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Comparison of the performance of solid-phase extraction techniques in recovering organophosphorus and organochlorine compounds from water

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Abstract

Solid-phase extraction (SPE) of 11 organochlorine and 24 organophosphorus compounds from aqueous solution was evaluated using different Amberlite (XAD-2 and XAD-7) resin mixtures, reversed-phase C₁₈ bonded-silica disks, and poly(styrene–divinylbenzene) (SDB) co-polymer disks. Macroreticular resins provided low recoveries and unacceptable reproducibility for some compounds including malathion, methylparathion, ethylparathion, chlorthion and endosulfan compounds. This is probably due to irreversible adsorption or chemical degradation. No relationship was observed between the recoveries and the log K_{ow} of the compounds. Octadecyl-bonded silica and styrene–divinylbenzene disks provided comparable results for the selected compounds with recovery efficiencies depending on the polarity of the compounds. Good recoveries were achieved for compounds with water solubilities below 300 mg/l or with log K_{ow} greater than 2. Poor recoveries were obtained for dichlorvos, monocrotophos and dimethoate.

Keywords: Solid-phase extraction; Extraction disks; Extraction resins; Environmental analysis; Organophosphorus compounds; Organochlorine compounds; Pesticides

1. Introduction

Pesticides in drinking water are generally present at levels such that their determination requires the use of preconcentration techniques. The EC Drinking Water Directive (EEC 80/778) states that individual pesticides should not exceed 0.1 $\mu\text{g/l}$, but the increasingly strict environmental regulations may require legal de-

tection limits as low as 0.1 ng/l during the next few years.

Sorbents provide a convenient means for isolating organic material from large volumes of water compared with conventional liquid–liquid extraction [1]. The two main processes of solid-phase extraction (SPE) are (i) adsorption of the dissolved substance onto a solid support, and (ii) partitioning of the dissolved compound preferentially into a solid sorbent.

Adsorption experiments with resins have suggested that sorption of organic solutes is due to Van der Waals forces, which allow easy desorp-

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tion of the adsorbed molecules [2]. The adsorptive capacity of an adsorbent depends, in part, on its treatment, manufacturing conditions and its composition. The polymers most commonly used are styrene–divinylbenzene copolymers, such as Amberlite XAD-2 and XAD-4, and acrylate polymers (Amberlite XAD-7 and XAD-8).

Bonded-silica groups which interact with the dissolved compounds, can be functional groups of different polarity such as C_8 and C_{18} hydrocarbons, cyano and amino groups. Octadecyl-bonded silica is one of the most commonly used because of its large capacity, as compared with other bonded silicas. The mechanism of C_{18} bonded-phase extraction is based on non-polar interactions between the carbon–hydrogen bonds of the sorbent and the carbon–hydrogen bonds of the analyte. The use of octadecyl-bonded SPE has been proposed by the U.S. Environmental Protection Agency (EPA) in the analysis of basic and neutral organics from drinking water (Method 525). The more recent use of SPE disks overcomes some limitations of the more traditionally used cartridges. A great number of small-sized particles on the disk create a high surface area permitting a faster flow-rate and a very uniform particle distribution which eliminates the channeling observed in packed columns. Moreover, they also give lower interference levels when compared to conventional SPE cartridges with polyethylene frits [3,4].

Bonded-phase silica sorbents have several advantages over polymeric resins. They do not require extensive clean-up, there are usually fewer chromatographic interferences during analyses [4–8] and they permit faster analyses and less consumption of solvents. On the other hand, XAD-resins are less expensive and allow the extraction of larger volumes of water with higher flow-rates.

Up until now, C_{18} cartridges and Amberlite columns have been widely applied for the extraction of pesticides from the water [9–32] but advantages of the new adsorbents [C_{18} and styrene–divinylbenzene copolymer (SDB)] in the form of Empore disks require further investigation. Only few studies have reported the use of these new C_{18} membrane disks for the analyses

of organophosphorus and organochlorine pesticides [33–37] and no data for these compounds exist using the new SDB Empore disks. In the present paper, we examine and compare the performance of C_{18} and SDB Empore disks and Amberlite resins XAD-2 and XAD-7 for the extraction and concentration of 24 organophosphorus and 11 organochlorine compounds from water. This study provides a basis for recovery of important pollutants, but future investigations will need to address the influence of the dissolved organic carbon on the extraction efficiencies of the pesticides from natural waters.

2. Experimental

2.1. Materials and reagents

Macroreticular Amberlite XAD-2 and XAD-7 of 20–50 mesh (840–300 μm), were purchased from Fluka (St. Quentin Fallavier, France) and appropriate Teflon beads ('coats') from the Filtration Etudes Conseil Company (Marseille, France). The glass columns containing the Amberlite resin were 20 cm \times 3 cm diameter with glass frits at the base and glass wool at the surface. The average pore diameters for XAD-2 and XAD-7 were respectively 90 \AA and 80 \AA , with specific surface areas of 330 m^2/g for XAD-2 and 450 m^2/g for XAD-7.

Empore extraction disks of 4.6 cm and 9 cm diameter containing Bakerbond C_{18} and SDB copolymer were purchased from J.T. Baker (Noisy le Sec, France). The C_{18} disks comprised 10% fibrillated PTFE and 90% 8 μm (particle diameter) octadecyl-modified silica with 60 \AA pore size (corresponding to approximately 500 mg of the silica material for the small disk and 2000 mg for the larger disk). Particles in the SDB disks had an average particle diameter of 6.8 μm with an 80 \AA pore size and a 350 m^2/g surface area.

