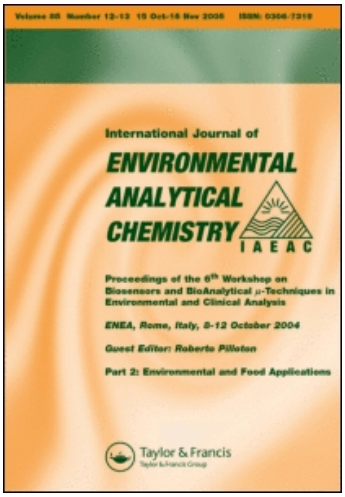

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Hassan Sabik[a]
[a] Environment Canada, St. Lawrence Centre, Quebec, Canada

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GRAPHITIZED CARBON BLACK CARTRIDGES FOR MONITORING POLAR PESTICIDES IN LARGE VOLUMES OF SURFACE WATER

HASSAN SABIK*

Environment Canada, St. Lawrence Centre, 105 McGill Street, 7th Floor, Montreal, Quebec Canada H2Y 2E7

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A method was developed to analyse 20 polar pesticides-9 organophosphorus, 9 organonitrogens and 2 degradation products of atrazine-simazine and propazine-in large volumes of surface water (1–20 L). During a recent study in our laboratory, the majority of these chemicals ($2 < \text{Log } K_{oc} < 4$) were found in the dissolved phase. This paper presents a new extraction method for pesticides in the dissolved phase, using a fibre glass filter with 0.7 μm porosity. Samples of filtered surface water (1–20 L) were extracted by means of a solid-phase technique, using cartridges filled with 500 mg of Carbopack B (60/80 mesh) graphitized carbon black as adsorbent. The pesticides were monitored by gas chromatography on two DB-5 and DB-210 capillary columns with a nitrogen-phosphorus detector (GC-NPD). With the exception of metribuzin, phosmet and anilazine, percent recoveries were high (70–100 %) for all pesticides in a volume of 17.85 L of Milli-Q water compared to percent recoveries in the same volume of filtered surface water (51–93%). Detection limits ranged from 0.1–4 ng/L.

Keywords: Surface water; polar pesticides; Carbopack B; SPE; large-volume extraction; colloids

INTRODUCTION

Previous studies have confirmed the presence of pollutants in the St. Lawrence River[1–3]. Because of the large-scale dilution of contaminants in the river, concentrations of many chemicals are below the detection limits of standard analytical and sampling methods[4–5]. A method was recently developed in our laboratory for the liquid-liquid extraction of organophosphorus and organonitrogen pesticides using the Goulden large-sample extractor (GLSE) followed by gas chromatography with nitrogen-phosphorus detector (GC-NPD)[6]. Although efficient and capable of reaching ng/L levels for the pesticides selected, this method

* Corresponding author. Fax: +1-514-496 7398. E-mail: hassan.sabik@ec.gc.ca.

was unable to determine the degradation products of some triazines. Furthermore, it requires large volumes of solvent (1 L of dichloromethane for each sample of water). Taking this into account, and given the dearth of information in the literature, a new method was needed to permit the simultaneous extraction and analysis of parent pesticides and their degradation products in large volumes of surface water, using less solvent.

Conventional liquid-liquid and solid-phase extraction (SPE) techniques use water samples of 1–2 litres[7–12]. However, they provide only a 1000- to 5000-fold concentration of the analytes, and are thus insufficient to detect such low levels as ng/L. To circumvent this problem, a 50 000-fold or greater concentration is needed.

Alternative techniques like solid-phase micro-extraction (SPME)[13,14] and semi-permeable membrane device (SPMD)[15,16] were used successfully in the 1980s to extract analytes from aqueous samples. However, the former technique is used only for small sample volumes (1–5 mL) and provide a 1000- to 5000-fold concentration of the analytes. The latter technique uses a thin film of neutral lipid and is capable of extracting only non-polar contaminants.

