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# Stability of organophosphorus insecticides on graphitized carbon black extraction cartridges used for large volumes of surface water

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## Abstract

The stability of nine organophosphorus insecticides (azinphos-ethyl, azinphos-methyl, diazinon, EPN, ethion, fonofos, malathion, phosmet and parathion-methyl) was evaluated under a variety of storage conditions. Large volumes of surface water (4 l) were extracted using large-particle-size graphitized carbon black cartridges (Carbopack B 60–80 mesh). The effects of temperature, matrix type and drying of cartridges on the recovery of these contaminants, after different storage periods, were studied and compared to the conservation of surface water in bottles. After a 2-month period, all the chemicals stored on cartridges and kept at  $-20^{\circ}\text{C}$  remained stable, with recoveries ranging from 70 to 134%. By contrast, phosmet and EPN could no longer be recovered from the bottled surface water. Cartridges kept at  $-20^{\circ}\text{C}$  fared better than did those stored at  $4^{\circ}\text{C}$  and  $20^{\circ}\text{C}$ . The type of matrix water selected appears to have kept the target pesticides stored on cartridges from degrading, compared to the Milli-Q water, in which malathion and phosmet were unstable. The effect of the cartridges being either wet or dry made no difference in terms of improving the recovery of chemicals. After immediate surface water extraction, the most practical storage condition for the target insecticides was found to be storage on cartridges in the dark at  $-20^{\circ}\text{C}$ , with no drying or solvent washing of the Carbopack B material. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Environmental surveys require the analysis of a large number of samples. Field samples should be analysed immediately after collection to avoid any chemical, physical and biological analyte alterations. For a number of reasons, however, this is simply impossible. The loss of pesticides in water can be due to several processes, including hydrolysis, photolysis, biodegradation and oxidation. Indeed, the US Environmental Protection Agency (EPA) cited these processes for its decision to remove organophosphorus

pesticides from the National Pesticide Survey (NPS) list [1,2]. By contrast, some of these chemicals have been placed on the Commission of the European Union's list of pesticides (council directive 76/464/EEC) to be monitored in the aquatic environment [3], including azinphos-methyl and parathion. Many organophosphorus insecticides, including diazinon and phosmet, are reported to be unstable and suffer 100% loss when stored at  $4^{\circ}\text{C}$  for 14 days in biologically-inhibited well water [2]. Beyond that, it is essential to ensure the integrity of pesticide samples, from their collection to the data reporting phase. A sample preservation study should therefore be performed as part of any analytical procedure.

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Standard preservation techniques have been recommended by different government organisations for the storage of water samples in containers or after liquid–liquid extraction [4,5]. Studies on alternative pesticide stabilization techniques, including the use of freeze-drying, have been published [6]. The results obtained with this technique show that the stability of the compounds depends on their water solubility and vapour pressure. Other recent papers have demonstrated that solid-phase extraction (SPE) is a good alternative to the storage of pesticides preconcentrated from water samples [2,4,7–9]. Studies dealing with the stability of organic contaminants on filter or cartridge-extraction material [ $C_{18}$ , graphitized carbon black (GCB), XAD-2] have already been published [2,4,7–9], although only two papers have focused on the use of GCB cartridges for stabilising pesticides [7,10]. None, however, deals with the extraction of organophosphorus insecticides from large volumes of surface water using large-particle-size GCB cartridges. On the one hand, the use of large volumes of surface water may increase the quantity of dissolved organic carbon (DOC) and microbial biomass retained by the cartridge material; on the other, the use of large-particle-size GCB cartridges may facilitate their passage, minimising retention. Moreover, the main factors affecting the stability of analytes in water samples – in addition to the nature of the sample in terms of pH, DOC, microbial biomass, and oxygen – are sample container-type and storage conditions (temperature, light, use of preservatives, and time interval between sampling and analysis).