Standard Millipore (47-mm) and Baker (90-mm) filtration glassware were used to support the disks during extraction of the water samples. A Soxhlet system, as described by Ehrhardt [38], was used to extract the Amberlite columns.

Solvents used were of high-purity pesticide quality (Burdick and Jackson Labs., Muskegon, MI, USA)

Authentic organophosphorus (OPs) standards (azinphos-ethyl, azinphos-methyl, chlorpyrifos, chlorthion, coumaphos, diazinon, dichlorvos, dimethoate, EPN, ethion, fenitrothion, leptophos, malathion, methidathion, methylchlorpyrifos, methylparathion, monocrotophos, parathion, sulfotep, tetrachlorvinphos, tributylphosphate, triisobutylphosphate, tris(2-ethylhexyl)phosphate, triphenylphosphate) were purchased from Riedel-de Haën (Seelze, Germany) and stock solutions of the OPs were prepared in ethyl acetate and diluted further with acetonitrile to spike aqueous samples. Ethyl acetate was the diluent for the GC standards. Organochlorine (OCs) standards (PCB 52, PCB 153, PCB 180, α -endosulfan, β -endosulfan, endosulfan sulfate, hexachlorobenzene (HCB), lindane, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT) were purchased from Promochem (Molsheim, France) and stock solutions were prepared in *n*-hexane and diluted further with methanol to spike the aqueous samples, and with ethyl acetate or hexane for GC calibration standards.

2.2. Solid-phase extraction

Recoveries were assessed from bidistilled water spiked with a 2-ml solution containing a mixture of each organophosphorus (in acetonitrile) and organochlorine standards (in methanol) which provided concentrations of between 150 and 400 ng/l for organophosphorus and 10–50 ng/l for organochlorine compounds.

Amberlite protocols

Commercial Amberlite XAD-2 and XAD-7 were rinsed several times with water and 'fines' were removed by slurring in methanol. Adsorbed contaminants were removed from the resin by sequential extraction using methanol, acetonitrile and acetone according to Ehrhardt [38].

A 250-ml volume of bidistilled water followed by the spiked water samples (2.5 l) were passed through the Amberlite columns at a flow-rate of

300 ml/min using a Cole Palmer pump (Master-Flex Model No. 7015.20). Sorbed compounds were recovered from the Amberlite columns by Soxhlet extraction (8 h) with acetonitrile for OCs and acetone for OPs. The aqueous-acetonitrile extracts were diluted with 500 ml saline (60 g NaCl/l) bidistilled water and the mixtures were then extracted with 3 consecutive portions (60 ml each) of *n*-hexane. Acetone present in the aqueous-acetone extracts was removed using a rotator evaporator and the remaining water phase (approximately 60 ml) was saturated with NaCl (6 g) and extracted 3 times with 25 ml methylene chloride. Prior to gas chromatographic analyses, both extracts were dried with Na_2SO_4 , and the methylene chloride solvent was exchanged with ethyl acetate.

Empore disk protocols

Octadecyl-silica and polystyrene-divinylbenzene co-polymer disks were first activated by wetting with methanol and were then washed with 3×10 ml ethyl acetate and were vacuum-dried. Methanol (15 ml), and bidistilled water (20 ml) were then pulled through the disks prior to use. The sample (1 or 5 l) containing 1% of wetting solvent (methanol or acetonitrile) were extracted at a rate of 30 ml/min and 70 ml/min for the 4.7 cm and 9 cm disks, respectively. The disks were dried briefly under vacuum, and compounds were eluted with 3×10 ml ethyl acetate for the 4.7 cm diameter membrane and 3×25 ml for the 9 cm membrane. Finally, the extract was dried over anhydrous sodium sulfate and concentrated to a 2 ml final volume. Extracts were then analysed by gas chromatography.

2.3. Chromatographic conditions

Organochlorine compounds were analysed using a Hewlett-Packard Model 5890 Series II gas chromatograph (Palo Alto, CA, USA) equipped with a split-splitless injector and an electron-capture detector. A 25 m \times 0.25 mm I.D. \times 0.32 μm film thickness fused-silica capillary column coated with SE-54 (Hewlett-Packard Ultra-2) was used for the analyses. The GC conditions were as follows: carrier gas nitrogen at

a flow-rate of 1.2 ml/min; temperature programme: 70°C for 2 min, 70°C to 260°C at 3°C/min, 260°C isothermal for 20 min; injector temperature 250°C; detector temperature 300°C. Organophosphorus compounds were analyzed using an HP 5890 gas chromatograph with flame photometric detection (FPD) equipped with a phosphorus filter (526 nm) (Palo Alto, CA, USA). A 25 m × 0.25 mm I.D. × 0.20 μm Chrompack OV-1701 was used for the analyses. The GC system conditions were as follows: carrier gas helium at a flow-rate of 1.5 ml/min; temperature programme: 60°C for 1 min, 60°C to 190 at 25°C/min, 190°C to 225°C at 2°C/min, 225°C to 280°C at 5°C/min, 280°C isothermal for 10 min; injector temperature 250°C; detector temperature 225°C.

Aliquots of 1–2 μl were injected in the splitless mode using a 'hot needle technique'.