SPE is by far the best method to isolate pesticides in water[9,11], but the specific nature of adsorbents and the size of particles available commercially limit its use for large-volume water samples (>5 L). Molto et al. (1991) demonstrated that, with C_{18} solid-phase extraction cartridges, recoveries of organophosphorus pesticides decrease when water samples reach a volume of 10 L. They concluded that the best recovery rate was achieved using 1-L samples. There are several reports in the literature of methods employing cartridges filled with different types of graphitized carbon black material (Carbopack B 120/400 mesh, Carbograph, etc.)[8,9]. Di Corcia et al. (1993) demonstrated that it was possible to extract simultaneously organophosphorus and organonitrogen pesticides and some of their degradation products from water with the Carbopack B (120–400 mesh), provided that sample volumes not exceed 1 L for drinking water and 0.5 L for surface water. Albanis and Hela[12] used C_{18} Empore solid-phase extraction discs with 1-L samples for multi-residue pesticide analysis.

The aim of this study was as follows:

i. To select the graphitized carbon black adsorbent and the particle size appropriate to the best percent recoveries for organophosphorus and organonitrogen pesticides and their degradation products in large volumes of surface water.

ii. To determine the parameters affecting percent recoveries for the target pesticides.

This paper describes a method for the extraction and analysis of 18 organophosphorus and organonitrogen pesticides and two degradation products of atrazine-simazine and propazine in large volumes of surface water. Samples of surface water (1–20 L) were filtered on fibre glass filters (0.7 μm), then extracted by solid-phase extraction using cartridges filled with 500 mg of Carbopack B (60/80 mesh) graphitized carbon black adsorbent. The pesticides were analysed by gas chromatography on two capillary columns (DB-5 and DB-210) with a nitrogen-phosphorus detector (GC-NPD).

MATERIALS AND METHODS

Reagents and chemicals

All pesticides were obtained from different suppliers. Ametryn, azinphos-ethyl, ethion (used as surrogate), malathion, parathion-methyl, phosmet, propazine and simazine were obtained from U.S. EPA. Azinphos-methyl, EPN, fonofos and tetrachlorvinphos (used as internal standard) were purchased from Chem Service (West Chester, Pa., U.S.A.). Atrazine, cyanazine, desethylatrazine, desisopropyl-atrazine, metribuzin, metolachlor and prometryn (used as surrogate) were purchased from Riedel-de-Haën, distributed by Fisher Scientific (Montreal, Que., Canada). Diazinon was obtained from Ultra-Scientific, distributed by Fisher Scientific. Anilazine was obtained from PolyScience Corp., distributed by Chromatographic Specialties (Brockville, Ont., Canada).

Ethyl acetate and hexane (both distilled-in-glass grade) were purchased from Caledon Laboratories Ltd. (Georgetown, Ont., Canada) and used without further cleanup. Anhydrous sodium sulfate was heated at 650°C overnight, then cooled in a dessicator before use. Reagent water was taken from a Milli-Q-UV Plus reagent-grade water system from Millipore (Bedford, Mass., U.S.A.).

A 293-mm Millipore stainless steel filter holder and 293-mm-diameter Gelman fibre glass filter (TCLP type with 0.7 μm nominal porosity) were used. The filters had been previously fired at 450°C overnight and kept in a clean Teflon bag before use.

Twenty-litre stainless steel pressure containers (containing 17.85 L of liquid), purchased from Spartanburg Steel Products (Spartanburg, S.C., U.S.A.), were used to collect and store samples.

Standard solutions

Primary stock solutions of all pesticides were prepared individually at a concentration of 1 mg/mL by weighing about 10 mg of each substance in a 10-mL volu-

metric flask and diluting to volume with ethyl acetate. Spiked solutions of the target pesticides were then prepared from these solutions in the same solvent at concentrations of 0.5–1 mg/L for the organophosphorus pesticides, 1–2 mg/L for triazines and their degradation products, and 2–4 mg/L for metolachlor. Spiked solutions of surrogate compounds were prepared in ethyl acetate at a concentration of 5 mg/L for ethion and 10 mg/L for prometryn. Tetrachlorvinphos served as the internal standard (IS) and a working solution of 10 μg/mL was prepared in hexane. Working solutions containing the target pesticides, surrogates and internal standard were prepared in ethyl acetate to construct the calibration curve. Concentrations of the targeted compounds and the surrogates ranged from 0.1–4 μg/mL, with the internal standard at a concentration of 1 μg/mL.

