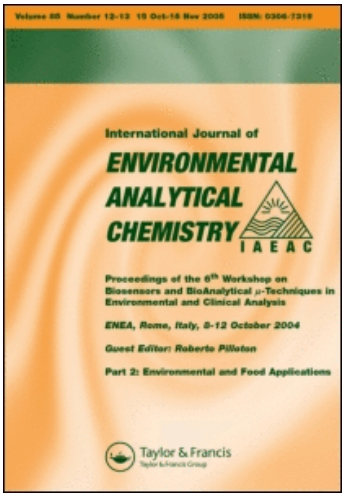

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Simultaneous Filtration and Solid-Phase Extraction Combined with Large-Volume Injection in GC/MS for Ultra-Trace Analysis of Polar Pesticides in Surface Water

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SIMULTANEOUS FILTRATION AND SOLID-PHASE EXTRACTION COMBINED WITH LARGE-VOLUME INJECTION IN GC/MS FOR ULTRA-TRACE ANALYSIS OF POLAR PESTICIDES IN SURFACE WATER

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A method combining simultaneous filtration and solid-phase extraction (SPE) with large-volume injection (LVI) in gas chromatography/mass spectrometry (GC/MS) was developed to determine 13 polar pesticides in surface water. The selected pesticides – 4 organophosphorus, 7 organonitrogens and 2 triazine degradation products – were extracted from 0.5-L samples of filtered and raw water using cartridges filled with a silica-bonded material (1 g of ISOLUTE triazine, C-18) and a depth filter. No obstruction was observed during the extraction of raw water drawn from the St. Lawrence River (concentration of suspended particulate matter (SPM) ranging from 2 to 58 mg L^{-1}). Overall percent recoveries were satisfactory for all the target pesticides ($>60\%$) except desisopropyl-atrazine (more polar), which varied from 29 to 46% according to sample pH. The coefficient of variation was below 10% for the majority of the target pesticides and detection limits ranged from 0.1 to 0.8 ng L^{-1}. Applied to real samples drawn from the St. Lawrence River, this method allowed for the detection of atrazine, cyanazine, desethyl-atrazine (DEA), desisopropyl-atrazine (DIA), metolachlor and simazine, at concentrations of 6 to 91 ng L^{-1}. Using atrazine and metolachlor as examples, the correlation between filtered and raw water samples was more significant for the former ($r=0.87$) than for the latter ($r=0.67$). Temporal variations in atrazine and metolachlor in filtered water drawn from the St. Lawrence River, for example, were similar whether using the established method, based on liquid–liquid large-volume extraction (LVE) combined with GC/NPD analysis, or the one proposed herein. The latter method, however, systematically found atrazine concentrations 62% higher than those obtained by the older one, applied to the same field samples. Thus, the switch to the new analytical method will require the application of a correction factor to the atrazine concentration time series acquired with the previously used method.

Keywords: Pesticide; Water analysis; Filtration; Solid-phase extraction; Gas chromatography/mass spectrometry; Large-volume injection

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INTRODUCTION

The monitoring of pesticides in diluted waters at ng L^{-1} levels is not a simple task. Few studies have been done to date on the contamination of the St. Lawrence River by pesticides [1,2]. The St. Lawrence Centre of Environment Canada started a monitoring program a few years ago to determine the sources and transport pathways of pesticides in this river. At that time, the challenge was to detect all possible traces of pesticides. To this end, preliminary methods were tested. Lemieux *et al.* (1995) [1] extracted 40–60 L of filtered surface water (0.2–0.6 μm nominal porosity) using three liquid–liquid extraction (LLE) steps in 17.85-L stainless steel containers with dichloromethane (DCM). Following mechanical agitation, the bottom layer (i.e. DCM) was aspirated, then dried, concentrated and analysed by injecting 2 μL of the extract in a gas chromatograph (GC) equipped with a nitrogen phosphorus detector (NPD). Another method, based on continuous LLE with DCM using the Goulden large-sample extractor (GLSE) and GC/NPD analysis, was developed to extract 40 L of filtered surface water (0.7 μm nominal porosity) [3]. Although the latter is both more practical and more efficient, it still presents several disadvantages, including the need for large quantities of DCM (1 L of solvent for each sample extracted). Moreover, it is time-consuming and incapable of recovering certain degradation products, such as desethyl-atrazine (DEA) and desisopropyl-atrazine (DIA). To fill in some of these gaps, another method based on solid-phase extraction (SPE) using graphitized carbon black (GCB) cartridges (Carbopack B, 60–80 and 120–400 mesh) followed by GC/NPD analysis, was developed to extract pesticides from 1 to 20 L of filtered surface water (0.7 μm nominal porosity) [4]. This method was satisfactory for filtered water, but it is not suitable for raw water as obstruction often occurs during the extraction of this matrix.

