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FIELD TESTING OF A LARGE VOLUME LIQUID-LIQUID EXTRACTION DEVICE FOR TRACE ORGANICS IN NATURAL WATERS

B.G. Oliver and K. Nicol

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Environmental Contaminants Division
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, Canada L7R 4A6

MANAGEMENT PERSPECTIVE

The APLE extractor could provide a useful monitoring tool to find out whether or not loading objectives are being met. Many of the critical detailed methodology and data quality questions about the APLE extractor have been answered in this paper.

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POINT DE VUE DE LA DIRECTION

L'extracteur APLE pourrait constituer un outil de contrôle utile pour déterminer si l'on a atteint ou non les objectifs relatifs à la charge de produits chimiques. Cette communication répond à de nombreuses questions importantes concernant les détails des méthodes et la qualité des données obtenues avec l'extracteur APLE.

Essais in situ d'un extracteur liquide-liquide à grand volume servant à extraire des produits organiques dans les eaux canadiennes

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EXECUTIVE SUMMARY

In this paper we report the laboratory testing and (more importantly) the field testing of a large volume (200 L) liquid-liquid extraction device (APLE) developed by the Ontario Region, Water Quality Branch and the Engineering Section at CCIW. The device permits the lowering of the detection limits for organic contaminants by two orders of magnitude (100) over conventional 1 - 2 L volume samples. The extractor is particularly useful in situations like the Niagara River where even though concentrations can be low the large flow can still lead to significant chemical loading (for example a chemical concentration of 1 ng/L in the Niagara River corresponds to a loading of 200 kg/year to Lake Ontario).

Extraction of both laboratory (4 samples) and field (24 samples) samples showed that the device could extract organics efficiently (40-70%) and reproducibility (±20%). Detailed concentration and cleanup procedures for the sample extract are described. These procedures must be closely followed to maintain sample integrity. The addition of surrogate spikes (chemicals with similar properties to the contaminants but which are not present in the sample) to each sample at the time of collection is recommended as a quality assurance technique.

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RÉSUMÉ À L'INTENTION DE LA DIRECTION

Ce rapport décrit l'essai en laboratoire et (ce qui est plus important) l'essai *in situ* d'un extracteur liquide-liquide à grand volume (200 L) (extracteur APLE) mis au point par la Direction de la qualité des eaux de la Région de l'Ontario et la Section technique du Centre canadien des eaux intérieures. Cet extracteur permet d'obtenir, dans le cas de contaminants organiques, des limites de détection 100 fois plus faibles (deux ordres de grandeur) que celles obtenues avec des échantillons classiques de 1 ou 2 litres. L'extracteur est particulièrement utile dans des situations comme celle de la rivière Niagara où un débit élevé peut néanmoins produire un apport important de produits chimiques, malgré des concentrations faibles (par exemple, une concentration de 1 ng/L dans les eaux de la rivière Niagara se traduit par un apport de 200 kg/an dans le lac Ontario).

L'extraction d'échantillons en laboratoire (4 échantillons) et *in situ* (24 échantillons) a révélé que l'extracteur permettait d'extraire les produits organiques de façon efficace (40-70 p. 100) et reproductible ($\pm$ 20 p. 100). On décrit en détail les méthodes de concentration et de purification des extraits. Il faut suivre ces méthodes à la lettre pour maintenir l'intégrité des échantillons.

Comme technique d'assurance de la qualité, on recommande, au moment du prélèvement, d'enrichir chaque échantillon avec un produit substitut (c.-à-d. un produit présentant des propriétés semblables à celles des contaminants mais que l'on ne retrouve pas dans l'échantillon).

Essais in situ d'un extracteur liquide-liquide à grand volume servant à extraire des produits organiques dans les eaux canadiennes

ABSTRACT

The testing of a large volume (200 litre) liquid-liquid extractor for trace organics in the laboratory and in the field is described. The recovery efficiency of the device, as measured by laboratory spiking experiments and field spiking of five surrogate chemicals, was reasonably consistent and in the 40-70% range. Concentration and cleanup procedures for the extract are described in detail. The device reduces the detection limits of the organic chemicals by one or two orders of magnitude over those achieved with conventional small volume (1-10 L) samples.

RÉSUMÉ

On décrit l'essai d'un extracteur liquide-liquide à grand volume (200 litres) servant à extraire en laboratoire et *in situ* des produits organiques à l'état de trace. Les taux de récupération de l'extracteur, mesurés par enrichissement en laboratoire et *in situ* avec cinq produits substituts, concordaient raisonnablement bien et étaient de l'ordre de 40-70 p. 100. Les méthodes de concentration et de purification des extraits sont décrites en détail. Cet extracteur permet d'obtenir des limites de détection de 10 à 100 fois plus faibles que celles obtenues avec des échantillons classiques de faible volume (1 à 10 L).