Sampling and filtration

Homogeneous surface-water samples (17.85 L) were collected at a one-metre depth using a Teflon pneumatic pump, then filtered through 293-mm-diameter fibre glass filters and held in a 293-mm-diameter stainless steel filter holder[17]. Filtered water samples were collected in Spartanburg 20-L stainless steel containers. The characteristics[18] of selected surface waters are shown in Table I.

TABLE I Characteristics of distilled water and surface water from the St. Lawrence River at the Quebec City sampling station. Values are the minimum and the maximum observed during 1995 (mean of values)

Sample origin	*pH n = 90*	*Conductivity (μS/cm) n = 90*	*DOC (mg/L) n = 90*	*POC (mg/L) n = 90*	*TOC (mg/L) n = 90*
Distilled water	5.95	5	-	-	-
Surface water	6.7–8.0 (7.6)	162–279 (234)	2.15–6.05 (3.7)	0.13–1.66 (0.51)	2.5–6.87 (4.22)

DOC: dissolved organic carbon; POC: particulate organic carbon; TOC: total organic carbon.

Extraction

Upon arrival at the laboratory, filtered water samples were separated into two identical volumes (either 1, 4, 10 or 17.85 L). The first sample (analytical sample) was used to quantify the pesticides contained in the surface water, whereas the second, spiked sample was used to calculate the percent recoveries of the target pesticides. First, 100 μL of spiked solution of the surrogates (1 μg of ethion and 2 μg of prometryn) was added to the analytical sample. Then, a volume of 1 mL of spiked solution of the target pesticides (0.5, 1 and 2 μg of organophos-

phorus pesticides, triazines and degradation products, and metolachlor, respectively) was added to the spiked sample. Both samples were stirred for 5 min and set aside for 1 hour before extraction. A solid-phase extraction system (VAC ELUT SPS 24 SPE, purchased from Analytichem International) was used to aspirate each sample through a graphitized carbon black cartridge filled with 500 mg of Carbopack B (60/80 mesh) (6.5 × 1.4 cm internal diameter, polypropylene, purchased from Supelco, Oakville, Ont., Canada). These cartridges were first conditioned with 6 mL of ethyl acetate, then with 20 mL of an acidic solution (10 g/L of ascorbic acid, adjusted to pH 2 with concentrated HCl). Extraction took approximately 3 hours and was carried out using a water pump at a rate of 2.4 kPa of pressure and 17.85 L of water (flow rate of 100 mL/min). Following sample application, the cartridge was rinsed with 6 mL of Milli-Q water, then aspirated for 2 min to remove residual water. The target pesticides were then eluted by running 100 mL of hexane/ethyl acetate (90:10 v/v) through the cartridge, followed by 50 mL of hexane, at a rate of 5 mL/min with a hypodermic syringe. The eluent was dried immediately afterward on a glass column (15 × 2.5 i.d.) filled with 25–30 g of anhydrous sodium sulfate, concentrated to 2 mL by rotary evaporation in a 250-mL flask and then transferred into a conical 15-mL test tube. The flask was rinsed three times with 1 mL of ethyl acetate and the extracts were mixed together. Lastly, the extract was reduced to 100 µL for analytical samples and 450 µL for spiked samples by a nitrogen stream at 25°C. A volume of 10 µL (100 µg) and 50 µL (500 µg) of the internal standard solution was added to each of the analytical and spiked samples, respectively. Before injection in GC-NPD, extracts were centrifuged at 2000 rpm for 10 min.

A method blank was performed periodically (one blank for every five samples) using a volume of 4 L of Milli-Q water. Extraction was the same as for surface-water samples. No traces of the targeted chemicals, nor interference either were detected on the blanks.

Chromatographic analysis

The sample extracts were analysed using a Varian model 3400 gas chromatograph equipped with a septum programmable injector (SPI) at a controlled flow and a nitrogen-phosphorus detector (NPD). DB-5 (5% phenyl/95% methyl) and/or DB-210 (50% trifluoropropyl/50% methyl) capillary columns (30 m × 0.25 mm i.d., 0.25 µm coating thickness), obtained from J&W Scientific (Folsom, Ca., U.S.A), were used with helium as the carrier gas with linear velocities of 34 cm/sec set at 214°C for the DB-5 column and 35 cm/sec set at 181°C for the DB-210. The detector gas flows were hydrogen at 4 mL/min, air at 169 mL/min and nitrogen as detector make-up at 25.8 mL/min. The detector temperature was set at 300°C when the DB-5 column was used and at 250°C for

the DB-210 column. One microlitre of the extract in ethyl acetate was injected without cleanup. Chromatograms and quantitation were done with Varian Star version 4.0 software.

