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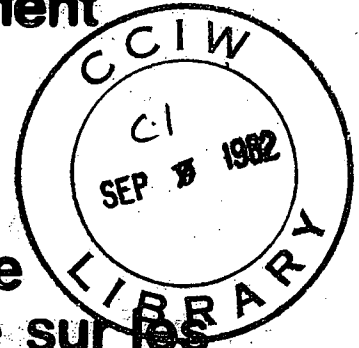


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Abstract

An automated rain sampler was designed, built and evaluated as a collecting device for persistent organic chemicals in rain. It consists of a large teflon coated funnel (0.209 m²) with an automated lid and a teflon column containing XAD-2 or 7 resin. The sampler was tested for recoveries and field precision with a number of organochlorine substances and PCBs frequently found at the nanogram per litre level in rain. Recoveries averaged 86% and the mean coefficient of variation for α -BHC, lindane and PCB's was 33% under field conditions where samples of 0.4-22 litres of rain were collected. The sampler is recommended for use in network sampling for such substances.

Introduction

Atmospheric deposition of persistent organic chemicals has been identified as a major pathway for the entry of such chemicals to the Great Lakes ecosystem (Science Advisory Board, 1981; Eisenreich et al 1980). They have also been reported elsewhere although attempts to calculate their budget significance have seldom been undertaken. Locations for earlier studies of such deposition included Hawaii (Benvenue et al, 1972), Norway (Lunde et al, 1977), Tokyo (Masahiro and Takahisa, 1975), the Caribbean (Bidleman and Olney, 1974) among others and are illustrative of the global aspects of this depositional pathway. Concentrations in various samples of biota from sites not expected to be subject to inputs from other mechanisms also emphasize the widespread nature of this problem (Peterle, 1969; Sodergren et al., 1972; Clausen et al, 1975; Swain, 1978). Compounds such as PCBs, HCB, DDT and isomers of benzene hexachloride have all been noted, none having vapour pressures indicative of likely presence in atmosphere. Further, PCBs and DDT, have been restricted or banned from North American usage since 1971 and this would suggest they should no longer be present in the atmosphere ten years later. That they are (Murphy and Rzesutko, 1977; Strachan et al, 1979; Swain 1980) indicates a need to precisely determine their levels and those of other such chemicals in order to provide information necessary to locate sources and evaluate trends.

"Precipitation" can be loosely categorized as wetfall and dryfall. Vapour-water or soil exchange may also be of importance in determining the atmospheric contribution of these chemicals to the ecosystem. Conflicting reports exist about whether these materials are mainly present in the atmosphere adsorbed to particulates, as aerosols or in the vapour state. The report by Eisenreich et al (1980) included a review, which addressed the question of the atmospheric form of these substances and indicated that loading to the aquatic

compartment is mainly a question of particulate levels and types and of sampling methodology. Eventhough the conclusion is that a high proportion (80-100%) of the quantity of such airborne contaminants is present in the vapour phase, it is the material reaching the surface of the land or water which has raised the greatest concern.

Dryfall particulate deposition of toxic organic chemicals is quantitatively an unknown factor. Theoretical models are available for vapour phase transfer using equilibrium constants and transfer coefficients (Smith et al., 1981; Wolff and van der Heijde, 1982). For particulate fluxes, only crude estimates have been made (Eisenreich et al., 1980) and the concentrations of persistent organic substances in or on this material is equally unknown. The nature of dryfall samplers is a major difficulty since most designs to obtain the quantities needed depend upon a a flow of air across a filter which may result in loss of sorbed contaminant from the particulates. While this type of sampling is of considerable interest, however, the topic of this report is wetfall sampling.