Essais *in situ* d'un extracteur liquide-liquide à grand volume servant à extraire des produits organiques dans les eaux canadiennes.

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INTRODUCTION

In most environmental research, there is a need to measure the concentration of organic chemicals in the water phase. For wastewater samples, simple liquid-liquid extraction procedures on sampler volumes of 4L or less are usually adequate to provide sufficient analytical sensitivity. When wastewater discharges have been diluted and chemicals are lost from the water phase by volatilization and/or association with suspended sediments or biota, the concentrations in the aqueous phase are usually very low (less than 1 ng/L)[1,2]. In a large river such as the Niagara (flow 6400 m^3/s), a concentration of 1 ng/L in the water phase corresponds to a loading of 200 Kg/y of chemical to Lake Ontario[3]. So measurement of concentrations in the subnanogram-per-liter range is sometimes necessary to see whether loading objectives are being met.

In this paper we describe the testing of a large volume, 200 liter, aqueous phase liquid-liquid extraction device, APLE, which can be used to lower detection limits to well below 1 ng/L for many chlorinated organic chemicals. Several investigators[4,5] have described continuous flow liquid-liquid extraction devices of partial glass construction. The APLE extractor is constructed of metal and is rugged enough for use in small boats in the field.

EXPERIMENTAL

The design of the APLE extractor has been described in detail by McCrea et al.[6,7]. Briefly, the extractor consists of a 200 L stainless-steel barrel and a circulating pump. The pump sprays dichloromethane (DCM) through the sample as fine droplets with the aid of a spray bar mounted in the barrel. In the field a water sample is pumped from the required depth using a submersible pump and Teflon-lined stainless steel tubing. The sample is then passed through a Westfalia continuous-flow centrifuge at 5-6 L/min to remove the suspended sediments and then into the extractor. After the extractor is half-filled with water, 10 mL of a methanol solution containing five surrogate spiked chemicals is added, and then the drum is filled to the 200 L mark. Eight liters of high purity DCM are then added to the extractor and the water is extracted for a period of 30 min. The pump is shut off and the extractor is allowed to stand for 15 min before the DCM is drained out of the bottom valve back into the original DCM containers. Only about 5-6 L of DCM is recovered because of its finite solubility in water. The approximate total time required for processing a sample is 90 min.

In the laboratory the DCM is placed in a large (5 L) round bottom flask with 30 mL of hexane and evaporated to ≈100 mL at a rate of 1 L/hr using a heating mantel and a 12-ball Snyder condenser. This extract is filtered through Na_2SO_4 into a 100 mL evaporation flask

(100 mL round bottom with 2 mL conical portion of a centrifuge tube attached)[8] and evaporated to 1 mL with a Kurderna-Danish, K-D, condenser using a water bath. This 1 mL extract is cleaned up through an 8 mm I.D. by 100 mm long disposable pipette packed with 1 cm Na_2SO_4 (top), 4 cm 40% H_2SO_4 on silica gel, and 2 cm of Florisil (deactivated with 5% water). A total of 10 mL of hexane eluate is collected and this is reevaporated to 1 mL using the evaporation flask and K-D condenser. The evaporation and cleanup procedures for 200 mL extracts have previously been shown to recover greater than 80% of the study chemicals[9,10].

A list of the 28 study compounds and the five surrogate chemicals, their abbreviations and detection limits for 200 liter water samples at a signal to noise ratio of 5 to 1 are shown in Table I. The bromobenzenes were chosen as surrogates because they have similar properties to the chlorobenzenes and chlorotoluenes, and because they have not been produced in significant quantities in the study area. PCB 65 was chosen as a surrogate for the PCB's because it is absent from industrial PCB mixtures (Aroclor, Clophens)[12]. Octachloronapthalene was selected as a surrogate for highly chlorinated chemicals of low volatility and because it is not produced industrially in significant quantities. A scan of Niagara River water extracts showed that none of the above surrogate compounds were present.

Quantification was carried out using dual, 30 m, fused silica capillary columns (SE54 and OV17) in a Varian 4600 gas chromatograph equipped with electron capture detectors. Splitless injection with an autosampler was employed and the gas chromatographic conditions were: injector, 250°C; detectors, 350°C; columns, 50-250°C at 1°C/min, 20 min final hold; carrier gas helium, linear velocity 20 cm/s. The mean concentration from the two columns was used except when discrepancies between the columns were greater than 20% in which case the lowest value was used. The precision of replicate injections of the sample extract was ±10%.