DB-5 column

The temperature of the injector was initially set at 60°C for 0.5 minutes. It was increased to 280°C at a rate of 140°C/min, then held for 30 min. The temperature of the column was initially set at 60°C for 2 min. It was increased to 180°C at a rate of 20°C/min, then to 220°C at a rate of 3°C/min, then to 260°C at a rate of 15°C/min, and finally to 300°C at a rate of 4°C.

DB-210 column

The temperature of the injector was initially set at 60°C for 0.5 minutes. It was increased to 250°C at a rate of 140°C/min, then held for 27 min. The temperature of the column was initially set at 60°C for 2 min. It was increased to 160°C at a rate of 20°C/min, then to 240°C at a rate of 5°C/min and held for 5 min. Finally, it was increased to 250°C at a rate of 5°C/min.

RESULTS AND DISCUSSION

The target pesticides were selected based on their intensity of use and on residual levels in the Great Lakes and the St. Lawrence River and its tributaries[3,19-22]. The characteristics of these chemicals are shown in Table II.

Selection of the eluent

Like Di Corcia and Marchetti[8], we initially used the Carbopack B (120/400 mesh). Different volumes (from 1 to 100 mL) of the following eluents were tested: ethyl acetate, acetone, acetonotrile, hexane, methanol, dichloromethane-hexane-acetone (60:20:20), dichloromethane-acetone (80:20), dichloromethane-acetonitrile (80:20), dichloromethane-methanol (80:20), ethyl acetate-5 M sodium hydroxide (99.9:0.1) and hexane/ethyl acetate (50:50; 75:25; 80:20 and 90:10, v/v). The cartridges (500 mg of Carbopack B 120/400 mesh) were first washed with 6 mL of ethyl acetate followed by 20 mL of an acidic solution (10 g/L of ascorbic acid, adjusted to pH 2 with concentrated HCl). A volume of 10 mL of spiked Milli-Q water (cf. Extraction), was run through the cartridge, which was then eluted with several fractions of the selected eluent. Except for hexane, which eluted a fraction of the target pesticides, and the mixture of hex-

ane/ethyl acetate (90:10), which did not elute anilazine, all the other selected solvents completely eluted these pesticides when solvent volume was at least 50 mL. Below this volume some pesticides, particularly anilazine, will not be completely eluted. All eluents were exchanged for ethyl acetate before chromatographic analysis. Ethyl acetate was first selected as eluent because of its efficiency, its low volume use and its compatibility with the GC-NPD. This eluent was later replaced by a mixture of hexane/ethyl acetate (90:10). Indeed, ethyl acetate, more polar than hexane/ethyl acetate (90:10), extracts more polar contaminants, thereby affecting chromatographic analysis. Methanol was not chosen because it can contribute to the hydrolysis of EPN and phosmet, when acetone and acetonitrile are not compatible with GC-NPD and/or with the capillary columns being used.

TABLE II Solubility in water and log K_{oc} (g/mL) of selected pesticides[23]

ID Pesticide	*Class*	*Solubility in water at 20–25°C (mg/L)*	*Log K_{oc}*
1 Desisopropyl-atrazine	Degradation product	NA	NA
2 Desethylatrazine	Degradation product	NA	NA
3 Simazine	Triazine (H)	6.2	2.11
4 Atrazine	Triazine (H)	33	2.00
5 Propazine	Triazine (H)	8	2.19
6 Fonofos	Phosphorodithioate (I)	17	2.94
7 Diazinon	Phosphorothioate (I)	60	3.00
8 Metribuzin	Triazine (H)	1220	1.78
9 Parathion-methyl	Phosphorothioate (I)	60	NA
10 Ametryn	Triazine (H)	185	2.48
11 Prometryn	Triazine (H)	33	2.60
12 Malathion	Phosphorodithioate (I)	130	3.26
13 Metolachlor	Acetanilide (H)	530	2.30
14 Cyanazine	Triazine (H)	170	2.28
15 Anilazine	Triazine (F)	8	3.48
IS Tetrachlorvinphos	Organophosphate (I)	11	NA
16 Ethion	Phosphorodithioate (I)	1.1	4.00
17 Phosmet	Phosphorodithioate (I)	25	NA
18 EPN	Phosphorothioate (I)	0.5	4.11
19 Azinphos-methyl	Phosphorodithioate (I-A)	29	3.00
20 Azinphos-ethyl	Phosphorodithioate (I-A)	NA	NA

IS = internal standard, I = insecticide; H = herbicide; F = fungicide; A = acaricide.
NA = Not available.

