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Determination of organonitrogen pesticides in large volumes of surface water by liquid–liquid and solid-phase extraction using gas chromatography with nitrogen–phosphorus detection and liquid chromatography with atmospheric pressure chemical ionization mass spectrometry

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Abstract

During a recent study to determine the fluxes and fates of contaminants in the St. Lawrence River, the majority of organonitrogen pesticides analysed in samples of surface water were found in the dissolved phase. This paper compares two extraction techniques and two analytical techniques for 10 chemicals (metolachlor, seven triazines and two degradation products of atrazine–cyanazine–propazine and simazine) in the dissolved phase in large volumes of surface water, using a fibre glass filter with 0.7 μm porosity. Samples of filtered surface water (1–20 l) were extracted by means of a liquid–liquid technique using the Goulden large-sample extractor, and by means of a solid-phase extraction technique, using cartridges filled with 500 mg of a large particle-size graphitized carbon black as adsorbent: Carbopack B (500–666 μm). The pesticides were analysed by gas chromatography on two DB-5 and DB-210 capillary columns with nitrogen–phosphorus detection (GC–NPD) and by liquid chromatography coupled with mass spectrometry equipped with an atmospheric pressure chemical ionization interface (LC–APCI-MS). The recoveries were high (67–100%) for the majority of the target pesticides in a volume of 17.85 l of Milli-Q water, compared to recoveries in the same volume of filtered surface water (51–102%). The detection limits ranged from 0.4 to 4 ng/l and from 0.6 to 3 ng/l for GC–NPD and LC–ACPI-MS techniques, respectively.

Keywords: Water analysis; Extraction methods; Environmental analysis; Pesticides

1. Introduction

The intensive use of pesticides in agriculture, their high water solubility as well as their persistent nature frequently result in the contamination of natural waters by infiltration, spills, spray drift or surface run-off, and have a generally negative impact on the ecosystem [1]. Herbicides make up 81% of all pesticides used in Canada [2]. Those most frequently used are from the triazine and acetamide classes [3,4]. In order to control the quality of natural waters, standards have been established for the protection of aquatic life and for drinking water for each such chemical. In the European Union, the

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maximum recommended limit for each individual pesticide, has been set at 0.1 μg/l for drinking water. In Canada, the maximum recommended limit for atrazine, one of the world's most widely used pesticides, has been set at 2 μg/l in surface water for the protection of aquatic life [5].

Previous studies have confirmed the presence of pollutants in the St. Lawrence River [6–8]. 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 [9,10]. Consequently, the lowest detection limits possible are required to study the fate and the transport of contaminants in this river. Furthermore, in view of the increasingly stringent environmental measures being implemented, future regulations may well demand even lower detection limits.

Several methods have to be used to screen organic environmental pollutants (parents and degradation products), because the polarity and other chemical properties of the components vary considerably. A variety of extraction techniques have been employed over the years to determine pesticides and their degradation products, including liquid–liquid extraction (LLE) [11], solid-phase extraction (SPE) [12,13], solid-phase microextraction (SPME) [14,15], semi-permeable membrane device (SPMD) [16,17] and supercritical fluid extraction [18], followed by various chromatographic techniques such as gas and liquid chromatography (GC and LC) coupled with nitrogen–phosphorus (NPD) [19], electron-capture (ECD) [20], diode-array [21], fluorescence [22] or mass spectrometry (MS) detection systems [23]. A number of papers have been written on the determination of pesticides using LC–atmospheric pressure chemical ionization interface mass spectrometry (LC–APCI-MS) [24–28]. None, however, deal with the use of large sample volumes of surface water.

Conventional LLE and SPE techniques use water samples of 1–2 l [29–34]. 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.

The purpose of this study was to determine eight organonitrogen pesticides and two degradation products of atrazine–cyanazine–propazine and simazine (desethylatrazine and deisopropylatrazine) in large volumes of surface water, and to find the most appropriate method to do so by: (i) comparing a LLE technique using the Goulden large-sample extraction (GLSE) instrument with a SPE technique using cartridges filled with a large particle-size graphitized carbon black as adsorbent: Carbopack B (500–666 μm); and (ii) comparing GC–NPD using two DB-5 and DB-210 capillary columns with LC–APCI-MS.