3. Results and discussion

Organophosphorus compounds exhibit a great variation in their physico-chemical properties and, consequently, their analyses require the use of polar solvents in liquid–liquid extraction to recover the most polar compounds (monocrotophos, dimethoate, dichlorvos) from an aqueous phase. This is illustrated in Table 1 where the recoveries and reproducibility (R.S.D.) are shown for OPs obtained with *n*-hexane (a non-polar solvent), *n*-hexane–dichloromethane (75:25) and dichloromethane (a more polar solvent). It is apparent that dichlorvos, monocrotophos, and dimethoate were not quantitatively recovered with *n*-hexane solvent extraction. Recoveries of the non-polar organochlorine analytes from the aqueous phase, however, with *n*-hexane and dichloromethane were all higher

Table 1

Mean recoveries (%) and R.S.D. (%; in parentheses) from triplicate extractions of 1 l organophosphorus-spiked NaCl saturated (60 g/l) bidistilled water with different solvents: *n*-hexane, *n*-hexane–dichloromethane (75:25) and dichloromethane

	Spiked at (ng/l)	<i>n</i> -Hexane	<i>n</i> -Hexane–CH ₂ Cl ₂ (75:25)	CH ₂ Cl ₂
Dichlorvos	360	21 (35)	72 (57)	60 (17)
TiBP	360	94 (17)	88 (32)	81 (10)
TBP	380	84 (15)	89 (24)	90 (10)
Sulfotep	360	91 (19)	74 (29)	73 (12)
Diazinon	360	107 (8)	86 (17)	89 (7)
Monocrotophos	808	0	0	65 (15)
Methylchlorpyrifos	380	104 (8)	85 (22)	113 (18)
Dimethoate	400	0	51 (11)	110 (17)
Chlorpyrifos	400	108 (10)	85 (11)	95 (4)
Parathion-methyl	360	90 (8)	87 (17)	94 (6)
Malathion	400	95 (10)	89 (8)	103 (4)
Fenitrothion	400	99 (6)	87 (11)	100 (7)
Parathion-ethyl	400	100 (8)	94 (8)	98 (4)
Chlorthion	398	98 (9)	93 (7)	101 (5)
Tetrachlorvinphos	720	74 (4)	94 (4)	106 (5)
Methidathion	720	87 (4)	90 (6)	105 (6)
Ethion	400	103 (13)	95 (3)	105 (5)
Tris(2-ethylhexyl)phosphate	1980	85 (13)	97 (6)	104 (12)
Tributoxiethylphosphate	2380	0	24 (56)	104 (15)
Leptophos	816	105 (16)	97 (7)	111 (16)
EPN	830	107 (22)	100 (6)	109 (10)
Azinphos-methyl	1594	50 (16)	72 (5)	74 (27)
Azinphos-ethyl	1626	81 (6)	95 (5)	107 (13)
Coumaphos	1590	91 (3)	99 (10)	97 (15)

than 70% with good reproducibility (R.S.D. < 15%).

3.1. Amberlite recoveries

The large quantities of water which are adsorbed in the Amberlite column compels the use of a solvent which is miscible with water to extract the column. A low-boiling point solvent is preferred so that it can be easily removed from the aqueous phase prior to extraction with a polar solvent (dichloromethane). Thus, acetone is generally used to extract these resins, although interferences are frequently observed during the determination of organochlorine compounds using GC-ECD. Moreover, only 40% of hexachlorobenzene was recovered owing to losses during the removal of acetone from the aqueous-acetone extract. During subsequent tests, organochlorine compounds sorbed onto the Amberlite resin were extracted with acetonitrile, diluted with saline distilled water and re-extracted with *n*-hexane as described above. Recoveries and reproducibility achieved with pure XAD-2, XAD-2 mixed with Teflon beads and XAD-2 mixed with XAD-7 are indicated in Table 2.

Owing to the limitations of *n*-hexane to recover some of the more polar organophosphorus analytes, acetone was used to extract these compounds from the resin because after its evaporation, the remaining water phase could be conveniently extracted with dichloromethane. Table 2 also gives the recoveries and reproducibilities obtained using the selected resin columns.

Recoveries of the compounds under investigation are generally similar to those reported by other authors [9–11,19,20]. However, some of the compounds (malathion, methylparathion, parathion, chlorthion, lindane, α -endosulfan and β -endosulfan) appear to suffer irreversible adsorption onto the resins. Repeated solvent extraction failed to recover more of the compounds. Moreover, a decrease in the aqueous flow-rate (to 100 ml/min) to attempt enhanced extraction did not significantly improve recoveries. Solvent extraction of the water that passed through the Amber-

lite XAD-2 revealed that, of the compounds under investigation, lindane was the only pesticide for which a significant proportion was not sorbed by the column (only 30%). These data suggest that low recoveries and poor reproducibility for malathion, chlorthion, and the families of parathion and endosulfan did not result from poor extraction efficiencies. Indeed, other authors have suggested that some compounds are not completely desorbed from XAD-2 or are difficult to elute from the resin [21]. It has also been reported that strong binding due to the charge transfer complexation between the electron pair donor of the styrene-divinylbenzene and the electron pair acceptors of nitro, phenol and quinone groups, could account for this irreversible desorption [39].

XAD-7 resin, which exhibits non-ionic but highly hydrophilic properties, shows more losses than XAD-2, probably due to chemical interactions resulting in degradation [22]. Higher reproducibility was, however, observed for the more polar organophosphorus analytes (monocrotophos, dimethoate and dichlorvos) with XAD-7.

