

**TRACE ANALYSIS OF ATMOSPHERIC
PRECIPITATION SAMPLES**

W.M.J. STRACHAN

NWRI Contribution No. 90-33

TD
226
N87
No. 90-
33
c. 1

EXECUTIVE SUMMARY

The paper presents data on precipitation (rain) sampling collected with the NWRI sampler which has become the standard for organic rain samplers in Canada and the U.S. and with other, prototype equipment used with air samples (vapour state and dryfall particulates). Replicate data is given which identifies the level of precision obtained with the different equipment. A plea is made to the participants at the 3rd Ecological Quality Assurance Workshop to concern themselves with developing a quality assurance programme for these types of samples.

Résumé

Le rapport présente des données sur les échantillons de précipitation (pluie) recueillis à l'aide d'un collecteur de précipitation de l'INRE, devenu l'instrument standard pour prélever des échantillons de pluie organique au Canada et aux États-Unis, et à l'aide d'un autre instrument expérimental utilisé pour l'échantillonnage de l'air (état de vapeur et particules de résidus à faible adhérence). Des données témoins sont fournies, qui permettent de déterminer le niveau de précision obtenu avec les divers instruments utilisés. On demande aux participants au 3^e atelier sur le contrôle de la qualité écologique de bien vouloir mettre au point un programme de contrôle de la qualité pour ces types d'échantillons.

TRACE ANALYSIS OF ATMOSPHERIC PRECIPITATION SAMPLES

ABSTRACT

Most of the persistent organic contaminants found in environmental samples from the Great Lakes reached there via long range transport through the atmosphere. Historically, analyses have focussed on the more readily determined levels in biota and sediments but present and future demands for modelling and prediction require that the basic compartments, particularly the mobile ones -- air and water -- be assessed.

Rain samples have been collected with equipment designed at Canada Centre for Inland Waters which utilizes XAD-2 resin sorption to concentrate the sample analytes in the field. Discussion will focus on the concentration levels and the variability to be expected in such samples. Substances of particular concern include total PCBs (the future will require congener specific analyses), the hexachlorocyclohexanes (α -HCH and lindane), DDT residues, dieldrin, HCB and others. Levels in rain observed across Canada vary from <0.1 ng/L to nearly 30 ng/L and account for direct inputs to some of the lakes of literally tonnes/annum.

KEYWORDS

Rain, air, atmosphere, PCB, lead, DDT.

Résumé

La plupart des agents de contamination organiques persistants relevés dans les échantillons environnementaux des Grands Lacs sont parvenus à cet endroit après avoir été transportés dans l'atmosphère sur de grandes distances. Dans le passé, les analyses se sont concentrées sur les teneurs plus faciles à déterminer dans le biote et les sédiments, mais les besoins actuels et futurs de modélisation et de prévision nécessitent une évaluation des vecteurs de base, surtout des vecteurs mobiles, c'est-à-dire l'air et l'eau.

Des échantillons de précipitation ont été recueillis à l'aide d'un équipement conçu au Centre canadien des eaux intérieures, qui recourt à la sorption de XAD-2 résine pour concentrer l'échantillon à analyser sur les lieux. L'étude sera axée sur les teneurs et sur la variabilité prévisibles de tels échantillons. Les substances qui nous préoccupent surtout sont notamment les BPC (on devra dans l'avenir recourir à des analyses par congénère), les hexachlorocyclohexanes (α -HCH et le lindane), les résidus de DDT, la dieldrine, les HCB et les autres. Les teneurs des précipitations observées à travers le pays varient, passant d'un niveau inférieur à 0,1 ng/L à un niveau avoisinant 30 ng/L, ce qui explique les apports directs dans certains lacs de l'ordre de plusieurs tonnes par année.

MOTS CLÉS

Précipitation, air, atmosphère, BPC, plomb, DDT

TRACE ANALYSIS OF ATMOSPHERIC PRECIPITATION SAMPLES

INTRODUCTION

In the Great Lakes, and elsewhere, the major mechanism by which many toxic chemical pollutants are introduced to the terrestrial and aquatic parts of the ecosystem is via atmospheric transport from remote distances (International Joint Commission, 1987). This applies to such notable contaminants as the polychlorinated biphenyls, DDT residues, dieldrin, lead and other substances. They reach the system from intercontinental distances, in some cases, and are deposited in the form of rain (and snow), dryfall particulate matter and vapour state exchange with water and soil/leaf material.