2. Experimental

2.1. Reagents and chemicals

All pesticides were obtained from different suppliers. Ametryn, propazine and simazine were obtained from the US Environmental Protection Agency (EPA). Atrazine, cyanazine, desethylatrazine (DEA), deisopropylatrazine (DIA), metribuzin, metolachlor, prometryn (used as surrogate) and terbutylazine (used as internal standard) were purchased from Riedel-de Haën, distributed by Fisher Scientific (Montreal, Canada).

Ethyl acetate, hexane, dichloromethane (DCM) and methanol (all distilled-in-glass grade) were purchased from Caledon Labs. (Georgetown, Canada) and used without further clean-up. 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, MA, USA).

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 PTFE bag before use.

Twenty-litre stainless steel pressure containers (containing 17.85 l of liquid), purchased from Spartanburg Steel Products (Spartanburg, SC, USA), were used to collect and store samples.

2.2. Standard solutions

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

volumetric 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 1 mg/l for triazines and their degradation products, and 2 mg/l for metolachlor. A spiked solution of surrogate compound (prometryn) was prepared in ethyl acetate at a concentration of 10 mg/l. Terbutylazine served as the internal standard (I.S.) and a working solution of 10 mg/l was prepared in ethyl acetate. Working solutions containing the target pesticides, surrogate and internal standard were prepared in ethyl acetate (for GC–NPD) and in methanol (for LC–APCI-MS) to construct the calibration curve. Concentrations of the targeted compounds and the surrogate ranged from 0.2–4 and 0.025–2.6 mg/l for GC–NPD and LC–APCI-MS, respectively, with the internal standard at a concentration of 1 mg/l.

2.3. Sampling and filtration

Homogeneous surface water samples (17.85 l) were collected at a 1-m depth using a PTFE pneumatic pump, then filtered through 293-mm diameter fibre glass filters and held in a 293-mm diameter stainless steel filter holder [35]. Filtered water samples were collected in Spartanburg 20-l stainless steel containers. The characteristics [36] of selected surface waters are shown in Table 1.

2.4. Extraction

2.4.1. Liquid–liquid extraction

Upon reception at the laboratory, filtered water samples were extracted with 200 to 400 ml of DCM using the GLSE instrument manufactured by Lasalle Scientific, Guelph, Canada. The surrogate solution was prepared in 100 ml of methanol just before extraction (2 μg of prometryn), and then metered into the GLSE instrument during sample extraction at a rate of 2 ml/min. The flow-rates of feed water and solvent make-up pumps were set at 500 and 10 ml/min, respectively. Typical extraction time is 40 min for 17.85 l of water. The DCM extract was recovered in an amber coloured glass bottle, dried on anhydrous sodium sulfate, and reduced in volume to a few milliliters by rotary evaporation under reduced pressure. DCM was exchanged for ethyl acetate, then concentrated again by rotary evaporation, transferred to a centrifuge tube and further concentrated to about 100 μl under a gentle stream of nitrogen. A 10-μl aliquot of the internal standard working solution (0.1 μg) was added to the extract just prior to chromatographic analysis. Lastly, the extract was centrifuged at 2000 rpm for 10 min and an aliquot of 1 μl was injected in GC–NPD mode with an autosampler.

A GLSE blank was performed periodically. Blank samples of 10 l of Milli-Q UV Plus reagent water were extracted in the same manner as for surface water samples. No trace was found of the target chemicals, nor was interference detected in the blanks.