XAD-2 mixed with Teflon beads is shown to give better recoveries than XAD-2 and the XAD-2-XAD7 mixture, probably because the inert Teflon reduces the above-mentioned irreversible adsorption or degradation. As the height of the XAD-2-Teflon bed is identical to that of the other supports, the reduction in irreversible adsorption or degradation might simply be attributable to the effect of the ratio: solution mass-XAD-2 resin mass. Hence, recoveries for α -endosulfan and β -endosulfan from XAD-2 mixed with Teflon beads are almost double those obtained using pure XAD-2. High recoveries achieved for *p,p*-DDE in all resins might result from the degradation of *p,p*-DDT.

Recoveries of a compound can vary when the same sorbent is used by various analysts. These differences relate to variations in the selected protocols, e.g. the amount of sample, flow-rate, choice of the eluting solvent and even the origin of the sorbent. Some analysts report good recoveries using XAD-2 [9,10,19,20,23–25], XAD-7 [20,24,26], or XAD-2 mixed with XAD-7 [11],

Table 2

Mean recoveries (%) and R.S.D. (%) (in parentheses) of organochlorine and organophosphorus compounds from 2.5 l spiked bidistilled water using different Amberlite resins: XAD-2, XAD-2 mixed with Teflon beads and XAD-2 mixed with XAD-7 (XAD2–XAD7)

	Spiked at (ng/l)	XAD-2	XAD2–Teflon	XAD2–XAD7
<i>Organochlorine</i>		(n = 6)	(n = 5)	(n = 5)
Hexachlorobenzene	2	68 (14)	74 (10)	57 (6)
Lindane	5	40 (47)	57 (27)	10 (72)
PCB 52	16	87 (6)	87 (5)	79 (10)
α -Endosulfan	10	20 (18)	45 (17)	2 (11)
<i>p,p</i> -DDE	10	123 (15)	118 (13)	155 (31)
β -Endosulfan	10	28 (44)	54 (11)	3 (112)
<i>p,p</i> -DDD	20	102 (9)	103 (5)	85 (5)
PCB 153	17	77 (13)	80 (9)	74 (11)
Endosulfan sulphate	10	51 (18)	58 (8)	18 (52)
<i>p,p</i> -DDT	30	53 (35)	66 (14)	31 (60)
PCB 180	13	72 (14)	71 (15)	68 (11)
<i>Organophosphorus</i>		(n = 7)	(n = 4)	(n = 3)
Dichlorvos	144	60 (37)	71 (43)	52 (24)
TiBP	144	76 (22)	77 (21)	73 (15)
TBP	152	87 (16)	89 (11)	86 (6)
Sulfotep	144	80 (16)	86 (9)	85 (10)
Diazinon	144	86 (15)	91 (16)	85 (10)
Monocrotophos	323	96 (36)	97 (40)	79 (8)
Methylchlorpyrifos	152	88 (21)	79 (12)	76 (11)
Dimethoate	160	104 (15)	99 (18)	93 (2)
Chlorpyrifos	160	92 (13)	82 (15)	84 (9)
Parathion-methyl	144	75 (39)	63 (24)	60 (47)
Malathion	160	57 (35)	72 (29)	44 (87)
Fenitrothion	160	98 (18)	87 (16)	88 (9)
Parathion-ethyl	160	81 (34)	64 (24)	66 (47)
Chlorthion	159	71 (50)	60 (28)	54 (54)
Tetrachlorvinphos	288	104 (9)	92 (9)	94 (7)
Methidathion	288	105 (11)	98 (13)	94 (5)
Ethion	160	95 (9)	94 (14)	89 (5)
Tris(2-ethylhexyl)phosphate	792	59 (10)	61 (23)	58 (3)
Tributoxiethylphosphate	952	88 (16)	85 (15)	82 (4)
Leptophos	326	86 (7)	89 (12)	82 (10)
EPN	332	78 (19)	66 (22)	61 (38)
Azinphos-methyl	638	74 (18)	81 (26)	71 (16)
Azinphos-ethyl	650	91 (10)	95 (12)	90 (9)
Coumaphos	636	91 (13)	100 (13)	91 (9)

The extracting solvents of the resins were acetonitrile for organochlorine compounds and acetone for organophosphorus analytes (n = number of assays).

whilst others fail to achieve good reproducibility [21,27,28] or to recover hydrophobic mutagens from treated water [40].

The eluting capacity of the water for analytes sorbed at very low concentrations on Amberlite was investigated. For this test, 20 l of bidistilled

water was passed through the resin after the sorption of the pesticide-spiked samples (2.5 l) on XAD-2 (for the OP compounds) and on XAD-2 mixed with Teflon (for the OC com-

pounds). Results are given in Table 3. A decrease in recovery, especially for the more polar compounds (dichlorvos, monocrotophos and dimethoate), demonstrates that excessive water can

Table 3

Mean average recoveries (%) and R.S.D. (%; in parentheses) for 2.5 l of spiked-pesticide water samples without, and after, passing 20 l of bidistilled water