Previous studies have reported the presence of contaminants in the St. Lawrence River [11–15]. Due to the large-scale dilution of these contaminants, large volumes of surface water (10 to 40 l) have been necessary to detect such chemicals. An SPE technique using large-particle-size GCB cartridges (Carbopack B 60–80 mesh) has been recently developed for extracting organophosphorus insecticides from large volumes of surface water (up to 20 l) [13]. This technique could be easily used for on-site extraction of up to 24 samples at a time, making it ideal for extracting samples immediately after collection in order to avoid possible analyte alterations. The small volume of the cartridges allows for easy storage until elution/purification and analysis.

The aim of this study was to evaluate the stability, under a variety of storage conditions, of nine organophosphorus insecticides extracted from large volumes of surface water using large-particle-size GCB cartridges (Carbopack B 60–80 mesh). In addition to the advantage of the SPE technique for on-site extraction, positive results would mean reduced time and space requirements, since cartridges would be stored instead of surface water.

## 2. Experiment

### 2.1. Reagents and chemicals

All pesticides were obtained from different suppliers. Azinphos-ethyl, ethion, malathion, parathion-methyl and phosmet were obtained from the EPA. Azinphos-methyl, EPN, fonofos and tetrachlorvinphos (used as internal standard) were purchased from Chem Service (West Chester, PA, USA). Diazinon was obtained from Ultra-Scientific, distributed by Fisher Scientific (Montreal, Canada).

Ethyl acetate and hexane (all distilled-in-glass grade) were purchased from Caledon Labs. (Georgetown, Canada) and used without further clean-up. 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 a 293-mm diameter Gelman fibre glass filter (TCLP type with 0.7  $\mu\text{m}$  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 samples. Water was stored in 4-l umber glass bottles.

### 2.2. Standard solutions

Primary stock solutions of all insecticides 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 chemicals were then prepared from these solutions in the same

Table 1

Characteristics of distilled water and surface water from the St. Lawrence River at the Lévis sampling station<sup>a</sup>

Sample origin	pH (n=90)	Conductivity ( $\mu\text{S}/\text{cm}$ ) (n=90)	DOC (mg/l) (n=90)	POC (mg/l) (n=90)	Faecal coliforms (FCU/100 ml) (n=223)
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)	10–2000 (206)

<sup>a</sup> Values are the minimum and the maximum observed during 1995 (mean of values). Note: DOC=dissolved organic carbon; POC=particulate organic carbon; TOC=total organic carbon; FCU=faecal coliform units.

solvent at concentrations of 0.5 mg/l. Tetrachlorvinphos served as the internal standard (I.S.) and a working solution of 10 mg/l was prepared in hexane. Working solutions containing the target insecticides and internal standard were prepared in ethyl acetate to construct the calibration curve. Concentrations of the targeted compounds ranged from 0.1 to 2 mg/l, 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 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 River water mass [16]. Surface water was sampled 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 [17]. Filtered water samples were collected in Spartanburg 20-l stainless steel containers. The characteristics [18] of selected surface waters are shown in Table 1.

### 2.4. Storage treatment

Six experiments were conducted using 4-l sample

volumes of filtered surface water to determine the best storage conditions for the target insecticides. We evaluated and compared the effect of temperature, matrix (pH, DOC, microbial biomass) and drying on the recovery of the selected contaminants, after different storage periods, to their recovery in the bottled surface water. The effect of light exposure on these compounds was not studied. All the cartridges were covered with aluminum paper and stored, as were the bottles of surface water, in the dark. The list of storage treatments is presented in Table 2.

### 2.5. Solid-phase extraction

Upon its arrival at the laboratory, the filtered water was divided into 4-l sample volumes. Each sample was spiked with 0.5 ml of spiked solution (0.5 mg/l), then stirred for 5 min and set aside until extraction. All the samples used in the cartridge storage experiments were extracted immediately and the cartridges were stored in defined conditions (Table 2). The surface waters used for sample conservation were stored in 4-l umber glass bottles at 4°C in the dark until extraction. The selected SPE technique has been well described by Sabik [13]. Briefly, an SPE system (Vac Elut SPS 24 SPE, purchased from Analytichem International) was used to aspirate each sample through a cartridge filled