2.4.2. Solid-phase extraction

Upon arrival at the laboratory, filtered water samples were spiked with the surrogate solution (2 μg of prometryn), then stirred for 5 min and set aside for 1 h before extraction. An SPE system (Vac-Elut SPS 24 SPE, purchased from Analytichem International) was used to aspirate each sample through a cartridge filled with 500 mg of Carbopack B (500–666 μm) graphitized carbon black (6.5×1.4 cm I.D., polypropylene, purchased from Supelco, Oakville, 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 h and was carried out using a water pump

Table 1
Characteristics of distilled water and surface water from the St. Lawrence River at the Quebec City sampling station

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)

Values are the minimum and the maximum observed during 1995 (mean of values).
DOC=dissolved organic carbon; POC=particulate organic carbon; TOC=total organic carbon.

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 eluted by running 50 ml of ethyl acetate through the cartridge at a rate of 5 ml/min with a hypodermic syringe. For LC–APCI-MS analysis, the eluent was concentrated to 2 ml by rotary evaporation in a 125-ml flask and 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 near dryness under a nitrogen stream and transferred into 500 μl of a mixture of methanol–water (50:50, v/v) containing 0.5 μg of the internal standard. The extract was cleaned up before GC–NPD analysis (cf. Section 2.5).

A method blank was performed periodically (one blank for every five samples) using a volume of 10 l of Milli-Q water. Extraction was the same as for surface water samples. No trace was found of the target chemicals, nor was interference detected in the blanks.

2.5. Clean-up

Clean-up was performed by partitioning 50 ml of Milli-Q water containing 4% chloride sodium and 75 ml of a mixture of hexane–ethyl acetate (eluent) (30:70, v/v). The organic phase was recovered and dried immediately afterward on a glass column (15× 2.5 cm I.D.) filled with 25–30 g of anhydrous sodium sulfate, then concentrated to 2 ml by rotary evaporation in a 125-ml flask and 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. The extract was then reduced to 100 μl by a nitrogen stream at 25°C, and a volume of 10 μl (0.1 μg) of the internal standard solution was added. Lastly, the extract was centrifuged at 2000 rpm for 10 min and an aliquot of 1 μl was injected in GC–NPD mode with an autosampler.

2.6. Chromatographic analysis

2.6.1. GC 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 an NPD system. 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, USA), were used, with helium as the carrier gas, with linear velocities of 34 cm/s set at 214°C for the DB-5 column and 35 cm/s 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 microliter of the extract in ethyl acetate was injected. Chromatograms and quantitation were carried out with Varian Star version 4.0 software.

2.6.1.1. DB-5 column

The temperature of the injector was initially set at 60°C for 0.5 min. 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/min.

2.6.1.2. DB-210 column

The temperature of the injector was initially set at 60°C for 0.5 min. 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.

2.6.2. LC analysis

This work was performed on a Varian LC system coupled with a Finnigan SSQ 7000 mass spectrometer and equipped with an APCI interface.

2.6.2.1. Liquid chromatography

LC separations were performed on a 25 cm×4.6 mm I.D. Kromasil column packed with 5-μm particles coated with C_{18}-bonded silica phase. LC was carried out using a Varian 9012 pump system, a Varian 9100 Autosampler and a Varian UV 9065

Polychrom diode-array detector. The flow-rate of the mobile phase was 1 ml/min with an injection volume of 20 μl. Linear gradient was 15–60% acetonitrile in water for 50 min, then held for 15 min. For calibration and to determine the linearity of the concentration range, we injected 20 μl of standard solution in methanol containing 25, 50, 130, 260, 520, 1040, 2600 μg/l of the analytes.

2.6.2.2. MS detection

The LC–APCI-MS experiments were performed on an SSQ 7000 quadrupole mass spectrometer equipped with an APCI interface and coupled to a Digital data system.

Atmospheric ion source parameters were set to a capillary temperature of 225°C, APCI vaporizer temperature of 400°C and Corona discharge intensity of 5 μA. Sheath gas was nitrogen at a pressure of 35 p.s.i. (1 p.s.i.=6894.76 Pa); auxiliary gas was also nitrogen, at a flow-rate of 5 ml/min. Data acquisition was set to full scan mode, with scanned mass ranging from 50 to 450 u.