Wetfall deposition of chemicals, which may be either adsorbed on particulates or dissolved in the rainfall, has been investigated extensively for metals and inorganic substances (review by Allen and Halley, 1980). For organic compounds, however, it is only in the last few years that quantitative efforts have been undertaken in the Great Lakes region (Murphy and Rzeszutko, 1977; Strachan and Huneault, 1979; Swain 1980). Even then it is seldom that substances other than PCB's or DDT are investigated. Large samples must be collected and the substances concentrated in order to permit their analytical determination. In this laboratory, we have previously employed large (2 m^2 and 0.36 m^2) stainless steel collectors but have often observed fine particulate matter adhering to the metal surface. This is of considerable concern since preliminary observations (Strachan et al, 1980) indicated that much of the organic

wetfall loading of these chemicals was via the particulate matter. It is also desirable that wetfall samplers should be capable of being left unattended in the field for considerable periods of time without affecting the integrity of the sample. Co-distillation, plus biological and abiotic transformations make samples stored in the aqueous phase suspect. These factors, and the need to distinguish wetfall from dryfall, led to the development of the sampler described in this report.

Description of Sampler

In the Great Lakes region, and elsewhere in Canada, monthly average rainfalls of 5-10 cm may be expected and individual events of 1 cm are not infrequent. It was desired to develop a sampler which could be used for sampling both types of situation (monthly and event). A surface area of approximately 0.2 m^2 was therefore indicated in order to acquire samples of at least 1 litre. This volume is necessary in order to reach the quantification limits of 0.5-5.0 ng of compound/sample based on concentrations observed in the area (Strachan et al., 1979).

The material chosen for the sampler was teflon coated stainless steel. Uncovered metals are potentially problematic because charged particles and metal surfaces have been observed to result in strong retentions of particulates albeit under dryfall conditions. If this were to occur to any extent during wetfall, it would lower the levels observed. Teflon is generally understood to be an inert material and, for the exposure times experienced during rainfall events, has not leached interfering substances or apparently adsorbed any of the investigated substances. It can be readily coated on metal surfaces and for these reasons was the material of choice for both the funnel surface and the column.