Several techniques, including SPE [5–8], solid-phase micro-extraction (SPME) [9,10], semi-permeable membrane device (SPMD) [11,12] and immuno-extraction [13,14] have been reported in the last decade for the extraction of pesticides and degradation products in aqueous samples. SPE, using either cartridges or disks filled with different adsorbents, was found to be a suitable technique to isolate various pesticides in water [6,8]. However, many analytical chemists have been confronted with two challenges: achieving satisfactory recoveries for degradation products and reaching lower detection limits (e.g. pg–ng L^{-1} in water) [6,15]. Gas or liquid chromatography coupled with mass spectrometry remain the methods of choice for the majority of researchers to analyse pesticides and degradation products in environmental samples [5,8,9,16]. These analytical techniques allow for good selectivity and high sensitivity to be achieved.

The aim of the present work was as follows.

(i) To devise a simple, efficient and cost-effective method for the determination of 13 polar pesticides in surface water at ultra-trace levels. It consists of simultaneous filtration and SPE using ISOLUTE triazine, combined with large-volume injection (LVI; up to 40 μL) in a gas chromatograph/mass spectrometer (GC/MS).
(ii) To compare concentrations of target pesticides in filtered water and raw water samples.
(iii) To compare concentrations of target pesticides during a one-year monitoring period obtained with a GLSE system and GC/NPD analysis and the proposed method.

EXPERIMENTAL

Reagents and Chemicals

All pesticides, including atrazine-d_5 (used as the internal standard), were obtained from different suppliers: U.S. EPA; Chem Service (West Chester, Penna., USA); Ultra-Scientific and Riedel-de-Haën, distributed by Fisher Scientific (Montreal, Quebec, Canada).

All solvents (distilled-in-glass grade), purchased from Caledon Laboratories Ltd. (Georgetown, Ontario, Canada), were used without further cleanup. Cartridges filled with anhydrous sodium sulfate were purchased from IST, distributed by Chromatographic Specialties (Brockville, Ontario, Canada). Reagent water was taken from a Milli-Q-UV Plus reagent-grade water system from Millipore (Bedford, Mass., USA).

Standard Solutions

Primary stock solutions of all pesticides were prepared individually at a concentration of $1\,g\,L^{-1}$ by weighing about 10 mg of each substance in a 10-mL volumetric flask and diluting to volume with acetone. Working solutions containing the target pesticides and the internal standard (atrazine-d_5) were prepared in DCM to construct the calibration curve at concentrations ranging from 0.02–2 $mg\,L^{-1}$, with atrazine-d_5 at a concentration of $0.20\,mg\,L^{-1}$.

Sampling and Filtration

Homogeneous surface-water samples were collected at the Lévis station (opposite Quebec City) from the municipality's drinking water intake; a previous study has shown that water collected at this site is representative of the St. Lawrence water mass [17]. Surface water was sampled using an all-Teflon pneumatic pump (PFD1 type, ASTI®) and Teflon tubing. Filtered water samples were filtered through glass fibre filters (293 mm diameter, ~0.7 μm porosity, TCLP type, Gelman®) held in a Millipore® filter holder equipped with a Teflon-coated grid support [18]. Filtered and raw water samples were stored at 4°C in 0.5-L amber glass containers until extraction could be carried out at the laboratory, usually within 8–16 h of sampling. The characteristics [19] of selected surface waters are shown in Table I.

