

# Environment Canada

Water Science and  
Technology Directorate

---

Direction générale des sciences  
et de la technologie, eau

# Environnement Canada

Trace Metals in Cloudwater and Precipitation

By:

H. Wong, M. Banic, W. Strachan

NWRI Contribution # 93-20

## MANAGEMENT PERSPECTIVE

The mechanism of trace metal deposition in the rain has been investigated. Sampling within clouds has required development of customized cloudwater and rain collectors and the low levels of metals encountered required extreme care and attention to contamination avoidance.

This report is a preliminary presentation at a conference. It outlines measures taken to ensure meaningful data on trace metal levels in cloudwater and rainfall. Results show that there is little difference between levels in cloudwater and those in rain. A consequence of this is the conclusion that below cloud scavenging of metals is not a likely contributor to levels in rain. This could have implications on how metals loadings to the surface, including the Great Lakes, are calculated.

## TRACE METALS IN CLOUDWATER AND PRECIPITATION

H. K. T. Wong\*, C. M. Banic\*\* and W. M. J. Strachan\*

### ABSTRACT

Clean laboratory and field methods were used to minimize background metal contamination in the collection, preservation and analysis of cloud water and of ground level precipitation. Total Cu, Ni, Pb, Zn and Cd levels in cloud water in October, 1992 in the southern Ontario region were: 2.0-15, 0.1-1.2, 0.3-2.0, 3.5-10., 0.8-3.0, <0.2-0.8 and <0.1-0.8 µg/L, respectively. For rain at Point Petre on Lake Ontario concentrations were: 0.7-4.0, 0.03-0.5, 0.01-3.0, 0.08-3.5 and 0.04-0.2 µg/L, respectively. These preliminary results indicate that rainfall burdens are derived from cloud aerosol rather than below cloud scavenging.

### INTRODUCTION

The search for reduced contamination in collecting, preserving, and analysing low levels of metals in water, coupled with a need to provide precise and accurate loadings estimates under the Canada-U.S. Great Lakes Water Quality Agreement (GLWQA) resulted in the present study. Work was aimed at assessing field and laboratory protocols intended to provide meaningful data on levels of trace metals in rain and cloud water. This report presents information on the blank levels achieved. Metal concentrations in cloud waters and in related precipitation are given and compared with results for conventional collections.

### METHODS

Precipitation: Ground level rain was collected at Point Petre, on Lake Ontario (Integrated Atmospheric Deposition Network, IADN, GLWQA Annex 15). Samplers were modified wet-only collectors (MIC Type B, [1]) for the "clean" samples and wet-only MIC Type A collectors for the routine network samples. The modified collector had all exposed metal surfaces coated with epoxy resin paint or replaced with non-metallic parts. Collection with this instrument was in a 0.2 m<sup>2</sup> linear polyethylene (LPE) funnel draining to a 4.5 litre LPE bottle. Samples were retained, un-acidified, in the LPE collection bottles and shipped every two weeks by courier. They were stored at 5 C in the dark in the laboratory until analysis.

IADN network samples were collected October 8 through November 5, 1992 in precleaned polyethylene bags, heat sealed in the field and shipped to the laboratory at the same frequency as the "clean" samples. A sub-sample was removed for As and the balance acidified and left overnight to re-extract any adsorbed metals. Both subsamples were stored at 5 C until analysis.

---

\* National Water Research Institute, P.O.Box 5050, Burlington, Ontario, Canada, L7R 4A6.

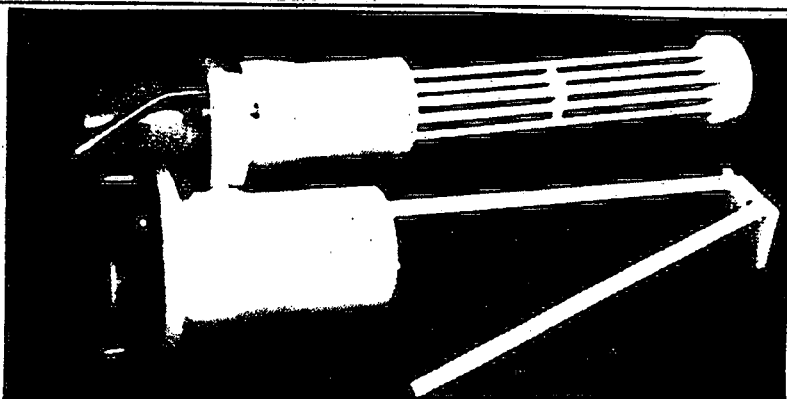
\*\* Atmospheric Environment Service, Environment Canada, 4905 Dufferin St., Toronto, Ontario, Canada, M3H 5T4.