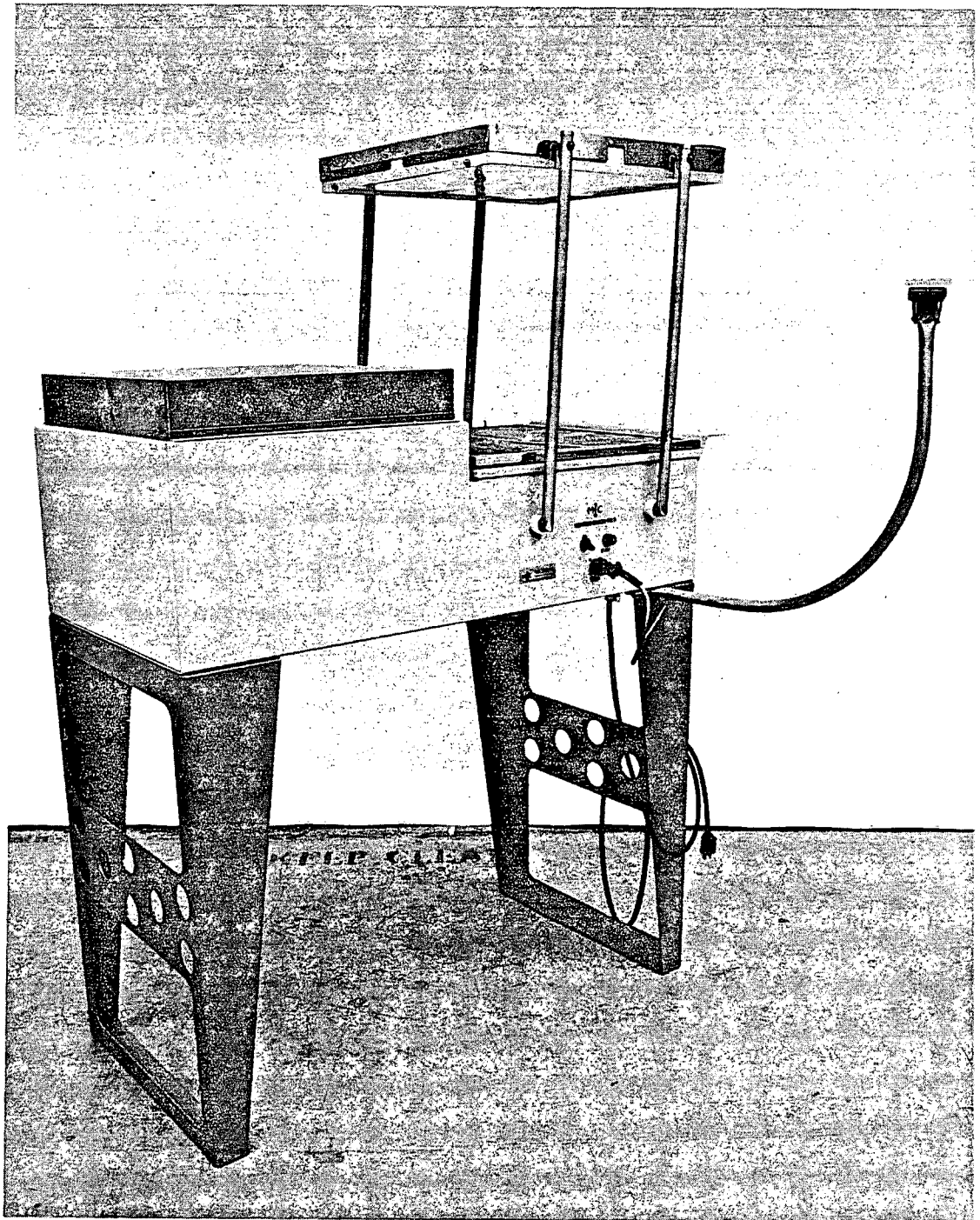


Figure 1. Organic Automated Rain Sampler (lid half open).

The sampler was constructed by M.I.C. Co. (Thornhill, Ontario, Canada) to a design and specifications prepared by the authors. The final prototype is shown in Figure 1. It consists of a square funnel (0.46 m X 0.46 m) and a lid, both of which are constructed of stainless steel. A funnel lip of 10 cm is used and the funnel surface is sloped 20° towards the centre in order to provide rapid drainage to a column attached below. All surfaces in contact with the sample are coated with 0.076 cm (30 mil) teflon. The legs and chassis are constructed of 0.318 cm (1/8 inch) cast aluminium and are detachable for transport. Splash from horizontal surfaces into the sampler is eliminated by the use of stainless steel screening. Total weight of the sampler is 47 kg. The overall dimensions of the closed sampler are 0.5m (w) X 1 m (l) X 1.2 (h); when open the lid adds an additional 0.5 m to the length.

The lid is automated to be open only during rainfall conditions. The rain sensor is set on an arm 0.5 m from any part of the sampler. It has two sensing faces set at 20° from the horizontal which are slightly heated to ensure response only during rainfall. The control electronics are modified from the Sangamo inorganic rain sampler and operate a 1/50 h.p. fractional gearmotor at 120 VAC. A small heater in the central electrical chassis avoids condensation which otherwise occurred.

The outlet of the funnel is threaded to receive an all-teflon column (2 cm i.d. X 25 cm) fitted with a support disk at the bottom. The outlet of the column is equipped with a U-tube to ensure that the resin remained wet. Under normal use, a head of at least 10 cm is maintained. Flow through the column under these conditions is 20-50 ml/min. The XAD resins in the column were successively soxhlet extracted for three hours with each of acetone and methanol; storage was in methanol. Prior to installation under the funnel, the resin was added to the column as a methanol slurry

(fired glass wool plugs are required above and below the 30-40 ml resin bed) and washed with 5-10 bed volumes of organic free water. While it was not done for this report, the columns could be detached and capped thus providing a suitable conveyance for mailing the resin; they could also be provided to field personnel in a pre-washed condition.