Quality assurance programmes, understandably for the Great Lakes, have focussed on relatively homogeneous samples such as water. To a lesser extent, biota and sediments have been the media but in most cases, it seems to this researcher that metals and inorganic anions have been the analytes. This may be the consequence of historic analytical detection limits which precluded working with the low levels of the persistent organic pollutants found in the basic media -- air, water and sediment/soil, and the suspended matter found in the first two. The present state of analytical art, however, is much advanced over that of ten years ago and it is appropriate that analytical and quality assurance investigators turn their attention there. These sample media, and the properties of the individual chemicals,

govern the distribution of chemicals in the environment and are therefore those which will determine how long the problems of such toxicants will last. It is appropriate, therefore that these sample matrices receive more attention than they have in the past. The subject of this paper relates to samples from atmospheric sources (and their attendant quality assurance aspects) but the other basic media are equally in need of investigation.

ATMOSPHERIC SAMPLE TYPES

Precipitation, in this presentation, is taken very broadly to include all sample types which result in the transfer between the air and the terrestrial or aquatic compartments of the environment. In a practical sense, work has largely focussed on the air-water interactions and all comments are restricted to these two compartments unless noted. This limits the sample types to rain, dryfall air particles and vapour state. There is less information on the latter two; consequently, most comments are derived from experience with rain.

The samples for rain are usually large relative to traditional water samples — tens of litres — although this often corresponds to a few centimetres of wetfall which can be achieved in a single, heavy rainfall (Strachan and Huneault, 1984). Routine sample collection, however, usually composites a number of precipitation events collected unfiltered either on an XAD resin column or in a solvent. Samples may sit adsorbed to the column material for

up to a month, are shipped via post, and processed in the laboratory at anything up to a month or two following receipt there; they are refrigerated during this latter period although not for other times.

Samples for the air compartment are usually collected on large glass filters (for particulates) which are placed before a vapour state trap (polyurethane foam plug, XAD or Tenax trap, etc.). These two collectors are part of a "high volume" (Hi-Vol) sampler pumping at the rate of cubic metres per minute. There is a lot of uncertainty about whether pollutants sorbed on the particulates (trapped on the filter) are retained there or whether they desorb and increase the apparent atmospheric vapour state load (e.g., Konig et al., 1980; Broddin et al., 1980; Grosjean, 1983). The Atmospheric Environment Service (Canada) together with the Ontario Research Foundation (now ORTECH International) has developed a sampler which separates vapour and particle using the denuder principle (Lane et al., 1988). This involves the vapour being selectively removed by absorption into a Tenax/silicon gum coating on concentric glass tubes; the particles are trapped on a conventional filter backed up by a Tenax trap. The filter and backup are determined following refrigeration in the field and processing and workup in the laboratory usually within a few weeks of returning to the laboratory. Vapour state is found as the difference between total (no denuders) and the particulates as described.

In all cases, the analytes must be removed from the sample trap medium. Except for systems using solvents to concentrate in the field, this involves eluting with a solvent, subsequent cleanup and possible fractionation, and analysis by gas-chromatography. Because environmental samples are inherently heterogeneous, there is substantial variability in apparently equivalent samples. There are also differences in technique among the several laboratories and collecting agencies while at the same time there is a declared desire to ensure that results from the various programmes are "compatible", "comparable" and "reliable". Presentation of a statistical evaluation is important in establishing confidence in the reported levels of contaminants. This is especially important in the Great Lakes region where the assessments will be used in judging successes under the Great Lakes Water Quality Agreement and the nature of additional, possibly costly control measures.

LEVELS AND PRECISION OF CONTAMINANTS IN RAIN AND AIR

Replicated results are available using a large (0.2 m^2) rain collector and from a prototype air sampler. The levels given here mainly indicate the levels of contaminants which can be expected in the several media and the present levels of imprecision. Sampling sites, during 1981-1984, are from across Canada -- Cree Lake is in northern Saskatchewan, Kouchibouguac is on the Atlantic coast in New Brunswick, Fifty Mile Point is on western Lake Ontario and the remaining locations are all around Lake Superior. These samples are singled out from among many others because triplicate samples

were available for the sampling periods indicated. Other samples, however, indicate that the levels of the more prominent organochlorine contaminants are uniform (to within a factor of 2X to 3X) across Canada. For purposes of perspective, a concentration of 10 ng/l in rain falling on 80,000 km² (an area approximating Lake Superior) would result in a loading of nearly 1 metric tonne.

Analytes investigated with the rain sampler include the PCBs and most of the common organochlorine pesticides; those reported in Table 1 are those most commonly found from replicated (three) samplers (Strachan and Huneault, 1984; Strachan, 1985, 1988) placed to collect "ambient" samples rather than those from urban or known contamination sources. In all cases presented here, the results were for samples which were found in all three samplers but no additional discrimination has been applied.