Table 2

Storage treatments for target pesticides

Experiment	No. pesticides	Matrix	Total storage period (days)	Storage treatment
A	9	SLR water	60	GCB cartridge stored dry at -20°C
B	9	SLR water	60	GCB cartridge stored dry at 4°C
C	9	SLR water	60	GCB cartridge stored dry at 20°C
D	9	SLR water	60	GCB cartridge stored wet at 4°C
E	9	SLR water	60	Bottle stored at 4°C
F	9	Milli-Q water	60	GCB cartridge stored dry at 4°C

with 500 mg of large-particle-size GCB material (Carbopack B 60–80 mesh) ( $6.5 \times 1.4$  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). The samples were applied to the cartridges, which were then rinsed with 6 ml of Milli-Q water. The target pesticides were completely eluted by running 50 ml of ethyl acetate through the cartridge. The final extract volume was reduced to 500  $\mu$ l of hexane containing 0.5  $\mu$ g of the internal standard.

### 2.6. 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 detection (NPD) system. DB-5 (5% phenyl–95% methyl) and/or DB-210 (50% trifluoropropyl–50% methyl) capillary columns ( $30 \text{ m} \times 0.25 \text{ mm}$  I.D.,  $0.25 \mu\text{m}$  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  $214^\circ\text{C}$  for the DB-5 column and 35 cm/s set at  $181^\circ\text{C}$  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  $300^\circ\text{C}$  when the DB-5 column was used and at  $250^\circ\text{C}$  for the DB-210 column. A 1- $\mu\text{l}$  volume of the extract in hexane was injected. Chromatograms and quantitation were done with Varian Star version 4.0 software. The details of the analytical technique have been well described by Sabik [13].

## 3. Results and discussion

The target insecticides were selected for this study based on their toxicity, intensity of use and instability in water [7,19–21]. Large-particle-size GCB material (Carbopack B 60–80 mesh) was chosen because it allows for the extraction of large volumes of surface water (up to 20 l). This was not possible with small-particle-size material (Carbopack B 120–400 mesh) [13].

All selected insecticides exhibited satisfactory recoveries. For example, the recoveries for target chemicals stored on cartridges at  $-20^\circ\text{C}$  for 2 months ranged from 70 to 134% (Table 3). These values were similar to the rates obtained by Sabik [13]. They were obviously lower than those obtained with the small-particle-size GCB material (Carbopack B 120–400 mesh), used for sample volumes of up to 1 l [10]. 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. Given the large volumes of surface water involved in this study, it is difficult to consider samples in triplicate or to increase the number of sampling sites. Furthermore, previous studies have already shown that water collected at the sampling site selected for this study is representative of the St. Lawrence River water mass [16], and that the extraction of large volumes of water by GCB cartridges (Carbopack B 60–80 mesh) has good reproducibility [13].

### 3.1. Factors affecting pesticide losses during cartridge storage

#### 3.1.1. Temperature

Three experiments were conducted at different temperatures:  $-20^\circ\text{C}$  (experiment A),  $4^\circ\text{C}$  (experiment B) and  $20^\circ\text{C}$  (experiment C). All cartridges were stored in the dark after drying. Our results showed that temperature had a major effect on the storage of the target chemicals retained on the cartridge material. After 2 months, recoveries for selected organophosphorus insecticides decreased by between 14 to 54% and between 22 to 66% (Table 3) when cartridges were stored at  $4^\circ\text{C}$  or  $20^\circ\text{C}$ , respectively, instead of  $-20^\circ\text{C}$ . This was not surprising; indeed, Bussiere et al. [21] had previously reported that the activation energy ( $E_a$ ) values depend on temperature: the greater the  $E_a$  value, the greater the dependence on temperature (i.e., the degradation kinetics speed up as the temperature increases). No significant new peak was observed on the chromatograms corresponding to different storage periods either at  $4^\circ\text{C}$  or  $20^\circ\text{C}$ . Chromatograms corresponding to samples A60 (cartridge stored dry at  $-20^\circ\text{C}$ ) and