Selection of the adsorbent

Experiments were conducted to compare the efficiency of different graphitized carbon black cartridges-Carbopack C (60/80 mesh), Carbopack B (60/80 mesh), a large particle-size adsorbent, and Carbopack B (120/400 mesh), a small particle-size adsorbent-using 17.85 L of spiked Milli-Q water. Water samples were spiked with 0.5, 1 and 2 μg of organophosphorus pesticides, triazines and their degradation products, and metolachlor, respectively (cf. Extraction). Extraction time for this volume was 3 h for Milli-Q water and 4 h for surface water with Carbopack C (60/80 mesh); 3 h for Milli-Q water and 4 h for surface water with Carbopack B (60/80 mesh); and 15 h for Milli-Q water and more than 24 h for surface water with Carbopack B (120/400 mesh). Although Carbopack B (120/400 mesh) yielded percent recoveries that were slightly superior to those obtained with Carbopack B (60/80 mesh), we selected the latter because of its relatively short extraction time. Final extract volume was 500 μL. Percent recoveries obtained for each pesticide using selected adsorbent materials are shown in Table III.

TABLE III Percent recoveries of pesticides using different adsorbents. Matrix and volume used: 17.85 L of Milli-Q water. Weight of adsorbent: 500 mg. Spike level: 0.5–2 μg in 1 mL of ethyl acetate

ID Pesticide	*Mean recovery* (%) ± C.V. (%)*		
	Carbopack C (60/80) (n = 2)	*Carbopack B (60/80) (n = 3)*	*Carbopack B (120/400) (n = 2)*
1 Desisopropyl-atrazine	14 ± 1	86 ± 17	110 ± 1
2 Desethylatrazine	24 ± 1	85 ± 16	115 ± 4
3 Simazine	48 ± 1	97 ± 10	109 ± 2
4 Atrazine	42 ± 2	98 ± 8	105 ± 1
5 Propazine	30 ± 1	97 ± 5	103 ± 1
6 Fonofos	50 ± 3	93 ± 5	89 ± 2
7 Diazinon	53 ± 4	94 ± 7	94 ± 1
8 Metribuzin	00 ± 0	62 ± 3	48 ± 4
9 Parathion-methyl	56 ± 3	94 ± 5	99 ± 1
10 Ametryn	48 ± 6	73 ± 14	88 ± 1
11 Prometryn	44 ± 4	92 ± 6	93 ± 1
12 Malathion	51 ± 4	95 ± 5	98 ± 1
13 Metolachlor	47 ± 3	100 ± 6	106 ± 1
14 Cyanazine	45 ± 4	91 ± 8	102 ± 2
15 Anilazine	48 ± 1	83 ± 15	70 ± 8
16 Ethion	54 ± 2	86 ± 4	86 ± 4

ID Pesticide	Mean recovery* (%) ± C.V. (%)		
	Carbopack C (60/80) (n = 2)	Carbopack B (60/80) (n = 3)	Carbopack B (120/400) (n = 2)
17 Phosmet	47 ± 4	74 ± 6	83 ± 1
18 EPN	57 ± 6	90 ± 4	94 ± 2
19 Azinphos-methyl	48 ± 4	70 ± 7	85 ± 1
20 Azinphos-ethyl	50 ± 8	76 ± 6	85 ± 0

* Elution was carried out with 50 mL of ethyl acetate.

Volume of surface water sample

All these experiments were performed with surface water drawn from the St. Lawrence River (Table I). Samples were spiked one hour before extraction with 0.5, 1 and 2 µg of organophosphorus pesticides, triazines and their degradation products, and metolachlor, respectively (cf. Extraction). Percent recoveries obtained for each pesticide are shown in Table IV.