Thus, the positive ionization mode was selected for the LC–APCI-MS. The high intensity protonated quasi-molecular ion was registered for each analyte and selected for measurement. In the APCI mass spectra, cluster ions derived from acetonitrile-added quasi-molecular ions were also found (e.g., atrazine+CH_3CN+H =257). Tuning of the APCI interface was performed with methanol containing DIA, atrazine, isoproturon and tebuconazole, at a concentration of 5 μg/ml for each.

3. 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 [3,4,8,37,38].

3.1. Detection limits

Table 2 shows the detection limits calculated for each pesticide by preparing dilutions of the final extracts (100 μl) issued from 10-l filtered water samples (signal-to-noise ratio 5).

Table 2
Detection limits (LODs) for selected pesticides

	Pesticide	LOD (ng/l)		Selected ion
		GC	LC	
1	DIA	0.4	1	174
2	DEA	0.4	1	188
3	Simazine	0.4	0.7	202
4	Atrazine	0.4	0.6	216
5	Propazine	0.4	0.7	230
6	Metribuzin	0.8	3	215
7	Ametryn	0.4	0.8	228
8	Prometryn	0.4	2	242
9	Metolachlor	4	3	284
10	Cyanazine	0.4	2	241

3.2. Recoveries

Water samples were spiked with 100 μl of the surrogate solution (2 μg of prometryn) and 1 ml of the spiked solution of the target pesticides (1 μg of triazines and degradation products, and 2 μg of metolachlor). For the SPE technique, samples were then stirred for 5 min and set aside for 1 h before extraction. Recoveries obtained for each pesticide are shown in Table 3. An APCI positive total ion chromatogram of a St. Lawrence River sample spiked with 1 μg of each analyte and using a 20 μl injection on LC column is shown in Fig. 1. Ion extracted chromatograms of the same sample spiked with 1 μg of each analyte using a 20 μl injection on LC column are shown in Fig. 2a and Fig. 2b. The ions selected for each pesticide were as follows:: DIA (m/z=174); DEA (m/z=188); simazine (m/z=202); metribuzin (m/z=215); atrazine (m/z=216); ametryn (m/z=228); propazine (m/z=230); cyanazine (m/z=241); prometryn (surrogate) (m/z=242); metolachlor (m/z=284).

With the exception of metribuzin, all pesticides were recovered at relatively high levels (67– 100%) in a volume of 17.85 l of Milli-Q water, compared to recoveries in the same volume of filtered surface water (51–102%). The fact that DIA [solubility (s)=3200 mg/l], which is more polar than metribuzin (s=1220 mg/l), exhibited the best recovery would lead one to conclude that the low recovery obtained for metribuzin is not due to its solubility. It is, rather, related to its chemical structure and interaction with the SPE sorbent. A recent study conducted by Sabik

Table 3
Recoveries of pesticides

	Pesticide	Mean recovery (%)±R.S.D. (%)					
		Milli-Q water		Surface water			
		GLSE	SPE	GLSE	SPE		
		17.85 l (n=3)	17.85 l (n=3)	17.85 l (n=3)	1 l (n=1)	10 l (n=1)	17.85 l (n=1)
1	DIA	NR	85±16	NR	71	60	51
2	DEA	NR	86±17	NR	75	62	52
3	Simazine	67±10	97±10	70±4	81	68	59
4	Atrazine	84±5	98±8	92±6	84	71	60
5	Propazine	87±1	97±5	88±1	85	75	61
6	Metribuzin	70±9	62±3	69±2	42	7	5
7	Ametryn	86±7	73±14	91±1	79	86	79
8	Prometryn	83±3	92±6	92±1	96	96	84
9	Metolachlor	92±4	100±6	102±4	97	85	82
10	Cyanazine	81±1	91±8	85±1	97	87	80

NR=Not recovered.