Table 3  
Results of recoveries (%) for target insecticides<sup>a</sup>

Sample reference <sup>b</sup>	Recovery (%)								
	Fonofos	Diazinon	Parathion-methyl	Malathion	Ethion	Phosmet	EPN	Azinphos-methyl	Azinphos-ethyl
A00	28	70	92	90	70	72	54	92	102
A01	24	70	90	90	66	76	54	94	100
A07	72	90	100	106	87	84	68	112	122
A30	84 (+27)	90 (+7)	104 (+31)	106 (+40)	87 (+8)	80 (+41)	68 (+14)	128 (+36)	120 (+13)
A60	94 (+39)	94 (+15)	106 (+39)	102 (+32)	89 (+16)	70 (+34)	72 (+27)	134 (+39)	134 (+26)
B00	28	70	92	90	70	72	54	92	102
B01	22	70	80	88	66	80	54	92	104
B07	62	86	86	94	81	72	66	54	112
B30	66 (+9)	88 (+5)	88 (+15)	84 (+18)	77 (-2)	64 (+25)	66 (+12)	98 (+6)	116 (+9)
B60	44 (-11)	78 (-1)	62 (-5)	78 (+8)	72 (-1)	42 (+6)	50 (+5)	80 (-15)	92 (-16)
C00	28	70	92	90	70	72	54	92	102
C01	18	66	72	78	62	60	52	70	86
C07	71	61	70	76	60	74	60	74	78
C30	16 (-41)	72 (-11)	14 (-59)	48 (-18)	64 (-15)	18 (-21)	52 (-2)	22 (-70)	54 (-53)
C60	38 (-17)	72 (-7)	54 (-13)	72 (+2)	68 (-5)	42 (+6)	50 (+5)	68 (-27)	92 (-16)
D00	28	70	92	90	70	72	54	92	102
D01	18	70	70	84	65	74	52	84	100
D07	68	84	88	92	80	72	66	100	118
D30	74 (+17)	90 (+7)	94 (+21)	90 (+24)	83 (+4)	72 (+33)	70 (+16)	114 (+22)	126 (+19)
D60	50 (-5)	78 (-1)	72 (+5)	78 (+8)	74 (+1)	54 (+18)	54 (+9)	92 (-3)	100 (-8)
E00	28	70	92	90	70	72	54	92	102
E01	26	58	80	72	62	30	36	94	94
E07	68	80	96	90	79	8	58	120	118
E30	52 (-5)	56 (-27)	72 (-1)	70 (+4)	72 (-7)	0 (-39)	0 (-54)	96 (+4)	102 (-5)
E60	84 (+29)	88 (+9)	86 (+19)	84 (+14)	81 (+8)	0 (-36)	0 (-45)	126 (+31)	134 (+26)
F00	42	86	104	118	90	112	74	112	124
F01	60	84	102	106	82	98	74	102	116
F07	66	98	110	66	90	58	76	124	146
F30	52 (-5)	104 (+21)	66 (-7)	0 (-66)	93 (+14)	0 (-39)	66 (+12)	92 (0)	124 (+17)
F60	22 (-33)	62 (-17)	22 (-45)	6 (-64)	56 (-17)	10 (-26)	44 (-1)	68 (-27)	98 (-10)
Mean 30 <sup>c</sup>	57	83	73	66	79	39	54	92	107
Mean 60 <sup>c</sup>	55	79	67	70	73	36	45	95	108

<sup>a</sup> Cartridges were stored under different conditions.

<sup>b</sup> Note: Numbers appearing alongside sample references A to F indicate time before cartridge elution, except for experiment E which refers to time before extraction (e.g., samples A00 to F00 were both extracted and cartridges eluted immediately; samples A01 to D01 and F01 were extracted immediately and cartridges eluted after one day of storage, etc.). Samples in experiment E01 to E60 were extracted after storage time indicated and eluted immediately after extraction.