Extracts were injected without cleanup: the quality of the extract, the selectivity of the NPD detector and the chromatographic separation carried out on two columns made cleanup unnecessary. When sample volume exceeds 10 L, however, cleanup is recommended before extract injection, even though percent recoveries of the target pesticides will decrease. The partitioning of water and ethyl acetate or dichloromethane (50:50, v/v) improved the quality of the extract. Indeed, Carbopack B adsorbents are not selective, so when the volume of surface-water samples increases, all interference substances present in the matrix will be concentrated in the extract, thereby affecting chromatographic analysis. Active sites, possibly the result of nonvolatile compounds (colloids, surfactants, etc.) or polymerization, were observed in the capillary columns for non-purified extracts issued from a large volume of surface water (> 10 L). Nevertheless, both analytical interference and the formation of active sites depend on the time and place of sampling. As a matter of fact, surface water matrices vary depending on geographic factors and within a geographical location the matrix can vary with depth of surface water, with time, as a result of local and/or upstream weather and seasonal change, and as a result of human activities. This method should be validated for each type of surface water sample prior to its application. With the exception of metribuzin, phosmet and anilazine, all pesticides were recovered at relatively high levels (70–100 %) in a volume of 17.85 L of Milli-Q water compared to percent recoveries in the same volume of filtered surface water (51–93%). Indeed, metribuzin is a very polar pesticide, its solubility in water being 1220 mg/L (Table II). The weak percent recoveries of phosmet and anilazine may be due to hydrolysis or to some interaction between these compounds and the humic substances present in water. Haider et al. (1993) have reported that the

binding of anilazine occurs in the form of ethers and esters with various functional OH-groups of humic molecules.

TABLE IV Effect of sample volume of surface water on percent recoveries on a Carbopack B (60/80 mesh) cartridge containing 500 mg of the adsorbent. Spike level: 0.5–2 μg in 1 mL of ethyl acetate

ID Pesticide	*Percent recovery* (%)*			
	1 L	*4 L*	*10 L*	*17.85 L*
1 Desisopropyl-atrazine	71	70	60	51
2 Desethylatrazine	75	72	62	52
3 Simazine	81	80	68	59
4 Atrazine	84	79	71	60
5 Propazine	85	84	75	61
6 Fonofos	81	80	75	76
7 Diazinon	80	78	75	77
8 Metribuzin	42	42	7	5
9 Parathion-methyl	87	82	76	73
10 Ametryn	79	93	86	79
11 Prometryn	96	95	96	84
12 Malathion	89	86	79	73
13 Metolachlor	97	98	85	82
14 Cyanazine	97	99	87	80
15 Anilazine	52	9	0	0
16 Ethion	70	90	88	87
17 Phosmet	80	75	62	30
18 EPN	91	89	84	75
19 Azinphos-methyl	92	82	70	60
20 Azinphos-ethyl	105	102	100	93

* Except for anilazine (results obtained from an elution with 50 mL of ethyl acetate), all other pesticides were eluted with 100 mL of hexane/ethyl acetate, followed by 50 mL of hexane.

The surrogates were used to determine the effectiveness of the extraction technique and were chosen to represent the two classes of pesticides studied. Because the matrix of surface water changes continuously as a function of time and space, we are of the opinion that for each sample, the pesticides analysed should be corrected with percent recoveries calculated for the same sample (cf. Extraction).

Detection limits

Table V shows the detection limits calculated for each pesticide in 100 µL of the final extracts issued from 10-L filtered water samples (signal-to-noise ratio 5), and their retention times on DB-5 and DB-210 columns.

TABLE V Retention times and detection limits (LODs) for selected pesticides

ID Pesticide	*Retention time (min)*		*LODs*
	DB-5 column	*DB-210 column*	*Water (ng/L)*
1 Desisopropyl-atrazine	9.86	10.09	0.4
2 Desethylatrazine	9.98	10.19	0.4
3 Simazine	10.83	11.01	0.4
4 Atrazine	10.95	11.09	0.4
5 Propazine	11.05	11.16	0.4
6 Fonofos	11.43	11.21	0.1
7 Diazinon	11.61	10.56	0.1
8 Metribuzin	12.74	12.30	0.8
9 Parathion-methyl	12.99	16.16	0.1
10 Ametryn	13.22	12.58	0.4
11 Prometryn	13.34	12.54	0.4
12 Malathion	14.23	15.93	0.1
13 Metolachlor	14.45	15.44	4
14 Cyanazine	14.60	18.30	0.4
15 Anilazine	15.87	14.24	0.8
IS Tetrachlorvinphos	17.31	18.08	0.1
16 Ethion	20.62	18.60	0.1
17 Phosmet	23.60	24.28	0.1
18 EPN	23.74	23.90	0.1
19 Azinphos-methyl	24.66	25.37	0.1
20 Azinphos-ethyl	25.64	26.29	0.1