Experimental

Recoveries: A stock solution of approximately 0.1-0.5 mg/ml each of a number of organochlorines was made up in acetone. Spikes (2.0 μ l) of this were injected into 2.0 L samples of organic-free water obtained by passing glass-redistilled water through a freshly prepared and washed XAD-2 resin column. After 15 minutes of stirring, three of these samples were slowly poured over the surface of the funnel and thence through separate columns which were partially filled with either XAD-2 or XAD-7 resin. The flow rates were approximately 20 ml/min. The resins were removed from the columns, extracted with 50-75 ml ether, 1 ml iso-octane keeper added and concentrated to 1 ml. The concentrates were analysed by chromatography (25 m OV-1 capillary column, programmed from 90-260°C at 4°/min., electron capture detector). Results of these recovery experiments are presented in Table 1 for both XAD-2 and XAD-7 resins.

Field: Precision of the total sampling and analysis technique was assessed for normal field conditions. Three samplers were employed to collect samples from a CCIW field site at 50 Mile Point near Hamilton, Ontario - a location 10 km downwind from a heavily industrialized area of approximately 300,000 inhabitants. Samples were collected during April and early May of 1981. The samplers were subsequently moved to the Turkey Lakes acid-rain watershed site near Sault Ste. Marie, Ontario - a "remote" area 50 km from that city of 80,000 persons. Collections there occurred during July and August, 1981. At

Table 1: Recoveriesa) XAD-2 Resin

	<u>Test Conc.</u> ($\mu\text{g/L}$)	<u>Mean</u> ($\mu\text{g/L}$)	<u>Coeff. Var.</u> (%)	<u>Recovery</u> (%)
α -BHC	0.29	0.25	3	87
Heptachlor	0.42	0.32	8	76
Aldrin	0.22	0.16	9	73
γ -Chlordane	0.55	0.46	15	83
α -Chlordane	0.55	0.54	17	98
Dieldrin	0.22	0.20	13	88
Endrin	0.65	0.63	13	98
pp'-DDT	0.41	0.35	25	85
Average recoveries				86

b) XAD-7 resin

HCB	0.12	0.077	8	63
Lindane (γ -BHC)	0.25	0.11	7	42
Heptachlor	0.12	0.029	(90)	(25)
Aldrin	0.067	0.045	16	67
γ -Chlordane	0.71	0.74	5	103
α -Chlordane	0.48	0.34	6	72
Endosulfan	0.42	0.34	6	82
pp'-DDE	0.54	0.29	9	53
pp'-TDE	0.41	0.29	4	80
pp'-DDT	0.36	0.21	7	57
Methoxychlor	0.51	0.29	12	58
Average recoveries				68

Table 2: Field Sampling Details

<u>Sample Number</u>	<u>Dates (1981)*</u>		<u>Rainfall</u>	
	<u>(From)</u>	<u>(To)</u>	<u>(mm)</u>	<u>(Litres)</u>
<u>50 Mile Point</u>				
50-1104	8/4	13/4	2.0	0.42
50-1404	13/4	14/4	9.9	2.07
50-2404	22/4	27/4	10.2	2.12
50-2804	27/4	29/4	10.4	2.18
50-0505	29/4	6/5	4.8	1.01
<u>Turkey Lakes</u>				
TL-0206	2/6	4/6	86.1	18.0
TL-0406	4/6	9/6	15.5	3.23
TL-0906	9/6	12/6	20.0	4.18
TL-1806	18/6	10/7	106.	22.2
TL-1007	10/7	14/8	72.	15.0

*Date/month. Integral numbers of events were collected.