	Spiked at (ng/l)	2.5 l	20 l
<i>Organochlorine (XAD-2-Teflon)</i>			
		(n = 5)	(n = 3)
Hexachlorobenzene	2	74 (10)	63 (21)
Lindane	5	57 (27)	49 (13)
PCB 52	16	87 (5)	97 (6)
α -Endosulfan	10	45 (17)	45 (39)
<i>p,p</i> -DDE	10	118 (13)	100 (3)
β -Endosulfan	10	54 (11)	48 (37)
<i>p,p</i> -DDD	20	103 (5)	84 (2)
PCB 153	17	80 (9)	65 (6)
Endosulfan sulphate	10	58 (8)	49 (10)
<i>p,p</i> -DDT	30	66 (14)	43 (17)
PCB 180	13	71 (15)	58 (6)
<i>Organophosphorus (XAD-2)</i>			
		(n = 7)	(n = 3)
Dichlorvos	144	60 (37)	45 (31)
TiBP	144	76 (22)	66 (34)
TBP	152	87 (16)	91 (12)
Sulfotep	144	80 (16)	65 (9)
Diazinon	144	86 (15)	71 (10)
Monocrotophos	323	96 (36)	50 (15)
Methylchlorpyrifos	152	88 (21)	67 (19)
Dimethoate	160	104 (15)	64 (14)
Chlorpyrifos	160	92 (13)	81 (3)
Parathion-methyl	144	75 (39)	53 (3)
Malathion	160	57 (35)	44 (63)
Fenitrothion	160	98 (18)	91 (10)
Parathion-ethyl	160	81 (34)	58 (9)
Chlorthion	159	71 (50)	44 (39)
Tetrachlorvinphos	288	104 (9)	92 (8)
Methidathion	288	105 (11)	99 (10)
Ethion	160	95 (9)	89 (10)
Tris(2-ethylhexyl)phosphate	792	59 (10)	61 (19)
Tributoxyethylphosphate	952	88 (16)	90 (2)
Leptophos	326	86 (7)	81 (14)
EPN	332	78 (19)	64 (4)
Azinphos-methyl	638	74 (18)	65 (11)
Azinphos-ethyl	650	91 (10)	89 (11)
Coumaphos	636	91 (13)	96 (3)

Organochlorine were sorbed on XAD-2 mixed with Teflon beads and the resin was extracted with acetonitrile. Organophosphorus was preconcentrated on a XAD-2 and the resin was extracted with acetone (see text for details) (*n* = number of assays).

desorb these pesticides. Thus, although limits of detection can be improved by increasing the volume of the sample, it must be appreciated that losses of, in particular, the more polar compounds will occur.

3.2. Octadecyl-silica and SDB disk recoveries

OC and OP analytes could not be eluted sequentially from the disks using *n*-hexane and ethyl acetate because some of the less polar organophosphorus compounds (e.g. chlorpyrifos) were eluted in the *n*-hexane fraction with the organochlorine compounds. Thus, all compounds were eluted together with ethyl acetate.

Table 4 shows the average recoveries and R.S.D. of the organochlorine and organophosphorus compounds spiked in 1 l distilled water using the C₁₈ and SDB Empore disks. Both disks provided acceptable recoveries and precision for the compounds under investigation, with the exception of the more polar compounds such as monocrotophos and dimethoate. As the copolymer structure of SDB contains a higher specific surface area than the C₁₈ bonded phase, higher recoveries were expected for these more polar compounds with the SDB disks. However, these results agree with the low recoveries reported for both disks with the more polar pesticides of the triazine and carbamate families [41].

The passage of large amounts of pure water through octadecyl-silica is known to change its nature and recoveries of analytes might decrease [35,42]. To compensate, a wetting agent (acetone-trile or methanol) is frequently added to maintain conditioning of the C₁₈. Low concentrations (1%) are used to avoid the early breakthrough of the more polar analytes. Tests were conducted to investigate the influence of the wetting agent. As is shown in Table 5, the addition of acetonitrile (1%) apparently gives slightly better recoveries than methanol (1%) or no solvent. Nevertheless, good recoveries were only achieved for compounds with water solubilities below 300 mg/l or with a log *K*_{ow} (octanol–water partition coefficient) higher than 2. Thus, poor recoveries from C₁₈ and SDB are obtained for monocrotophos, dichlorvos and dimethoate. For

Table 4

Mean recoveries (%) and R.S.D. (%) (in parentheses) from triplicate extractions of organochlorine and organophosphorus compounds spiked into 1 l of bidistilled water

	Spiked at (ng/l)	C ₁₈	SDB
<i>Organochlorine</i>			
Hexachlorobenzene	6	60 (20)	84 (4)
Lindane	12	110 (3)	103 (6)
PCB 52	40	59 (12)	90 (5)
α -Endosulfan	25	88 (6)	95 (5)
<i>p,p</i> -DDE	25	67 (12)	91 (5)
β -Endosulfan	25	105 (11)	98 (3)
<i>p,p</i> -DDD	50	108 (5)	100 (3)
PCB 153	42	69 (10)	92 (4)
Endosulfan sulphate	25	115 (5)	101 (4)
<i>p,p</i> -DDT	75	102 (9)	110 (3)
PCB 180	32	67 (9)	94 (6)
<i>Organophosphorus</i>			
Dichlorvos	360	48 (19)	66 (6)
TiBP	360	89 (5)	81 (4)
TBP	380	92 (10)	82 (3)
Sulfotep	360	87 (11)	85 (2)
Diazinon	360	92 (12)	82 (6)
Monocrotophos	808	7 (97)	0
Methylchlorpyrifos	380	97 (11)	83 (6)
Dimethoate	400	10 (25)	15 (7)
Chlorpyrifos	400	91 (12)	82 (7)
Parathion-methyl	360	82 (18)	83 (10)
Malathion	400	92 (12)	75 (9)
Fenitrothion	400	96 (16)	83 (9)
Parathion-ethyl	400	85 (7)	86 (7)
Chlorthion	398	99 (19)	79 (8)
Tetrachlorvinphos	720	92 (15)	92 (6)
Methidathion	720	91 (13)	85 (11)
Ethion	400	89 (11)	83 (9)
Tris(2-ethylhexyl)phosphate	1980	84 (15)	68 (11)
Tributoxiethylphosphate	2380	79 (9)	80 (8)
Leptophos	816	85 (18)	84 (9)
EPN	830	81 (10)	88 (12)
Azinphos-methyl	1594	84 (13)	88 (17)
Azinphos-ethyl	1626	86 (15)	89 (8)
Coumaphos	1590	84 (17)	84 (13)

