefore it may be concluded that within the duration of the sampling period (24 h), the distribution of these elements in the precipitation is inherently associated with such events. The observed concentrations of Pb, Cd and As in this study may be considered in the same way as those seen in a rural or nonindustrialized area elsewhere.

The sample collection and analytical data for Hg are shown in Tables 4 and 5 for 14 measurable events that occurred in this period. The samples, with only a few exceptions, contain very little Hg in this phase of the survey. Even for the positive samples Hg levels are insignificant. This is not surprising, since the element Hg is reported to be scavenged from the atmosphere by rain rather rapidly and its long-range transport mechanism involves terrestrial deposition and re-evaporation, which is governed by humidity, temperature and sunlight (25). Therefore the absence of Hg should not be considered to preclude the presence of other elements due to long-range transport.

This survey alone, however, cannot be used to make a distinction between contamination owing to the long-range transport of elements and that produced by the local contribution. A network of planned and strategically located sampling stations perhaps could provide such information in the future.

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Tables

Table 1. Collection Data on Precipitation Events, June to August 1981

Event No.	Sampling date	Time started	Sampling duration (h)	Standard gauge reading (mm)	Total sample volume (mL)	No. of samples collected	Samples analyzed including blank, standards and stock	Precipitation catch (%)
1	81-06-25	9:00 A.M.	24	25	1500	4	12	84.85
2	81-07-05	5:00 P.M.	17	3.5	230	1	6	92.93
3	81-07-06	9:30 A.M.	24	5.2	355	2	8	96.54
4	81-07-10	7:30 P.M.	36	7.6	515	3	10	95.83
5	81-07-13	9:30 A.M.	24	6.0	450	2	8	106.06
6	81-07-14	9:30 A.M.	24	12.2	780	4	12	90.41
7	81-07-21	9:30 A.M.	24	9.5	740	4	12	110.01
8	81-07-27	9:30 A.M.	24	19.0	1290	4	12	96.01
9	81-08-07	9:30 A.M.	24	8.0	530	3	10	93.69
10	81-08-16	9:30 A.M.	24	30	2000	4	12	94.28

Table 2. Data for Pb, Cd and As Contaminants in Precipitation from WITKOM Samplers

Event No.	Sampling date	Sample sequence	Metal concentration ($\mu\text{g/L}$)					
			Pb	Mean	Cd	Mean	As	Mean
1	81-06-25	1	29.8	21.80	6.0	5.10	0.15	0.135
			13.8		4.2		0.12	
		2	11.6	8.30	0.0	0.20	0.10	0.075
			5.0		0.4		0.05	
		3	7.0	7.0	0.0	0.10	0.10	0.100
			7.0		0.2		0.10	
		4	6.5	5.50	0.0	0.00	0.05	0.025
			4.5		0.0		0.00	
		B	0.0	2.20	0.0	0.00	0.00	0.000
			4.4		0.0		0.00	
		S	6.0	5.60	0.0	0.70	0.00	0.000
			5.2		1.4		0.00	
2	81-07-05	1	10.5	10.80	2.2	2.00	0.10	0.075
			11.0		1.8		0.05	
		B	0.0	0.00	0.0	0.00	0.00	0.000
			0.0		0.0		0.00	
		S	10.0	9.00	1.7	0.85	0.05	0.050
			8.0		0.0		0.05	
3	81-07-06	1	4.7	4.05	1.0	0.50	0.05	0.025
			3.4		0.0		0.00	
		2	7.5	7.0	2.2	1.10	0.00	0.000
			6.5		0.0		0.00	
		B	0.0	0.00	0.0	0.00	0.00	0.000
			0.0		0.0		0.00	
		S	9.1	8.00	1.5	0.75	0.00	0.010
			6.9		0.0		0.02	
4	81-07-10	1	22.0	19.30	4.9	4.80	0.30	0.300
			16.6		4.8		0.30	
		2	8.6	5.95	0.5	0.45	0.00	0.000
			3.3		0.4		0.00	
		3	5.0	4.00	0.4	0.20	0.00	0.000
			3.0		0.0		0.00	
		B	0.0	0.00	0.0	0.00	0.00	0.000
			0.0		0.0		0.00	
		S	9.0	10.25	2.5	2.63	0.00	0.000
			11.5		2.8		0.00	