Table 3 Field Sampling Results

Sample	Concentration (percent coefficient of variation)							
	α -BHC	Lindane	γ -Chlordane	Dieldrin (ng/L)	pp'-DDT	Endosulfan	Endrin	PCB's
50-1104								61(66)
50-1404	35(49)	7(20)						9(98)
50-2404	38(15)	11(15)			2(25)			11(9)
50-2804	29(29)	10(28)	0.9(11)					22(16)
50-0505	10(31)	5(35)						32(45)
TL-0206	5(3)	1(4)	0.1(41)	0.4(12)		0.7(69)	0.2(49)	1(36)
TL-0406	28(31)	7(60)						8(28)
TL-0906	48(14)	11(47)						3(20)
TL-1806	19(39)	7(51)			0.4(38)			1(65)
TL-1007	32(31)	9(14)		0.6(12)				2(33)
Average coeff. var. %	(27)	(30)	(20)	(12)	(38)	(37)	(49)	(42)

Quantitation limit (ng/sample) 0.5 0.5 1.0 1.0 1.0 3.0 1.5 2.0 5.0

both locations, a tipping bucket rain gauge was employed to measure rainfall and collected volumes were calculated using mm of precipitation and the area of the collecting funnel (0.209 m²). Efforts were made to ensure that at both sites the three samplers and the rainfall gauge were placed in open areas at least 3 m apart away from any objects of equivalent or greater height. Details of the samples are assembled in Table 2. Field samples were analysed as above but with an additional cleanup step according to established procedures of the Inland Waters Directorate (1979). Analytical results are given in Table 3. Only data for those substances and occasions when observed levels exceeded the analytical quantitation limits (0.5-5 ng/sample) are reported. Substances examined for (and their limits, ng/sample), in addition to those presented in Table 3, included hexachlorobenzene (0.5), heptachlor epoxide (1.0), α -chlordane (1.0), pp'-DDE (1.0), pp'-TDE (4.0), endosulfan (1.5), mirex(2.0), and methoxychlor (5.0).

Discussion

In the laboratory recovery experiments reported in Table 1, the mean coefficient of variation for the test compounds was 13% (range 3-25%) for the XAD-2 resin when heptachlor is excluded; the corresponding average for XAD-7 resin was 8% (range 4-16%). These values are comparable to the precision obtained for the gas chromatographic calibration standards (mean 9%, range 5-12%) and are better than the average 25% reported by IWD (1979). This latter improvement possibly results from the clean-up step which was not included in the laboratory recovery tests but which was included for the analyses of the field samples.

The recoveries for XAD-2 and XAD-7 (Table 1) averaged 86% (range 73-98%) and 68% (range 42-103%) respectively. The XAD-2

results compare favourably with those obtained in the IWD laboratories where 80% was the average with the identical procedures excluding a cleanup step using Porasil columns. The XAD-2 results are also better than those using XAD-7, a result to be expected considering the non-polar nature of all of the test substances. The XAD-2 resin was employed in all field sampling but for substances other than those investigated here, XAD-7 may offer some advantages. A mixed resin bed may be worth considering for general sampling of wetfall organics.

It can be seen from Table 3 that no systematic relationship exists between the coefficient of variation and the concentration levels observed in the field samples. Furthermore, no such bias was found with the quantities adsorbed. A somewhat higher but statistically insignificant incidence of detection of "other" compounds at the trace level was noted for samples from the Turkey Lakes site. In addition to those compounds reported in Table 3, endosulfan, methoxychlor, heptachlor epoxide and pp'-DDE were occasionally found at levels below the quantification limits. The usefulness of this data in evaluating sampling precision is questionable and they are not further commented upon in this report. Indeed, since only α -BHC, lindane (γ -BHC) and PCB's were observed with any degree of frequency and quantitative significance, only these are commented upon.