RESULTS AND DISCUSSION

The APLE extractor was first tested in the laboratory to determine its recovery efficiency for the study chemicals. Two hundred liters of carbon filtered Lake Ontario water was first extracted with DCM in the extractor to remove interfering organics. Next 1 mL of a concentrated stock solution containing the 28 organics and five surrogate compounds in methanol was added to the drum and mixed into the sample. The sample was then extracted with DCM as described in the experimental section. After the DCM was removed from the drum, a second extraction with DCM was performed to assess the efficiency of the first extraction. This experiment was repeated four times. In addition, 1 mL of concentrated stock solution was added

directly to 8 L of DCM and this DCM extract was taken through the entire concentration and cleanup procedure. A DCM blank (8 L of DCM to 1 mL) was run for each batch of DCM employed during the experiments and the field trials. With one exception, 1,2-DCB, there was minimal, if any interferences in the DCM. The blank for 1,2-DCB was, however, too high to permit any useful data to be generated for this chemical in the spiking experiment, but some data was generated in the field trials because different DCM batches or lots were used.

A summary of the data showing the spiking concentrations, the recoveries for the first and second extraction and for the direct evaporation experiment are shown in Table II. In general, the recoveries are good using the APLE extractor, although they are somewhat lower than those reported for direct liquid-liquid extraction of smaller volume samples[3,10]. Very little is recovered by the second extraction with DCM indicating that a single extraction with 8 L of DCM provides efficient recovery. A comparison of the APLE data with the recoveries from the concentration and cleanup of the directly spiked DCM shows close agreement. This strongly indicates that the major losses of chemicals is due to volatilization during the sample concentration from 5 to 8 L down to 1 mL (as mentioned earlier, minimal losses occur during the cleanup stage). The reproducibility of the recovery was good with the average standard deviation expressed as a percentage of ±11%. Table II also shows that the recovery of the surrogate compounds is in excellent agreement with those of the study chemicals.

The safest way to apply the APLE extractor for environmental samples is to add a surrogate spike to each sample as described in the experimental section. This allows one to obtain a recovery efficiency for each sample. Data for the five surrogate spikes for 24 samples - 12 from Lake Ontario, six from the Niagara River and six from the Detroit River - are shown in Table III. The data shows that the recoveries of the spike for the various samples is reasonably consistent and in good agreement with the laboratory recovery studies. The standard deviation in recovery expressed as a percentage is ±21%, about twice that observed for the laboratory samples. In a few cases the recoveries are too high, indicating a positive interference (perhaps the chemical itself) in the sample. In other cases low recoveries are obtained, perhaps due to incomplete recovery of DCM from the extractor during rough or stormy weather. The mean recoveries for the five chemicals exhibit a smaller range and standard deviation than observed for individual surrogates. We suggest that the mean recovery of the five chemicals (excluding outliers) be used to correct the observed concentrations. For example if the mean recovery of surrogate spikes was 50% in the sample, all the concentration data would be multiplied by two to obtain the actual water concentration for the chemical.

A comparison of direct liquid-liquid hexane extraction of 4 L samples[10] to APLE extractor data for four Niagara River samples is shown in Table IV for several chlorobenzenes that could be detected in

both extracts. Fairly good agreement between the methods is exhibited, average deviation ±29%, especially when it is considered that most of these chemicals were close to detection limits in the 4 L sample. Approximate detection limits for the 4L samples were: 1,4-DCB, 4 ng/L; 1,2,4-TCB, 0.3 ng/L; 1,2,3-TCB and 1,2,4,5-TeCB, 0.2 ng/L; and 1,2,3,4-TeCB, 0.1 ng/L.

An illustration of the application of the extractor to samples from Lake Ontario, and the Niagara and Detroit Rivers is shown in Table V. The chemical concentrations, particularly in the lake, are seen to be extremely low. Previous methods, which employed much smaller volume samples, would simply produce "ND's" or "not detected" values for most of the study chemicals, especially in Lake Ontario. These concentrations are mean values from a single sampling cruise at each site so we do not know how representative the data is for these waterbodies.

In summary, it has been shown that a large volume APLE sampler can be used to efficiently extract trace organic chemicals from water. The critical step in the recovery procedure appears to be the evaporation of the solvent from 5 - 8 L to 1 mL. This step must be performed carefully by a similar procedure to the one described here in order to maintain the integrity of the sample. It is also recommended that surrogate spikes be added to the sample at the time of collection so recovery data for each sample can be obtained and appropriate correction factors can be applied.