**Cloud Waters:** Cloud water was collected using custom-made samplers with all teflon/LPE slotted rods for warm clouds ( $>0^{\circ}\text{C}$ ); teflon tubes led from the rods through the samplers to LPE bottles sealed (threaded) into the sampler. For supercooled clouds ( $<0^{\circ}\text{C}$ ), a similar device with riming rods was used; samples were obtained by dislodging the frost into LPE sample bags. Individual parts of both samplers were cleaned with soap, rinsed with distilled water then acetone, leached in concentrated  $\text{HNO}_3$  for one hour and then in 5 N  $\text{HNO}_3$  for a minimum of one week. All parts were rinsed with Milli-Q water, allowed to soak in 0.5%  $\text{HNO}_3$  for several days, re-assembled under class-100 conditions, doubly sealed in acid-leached LPE bags and opened during flight for installation. Between flights, the used collectors were rinsed with 0.5%  $\text{HNO}_3$ , copiously rinsed with Milli-Q water and returned to doubly heat-sealed, acid-washed bags until used.

In the case of warm clouds, aerosols impact the rods, moisture is trapped in the slots where it accumulates to droplet size; these flow through the teflon tubing into the LPE sample bottles. The first few millimetres are discarded. For supercooled clouds, the aerosols are collected as rime formed by freezing on contact with the rods. This frost is dislodged from the rods into precleaned LPE bags and then heat-sealed. Both sample types are bagged again and stored cold and dark.

The samplers (Figure 1, [2]), protruded through the forward hull (roof) of a Twin Otter turboprop aircraft. Samples were collected while flying through the clouds at approx. 200 km/h on the dates and times indicated in Table 1.

**FIGURE 1:**  
Cloud Water  
Samplers



Top/Rear: slotted rod, warm cloud sampler (modified Mohnen)  
Bottom/Front: riming rod, supercooled cloudwater sampler shown  
with a partly detached rod

**Analysis:** Concentrations of metals and metalloids in cloud or rime water or in the "clean" samples of ground level rain were determined directly using a Varian Series 400 Graphite Atomic Absorption Spectrometer. Processing and analysis of these samples was carried out under clean-100 conditions. Details of the decontamination of LPE sample bottles, LPE surfaces, clean water supplies, reagents, etc. can be found in a recent publication by Nriagu et al. [3]. Quality assurance for the method was checked against SPEX multi-element plasma standard and against a riverine water reference sample from the National Research Council of Canada. Accuracy (percent of standards)

TABLE 1: Conditions for Cloud Sample Collections

Sample Type	Date (Oct.'92)	Sample Period (GMT)	Temp ( C)	Altitude (m)	LWC* (g/m <sup>3</sup> )
warm clouds	09	1540-1551	8	1550	0.12
	09	1647-1701	11	963	0.20
	09	1701-1710	11	965	0.22
	15	2000-2009	7	1542	0.13
	15	2009-2026	7	1536	0.05
	15	2028-2036	6	1750	0.08
	15	2053-2058	0	2788	0.04
supercooled clouds	28	1745-1806	-7	2150	0.13
	28	2042-2101	-9	2370	0.27
	28	2058-2110	-9	2320	0.27
	28	2100-2108	-9	2325	0.28
	28	2109-2115	-9	2270	0.28
	28	2116-2123	-9	2260	0.26
	28	2200-2500	-9	2300	0.27

\* LWC = liquid water content

and precision (s.d. as percent) for at least 10 assessments were, respectively: Cd - 79-94%, 5-20%; Cu - 95-96%, 2-5%; Ni - 110-130%, 3-30%; Pb - 92-110%, 2-10%; Zn - 80-95%, 2%.

Analysis of the network (conventional) samples of rain was done at Environment Canada's National Laboratory for Environmental Testing. Acid digestion, volume reduction and determination with ICP was used for trace metals; As was an acid/persulfate digestion and analysis by ICP of the metalloid hydride.

## RESULTS AND DISCUSSION

To obtain meaningful results for metals in samples, background contamination must be minimized since the apparent levels are near detection limits for some metals. Blank values obtained with the tested procedures are presented in Table 2; they are acceptable for the sample levels observed (Table 3). Frequent collection of field blanks and the use of "clean" equipment is considered essential in obtaining meaningful results from such sampling programmes -- cloud or precipitation -- as are described here. It is also noted that the equipment employed, with special emphasis on teflon or LPE materials and with protecting from inadvertent contamination from nearby metal surfaces, can provide samples with satisfactory results. Some improvement might be made by using laminar-flow work stations and HEPA filters but this is impractical in the field and nearly impossible in available airplanes.

These blanks are considerably lower than those from an earlier study (1991, [5]). In this previous study, field blanks for As, Ba, Cd, Cu, Mn, Pb and Zn were 1.5, 8, 20, 18, 125, 190 and 40 times the values in the present study. The intent here is not to disparage the earlier results but to indicate the value of scrupulous attention to contamination avoidance which is necessary when collecting samples with low concentrations of trace metals.