B—Sample blank

B—Blank provided by Environment Canada

S—Stock sample of a precipitation event

Table 2. Continued

Event No.	Sampling date	Sample sequence	Metal concentration ($\mu\text{g/L}$)					
			Pb	Mean	Cd	Mean	As	Mean
5	81-07-13	1	10.8	9.85	2.2	2.40	0.00	0.000
			8.9		2.6		0.00	
		2	0.0	3.23	0.0	0.00	0.00	0.000
			6.4		0.0		0.00	
		B	0.0	0.00	0.0	0.00	0.00	0.000
			0.0		0.0		0.00	
		S	6.9	9.40	1.2	1.50	0.00	0.000
			11.9		1.8		0.00	
6	81-07-14	1	5.0	5.00	0.2	0.25	0.00	0.000
			5.0		0.2		0.00	
		2	0.0	0.00	0.0	0.00	0.00	0.000
			0.0		0.0		0.00	
		3	0.0	0.00	0.0	0.00	0.00	0.000
			0.0		0.0		0.00	
		4	0.0	0.00	0.0	0.00	0.00	0.000
			0.0		0.0		0.00	
		B	0.0	0.00	0.0	0.00	0.00	0.000
			0.0		0.0		0.00	
		S	2.6	2.60	0.1	0.10	0.00	0.000
			2.6		0.1		0.00	
7	81-07-21	1	5.1	5.92	3.0	2.90	0.07	0.070
			6.8		2.8		0.07	
		2	2.5	2.62	2.6	2.55	0.00	0.000
			2.8		2.5		0.00	
		3	1.1	1.90	0.0	0.00	0.00	0.000
			2.7		0.0		0.00	
		4	1.1	1.90	0.0	0.00	0.00	0.000
			2.8		0.0		0.00	
		B	0.0	0.00	0.0	0.00	0.00	0.000
			0.0		0.0		0.00	
		S	5.0	5.00	2.6	2.35	0.05	0.073
			5.0		2.1		0.09	
8	81-07-27	1	15.0	10.50	0.0	2.20	0.14	0.140
			6.0		4.4		0.14	
		2	10.0	7.00	0.0	0.93	0.14	0.095
			4.0		1.8		0.05	
		3	4.0	3.00	0.0	0.60	0.02	0.022
			2.0		1.2		0.02	
		4	2.0	1.00	0.0	0.00	0.02	0.010
			0.0		0.0		0.00	

Table 2. Continued

Event No.	Sampling date	Sample sequence	Metal concentration ($\mu\text{g/L}$)					
			Pb	Mean	Cd	Mean	As	Mean
9	81-08-07	B	0.0	0.00	0.0	0.00	0.000	0.000
			0.0		0.0		0.000	
		S	7.0	4.50	0.7	0.70	0.06	0.075
			2.0		0.7		0.07	
		1	51.2	40.00	1.8	2.78	0.58	0.438
			28.8		3.8		0.30	
		2	13.0	11.50	1.0	0.50	0.21	0.210
			10.0		0.0		0.21	
		3	11.0	9.60	0.0	0.00	0.24	0.230
			8.2		0.0		0.21	
10	81-08-16	B	3.0	3.30	5.0	5.00	0.34	0.330
			3.6		5.0		0.32	
		S	9.0	8.60	0.0	0.00	0.25	0.125
			8.2		0.0		0.00	
		1	15.0	15.00	0.5	0.32	—	—
			15.0		0.2		—	
		2	20.0	20.00	0.4	0.52	—	—
			20.0		0.6		—	
		3	7.5	6.20	0.0	0.00	—	—
			5.0		0.0		—	
		4	3.0	3.00	0.0	0.00	—	—
			3.0		0.0		—	
		B	0.0	0.00	0.0	0.00	—	—
			0.0		0.0		—	
		S	3.0	2.70	0.0	0.10	—	—
			2.5		0.2		—	

Table 3. The Pb, Cd and As Distribution Ratios in Sequential and Stock Samples

Event No.	Mean sequential data ($\mu\text{g/L}$)			Ratio Pb/Cd	Mean stock data ($\mu\text{g/L}$)			Ratio Pb/Cd	Sample volume (L)
	Pb	Cd	As		Pb	Cd	As		
1	10.10	1.35	0.084	7.48	5.60	0.70	0.000	8.00	1.500
2	10.80	2.00	0.075	5.40	9.00	0.85	0.050	10.58	0.230
3	5.53	0.80	0.012	6.91	8.00	0.75	0.010	10.66	0.355
4	9.42	1.82	0.100	5.19	10.25	2.63	0.000	3.91	0.515
5	6.54	1.20	0.000	5.45	9.40	1.50	0.000	6.26	0.450
6	5.00	0.25	0.000	20.00	2.60	0.10	0.000	26.00	0.780
7	3.09	1.36	0.017	2.27	5.00	2.35	0.073	2.13	0.740
8	5.38	0.93	0.066	5.78	4.50	0.70	0.075	6.43	1.290
9	20.47	1.09	0.293	18.78	8.60	N.D.	0.125	—	0.530
10	11.05	0.26	—	42.50	2.70	0.10	—	27.00	2.000
Sequential average									
	8.74	1.106	0.072	7.90					
Volume-weighted average									
	5.28	0.77	0.028	6.86					

Note: The experimental data are from Table 2.