Extraction

Filtered and raw water samples (0.5 L) were aspirated through a C-18 cartridge filled with a silica-bonded material and a depth filter (1 g of ISOLUTE triazine in 6 mL polypropylene cartridges, purchased from IST Ltd., U.K., distributed by Chromatographic Specialties Inc., Ontario, Canada). Cartridges were first conditioned with 3×6 mL of DCM, then with 6 mL of acetone and 6 mL of Milli-Q water. Extraction took approximately 50 min for 0.5 L of water (flow rate of $10\,mL\,min^{-1}$) and was carried out using a water pump or aspirated under a vacuum pump using a SPE system (VAC ELUT SPS 24 SPE, purchased from Analytichem International). Following sample application, the cartridge was rinsed with 6 mL of Milli-Q water,

TABLE I Characteristics of distilled water and surface water from the St. Lawrence River at the Lévis sampling station. Values are the minimum–maximum (mean) observed during 1999–2000

Sample origin	*pH* $n=50$	*Conductivity* ($\mu s\,cm^{-1}$) $n=50$	*DOC* ($mg\,L^{-1}$) $n=50$	*POC* ($mg\,L^{-1}$) $n=50$	*TOC* ($mg\,L^{-1}$) $n=50$	*SPM* ($mg\,L^{-1}$) $n=50$
Distilled water	5.95	5	–	–	–	–
Surface water	7.4–8.2 (7.8)	178–262 (235)	2.5–4.6 (3.4)	0.14–1.64 (0.50)	2.8–5.7 (3.9)	2–58 (12)

DOC = dissolved organic carbon; POC = particulate organic carbon; TOC = total organic carbon; SPM = suspended particulate matter.

then aspirated for 15 min to remove residual water. A closed cartridge, filled with 2.5 g of dried anhydrous sodium sulfate (ISOLUTE sodium sulfate drying cartridge, purchased from IST Ltd., U.K., distributed by Chromatographic Specialties, Ontario, Canada) was then set up below the SPE cartridge. The target pesticides were eluted with 15 mL of DCM and acetone (80 : 20, v/v) at a rate of 1 mL min^{-1}. The eluent was collected in a conical 15-mL test tube, then reduced by a nitrogen stream at 25°C to 1 mL. A volume of 100 μL (50 ng) of the internal standard solution (atrazine-d_5) was added to the extract, then reduced to a final volume of 250 μL for GC/MS analysis.

Chromatographic Analysis and Optimization of the LVI System

Sample extracts were analysed using a Varian model 3400 GC equipped with a Varian LVI system model 1078 split–splitless programming temperature coupled with a Saturn IV ion trap MS. A splitless temperature ramp mode with an open deactivated capillary glass insert (2 mm internal diameter) was used as follows: The sample is injected at a very slow rate (2 μL s^{-1}) while the injector is set a few degrees below the solvent boiling point. The injector split valve is left open for a period of time to vent the solvent to the split vent. The split valve is then closed and the injector is rapidly heated to vapourize the solute material onto the GC column, where separation occurs.

GC/MS Analysis

A DB-5MS (5% phenyl/95% methyl) low-bleed MS capillary column (30 m × 0.25 mm i.d., 0.25 μm coating thickness, obtained from Restek, distributed by Chromatographic Specialties Inc., Ontario, Canada) and a deactivated Siltek guard column (5 m × 0.25 mm i.d., obtained from Restek) were used. The temperature of the column was initially set at 40°C for 5 min. It was increased to 300°C at a rate of 5°C min^{-1}, then held for 5 min. The temperature of the injector equipped with a deactivated Siltek liner from Restek was initially 40°C for 1 min. It was increased to 300°C at a rate of 180°C min^{-1}, then held for 58 min. Forty microlitres of the extract in DCM was injected in GC/MS without cleanup. A mass spectrometric analysis was performed by EI/MS in full scan mode from 47 to 450 u with ion extraction at specific m/z values listed in Table III. Chromatograms were drawn and quantitation done with Varian Saturn IV software.

RESULTS AND DISCUSSION

Repeatability of the LVI System

Forty microlitres of an extract, obtained from 0.5 L of spiked Milli-Q water, was injected ten different times to determine the repeatability of the detector when using the LVI. The coefficient of variation was less than 5%, thus showing the good repeatability of the LVI mode.

Calibration Curve and Linearity

The linearity of the MS detector's response was studied in relation to concentration and injection volume using the LVI mode. The MS detector's response was linear

for the target pesticides at a constant concentration and variable volumes ranging from 10 to 40 μL and at a constant injection volume (40 μL) and variable concentrations of standard solutions (20–2000 μg L^{-1}). The coefficient of variation was less than 5%, thus showing the good linearity of the LVI system. Its flexibility at different volume injections offers advantages for surface water analysis. Thus, highly contaminated and diluted samples could be extracted by the same technique (including SPE) using a small volume of water (0.5 L). The injection volume of extracts from these samples could be adjusted according to their concentration levels.