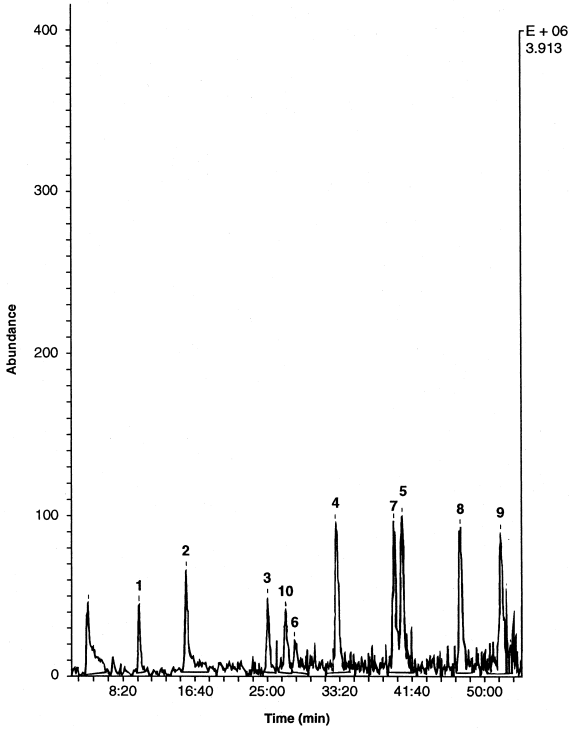

Fig. 1. APCI positive total ion chromatogram for the analysis of the St. Lawrence River sample spiked with 1 μg of each analyte using a 20 μl injection on an LC column. 1=DIA; 2=DEA; 3=simazine; 4=atrazine; 5=propazine; 6=metribuzin; 7=ametryn; 8=prometryn (surrogate); 9=metolachlor; 10=cyanazine.

[13] showed that the recovery of metribuzin improved when the ratio of water sample volume to the adsorbent material (Carbopack B, 500–666 μm) was decreased.

Recoveries obtained with the GLSE technique were slightly higher for surface water than those obtained by SPE using Carbopack B material. This could be due to the type of spike and to the ratio of solvent volume (GLSE) and adsorbent quantity (SPE) to sample volume. Indeed, when using the GLSE technique, pesticides may pass into the dichloromethane during spiking. This may reduce their contact with the colloids present in water samples and minimize adsorption. In a previous study, Sabik [13] demonstrated the use of two cartridges in series, each filled with 500 mg of Carbopack B (500–666 μm). In a surface water sample of 4 l, the author found 10–20% of the target pesticides in the bottom cartridge. This would lead one to conclude that a cartridge filled with 1 g of the adsorbent should yield the best recoveries.

The surrogate was used to determine the effectiveness of the extraction technique and was chosen to represent the class of pesticides studied.

3.3. Selection of the eluent for SPE technique

Different volumes (from 1 to 100 ml) of the following eluents were tested: ethyl acetate, acetone,