Samples were extracted using C₁₈ and SDB disks (without wetting agents).

reversed-phase sorbents such as octadecyl-silica, the breakthrough volume is a function of the hydrophobicity of the solute and the mass of sorbent used. This is illustrated in Table 6, when the use of a higher capacity disk (9 cm diameter) provides an increase in the recoveries of the

Table 5

Mean recoveries (%) and R.S.D. (%) in parentheses) from triplicate extractions of organochlorine and organophosphorus compounds spiked into 1 l of bidistilled water

	Spiked at (ng/l)	No wetting agent	1% MeOH	1% ACN
<i>Organochlorine</i>				
Hexachlorobenzene	6	60 (20)	68 (15)	59 (14)
Lindane	12	110 (3)	94 (2)	97 (9)
PCB 52	40	59 (12)	69 (7)	71 (12)
α -Endosulfan	25	88 (6)	78 (3)	79 (7)
<i>p,p</i> -DDE	25	67 (12)	77 (2)	82 (10)
β -Endosulfan	25	105 (11)	88 (3)	93 (5)
<i>p,p</i> -DDD	50	108 (5)	105 (7)	109 (7)
PCB 153	42	69 (10)	70 (6)	82 (7)
Endosulfan sulphate	25	115 (5)	117 (3)	112 (4)
<i>p,p</i> -DDT	75	102 (9)	108 (7)	109 (6)
PCB 180	32	67 (9)	74 (9)	83 (8)
<i>Organophosphorus</i>				
Dichlorvos	360	48 (19)	36 (7)	27 (11)
TiBP	360	89 (5)	83 (3)	83 (6)
TBP	380	92 (10)	87 (1)	88 (7)
Sulfotep	360	87 (11)	83 (4)	76 (9)
Diazinon	360	92 (12)	73 (27)	90 (7)
Monocrotophos	808	7 (97)	2 (173)	0
Methylchlorpyrifos	380	97 (11)	87 (3)	91 (7)
Dimethoate	400	10 (25)	6 (87)	6 (12)
Chlorpyrifos	400	91 (23)	84 (5)	101 (7)
Parathion-methyl	360	82 (18)	89 (7)	81 (8)
Malathion	400	92 (12)	87 (5)	96 (4)
Fenitrothion	400	96 (16)	88 (4)	94 (5)
Parathion-ethyl	400	85 (7)	90 (7)	90 (8)
Chlorthion	398	99 (19)	90 (4)	98 (5)
Tetrachlorvinphos	720	92 (15)	87 (3)	95 (3)
Methidathion	720	91 (13)	90 (1)	93 (4)
Ethion	400	89 (11)	84 (6)	94 (3)
Tris(2-ethylhexyl)phosphate	1980	84 (15)	77 (7)	65 (13)
Tributoxyethylphosphate	2380	79 (9)	82 (5)	96 (2)
Leptophos	816	85 (18)	82 (6)	96 (3)
EPN	830	81 (10)	84 (4)	105 (3)
Azinphos-methyl	1594	84 (13)	81 (3)	100(4)
Azinphos-ethyl	1626	86 (15)	81 (3)	99 (2)
Coumaphos	1590	84 (17)	79 (4)	102 (2)

Samples were extracted using C₁₈ disks: (i) without adding a wetting agent, (ii) with 1% methanol (MeOH), (iii) with 1% acetonitrile (ACN) (see text for details).

more soluble compounds (dichlorvos, monocrotophos and dimethoate).

When larger volumes (5 l) of water containing the same amounts of analytes were passed through the octadecyl-silica phase, no significant differences in the recoveries of all the com-

pounds was observed (Table 7). The method was shown to provide reliable extraction for concentrations ranging from 1.2 ng/l to 2.4 μ g/l with the exception of the more polar compounds (dichlorvos, monocrotophos and dimethoate). The maximum relative standard deviation of the

Table 6

Mean recoveries (%) and R.S.D. (%; in parentheses) from triplicate extractions of organophosphorus compounds spiked into 1 l of bidistilled water