Detection Limits and Recovery Studies

A method blank was performed for every five samples using a volume of 0.5 L of Milli-Q water. Extraction was the same as for surface-water samples. No traces of the target chemicals were detected on the blanks nor was interference except for propazine (0.9 ng L^{-1}), which surprisingly was present in the internal standard (atrazine-d_5) solution at a ratio of one per cent.

Recovery studies were performed by extracting the target pesticides, previously spiked at 0.05 to 0.1 ppb levels, from 0.5-L Milli-Q and surface-water samples using SPE on ISOLUTE triazine adsorbent (C-18), followed by a 40-μL injection (LVI mode) in the GC system. Detection limits (DLs) were determined for each analyte at a concentration providing a signal-to-noise ratio of three. The DLs and recoveries obtained for each pesticide are shown in Table II. Overall percent recoveries were satisfactory for all target pesticides (> 60%) except DIA (more polar), which ranged from 29 to 46%, depending on sample pH. The coefficient of variation was below 10% and DLs were between 0.1 and 0.8 ng L^{-1}.

Environmental Levels

Using ISOLUTE triazine cartridges for the extraction process, followed by GC/MS analysis with the LVI system, atrazine, cyanazine, DEA, DIA, metolachlor and simazine were detected at concentrations ranging from 6 to 91 ng L^{-1} in filtered and raw

TABLE II Detection limits (DLs) and recovery studies (%) for target pesticides

Pesticide	*DL* (ng L^{-1})	*Mean recovery (%) (n = 3)*		
		Milli-Q water		*Surface water*
		pH 7	*pH 2*	*pH 7*
Ametryn	0.6	107 ± 3	108 ± 3	105 ± 2
Atrazine	0.2	92 ± 4	92 ± 1	80 ± 3
Cyanazine	0.8	101 ± 25	125 ± 7	125 ± 6
Desethyl-atrazine	0.3	60 ± 3	59 ± 1	55 ± 3
Desipropyl-atrazine	0.3	35 ± 4	46 ± 2	29 ± 2
Diazinon	0.1	78 ± 8	66 ± 3	79 ± 3
Ethion	0.2	119 ± 5	115 ± 11	106 ± 6
Fonofos	0.1	78 ± 8	98 ± 6	70 ± 3
Malathion	0.2	119 ± 6	108 ± 6	102 ± 16
Metolachlor	0.1	117 ± 2	107 ± 5	116 ± 2
Prometryn	0.8	98 ± 2	81 ± 1	97 ± 2
Propazine	0.2	96 ± 7	88 ± 3	96 ± 6
Simazine	0.2	98 ± 4	97 ± 4	97 ± 2

water (0.5-L samples) drawn from the St. Lawrence River. Figure 1 shows ion chromatograms obtained from raw water drawn from the Lévis station. Pesticide concentrations present in the natural waters of the St. Lawrence River are shown, along with the ions selected for monitoring purposes (Table III).

Comparison Between Filtered and Raw Surface Water

The target pesticides found in filtered water exhibited log Koc around 2–4 [4]. A recent study has shown that the pesticides detected in the St. Lawrence River are mostly present in the aqueous phase (>99%) rather than in suspended particulate matter (SPM) [2].

In general, SPE is preceded by a filtration step to eliminate the particulate phase, thereby preventing cartridge blockage. The availability of depth filters combined with the adsorbent material inside the cartridges now allows for simultaneous filtration and extraction of highly-water-soluble pesticides. In this study, we evaluated the efficiency of SPE cartridges filled with ISOLUTE triazine adsorbent and a depth filter for certain polar pesticides in filtered and raw water. No obstruction was observed during the extraction of raw water drawn from the St. Lawrence River (concentration of SPM ranging from 2 to 58 mg L^{-1}, Table I). As expected, the correlation between concentrations obtained in filtered and raw water samples was quite satisfactory for the majority of detected pesticides, being more significant for compounds with lower