TABLE 2: Sampling and Analytical Values for Blanks ( $\mu\text{g/L}$ )

Element	IDL <sup>1</sup>	Lab. Blank <sup>2</sup>	Aircraft Aircraft <sup>3</sup>	Field Blanks Collector <sup>4</sup>	Precipitation Collector <sup>5</sup>
As	0.2	nd	nd	nd	---
Ba	0.1	0.1	nd	0.1	---
Cd	0.001	0.04	0.03	0.04	0.01
Cu	0.2	0.5	0.2	0.4	0.2
Mn	0.02	nd	nd	nd	---
Ni	0.02	0.02	0.12	0.02	0.05
Pb	0.01	nd	nd	nd	nd
V	0.2	nd	nd	nd	---
Zn	0.05	nd	nd	nd	0.4

<sup>1</sup> = instrument detection limit

<sup>2</sup> = 0.5% Seastar HNO<sub>3</sub>/Milli-Q water

<sup>3</sup> = 0.5% Seastar HNO<sub>3</sub>/Milli-Q water exposed to air in flight

<sup>4</sup> = field rinse of slotted collector with 30 mL Milli-Q water

<sup>5</sup> = simulated through funnel at site (pH 4.5, Milli-Q water)

nd = less than IDL

TABLE 3: Metal Concentrations in Cloud Water and In Rain ( $\mu\text{g/L}$ )

Element	----Cloudwater----		-----Rainfall-----	
	Warm	Supercooled	("clean")	(routine IADN)
As	0.2-0.8	0.2-0.7	---	0.3
Ba	0.5-3.5	1.5-2.2	---	2.8
Cd	1.5-3.0	0.9-5.0	0.02-0.8	0.1
Cu	2-115	2-15	0.7-3.0	1.2
Mn	0.3-2.6	1.6-6.0	---	8.0
Ni	0.02-0.3	0.02-1.2	0.2-1.3	0.6
Pb	0.4-1.2	0.3-2.0	0.1-0.3	3.4
V	0.2	0.2	---	0.4
Zn	3.5-6.0	6-10	1.8-15	11.

Aerosols can be atmospherically transported long distances and may be scavenged during formation of precipitation within clouds or when the precipitation falls through the air beneath the clouds. In Table 3, ranges of metal concentrations from cloud samples are presented together with results from the modified samplers and the volume weighted means for the IADN network samples [4] from the period of the aircraft sampling. Examination of the data shows that metal levels from both warm and supercooled clouds are very similar even though gathered on different dates and under different thermal conditions. The values reported here are lower than (for Mn and Pb) or similar to (As, Ba and Cd) those reported for the same area in [5]. The differences are due to improved blank levels and a greater number of quantitated values as a consequence.

Cloud water and precipitation samples are not directly comparable since the latter covered more than the period of the sampling flights and was not restricted to the three flight days. Despite this, metal results for the "clean" rain samples indicated that rain reaching the ground was, with the possible exception of Ni, not more concentrated in these contaminants than was the initial cloudwater. If the rain results are

representative of the cloud sample periods, then the conclusion can be drawn that below-cloud scavenging of metals by rain is not a major source of the wetfall metals. This may have implications for estimating loadings of the overall atmospheric inputs of trace metals to the Great Lakes and elsewhere.

#### ACKNOWLEDGEMENTS

The authors wish to thank the staff of the Canadian Institute for Aerospace Research for their assistance in the collection of the cloud water samples and for generously providing the time with their deHavilland Twin Otter aircraft. The technical assistance of Steve Basic who modified the collectors and did the aircraft instrumentation is also appreciated.

#### REFERENCES

1. Strachan, W. M. J. and H. Huneault. Environ. Science & Technol. 18: 127 (1984).
2. Leatich, W. R., G. A. Isaac, J. W. Strapp, C. M. Banic and H. A. Wiebe. J. Geophys. Research 97: 2463 (1992).
3. Nriagu, J. O., G. Lawson, H. K. T. Wong and J. Azcue. J. Great Lakes Research 19: 175 (1993).
4. Strachan, W. M. J.. Unpublished results (1993).
5. Banic, C. M., W. R. Leatich, G. A. Isaac and J. W. Strapp. In "Precipitation Scavenging and Atmospheric-Surface Exchange" Vol.1, Hemisphere Publ., p.421 (1992).

Environment Canada Library, Burlington



3 9055 1017 7943 6





Environment  
Canada

Environnement  
Canada

Canada

**Canada Centre for Inland Waters**

P.O. Box 5050  
867 Lakeshore Road  
Burlington, Ontario  
L7R 4A6 Canada

**National Hydrology Research Centre**

11 Innovation Boulevard  
Saskatoon, Saskatchewan  
S7N 3H5 Canada

**St. Lawrence Centre**

105 McGill Street  
Montreal, Quebec  
H2Y 2E7 Canada

**Place Vincent Massey**

351 St. Joseph Boulevard  
Gatineau, Quebec  
K1A 0H3 Canada

**Centre canadien des eaux intérieures**

Case postale 5050  
867, chemin Lakeshore  
Burlington (Ontario)  
L7R 4A6 Canada

**Centre national de recherche en hydrologie**

11, boul. Innovation  
Saskatoon (Saskatchewan)  
S7N 3H5 Canada

**Centre Saint-Laurent**

105, rue McGill  
Montréal (Québec)  
H2Y 2E7 Canada

**Place Vincent-Massey**

351 boul. St-Joseph  
Gatineau (Québec)  
K1A 0H3 Canada