Table 4. Collection Data on Precipitation Events, September to November 1981

Event No.	Sampling date	Time started	Sampling duration (h)	Standard gauge reading (mm)	Total sample volume (mL)	No. of samples collected	Samples analyzed including blank, standards and stock	Precipitation catch (%)
1	81-09-14	11:30 A.M.	24	4.2	308	2	12	103.70
2	81-09-19	12:00 P.M.	24	10.6	632	4	13	84.31
3	81-09-22	2:00 P.M.	24	14.4	1000	4	12	98.20
4	81-09-23	4:50 P.M.	26	24.6	537	3	11	30.87
5	81-09-24	5:00 P.M.	24	17.5	963	4	12	77.82
6	81-10-02	9:15 A.M.	24	25.0	1730	4	16	97.86
7	81-10-06	7:00 P.M.	22	19.0	995	4	12	74.05
8	81-10-07	5:15 P.M.	24	9.0	535	3	10	84.06
9	81-10-08	5:00 P.M.	27	13.0	715	4	12	77.78
10	81-10-09	8:00 P.M.	26	6.1	340	2	8	78.82
11	81-10-22	10:00 A.M.	48	22.0	1430	4	12	91.98
12	81-10-24	8:45 A.M.	24	17.4	1035	4	12	89.11
13	81-10-26	1:15 P.M.	24	12.2	765	4	12	88.67
14	81-11-06	12:00 P.M.	24	16.0	950	4	12	83.96

Table 5. Analytical Data for Hg Contamination in Precipitation Events

Sampling date	Sample sequence	Mercury ($\mu\text{g/L}$)		
		Sampler I	Sampler II	Mean
81-09-14	1	0.00	0.00	0.00
	B	0.00	0.00	0.00
	S	<0.02	<0.02	0.007*
81-09-19	1	0.00	0.00	0.00
	2	0.00	0.00	0.00
	3	0.00	0.00	0.00
	4	0.00	0.00	0.00
	B	0.00	0.00	0.00
	S	0.00	<0.02	0.003*
81-09-22	1	0.00	0.00	0.00
	2	0.00	0.00	0.00
	3	0.00	0.00	0.00
	4	0.00	0.00	0.00
	B	0.00	0.00	0.00
	S	0.05	0.00	0.025
81-09-23	1	0.00	0.00	0.00
	2	0.00	0.00	0.00
	3	0.00	0.00	0.00
	B	0.00	0.00	0.00
	S	0.00	0.00	0.00
81-09-24	1	0.00	0.00	0.00
	2	0.00	0.00	0.00
	3	0.00	0.00	0.00
	4	0.00	0.00	0.00
	B	0.00	0.00	0.00
	S	0.00	0.00	0.00
81-10-02	1	0.00	0.00	0.00
	2	0.00	0.00	0.00
	3	0.00	0.00	0.00
	4	0.02	0.017	0.018†
	B	0.00	0.00	0.00
	S	0.00	0.00	0.00
81-10-06	1	0.00	0.00	0.00
	2	0.00	0.00	0.00
	3	0.00	0.00	0.00
	4	0.00	0.00	0.00
	B	0.00	0.00	0.00
	S	0.026	0.004	0.015
81-10-07	1	0.00	0.00	0.00
	2	0.00	0.00	0.00
	3	0.00	0.00	0.00
	B	0.00	0.00	0.00
	S	0.00	0.00	0.00

* By extrapolation

† Control sample (0.02 ppb)

B—Sample blank

4—Blank provided by Environment Canada

S—Stock sample of a precipitation event

Table 5. Continued

Sampling date	Sample sequence	Mercury ($\mu\text{g/L}$)		
		Sampler I	Sampler II	Mean
81-10-08	1	0.00	0.00	0.00
	2	0.00	0.00	0.00
	3	0.00	0.00	0.00
	4	0.00	0.00	0.00
	B	0.00	0.00	0.00
	S	0.00	0.00	0.00
81-10-09	1	0.00	0.00	0.00
	2	0.00	0.00	0.00
	B	0.00	0.00	0.00
	S	0.00	0.00	0.00
81-10-22	1	0.00	0.00	0.00
	2	0.00	0.00	0.00
	3	0.00	0.00	0.00
	4	0.00	0.00	0.00
	B	0.00	0.00	0.00
	S	0.00	0.00	0.00
81-10-26	1	0.00	0.00	0.00
	2	0.00	0.00	0.00
	3	0.00	0.00	0.00
	4	0.00	0.00	0.00
	B	0.00	0.00	0.00
	S	0.00	0.00	0.00
81-11-06	1	0.00	0.00	0.00
	2	0.00	0.00	0.00
	3	0.00	0.00	0.00
	4	0.00	0.00	0.00
	B	0.00	0.00	0.00
	S	0.00	0.00	0.00

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