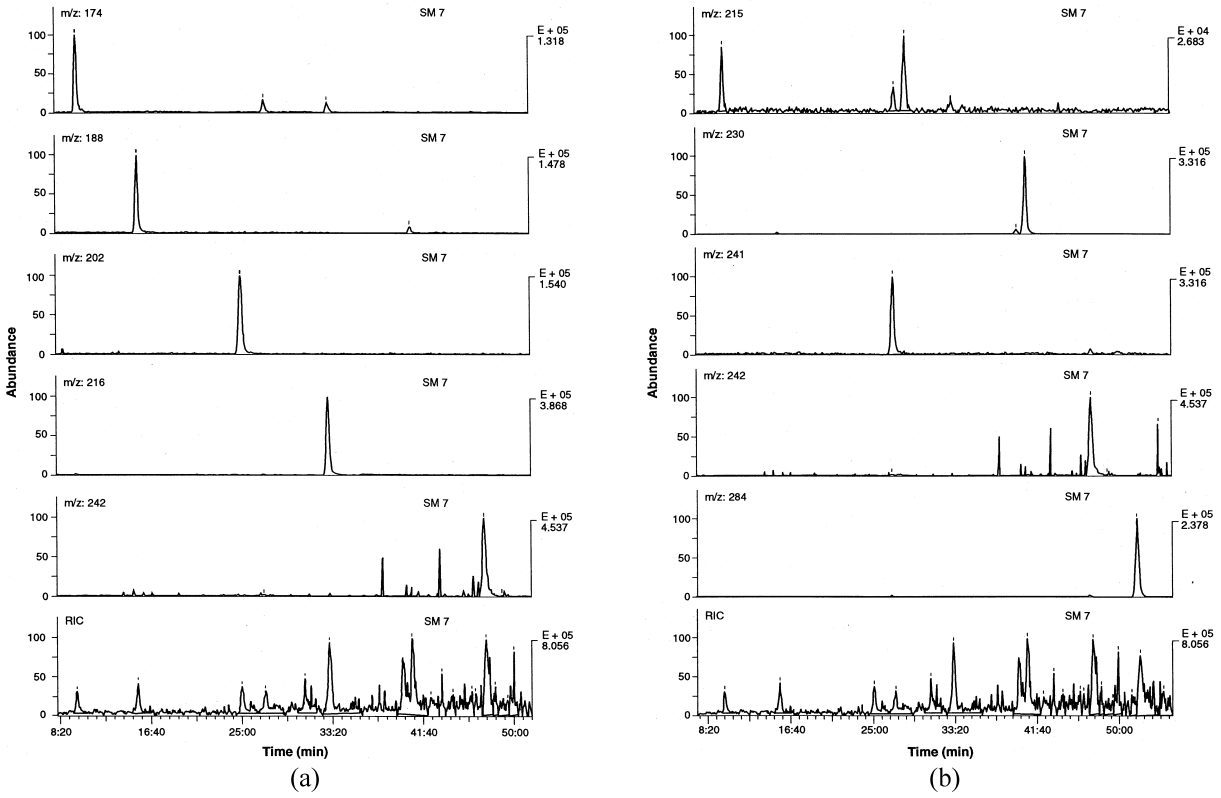

Fig. 2. (a, b) Ion extracted chromatograms for the analysis of the St. Lawrence River sample spiked with 1 μg of each analyte using a 20 μl injection on an LC column. DIA (m/z=174); DEA (m/z=188); simazine (m/z=202); metribuzin (m/z=215); atrazine (m/z=216); ametryn (m/z=228); propazine (m/z=230); cyanazine (m/z=241); prometryn (surrogate) (m/z=242); metolachlor (m/z=284).

acetonitrile, 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 (90:10). The cartridges 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. Sections 2.4 and 3.2), 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, all the selected solvents completely eluted these pesticides when solvent volume was at least 50 ml. All eluents were exchanged for ethyl acetate before GC analysis. Ethyl acetate was selected as eluent for its efficiency and its compatibility with GC–NPD. The extract was cleaned up before GC–NPD injection. Indeed, Carbopack B adsorbents are not selective. When the polarity of the eluent was increased, we observed that some of the substances present in the matrix were extracted, thereby affecting GC analysis. Active sites, possibly the result of non-volatile compounds (colloids, surfactants, etc.) or polymerization, were observed in capillary columns when the elution is carried out with a more polar solvent. This phenomenon was not observed when using LC–APCI-MS, whatever eluent was used.

3.4. Volume of surface water sample for SPE technique

All these experiments were performed with sur-

face water drawn from the St. Lawrence River. Samples were spiked 1 h before extraction, as explained in Section 3.2. In St. Lawrence surface water, sample volumes of 10 l were sufficient to detect the target pesticides. GC–NPD and LC–APCI-MS chromatograms of extracts issued from the St. Lawrence River are shown in Figs. 3 and 4. Extracts were injected without clean-up when using LC–APCI-MS, but this was not always the case for GC–NPD: the quality of the extract made clean-up unnecessary for some samples. 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.

