



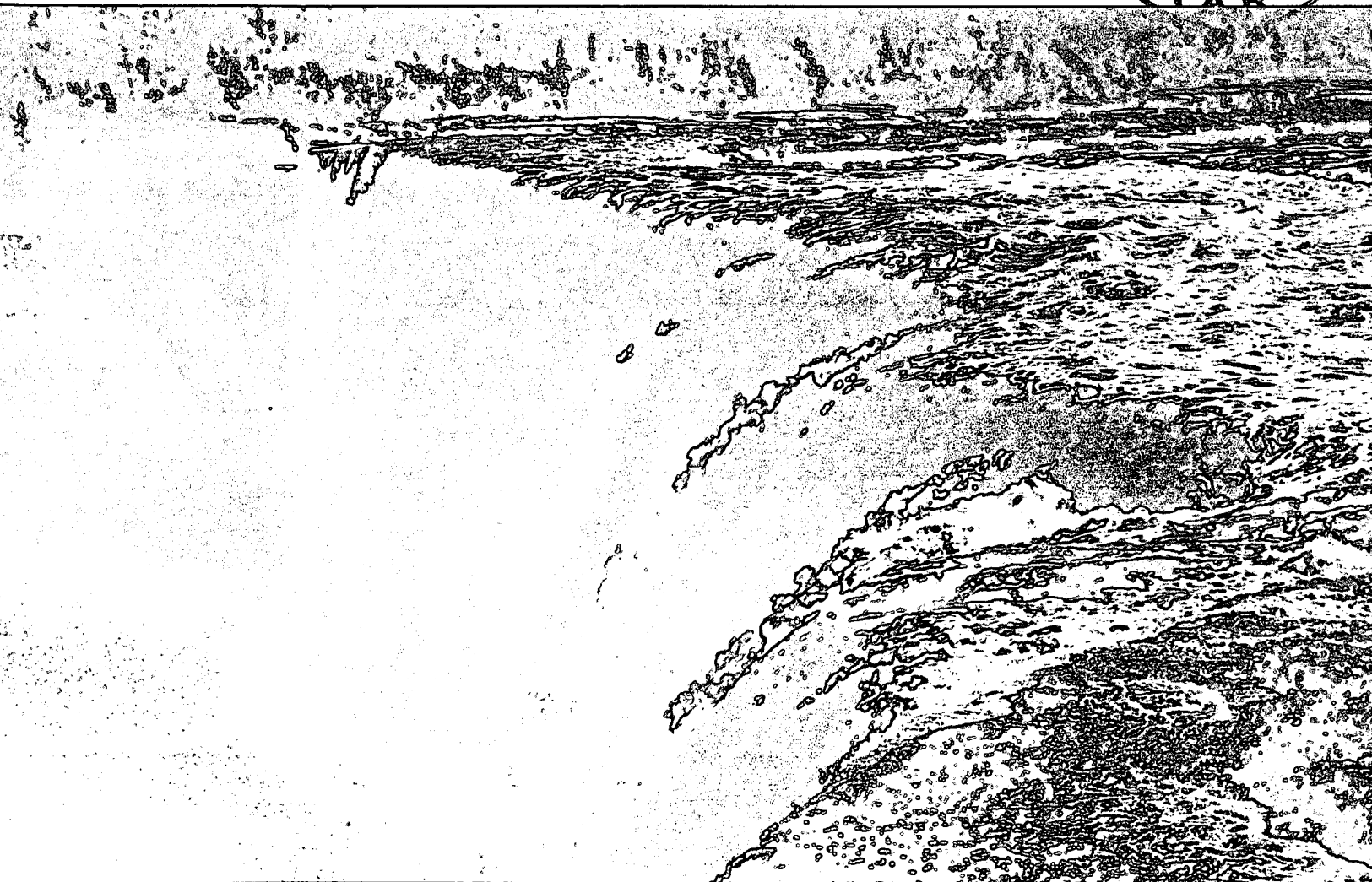
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# Evaluation of an Organic Automated Rain Sampler

W.M.J. Strachan and H. Huneault

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NATIONAL WATER RESEARCH INSTITUTE  
INLAND WATERS DIRECTORATE  
CANADA CENTRE FOR INLAND WATERS  
BURLINGTON, ONTARIO, 1982