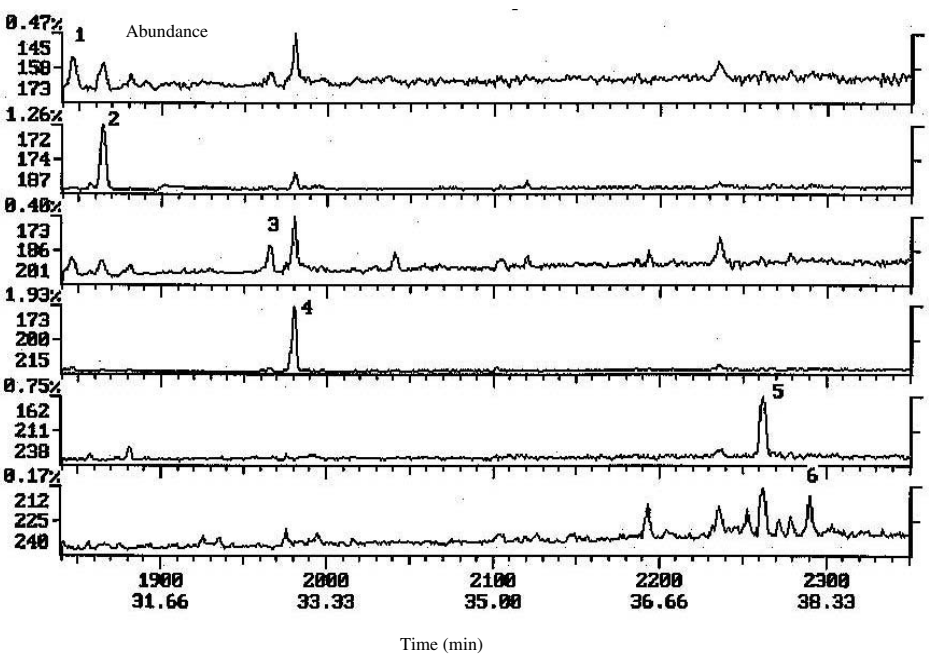

FIGURE 1 LVI/GC/MS (40 μL) ion chromatograms from an extract (250 μL in dichloromethane) obtained by SPE on 1 g ISOLUTE triazine of raw water drawn from the Lévis station. Peaks: 1 = DIA (16.0 ng L^{-1}); 2 = DEA (38.6 ng L^{-1}); 3 = simazine (6.0 ng L^{-1}); 4 = atrazine (45.1 ng L^{-1}); 5 = metolachlor (11.3 ng L^{-1}); 6 = cyanazine (13.4 ng L^{-1}).

TABLE III Mean pesticide concentrations in filtered and raw waters of the St. Lawrence River and selected ions (m/z) used for pesticide quantification by GC/MS

Pesticide	*Environmental level* ($ng\,L^{-1}$)	*Selected ions* (m/z)
Desipropyl-atrazine	7–38	145/158/173
Desethyl-atrazine	25–80	172/174/187
Simazine	< DL – 7	173/186/201
Atrazine	26–91	173/200/215
Propazine	ND	172/214/229
Fonofos	ND	109/137/246
Diazinon	ND	137/179/304
Ametryn	ND	170/212/227
Prometryn	ND	184/226/241
Malathion	ND	127/158/173
Metolachlor	8–25	162/211/238
Cyanazine	< DL – 13	212/225/240
Ethion	ND	97/153/231

ND: Not detected.

log Koc; atrazine ($r = 0.87$; log Koc = 2) and metolachlor ($r = 0.67$; log Koc = 2.3). Concentrations and temporal variations in atrazine and metolachlor, for example, in water drawn from the St. Lawrence River, were similar in both filtered and raw water samples (Fig. 2).

The seasonal distribution pattern of atrazine, for example, was similar to that previously reported by Pham *et al.* (2000) [2] for the St. Lawrence River. These authors explained seasonal variations by the dilution of the triazine-rich water from Lake Ontario by the triazine-poor waters from the north-shore tributaries (80% forested land), which constitute up to 55% of the water discharge during spring runoff. The highest atrazine concentrations correspond to the period of herbicide application in summer and were most likely influenced by high pesticide loading from the south-shore tributaries (farm land) of the St. Lawrence River.

Comparison between Large-Volume Extraction (LVE) of Filtered Surface Water and Large-Volume Injection (LVI) in GC

When considering long-term temporal variations in pesticide monitoring, one should be careful to avoid the introduction of a bias when analytical methods are changed.