3.5. Comparison of GLSE and SPE

Both GLSE and SPE take the same amount of time for large-volume water samples. However, SPE has the advantage of being less costly, more practical and it consumes less solvent than GLSE, which can be used for larger volumes of water samples (i.e., 10–40 l) [11]. With a large particle-size adsorbent (Carbopack B 500–666 μm), extraction took only 90 min for a 10 l surface water sample. As shown in Table 4, degradation products of atrazine were not recovered by GLSE, whereas they were well recovered by SPE using Carbopack B material.

3.6. Comparison of GC–NPD and LC–APCI-MS

Both GC–NPD and LC–APCI-MS allowed for the determination of the target pesticides and reached

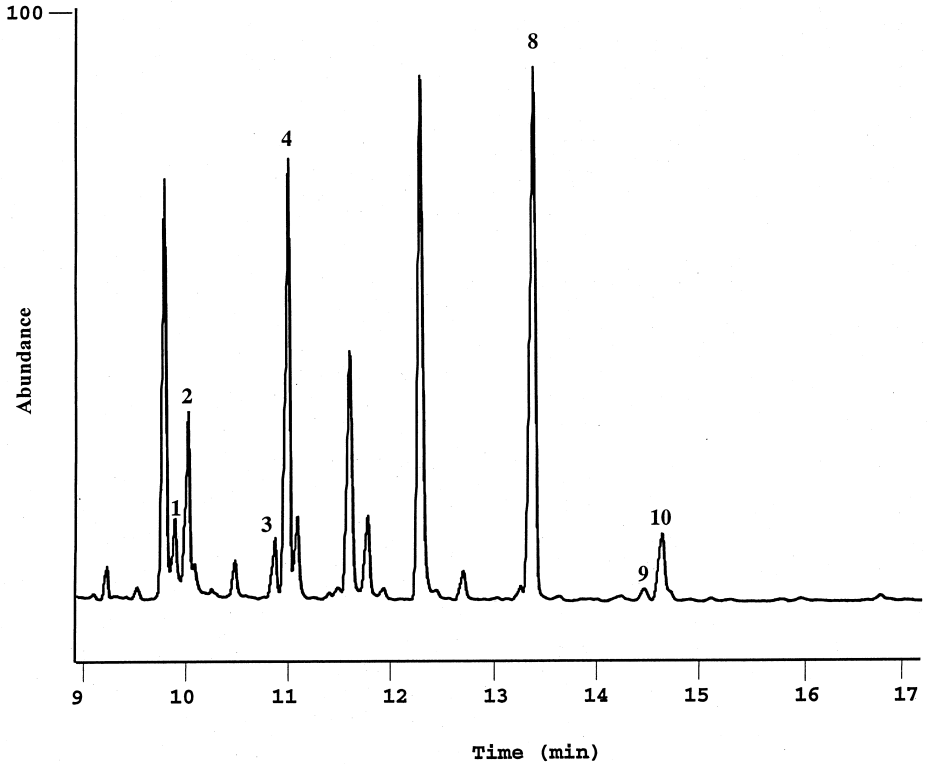

Fig. 3. GC–NPD chromatogram on a DB-5 capillary column of a 10-l filtered water extract drawn from the St. Lawrence River at the Quebec City sampling station. 1=DIA; 2=DEA; 3=simazine; 4=atrazine; 8=prometryn (surrogate); 9=metolachlor; 10=cyanazine.