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## Abstract

An automated rain sampler has been designed, built and evaluated as a collecting device for persistent organic chemicals in rain. It consists of a large Teflon-coated funnel ( $0.209 \text{ m}^2$ ) with an automated lid and a Teflon column containing XAD-2 or XAD-7 resin. The sampler was tested for recoveries and field precision with a number of organochlorine substances and polychlorinated biphenyls (PCB's) frequently found at the nanogram per litre level in rain. Recoveries averaged 86% and the mean coefficient of variation for  $\alpha$ -BHC, lindane and PCB's was 33% under field conditions where samples of 0.4-22 L of rain were collected. The sampler is recommended for use in network sampling for these persistent organic compounds.

## Résumé

On a conçu, construit et évalué un collecteur automatique de l'eau de pluie et de ses constituants organiques persistants. Il consiste en un grand entonnoir ( $0.209 \text{ m}^2$ ) revêtu de téflon, avec un couvercle relevable automatique et en une colonne de téflon contenant de la résine XAD-2 ou XAD-7. On en a vérifié le taux de récupération et la précision sur le terrain avec un certain nombre d'organochlorés et de biphényles polychlorés (BPC) que l'on trouve fréquemment dans la pluie à une concentration de l'ordre du nanogramme par litre. En moyenne, la récupération a été de 86 %, et le coefficient moyen de variation sur le terrain pour l' $\alpha$ -HCH, le lindane et les BPC a été de 33 %, pour des échantillons de pluie de 0.4 à 22 L. L'utilisation du collecteur est recommandée pour des réseaux d'échantillonnage de composés organiques persistants.

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## INTRODUCTION

Atmospheric deposition of persistent organic chemicals has been identified as a major pathway for their entry into the Great Lakes ecosystem (Eisenreich *et al.*, 1980). These chemicals 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), and the Caribbean (Bidleman and Olney, 1974) 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.*, 1974; Swain, 1978). Compounds such as PCB's, HCB, DDT and isomers of benzene hexachloride have all been noted, with none having vapour pressures indicative of likely presence in the atmosphere. Furthermore, PCB's and DDT have been restricted or banned from North American usage since 1971, which would suggest they should no longer be present in the atmosphere ten years later. Their presence (Murphy and Rzeszutko, 1977; Strachan *et al.*, 1980; Swain, 1978) indicates a need to determine precisely their levels and those of other such chemicals 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 whether these materials are mainly present in the atmosphere either adsorbed onto particulates, as aerosols or in the vapour state. The report by Eisenreich *et al.* (1980) included a review that 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. Although the conclusion is that a high proportion (80% to 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 that 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 are equally unknown. The nature of dryfall samplers is a major difficulty, since most designs to obtain the quantities needed depend upon a flow of air across a filter, which may result in loss of sorbed contaminant from the particulates. In this report wetfall sampling is discussed.

The wetfall deposition of chemicals, which may be either adsorbed onto 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 studies on the quantities deposited have been undertaken in the Great Lakes region (Murphy and Rzeszutko, 1977; Strachan and Huneault, 1979; Swain, 1978). Even then it is seldom that substances other than PCB's or DDT are investigated. Large samples must be collected and the substances concentrated to permit their analytical determination. In this laboratory, we have previously employed large (2 m<sup>2</sup> and 0.36 m<sup>2</sup>) 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 be capable of being left unattended in the field for considerable periods of time without affecting the integrity of the sample. Co-distillation and biological and abiotic transformations make samples stored in the aqueous phase suspect. These factors along with 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. Therefore a sampler that could be used for sampling both types of situation (monthly and event) was required. A surface area of approximately 0.2 m<sup>2</sup> was indicated to acquire samples of at least 1 L. This volume is necessary to reach the quantification limits of 0.5–5.0 ng of compound per sample based on concentrations observed in the area (Strachan *et al.*, 1980).

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.