	Spiked at (ng/l)	C ₁₈ 4.6 cm	C ₁₈ 9 cm
Dichlorvos	360	48 (19)	73 (9)
TiBP	360	89 (5)	74 (11)
TBP	380	92 (10)	78 (9)
Sulfotep	360	87 (11)	71 (8)
Diazinon	360	92 (12)	72 (13)
Monocrotophos	808	7 (97)	44 (25)
Methylchlorpyrifos	380	97 (11)	74 (14)
Dimethoate	400	10 (25)	63 (6)
Chlorpyrifos	400	91 (12)	72 (16)
Parathion-methyl	360	82 (18)	69 (15)
Malathion	400	92 (12)	69 (15)
Fenitrothion	400	96 (16)	72 (14)
Parathion-ethyl	400	85 (7)	72 (10)
Chlorthion	398	99 (19)	76 (10)
Tetrachlorvinphos	720	92 (15)	75 (10)
Methidathion	720	91 (13)	72 (12)
Ethion	400	89 (11)	82 (4)
Tris(2-ethylhexyl)phosphate	1980	84 (15)	79 (16)
Tributoxiethylphosphate	2380	79 (9)	85 (24)
Leptophos	816	85 (18)	84 (11)
EPN	830	81 (10)	73 (7)
Azinphos-methyl	1594	84 (13)	66 (13)
Azinphos-ethyl	1626	86 (15)	69 (15)
Coumaphos	1590	84 (17)	72 (13)

Samples were extracted using C₁₈ disks of different capacity (4.6 and 9 cm diameter) without wetting agent.

recoveries was less than 10%, except for the more volatile compounds such as hexachlorobenzene (15%). However, this method fulfills the requirements of the U.S. Environmental Protection Agency (EPA), which accepts recoveries in the range from 70 to 130% (with a maximum standard deviation of 30%).

Results reported herein for octadecyl-silica extraction disks are generally in good agreement with most data found in the literature [13,16,29,30,33,34], with low recoveries reported for dimethoate [15,31,32,37] and dichlorvos [31]. It may be pointed out, however, that other authors report a good recovery for monocrotophos [26] using C₁₈ cartridges. Other analysts [18] report a very poor recovery for

Table 7

Mean recoveries (%) and R.S.D. (%; in parentheses) from triplicate extractions of organochlorine and organophosphorus compounds spiked with 1 and 5 l of bidistilled water

	Spiked at (ng)	1 l	5 l
<i>Organochlorine</i>			
Hexachlorobenzene	6	59 (14)	66 (16)
Lindane	12	97 (9)	98 (6)
PCB 52	40	71 (12)	72 (4)
α -Endosulfan	25	79 (7)	72 (5)
<i>p,p</i> -DDE	25	82 (10)	82 (2)
β -Endosulfan	25	93 (5)	83 (7)
<i>p,p</i> -DDD	50	109 (7)	107 (8)
PCB 153	42	82 (7)	80 (7)
Endosulfan sulphate	25	112 (4)	113 (8)
<i>p,p</i> -DDT	75	109 (6)	116 (8)
PCB 180	32	83 (8)	83 (9)
<i>Organophosphorus</i>			
Dichlorvos	360	27 (11)	6 (21)
TiBP	360	83 (6)	86 (2)
TBP	380	88 (7)	99 (3)
Sulfotep	360	76 (9)	74 (5)
Diazinon	360	90 (7)	95 (1)
Monocrotophos	808	0	0
Methylchlorpyrifos	380	91 (7)	91 (1)
Dimethoate	400	6 (12)	0
Chlorpyrifos	400	101 (7)	92 (1)
Parathion-methyl	360	81 (8)	85 (4)
Malathion	400	96 (4)	99 (4)
Fenitrothion	400	94 (5)	96 (2)
Parathion-ethyl	400	90 (8)	90 (7)
Chlorthion	398	98 (5)	99 (2)
Tetrachlorvinphos	720	95 (3)	101 (5)
Methidathion	720	93 (4)	92 (2)
Ethion	400	94 (3)	97 (3)
Tris(2-ethylhexyl)phosphate	1980	65 (13)	73 (5)
Tributoxiethylphosphate	2380	96 (2)	103 (4)
Leptophos	816	96 (3)	100 (3)
EPN	830	105 (3)	103 (6)
Azinphos-methyl	1594	100(4)	106 (2)
Azinphos-ethyl	1626	99 (2)	102 (2)
Coumaphos	1590	102 (2)	105 (1)

Samples were extracted using C₁₈ disks (4.6 cm) with 1% acetonitrile (ACN) modifier (see text for details).

β -endosulfan. This is not in agreement with our results and might be accounted for through their use of a non-polar eluent (*n*-hexane) which is not able to elute the more polar β -endosulfan when water is still present in the solid phase.

3.3. Comparison between Amberlite resins, octadecyl-silica bonded phase and polystyrene-vinylbenzene copolymer disks

Fig. 1 shows the GC-ECD chromatograms obtained for the pesticide-spiked samples ex-

tracted using Amberlite resins and SDB disks. Fig. 2 illustrates the corresponding GC-FPD chromatogram for the organophosphorus compounds. It is demonstrated by the ECD chromatogram that the Amberlite resin is subject to higher interferences than the disks. These inter-