<sup>c</sup> Mean 30/Mean 60: mean recovery (%) for all experiments after 30 and 60 days. Values in parentheses are the difference between the experimental value and the mean calculated [e.g., A30 for fonofos: (+27)=A30–mean 30=84–57].

C60 (cartridge stored dry at 20°C) are presented in Fig. 1a and b. Because the analyses were carried out using gas chromatography without any derivatization, the detection of potential degradation products

remains difficult due to their high theoretical polarity. As the cartridges were washed with sterilised water before elution to evacuate bacteria, it is speculative at best to attribute this decrease in

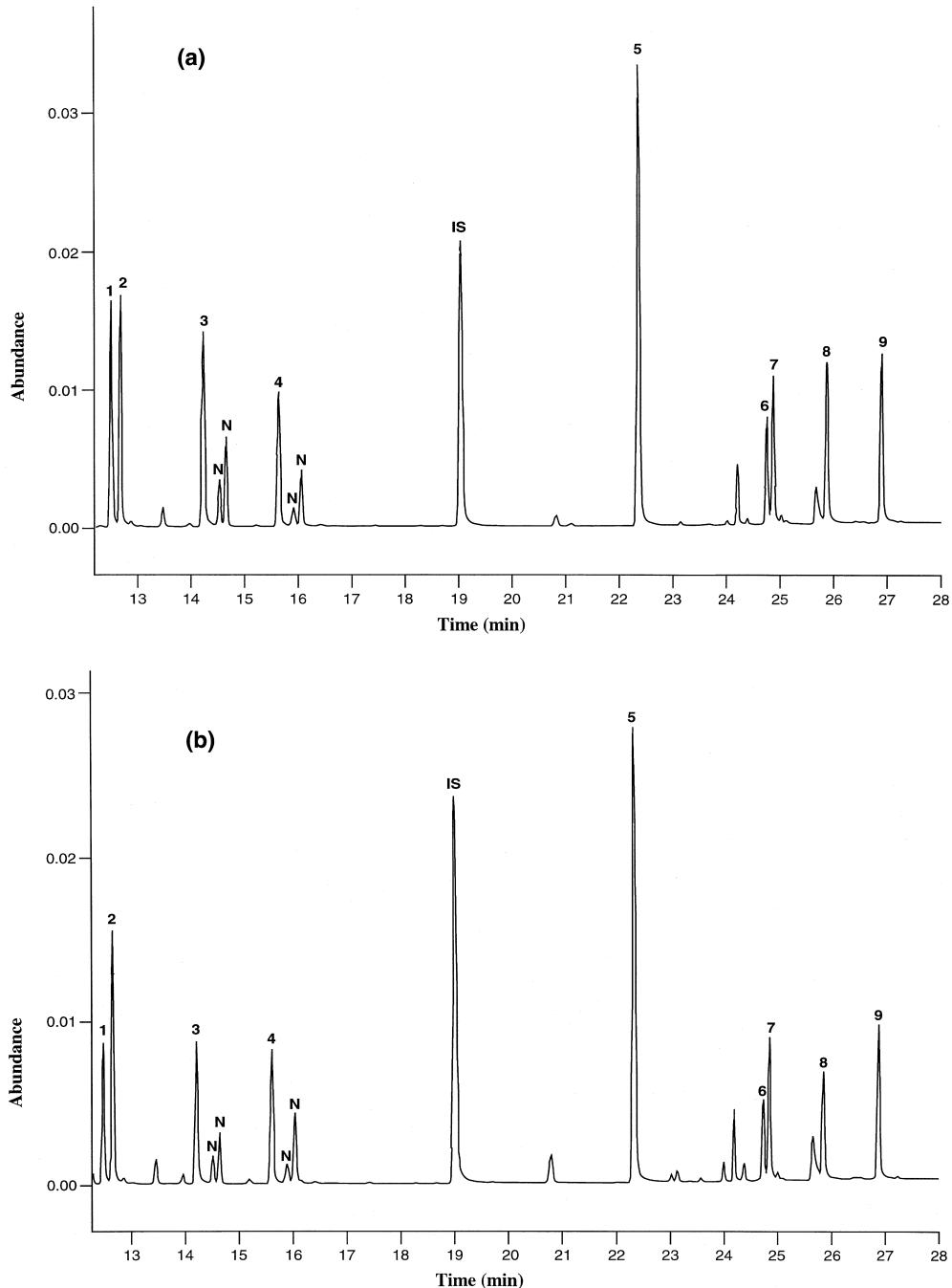


Fig. 1. (a) Chromatogram corresponding to sample A60 (surface water, cartridge stored dry at  $-20^{\circ}\text{C}$ ); 1=diazinon; 2=fonofos; 3=parathion-methyl; 4=malathion; 5=ethion; 6=phosmet; 7=EPN; 8=azinphos-methyl; 9=azinphos-ethyl; I.S.=tetrachlorvinphos (internal standard); N=organonitrogen pesticide. (b) Chromatogram corresponding to sample C60 (surface water, cartridge stored dry at  $20^{\circ}\text{C}$ ); peaks as in (a). (c) Chromatogram corresponding to sample D60 (surface water, cartridge stored wet at  $4^{\circ}\text{C}$ ); peaks as in (a). (d) Chromatogram corresponding to sample F30 (Milli-Q water, cartridge stored dry at  $4^{\circ}\text{C}$ ); peaks as in (a). (e) Chromatogram corresponding to sample E60 (surface water, bottle stored at  $4^{\circ}\text{C}$ ); peaks as in (a).