The sampler was constructed by M.I.C. Co. (Thornhill, Ontario) 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 × 0.46 m) and a lid, both of which are constructed of stainless steel. A funnel

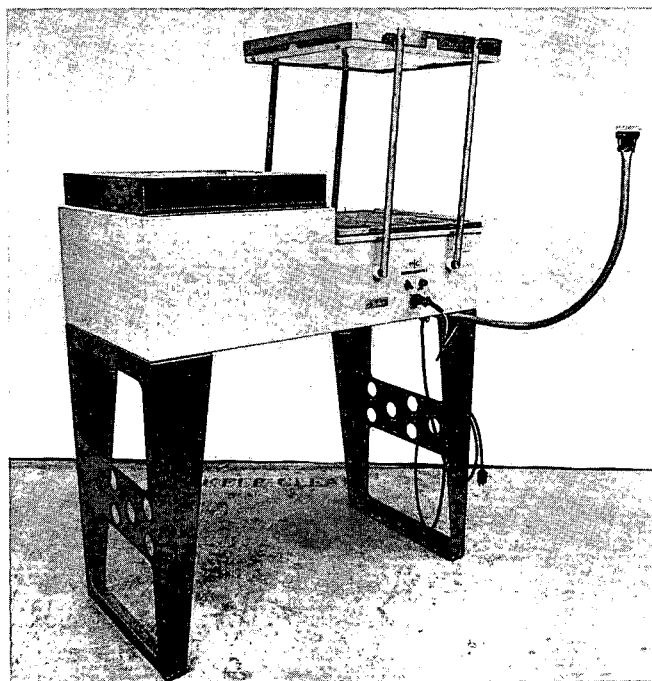


Figure 1. Organic automated rain sampler (lid half open).

lip of 10 cm is used, and the funnel surface is sloped 20° toward the centre 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 in.) cast aluminum and are detachable for transport. Splash from horizontal surfaces into the sampler is eliminated by the use of stainless steel screening. The total weight of the sampler is 47 kg. The overall dimensions of the closed sampler are 0.5 m (width) × 1 m (length) × 1.2 m (height); 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 hp fractional gear motor at 120 V AC. A small heater in the central electrical chassis avoids condensation which would otherwise occur.

The outlet of the funnel is threaded to receive an all-Teflon column (2 cm I.D. × 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 remains 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 3 h with acetone and then 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- to 40-mL resin bed) and washed with five to ten bed volumes of organic-free water. While it was not done for this report, the columns can be detached and capped, thus providing a suitable conveyance for mailing the resin; they can also be provided to field personnel in a pre-washed condition.

## EXPERIMENTAL

### Recoveries

A stock solution of approximately 0.1–0.5 mg/mL of each of a number of organochlorines was made up in acetone. Spikes (2.0 µL) 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 min of stirring, three of these samples were slowly poured over the surface of the funnel and then 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 and extracted with 50–75 mL ether, 1 mL iso-octane keeper was added, and then they were concentrated to 1 mL. The concentrates were analyzed by chromatography (25 m OV-1 capillary column, programmed from 90°C to 260°C at 4°/min, electron capture detector). Results of these recovery experiments are presented in Tables 1a and 1b for both the XAD-2 and XAD-7 resins.

Table 1a. Recoveries for XAD-2 Resin

	Test conc. (µg/L)	Mean (µg/L)	C.V. (%)	Recovery (%)
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
p,p'-DDT	0.41	0.35	25	85
Average recoveries				86

Table 1b. Recoveries for XAD-7 Resin

	Test conc. (µg/L)	Mean (µg/L)	C.V. (%)	Recovery (%)
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
p,p'-DDE	0.54	0.29	9	53
p,p'-TDE	0.41	0.29	4	80
p,p'-DDT	0.36	0.21	7	57
Methoxychlor	0.51	0.29	12	58
Average recoveries				68

\*Value not included in average.