The gas-air particle sampler (GAPS) is a prototype instrument designed to separate airborne particulates from vapour without filtration. It has only been evaluated for HCB and lindane (Lane et al., 1988) although there are some preliminary results with PCBs. The results in Table 2 are those from triplicate samples taken in a study at Little Turkey Lake north of Sault Ste. Marie (Johnson et al., 1989). Each sample was collected over approximately 46 hrs pumping air at 16.7 litres per minute; the "replicates" (three) were not exactly replicates since they were taken sequentially over a one week period.

Table 1: Environmental Means (and Relative Standard Deviations) of Rain Samples

<u>Sample Description</u>	<u>Volume</u> (litres)	<u>a-HCH</u>	<u>g-HCH</u>	<u>t-PCBs</u>	<u>t-DDT</u>	<u>Dield'n</u>	<u>HCB</u>
----- ng/L (percent) -----							
50MP, Apr. 1981	0.42			61(66)			
50MP, Apr. 1981	2.1	35(39)	7(20)	9(98)			
50MP, Apr. 1981	2.1	38(15)	11(15)	11(9)			
50MP, Apr. 1981	2.2	29(29)	10(28)	22(16)			
50MP, May 1981	1.0	10(31)	5(35)	32(45)			
TLake, June 1981	18.	5(3)	1(4)	1(36)		0.4(12)	
TLake, June 1981	3.2	28(31)	7(60)	8(28)			
TLake, June 1981	4.2	48(41)	11(47)	3(20)			
TLake, June 1981	22.	19(39)	7(51)	1(65)	0.4(38)		
TLake, July 1981	15.	32(31)	9(14)	2(33)		0.6(12)	
IRoyale, June 1983	18.	65(21)	16(26)	16(28)	0.1(50)		0.1(60)
IRoyale, Aug. 1983	17.	40(15)	8(14)	5(62)	0.7(95)	1. (32)	0.01(100)
IRoyale, Sept.1983	35.	19(11)	5(13)	1(53)	0.5(50)	0.6(27)	
Caribou, May 1983	7.9	9(16)	4(16)	48(21)	1. (53)	0.7(22)	
Caribou, June 1983	26.	46(3)	12(5)	6(56)	0.2(20)		0.1(12)
Caribou, Aug. 1983	34.	4(75)	2(27)	0.6(50)	0.2(100)	0.3(26)	0.02(69)
Caribou, Sept.1983	20.	6(3)	2(9)	2(75)	0.3(40)	0.2(25)	0.4(28)
Caribou, Oct. 1983	22.	5(16)	2(14)	2(51)	0.1(43)	0.3(6)	
Agawa, June 1984	21.	3(8)	2(17)	2(9)	0.2(22)	0.2(23)	0.03(24)
Agawa, July 1984	22.	4(11)	2(11)	5(70)	0.5(55)	0.6(37)	0.1(19)
Agawa, Aug. 1984	21.	3(24)	3(42)	4(21)	0.1(41)	0.7(41)	
Agawa, Sept. 1984	26.	15(22)	5(14)	2(33)		0.9(33)	
Caribou, May 1984	57.	4(21)	2(26)	3(45)	2. (58)	0.5(55)	
Caribou, June 1984	19.	4(10)	2(16)	3(45)	0.6(40)	1.0(47)	0.03(13)
Caribou, July 1984	20.	7(7)	3(31)	3(21)	1.0(41)	0.9(28)	0.2(38)
Caribou, Aug. 1984	18.	4(22)	4(24)	4(56)	0.2(37)	1.3(17)	0.1(74)
Caribou, Sept.1984	20.	12(16)	4(7)	1(0)	0.7(10)	0.8(5)	
Cree, June 1984	21.	4(11)	4(12)	0.6(28)	0.1(45)		
Cree, July 1984	31.	0.9(22)	0.5(39)	3(4)	0.1(31)		0.01(16)
Cree, Sept. 1984	5.	53(3)	14(22)	17(14)	2. (29)		
Kou'ac, June 1984	43.	2(14)	1(14)		0.06(16)	0.07(46)	0.01(28)
Kou'ac, July 1984	50.	6(26)	3(40)	0.7(11)	0.6(55)		0.1(5)
Kou'ac, Aug. 1984	18.	1(47)	0.5(71)	2(104)	0.1(18)		
Kou'ac, Sept.1984	20.	66(53)	34(38)	7(46)	0.9(55)	2. (24)	0.1(28)
Mean Rel.Std.Dev. (%)		(22)	(25)	(40)	(43)	(27)	(37)