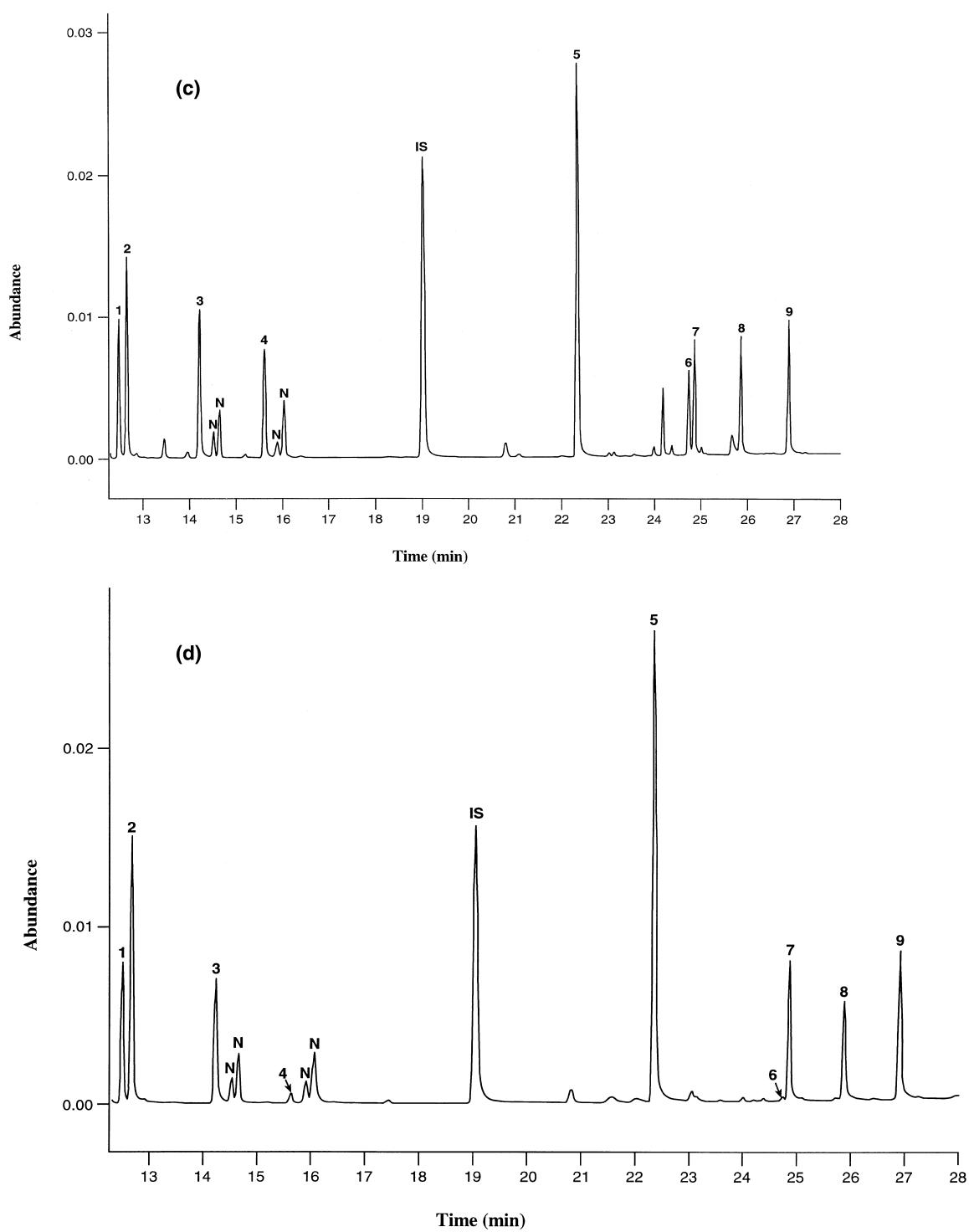


Fig. 1. (continued).

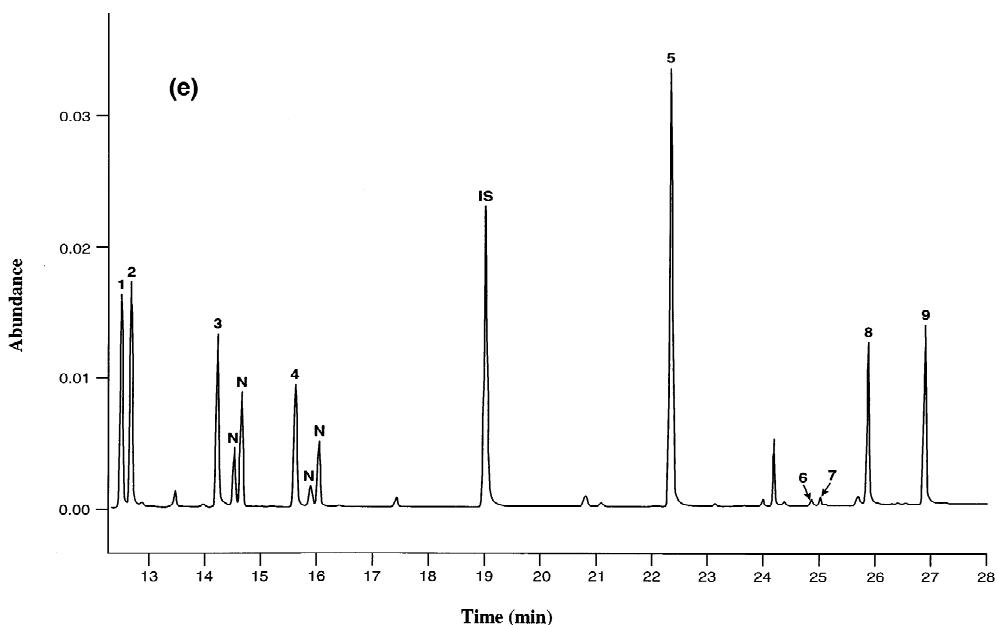


Fig. 1. (continued).

recoveries to the process of biodegradation. Additional studies should be carried out to determine how temperature affects the loss of selected chemicals on these cartridges.

### 3.1.2. Cartridge drying

Two experiments were set up to evaluate the effect of cartridge drying on the storage of pesticides. Experiments B and D consisted of storing the dried and undried cartridges used for the extraction of 4-l sample volumes. Both cartridges were stored in the dark at 4°C. Our results showed no differences in the target pesticides extracted from surface water, whether the cartridges were wet or dried (Table 3). We might thus conclude that, at 4°C, the chemicals did not hydrolyze on the cartridges when extracted from surface water. A chromatogram corresponding to sample D60 (cartridge stored wet at 4°C) is presented in Fig. 1c.