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TABLE I. Study Chemicals, Abbreviations and Detection Limits for 200L Water Sample.

Chemical	Abbreviation	Detection Limit (pg/L in water sample)
1,3-dichlorobenzene	1,3-DCB	25
1,4-dichlorobenzene	1,4-DCB	50
1,2-dichlorobenzene	1,2-DCB	25
1,3,5-trichlorobenzene	1,3,5-TCB	3
1,2,4-trichlorobenzene	1,2,4-TCB	3.5
1,2,3-trichlorobenzene	1,2,3-TCB	2
1,2,4,5-tetrachlorobenzene	1,2,4,5-TeCB	2
1,2,3,4-tetrachlorobenzene	1,2,3,4-TeCB	1
Pentachlorobenzene	QCB	0.5
Hexachlorobenzene	HCB	0.5
2,4,5-trichlorotoluene	2,4,5-TCT	3
2,3,6-trichlorotoluene	2,3,6-TCT	2.5
Pentachlorotoluene	PCT	0.5
2,5,2'-trichlorobiphenyl	PCB 18*	4
2,5,2',5'-tetrachlorobiphenyl	PCB 52	3
2,3,2',3'-tetrachlorobiphenyl	PCB 40	2
2,4,5,2',5'-pentachlorobiphenyl	PCB 101	2.5
2,4,5,2',4',5'-hexachlorobiphenyl	PCB 153	2.5
2,3,4,5,2',3',4,',5'-octachlorobiphenyl	PCB 194	2.5
Mirex	Mirex	3
1,1-dichloro-2,2-bis(p-chlorophenyl)-ethylene	p,p'-DDE	1
1,1,1-trichloro-2,2-bis(4-chlorophenyl)-ethane	p,p'-DDT	2.5
a and γ-1,2,3,4,5,6-hexachlorocyclohexane	α-BHC,γ-BHC	1
α and γ-chlordane	α-chlor, γ-chlor	1
Hexachlorobutadiene	HCBD	0.5
Octachlorostyrene	OCS	1
Surrogate Chemicals		
1,3-dibromobenzene	1,3-DBB	1.5
1,3,5-tribromobenzene	1,3,5-TBB	0.5
1,2,4,5-tetrabromobenzene	1,2,4,5-TeBB	0.5
2,3,5,6-tetrachlorobiphenyl	PCB 65	1.5
Octachloronaphthalene	OCN	1.5

* PCB numbering system of Ballschmiter and Zell[11].

TABLE II. APLE Extractor and Method Recovery Data (%) from Spiked Lake Ontario Water.

Chemical	Spiked Concentration (ng/L)	APLE First Extract	APLE Second Extract	Concentration/ Cleanup Method
1,3-DCB	1.5	43± 3	0	42± 2
1,4-DCB	3.3	41± 5	3± 1	47± 2
1,2-DCB	1.5	I*	I	I
1,3,5-TCB	0.3	58± 10	3± 1	57± 3
1,2,4-TCB	0.3	53± 8	3± 1	50± 1
1,2,3-TCB	0.1	53± 5	2± 1	51± 2
1,2,4,5-TeCB	0.2	63± 2	4± 2	62± 5
1,2,3,4-TeCB	0.1	54± 7	3± 1	59± 4
QCB	0.04	62± 2	6± 2	56± 5
HCB	0.05	67± 2	6± 2	71± 3
2,4,5-TCT	0.3	59± 5	4± 2	58± 3
2,3,6-TCT	0.3	56± 8	3± 1	57± 2
PCT	0.06	64± 3	4± 1	67± 3
PCB 18*	0.3	66± 6	7± 2	73± 4
PCB 52	0.2	68± 4	10± 3	73± 6
PCB 40	0.1	74± 5	7± 2	77± 4
PCB 101	0.1	69± 15	10± 3	76± 7
PCB 153	0.1	75± 12	9± 2	74± 7
PCB 194	0.1	70± 17	6± 1	79± 4
Mirex	0.1	76± 11	6± 2	72± 4
p,p'-DDE	0.1	73± 16	6± 2	74± 6
p,p'-DDT	0.1	63± 10	4± 1	71± 3
α-BHC	0.1	63± 9	6± 2	62± 2
γ-BHC	0.1	63± 4	3± 1	65± 2
α-chlor	0.1	69± 8	5± 1	76± 5
γ-chlor	0.1	66± 7	5± 1	71± 7
HCBD	0.03	53± 4	4± 2	54± 1
OCS	0.05	63± 9	10± 2	83± 3
1,3-DBB	0.1	59± 8	3± 1	50± 2
1,3,5-TBB	0.05	61± 6	3± 1	54± 1
1,2,4,5-TeBB	0.05	61± 2	3± 1	60± 2
PCB 65	0.1	62± 3	4± 2	68± 3
OCN	0.1	67± 2	4± 1	75± 1

*Interference from solvent.