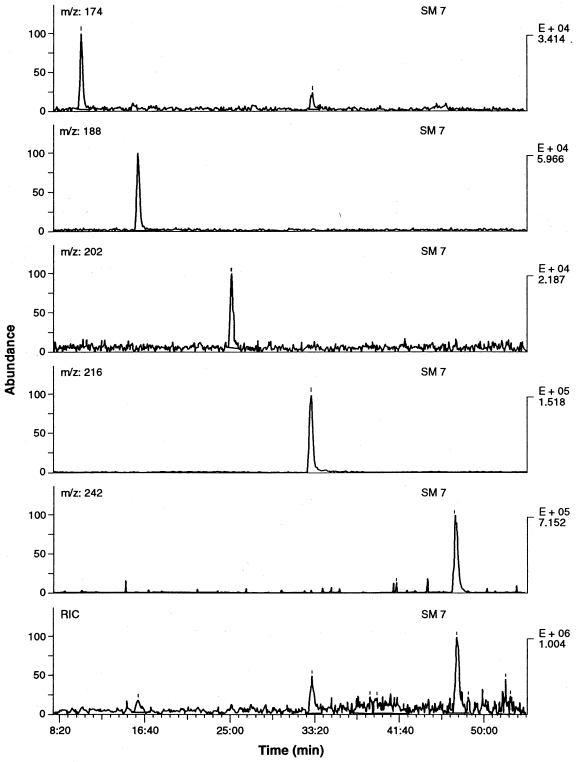

Fig. 4. Ion extracted chromatograms for the analysis of the St. Lawrence River sample using a 20 μl injection on an LC column. DIA (m/z=174); DEA (m/z=188); simazine (m/z=202); atrazine (m/z=216); prometryn (surrogate) (m/z=242).

low detection limits (0.4–4 ng/l for GC–NPD and 0.6–3 ng/l for LC–APCI-MS). When using SPE coupled with GC–NPD, it is important to either select the proper eluent to avoid undesirable co-extraction products, or else to clean-up extracts before injection. Indeed, co-extraction products can contaminate the capillary columns. In our case, a volume of 50 ml of ethyl acetate was necessary to extract the targeted pesticides. To avoid contamination of the capillary columns, clean-up using a partitioning of 50 ml of Milli-Q water containing 4% sodium chloride and 75 ml of a mixture of hexane–ethyl acetate (30:70, v/v) was necessary. There were no such problems with LC–APCI-MS, regardless of the eluent used.

3.7. Environmental levels

Using SPE followed by GC–NPD or LC–APCI-MS, atrazine, desethylatrazine, deisopropylatrazine, cyanazine, simazine and metolachlor were detected at concentrations ranging from 3 to 52 ng/l in filtered water drawn from the St. Lawrence River at the Quebec City sampling station. This was the first time that degradation products of atrazine–cyanazine–propazine and simazine were able to be detected in the St. Lawrence River. Only parent products were detected with the GLSE technique, and at approximately the same levels. No traces of the other targeted pesticides were detected in filtered water. Pesticide concentrations present in the natural waters of the St. Lawrence River are shown in Table 4.

4. Conclusions

GLSE or SPE (Carbopack B 500–666 μm, a large

Table 4
Pesticide concentrations in 10 l of St. Lawrence surface water drawn at the Quebec City sampling station

Sample origin	Compound	Level in filtered water[a] (ng/l)		
		30 July 1997	13 August 1997	10 September 1997
Quebec City	Atrazine	52	47	46
	Desethylatrazine	33	36	24
	Desisopropyl-atrazine	10	11	3
	Cyanazine	10	9	3
	Simazine	9	9	6
	Metolachlor	12	6	7

[a] Values are not corrected by percent recovery of each pesticide. Samples were extracted by SPE and analysis was performed by GC–NPD.

particle-size adsorbent) allowed for the recovery of a wide range of pesticides in large volumes of surface water. They provided a 50 000-fold concentration of the analytes and detected residual pesticides at ng/l levels. The percent recoveries were high (67–100%) for the majority of target pesticides in a volume of 17.85 l of Milli-Q water compared to recoveries in the same volume of filtered surface water (51–102%). The detection limits ranged from 0.4–4 and 0.6–3 ng/l for GC–NPD and LC–ACPI-MS, respectively.

When using SPE coupled with GC–NPD, it is important to select the proper eluent to avoid high polar co-extracts and non-volatile products, or else to clean-up extracts before injection. Indeed, co-extraction products could contaminate the capillary columns. This phenomenon was not observed when using LC–APCI-MS, whatever eluent was used.

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