Pesticides have been monitored in the St. Lawrence River since 1995 using a method based on the extraction of large volumes of filtered surface water and GC/NPD analysis. To substitute this method by the proposed alternative, the latter first had to be validated for temporal continuity. Thus, the data obtained by both methods – LVE of water samples (40 L) with the GLSE system followed by 1-μL injections in GC/NPD, and small-volume extraction (0.5 L) by SPE followed by 40-μL injections (LVI mode) in GC/MS – were compared. The two methods allowed for the determination of target pesticides at $ng\,L^{-1}$ levels. However, the new one has the advantage of being less costly, more practical, faster, more precise and more efficient as well as requiring less solvent and presenting less interference. In addition, it can be easily extended to other pesticides that cannot be recovered with the previous one.

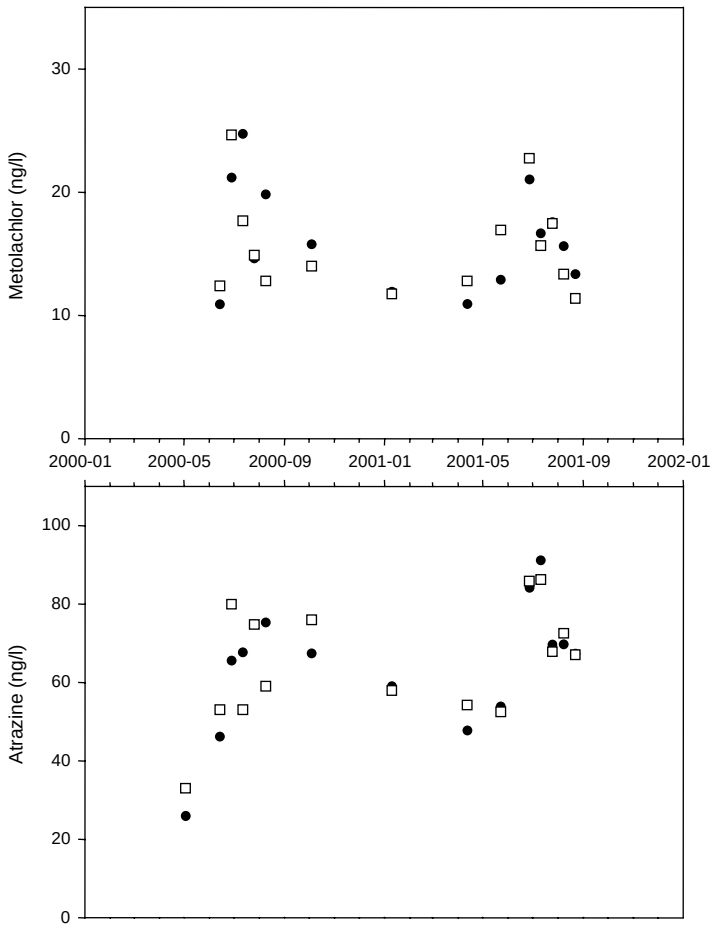

FIGURE 2 Comparison of atrazine and metolachlor concentrations determined by SPE/LVI/GC/MS in filtered (dots) and raw water (squares) samples drawn from the Lévis station.

As shown in Fig. 3, temporal variations in atrazine and metolachlor, for example, in filtered water drawn from the St. Lawrence River, were similar, whether using LVE with the GLSE system combined with GC/NPD analysis or the SPE filled with ISOLUTE triazine material combined with the LVI in GC/MS.

Statistical analysis A statistical analysis of atrazine and metolachlor comparative measurements was performed and a model of the sources of variability was fitted to the data. Sample concentration variations and daily laboratory performance were considered to be random factors whereas the systematic difference between analytic methods was modeled as a fixed factor. The sources of variation were partitioned similarly for both compounds, as follows: sample concentration variability (coefficient of variation) was on the order of 30% and variations associated with laboratory performance amounted to 10%, which left 20% of unexplained variation (random error).