Table 2: Environmental Means (and Relative Standard Deviations) of Air Samples

<u>Sample Description</u>	<u>a-HCH</u>	<u>g-HCH</u>	<u>t-PCBs</u>	<u>t-DDT</u>	<u>Dield'n</u>	<u>HCB</u>
	----- ng/m ³			(percent) *		
TLake, Fall 1986	0.36(29)	0.06(47)				0.13(14)
TLake, Spring 1987	0.29(6)	0.10(16)				0.09(20)
TLake, Summer 1987	0.46(3)	0.04(11)				0.07(39)
TLake, Fall 1987	0.20(6)	0.03(0)				0.08(6)
Mean Rel.Std.Dev. (%)	(11)	(19)				(20)

* - Each value represents the mean (and rel. std. dev.) of three separate samples of approximately 45 m³ all taken within one week.

There are no apparent systematic variations due to analyte level, sample size, location or season in the relative standard deviations in either the rain samples or in those for air. Mean levels for the imprecision estimates are therefore arrived at by simple averaging and are given in the two tables. It is apparent that the variabilities of the rain samples (Table 1) and those for the air (Table 2) are substantial and would affect the estimates of loadings required under the Agreement. When compared with the analytical variability for comparable levels of analytes, however, the contribution to the imprecision from the sampling process is seen to be moderate and may be the consequence of inherent variability rather than technique. In most cases where assessment of significance of the atmospheric input mechanism has been possible (Strachan and Eisenreich, 1988), even this level of variability does not negate the observation that this route is the dominant one for remote lakes and presumably also terrestrial areas.

The rain results are entirely from studies at NWRI and there is now building a body of information from the Ontario Ministry of the Environment and from the U. S. Environmental Protection Agency using the same resin field concentration and recovery methods. There are also data from a Great Lakes network which employs solvent extraction for concentration and in the very near future, there is to be a Great Lakes network utilizing the resin method for field processing of samples. It is partially with these different but similar systems in mind that a plea is made here for assistance in developing a quality assurance protocol now, before this network develops a "life" (i.e., direction) of its own!

The small amount of data available for the air samples pertains to the use of the prototype GAPS sampler in a limited number of situations. It too, however, may end up in the coming Great Lakes "international Atmospheric Deposition Network" called for under Annex 15 of the Great Lakes Water Agreement (1987 Protocol). There will be a need for quality assurance in all aspects of this since there will be several collecting agencies involved, a number of laboratories and different analytical protocols. Much of the required guidance is indicated in the several reports of the different work groups at the last Ecological Quality Assurance Workshop especially the practical aspects; those of us involved with establishing the atmospheric network look forward to hearing from those who have actively pursued the directions provided there.

REFERENCE

- Broddin, G., Cautreels, W. and van Cauwenberghe, K. (1980). On the aliphatic and polyaromatic hydrocarbon levels in urban and background aerosols from Belgium and the Netherlands. Atmos. Environ. 14: 895-901.
- Grosjean, D. (1983). Polycyclic aromatic hydrocarbons in Los Angeles air from samples collected on Teflon, glass and quartz filters. Atmos. Environ. 17: 2565-2573.
- International Joint Commission (1987). Summary Report of the Workshop on Great Lakes Atmospheric Deposition (October 1986). Int. Joint Comm., Windsor, 41 p.
- Konig, J., Funcke, W., Balfanz, E., Grosch, G. and Potts, F. (1980). Testing a high volume air sampler for quantitative collection of polycyclic aromatic hydrocarbons. Atmos. Environ. 14: 609-613.
- Johnson, N. D., Lane, D. A., ASchroeder, W. H., and Strachan, W. M. J. (1989). Measurements of selected organochlorine compounds in air near Ontario lakes: Gas-particle relationships. Presented at 32nd Annual Conference, International Association Great Lakes Research, Madison, Wisc., June 1989.

Lane, D. A., Johnson, N. D., Barton, S. C., Thomas, G. H. S., and Schroeder, W. H. (1988). Development and evaluation of a novel gas and particle sampler for semivolatile chlorinated organic compounds in ambient air. Environ. Science & Tech. 22: 941-947.

Strachan, W. M. J. (1985). Organochlorine substances in the rainfall of Lake Superior: 1983. Environ. Toxic. & Chemistry 4: 677-683.