Parameters affecting percent recoveries

We studied the effects of the following parameters on percent recoveries: addition of sodium sulfite and sodium chloride to the sample; acidification of Carbopack B; interval between spike and extraction; the method of cartridge elution

(forward- vs. back-flush technique), use of the same cartridge for more than one sample; and effect of colloids on extraction.

The antioxidant sodium sulfite did not improve the recovery rates of the target pesticides when added to surface-water samples, whereas percent recoveries for anilazine and phosmet dropped significantly. The reason for this transformation is not yet clear. Further study is needed to fully understand this phenomenon.

The acidification of Carbopack B increased the percent recovery of metribuzin by 50% in a volume of surface water of 4 L or less. Above this volume, acidification made no improvement to pesticide recovery. This would lead one to conclude that metribuzin was retained by ionic exchange. This result agrees with that obtained by Di Corcia et al. (1993) for a similar compound.

Sodium chloride, when added to surface-water samples, seemed to have the same effect as did acidification of the cartridge. Indeed, this reagent decreases the solubility of pesticides in water, particularly for metribuzin, and improves their retention on the Carbopack.

With the exception of phosmet, time between spiking and extraction of surface-water samples (1 to 24 h) did not seem to affect percent recoveries of the target pesticides. Twenty-four hours after spiking, phosmet could no longer be recovered. These results agree with those obtained by Lartiges and Garrigues (1995). As a matter of fact, phosmet, with a half-life of 7.1 h at 20°C and pH 7.4, is rapidly hydrolyzed[27].

No significant difference was observed between forward- and back-flushing when the cartridge was eluted with 50 mL of ethyl acetate. We preferred elution from the forward direction because it is more practical, as opposed to Di Corcia et al. (1993), who opted for the reverse direction because they were using a small volume of eluent and not drying the extract on sodium sulfate.

The use of two cartridges in series, each filled with 500 mg of Carbopack B (60/80 mesh), showed that, in a surface-water sample of 4 L, 10–20% of the target pesticides are found in the bottom cartridge. This would lead one to conclude that a cartridge filled with 1 g of the adsorbent should yield the best percent recoveries. This loss is related to the use of large particle-size-adsorbents. The "channeling" effect associated with the rapid flow of water samples through the cartridge can increase the equilibration time to the point whereby a fraction of the analytes, regardless of their nature, passes through the adsorbent bed unretained.

An experiment consisting of running 1 L of pesticide-free surface water through a cartridge filled with 500 mg of Carbopack B (60/80 mesh), followed by 1 L of spiked Milli-Q water, yielded the same result as for a spiked surface-water sample. Percent recoveries of selected pesticides were now lower in surface water than in Milli-Q water samples when using Carbopack B (Tables IV and V). This would

appear to suggest that the colloids present in surface water compete with pesticides for adsorption onto the Carbopack B, thereby affecting percent recoveries. This phenomenon becomes more important when the volume of surface water or the concentration of colloids increases in water. This hypothesis complements that of Johnson et al. (1991), who concluded, after using two C_{18} cartridges in series, that a fraction of pesticides bind with humic acids and pass through the cartridge without being retained by the adsorbent.

When a cartridge previously used for Milli-Q water samples is used a second time, percent recoveries of selected pesticides do not seem to be affected. However, this is not the case for surface-water samples. Indeed, a fraction of the chemicals present in surface water (colloids and others) seems to remain adsorbed on the Carbopack. This may affect its capacity for reuse.