The difference between the two methods for the metolachlor results was not significantly higher than expected from random fluctuations, with a confidence interval of -16 to $+26\%$. For atrazine, the new SPE/LVI/GC/MS method systematically

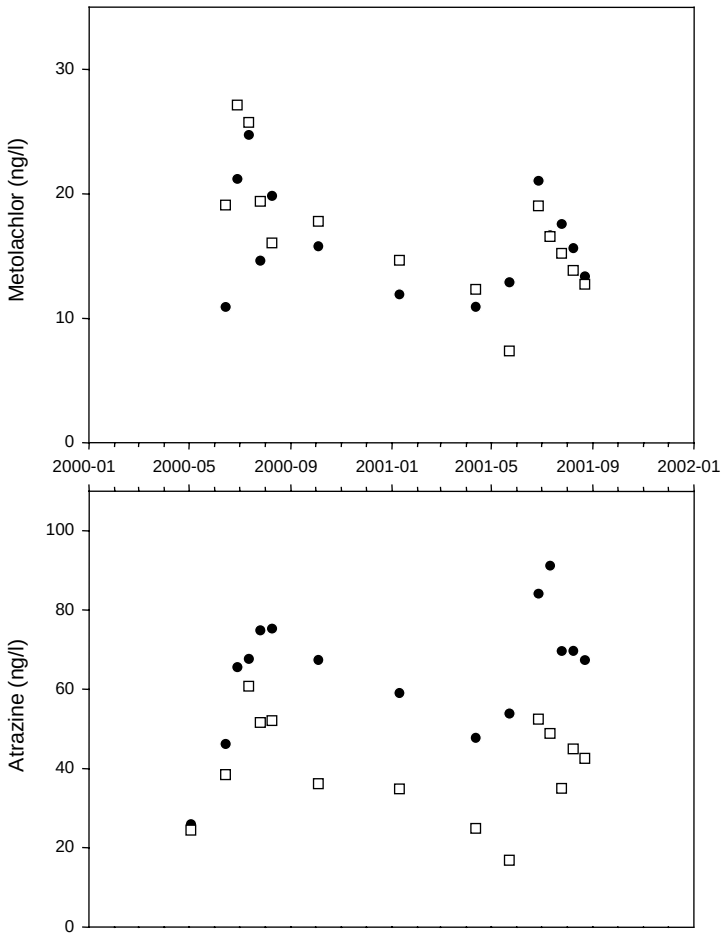

FIGURE 3 Comparison of temporal variations in atrazine and metolachlor concentrations determined by SPE/LVI/GC/MS (dots) *vs* LVE/GLSE/GC/NPD (squares) in filtered surface water samples drawn from the Lévis station.

found concentrations 62% higher than LVE/GLSE/GC/NDP applied to the same field samples.

This comparison of the methods is based on 14 pairs of measurements for each contaminant. Within the limited precision achieved by such a small sample size, it is clear that a change in favour of the new analytical method will require the application of a correction factor to atrazine concentration time series acquired with the old method.

Conclusion

The SPE method using ISOLUTE triazine (C-18) for 0.5-L raw surface water samples followed by GC/MS with an LVI (40 µL) system allowed for the ultra-trace analysis of a wide range of polar pesticides and some of their degradation products. Overall percent recoveries were satisfactory for all target pesticides ($>60\%$), except for DIA (more polar), ranging from 29 to 46%, depending on sample pH. The coefficient of

variation was below 10% for the majority of target pesticides and detection limits ranged from 0.1 to 0.8 ng L^{-1}. No blockage was observed during the extraction of raw water drawn from the St. Lawrence River (concentration of SPM ranging from 2 to 58 mg L^{-1}; Table I). Using atrazine and metolachlor as examples, the correlation between concentrations obtained in filtered and raw water samples were more significant for the former ($r = 0.87$; $\log \mathrm{Koc} = 2$) than for the latter ($r = 0.67$; $\log \mathrm{Koc} = 2.3$). Again, temporal variations in atrazine and metolachlor in filtered water drawn from the St. Lawrence River, for example, were similar whether using LVE in the GLSE system combined with GC/NPD analysis, or SPE filled with ISOLUTE triazine material combined with the LVI in GC/MS. However, the latter method systematically found atrazine concentrations 62% higher than those obtained by the previous method, applied to the same field samples. Thus, the change in favour of the new analytical method will require the application of a correction factor to atrazine concentration time series acquired with the previous method.

The proposed method, based on the extraction of small sample volumes of raw water using a SPE technique, followed by the injection of large volumes of the extracts in GC/MS, could easily be extended to other organic contaminants with log Koc around 2 (mostly dissolved). For pesticides having higher log Koc (e.g. > 4), a pre-filtration of raw water through 0.45-μm PTFE filters is recommended prior to SPE. Finally, this method would allow for savings of time and money, in addition to reducing the need for toxic solvents.

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