TABLE III. Recovery of Surrogate Spikes from Lake Ontario (LO), Niagara River (NR) and Detroit River (DR) Samples.

Chemical	LO1	LO2	LO3	LO4	LO5	LO6	LO7	LO8	LO9	LO10	LO11	LO12
1,3-DBB	86*	108*	90*	43	51	52	57	56	55	69	32	60
1,3,5-TBB	57	58	180*	52	64	54	49	61	56	64	49	55
1,2,4,5-TeBB	64	59	55	58	67	59	49	63	54	66	46	63
PCB65	51	58	50	64	45	55	51	67	53	68	33	62
OCN	44	55	40	56	65	56	45	61	49	62	34	57
Sample Mean	54±9	58±2	50±6	55±8	58±10	55±3	50±4	62±4	53±3	66±3	39±8	59±3

	NR1	NR2	NR3	NR4	NR5	NR6	DR1	DR2	DR3	DR4	DR5	DR6	Overall
1,3-DBB	102	70	54	48	61	63	55	55	59	64	77	68	60±14
1,3,5-TBB	83	72	68	49	65	56	50	70	53	42	57	48	58±9
1,2,4,5-TeBB	77	67	71	45	69	55	53	61	46	45	54	44	58±9
PCB65	82	64	50	50	62	65	55	66	45	32	51	41	55±12
OCN	67	67	64	51	75	62	67	58	46	16	52	28	53±14
Sample Mean	82±13	68±3	61±9	49±2	66±6	60±4	56±7	62±6	50±6	40±18	58±11	46±14	57±9

* Excluded from mean because of positive interference.

TABLE IV. A Comparison of Chlorobenzene Concentrations in four Niagara River Samples by the APLE Extraction Method (200L sample) and the Hexane Liquid-Liquid Extraction Method (4L sample).

Chemical	NR1		NR3		NR4		NR6	
	APLE	LLE	APLE	LLE	APLE	LLE	APLE	LLE
1,4-DCB	3.0	5.2	2.1	4.4	2.2	4.2	2.5	3.2
1,2,4-TCB	2.5	2.2	2.7	4.6	2.6	3.0	1.5	3.2
1,2,3-TCB	0.84	0.74	0.81	0.57	0.76	0.51	0.43	0.36
1,2,4,5-TeCB	0.42	0.55	0.47	0.39	0.50	0.55	0.31	0.31
1,2,3,4-TeCB	1.2	1.3	1.1	0.81	1.1	0.76	0.72	0.85

TABLE V. Mean Concentrations from a Single Sampling Cruise in Lake Ontario, Niagara River and Detroit River as Determined with the APLE Extractor (ng/L).

Chemical	Lake Ontario	Niagara River	Detroit River
1,3-DCB	0.07	2.0	0.4
1,4-DCB	1.7	5.7	7.1
1,2-DCB	1.0	4.5	0.4
1,3,5-TCB	0.05	0.1	0.07
1,2,4-TCB	0.4	3.8	0.4
1,2,3-TCB	0.1	1.0	0.1
1,2,3,5-TeCB	0.02	0.07	0.02
1,2,4,5-TeCB	0.05	0.5	0.1
1,2,3,4-TeCB	0.09	0.9	0.05
QCB	0.05	0.2	0.07
HCB	0.09	0.1	0.1
2,4,5-TCT	0.04	2.4	0.08
2,3,6-TCT	0.04	2.4	ND
PCT	0.02	0.09	ND
PCB 18	0.1	0.2	0.4
PCB 52	0.08	0.1	0.2
PCB 40	ND*	0.04	0.02
PCB 101	0.1	0.2	0.1
PCB 153	0.02	0.03	0.04
PCB 194	ND	ND	ND
Mirex	0.02	ND	ND
p,p'-DDE	0.08	0.1	0.1
p,p'-DDD	0.05	0.05	0.03
p,p'-DDT	0.01	0.03	0.01
α-BHC	5.8	5.1	5.6
γ-BHC	0.9	1.0	0.6
γ-chlor	0.02	0.04	0.04
HCBD	0.01	0.2	0.1
OCS	0.003	0.007	0.009

* Not Detected