### 3.1.3. Aqueous matrix

Two experiments were conducted to evaluate the effect of matrix water on the storage of pesticides. Experiments B and F consisted of storing cartridges used for the extraction of 4-l sample volumes of

surface and Milli-Q waters, respectively. Both cartridges were stored in the dark at 4°C. The type of matrix water selected appears to have kept the target pesticides stored on cartridges from degrading, compared to the Milli-Q water, in which malathion and phosmet showed a high instability for samples analysed after 30 days of storage. A chromatogram corresponding to sample F30 (Milli-Q water, cartridge stored dry at 4°C) is presented in Fig. 1d. As photodegradation (storage in the dark) and biodegradation (Milli-Q water matrix) cannot be considered in this study, the instability of these chemicals may be due to the pH and/or to the free-humic substances in this matrix. Indeed, it has been reported [22,23] that the degradation of malathion is regulated by the pH level in water (increases with alkaline pH) and the colloids present in surface water may protect some pesticides from degradation, increasing their half-lifetimes [23]. Lartiges and Garrigues [20] have demonstrated that phosmet has a high affinity for adsorption on particulates present in surface water. Taking this into account, one might expect that a fraction of the colloids present in surface water could be retained by the cartridges, resulting in the adsorption of chemicals until their elution. This was

not the case for the Milli-Q water. Processes such as sorption, degradation, and transformation have all been reported to be affected by DOC [24]. No DOC or microbial biomass analysis was performed after the sample water had been passed through the cartridges. Further studies should be carried out to determine how the surface water matrix with different properties (high vs. low DOC) can affect the loss of pesticides to these cartridges.

### 3.2. Comparison between surface water conservation and cartridge storage

Two experiments were conducted to compare surface water conservation and cartridge storage after surface water extraction. Experiment A consisted of storing the cartridges used to extract 4-l sample volumes of surface water, whereas experiment E consisted of extracting the same volume of surface water after sample conservation in bottles. Cartridges were stored at  $-20^{\circ}\text{C}$ , and surface water was stored at  $4^{\circ}\text{C}$ , both in the dark. After a 2-month period, all the chemicals stored on cartridges and kept at  $-20^{\circ}\text{C}$  remained stable, with recoveries ranging from 70 to 134%. By contrast, phosmet and EPN could no longer be recovered from the bottled surface water kept at  $4^{\circ}\text{C}$ . A chromatogram corresponding to sample E60 (bottle stored at  $4^{\circ}\text{C}$ ) is presented in Fig. 1e. In addition to the advantage of preserving target pesticides from degradation and their on-site application, cartridges are also easily maintained at much lower temperatures, offering time and space savings with no need to transport sample containers.

## 4. Conclusion

This study has shown that it is possible to preserve organophosphorus insecticides in large volumes of surface water, with no physical, chemical or biological alteration of these compounds, by using GCB cartridges (large-particle-size Carbopack B 60–80 mesh). This was not possible with the conservation of surface water in bottles. In addition to their ability to preserve target chemicals from degradation, cartridges are also easily maintained at much lower temperatures, offering time and space savings with

no need to transport sample containers. SPE using GCB cartridges can be used for on-site extraction, with the analysis being performed in a laboratory a few days or even weeks later. The use of large volumes of surface water may increase the quantity of DOC and microbial biomass retained by the cartridge material, whereas the use of large-particle-size GCB cartridges may facilitate the passage of these variables and minimise their retention by the cartridge material. The results have shown that only temperature and Milli-Q water can affect the storage of selected insecticides on GCB cartridges. No hydrolysis of target chemicals was observed on the cartridges when extracted from surface water. Cartridge dryness or wetness had no improved effect on recovery. Following immediate surface water extraction, the most practical storage condition for the target insecticides was found to be storage on cartridges in the dark at  $-20^{\circ}\text{C}$ , with no drying or solvent washing of the Carbopack B material.

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