Environmental levels

With this method, atrazine, desethylatrazine, deisopropyl-atrazine, cyanazine, simazine and metolachlor were detected at concentrations ranging from 6 to 52 ng/L in filtered water drawn from the St. Lawrence River at the Quebec City sampling station (Figure 1). No traces of the other target pesticides were detected in filtered water. All pesticides found in filtered water exhibit log Koc around 2 (Table II) and, consequently, are well distributed in the aqueous phase (> 99%) rather than in the suspended particulate matter[6]. Pesticide concentrations present in the natural waters of the St. Lawrence River are shown in Table VI.

TABLE VI Pesticide concentrations in 10 L of surface water drawn from the St. Lawrence River at the Quebec City sampling station

Sample origin	*Compound*	*Level in filtered water*** *(ng/L)*	
		July 30, 1997	*August 13, 1997*
Quebec City	Atrazine*	52	47
	Desethylatrazine*	33	36
	Desisopropyl-atrazine*	t10	11
	Cyanazine	10	9
	Simazine*	9	9
	Metolachlor	12	6

* Confirmed by liquid chromatography with mass spectrometry detector.
** Values not corrected by percent recovery of each pesticide.

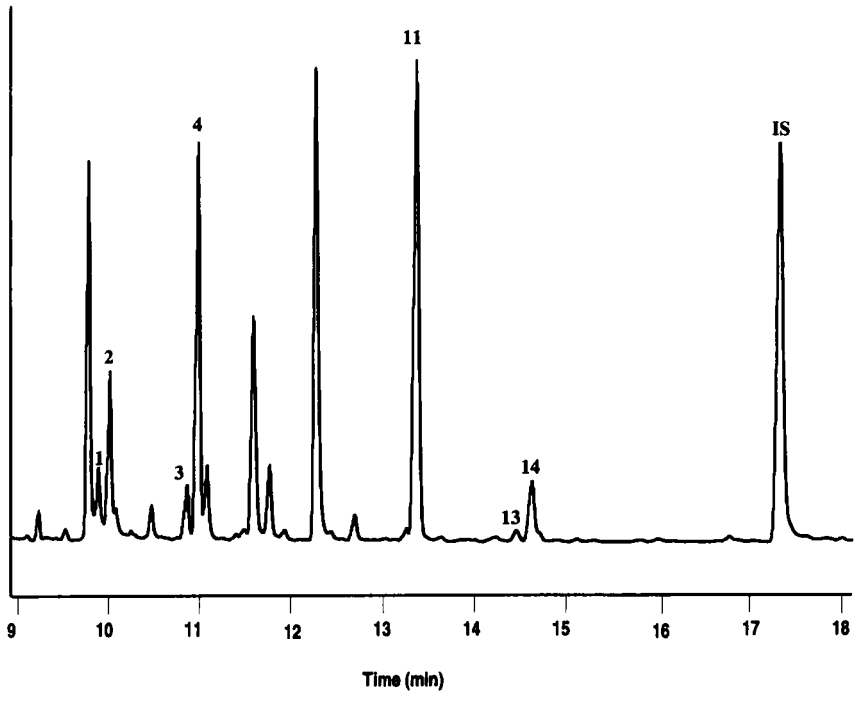

FIGURE 1 Chromatogram of a 10-L filtered water extract collected from the St-Lawrence River at the Quebec City sampling station on May 10, 1997, and analysed by GC-NPD on a DB-5 capillary column. Numbers on the peaks indicate the compounds listed in Table V

CONCLUSION

The use of cartridges filled with Carbopack B (60/80 mesh) allowed for the recovery of a wide range of pesticides and their degradation products. It provides a 50 000-fold concentration of the analytes and detects residual pesticides at ng/L levels. With the exception of metribuzin, phosmet and anilazine, all pesticides were recovered at relatively high levels (70–100%) in a volume of 17.85 L of Milli-Q water compared to percent recoveries in the same volume of filtered surface water (51–93%). Detection limits were between 0.1 and 4 ng/L. The colloids present in surface water have a minor effect on percent recoveries for the selected pesticides by rendering adsorption sites of Carbopack B less available. Some pesticides (e.g. anilazine) that are able to bind with colloids may pass through the cartridge without being retained. It is necessary to clean up extracts issued from surface-water samples taken from the St. Lawrence River when the

volume is greater than 10 L. This volume limit could be increased or decreased depending on the origin and the nature of the surface water used.

This rapid, reproducible, practical and ecological technique could be easily applied for monitoring other organic contaminants belonging to different chemical classes.

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