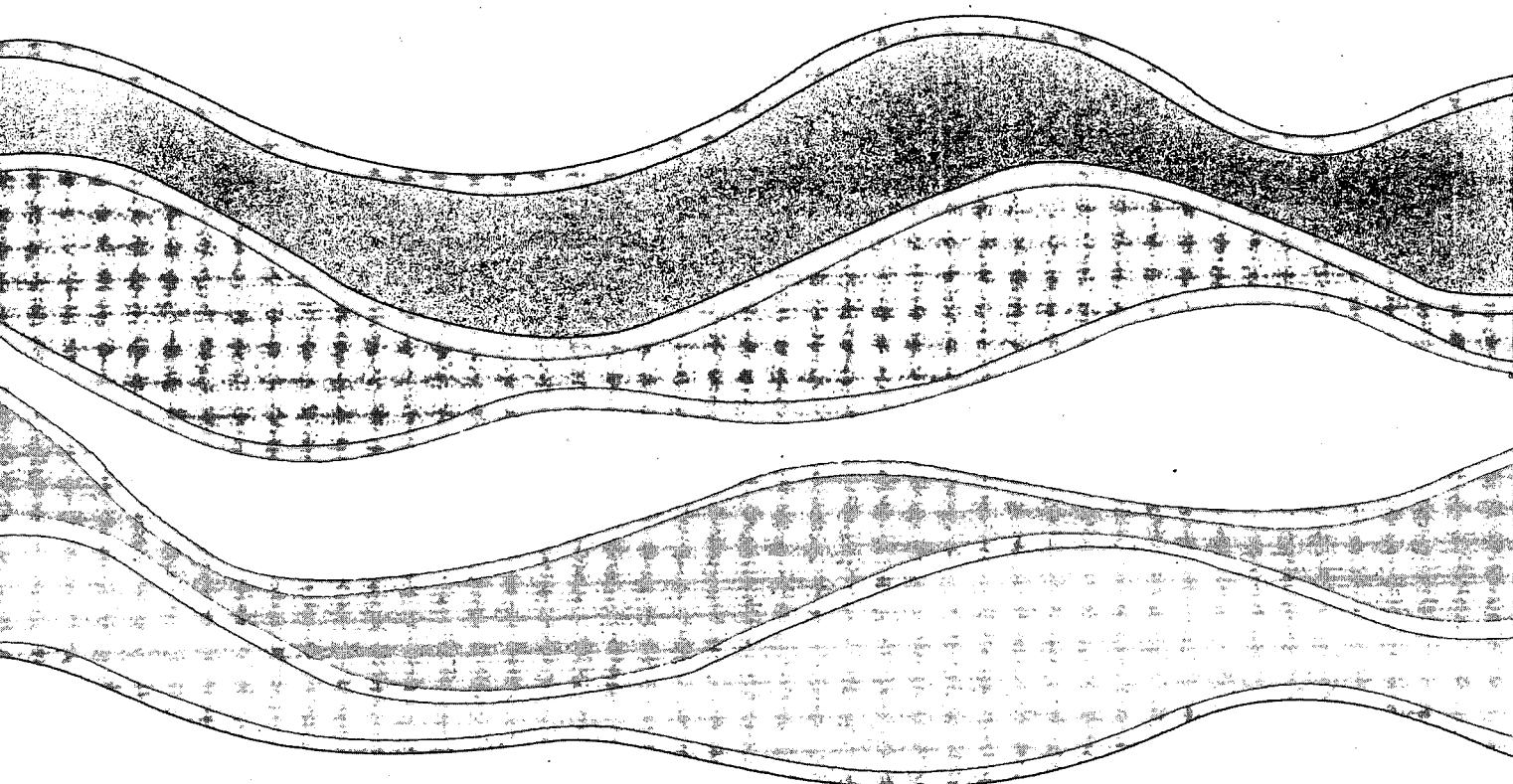
Strachan, W. M. J. (1988). Toxic contaminants in rainfall in Canada: 1984. Environ. Toxic. & Chemistry 7: 871-877.

Strachan, W. M. J. and Eisenreich, S. J. (1988). Mass Balancing of Toxic Chemicals in the Great Lakes: The Role of Atmospheric Deposition. Int. Joint Comm., Windsor, 113 p.

Strachan, W. M. J. and Huneault, H. (1984). Automated rain sampler for trace organic substances. Environ. Science & Tech. 18: 127-130.



3 9055 1017 0664 5



NATIONAL WATER RESEARCH INSTITUTE
P.O. BOX 5050, BURLINGTON, ONTARIO L7R 4A6

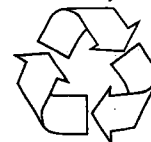


Environment Canada
Environnement Canada

Canada

INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX
C.P. 5050, BURLINGTON (ONTARIO) L7R 4A6

Think Recycling!



Pensez à Recycling!