## Field

Precision of the total sampling and analysis technique was assessed for normal field conditions. Three samplers were employed to collect samples from a Canada Centre for Inland Waters field site at Fifty Mile Point near Hamilton, Ontario, which is 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, which is a "remote" area 50 km from that city of 80 000 persons. Collections there occurred during June, July and August of 1981. At both locations, a tipping-bucket rain gauge was employed to measure rainfall, and collected volumes were calculated using millimetres of precipitation and the area of the collecting funnel (0.209 m<sup>2</sup>). 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 and away from any objects of equivalent or greater height. Details of the samples are given in Table 2. Field samples were analyzed as described above but with an additional cleanup step according to established procedures of the Inland Waters Directorate (Environment Canada, 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 per sample) are reported. In addition to the substances presented in Table 3, others investigated (and their limits in nanograms per sample) included hexachlorobenzene (0.5), heptachlor epoxide (1.0), α-chlordane (1.0), p,p'-DDE (1.0), p,p'-TDE (4.0), mirex (2.0) and methoxychlor (5.0). Some of these were observed at trace levels.

## DISCUSSION

In the laboratory recovery experiments reported in Tables 1a and 1b, the mean coefficient of variation for

Table 2. Field Sampling Details

Location	Sample No.	Dates*	Rainfall	
			(mm)	(L)
Fifty Mile Point	50-1104	81-04-08 to 81-04-13	2.0	0.42
	50-1404	81-04-13 to 81-04-14	9.9	2.07
	50-2404	81-04-22 to 81-04-27	10.2	2.12
	50-2804	81-04-27 to 81-04-29	10.4	2.18
	50-0505	81-04-29 to 81-05-06	4.8	1.01
Turkey Lakes	TL-0206	81-06-02 to 81-06-04	86.1	18.0
	TL-0406	81-06-04 to 81-06-09	15.5	3.23
	TL-0906	81-06-09 to 81-06-12	20.0	4.18
	TL-1806	81-06-18 to 81-07-10	106.	22.2
	TL-1007	81-07-10 to 81-08-14	72.	15.0

\*The samples were collected for the entire period of time indicated and corresponded to integer numbers of individual rainfall events.



Table 3. Field Sampling Results

Sample No.	$\alpha$ -BHC (ng/L)	Lindane (ng/L)	$\gamma$ -Chlordane (ng/L)	Dieldrin (ng/L)	p,p'-DDT (ng/L)	Endosulfan (ng/L)	Endrin (ng/L)	PCB's (ng/L)
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 C.V. (%)	(27)	(30)	(20)	(12)	(38)	(37)	(49)	(42)
Quantitation limit (ng/sample)	0.5	0.5	1.0	1.0	3.0	1.5	2.0	5.0

\*Numbers in parentheses indicate percent coefficient of variation (C.V.).

the test compounds was 13% (range 3% to 25%) for the XAD-2 resin; the corresponding average for XAD-7 resin was 8% (range 4% to 16%) when heptachlor was excluded. These values are comparable to the precision obtained for the gas chromatographic calibration standards (mean 9%, range 5% to 12%) and are better than the average 25% reported by Environment Canada (1979). This latter improvement could possibly result from the cleanup 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 (Tables 1a and 1b) averaged 86% (range 73% to 98%) and 68% (range 42% to 103%), respectively. The XAD-2 results compare favourably with those obtained in the Inland Waters Directorate laboratories where 80% was the average with 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 of the field sampling, but for substances other than those investigated here, XAD-7 may offer some advantages. It may be worth considering a mixed resin bed 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 the compounds reported in Table 3, methoxy-

chlor, heptachlor epoxide and p,p'-DDE were occasionally found at levels below the quantification limits. The usefulness of these data in evaluating sampling precision is questionable. Since only  $\alpha$ -BHC, lindane ( $\gamma$ -BHC) and PCB's were observed with any degree of frequency and quantitative significance, only these are discussed here.

The coefficients of variation for  $\alpha$ -BHC, lindane and PCB's in the field samples averaged 27%, 30% and 42%, respectively. The corresponding value for water samples reported by Environment Canada (1979), as noted previously, was 25% for replicate analyses on single samples. Therefore it would appear 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 affecting 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 that the latter is the cause, but this is by no means certain. The 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 substances in rainfall including both particulate and dissolved forms. It is not

appropriate for dryfall or for snow during the winter months, although efforts are underway to modify it for the latter purpose (C.H. Chan, Inland Waters Directorate, 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. Although few quality control studies have ever been attempted for this type of sample, 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 the Inland Waters Directorate and the Atmospheric Environment Service of Environment Canada.

### ACKNOWLEDGMENTS

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