The coefficients of variation for α -BHC, lindane and PCB's in the field samples averaged 27, 30 and 42% respectively. The corresponding value for water samples reported by IWD (1979), as noted previously, was 25% for replicate analyses on single samples. It would appear, therefore, that the sampling procedures reported here add only marginally to the imprecision and would tend to confirm the suitability of both the sampler and the use of XAD-2 resin columns in the field. The slightly higher variation observed may be the result of non-homogeneity either in the intensity of the rain itself or in

the concentrations impacting different samplers. Since most of these substances are washed out in the early phase of a given rainfall event (Strachan et al., 1980) it is likely the latter which is the cause but this is by no means certain. Proximity of elevated objects nearby or of the other samplers themselves could have an effect but this is not expected to be the case here given the precautions taken in separating the samplers and placing them at open sites.

Summary

The sampler described is designed to collect and concentrate persistent organic substance in rainfall including both particulate and dissolved forms. It is not appropriate for dryfall nor for snow during the winter months, although efforts are underway to modify it for this latter purpose (C.H. Chan, I.W.D., personal communication). It offers an average recovery of 86% for organochlorines with an average coefficient of variation of 33% on replicate samples collected under environmental conditions. Few quality control studies have ever been attempted for this type of sample but it is believed that these results are at least as good as those from any other technique. The sampler also offers the advantage of unattended operation for extensive periods and a simple method for field handling of samples since the columns can be readily exchanged and capped for delivery. It is therefore recommended that these samplers be employed in national sampling networks such as the CANSOC program of Inland Waters Directorate and Atmospheric Environment Service of Environment Canada.

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References

- Allen, H.E., and Halley, M.A. 1980. Assessment of airborne inorganic contaminants in the Great Lakes. Appendix B to the Science Advisory Board Report to the International Joint Commission, 1980.
- Benvenue, A., Ogata, J.N., and Hylén, J.W. 1972. Organochlorine pesticides in rainwater, Oahu, Hawaii, 1971-1972. Bull. Env. Cont. Toxic. 8:238-241.
- Bidleman, T.F., and Olney, C.E. 1974. Chlorinated hydrocarbons in the Sargasso sea atmosphere and surface water. Science 183:516-518.
- Clausen, J., Braestrup, L., and Berg, O. 1974. The content of polychlorinated hydrocarbons in Arctic mammals. Bull. Env. Cont. and Toxic 12:529-534.
- Eisenreich, S.J., Looney, B.B. and Thornton, J.D. 1980. Appendix A to the Science Advisory Board Report to the International Joint Commission 1980.
- Inland Waters Directorate 1979. Analytical methods Manual 1979 and updates, Inland Waters Directorate, Department of the Environment. August 1979.
- Lunde, G., Gether, J., Gjos, N., Lande, M-B.S. 1977. Organic micropollutants in precipitation in Norway. Atmosph. Envir. 11:1007-1014.
- Masahiro, O. and Takahisa, H. 1975. Alpha- and gamma-BHC in Tokyo rainwater (December 1968 to November 1969). Envir. Poll. 9:283-288.
- Murphy, T.J., and Rzeszutko, C.P. 1977. Precipitation inputs of PCB'S to Lake Michigan. J. Great Lakes Res. 3:305-312.

Peterle, T.J. 1969. DDT in Antarctic snow. Nature 224:620.

Smith, JH.H., Bomberger Jr., D.C., and Haynes, D.L. 1981. Volatilization rates of intermediate and low volatility chemicals from water. Chemosphere 10:281-289.

Sodergren, A., Svensson, B., and Ulfstrand, S. 1972. DDT and PCB in south Swedish streams. Env. Poll. 3:25-37.

Strachan, W.M.J., Huneault, H., Schertzer, W.M., and Elder, F.C. 1980. Organochlorines in precipitation in the Great Lakes region. In Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment. ed. Afghan, B.K. and Mackay, D. Plenum Press. p. 387-396.

Strachan, W.M.J. and Huneault, H. 1979. Polychlorinated biphenyls and organochlorine pesticides in Great Lakes precipitation.