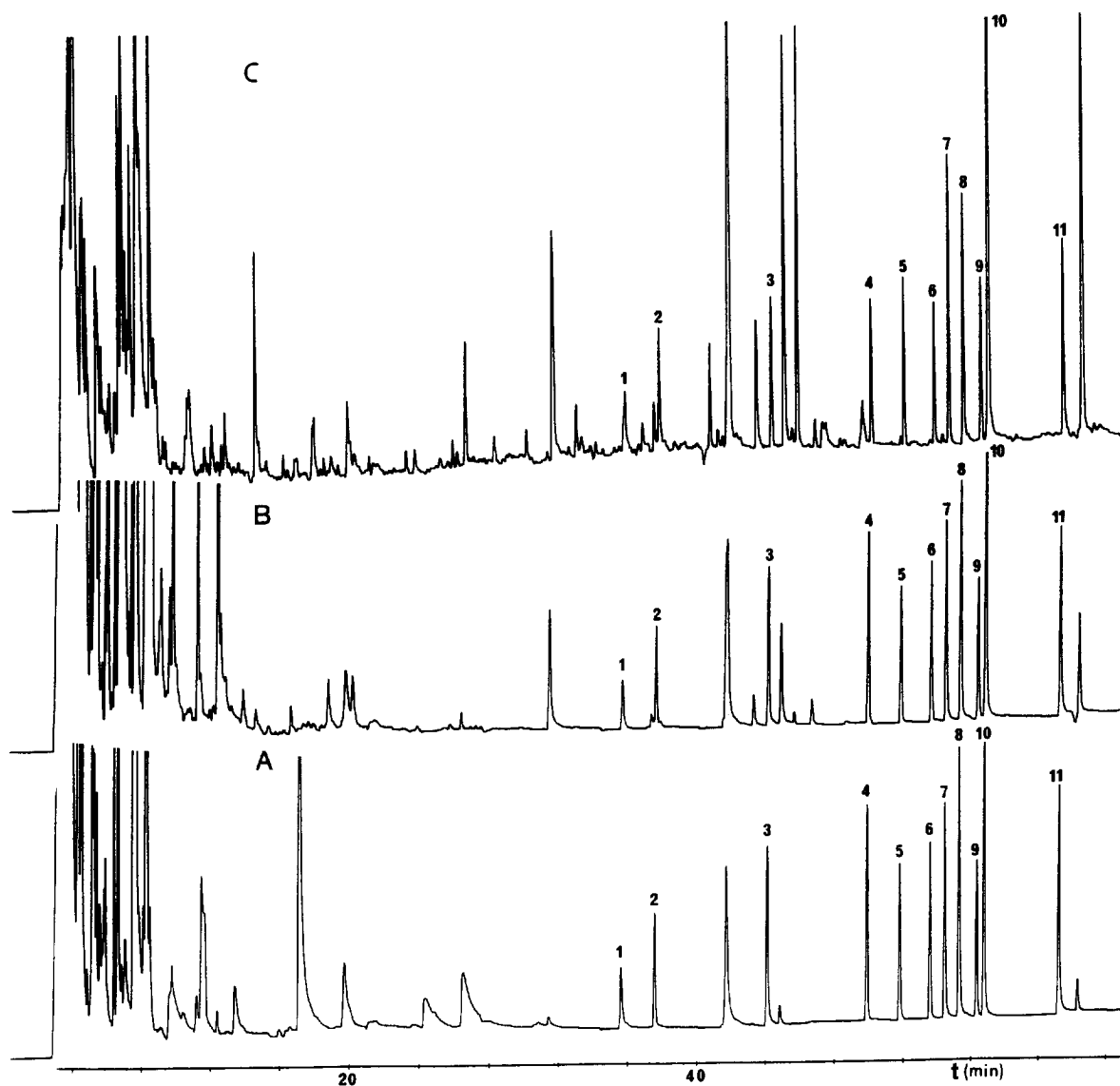


Fig. 1. GC-ECD chromatogram obtained for: (A) organochlorine standards; (B) 1 l distilled water spiked with organochlorines and extracted using a SDB disk; (C) 2.5 l distilled water spiked with organochlorine standards and extracted using XAD-2 mixed with Teflon beads. Chromatographic conditions as explained in the text. Peaks: 1 = hexachlorobenzene; 2 = lindane; 3 = PCB 52; 4 = α -endosulfan; 5 = *p,p*-DDE; 6 = β -endosulfan; 7 = *p,p*-DDD; 8 = PCB 153; 9 = endosulfan sulphate; 10 = *p,p*-DDT; 11 = PCB 180.

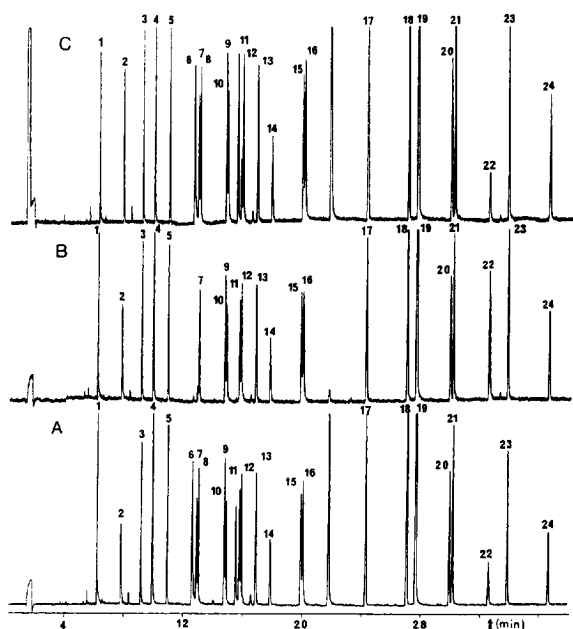


Fig. 2. GC-FPD chromatogram obtained for: (A) organophosphorus standards; (B) 1 l distilled water spiked with organophosphorus standards and extracted using an SDB disk; (C) 2.5 l distilled water spiked with organophosphorus standards and extracted using XAD-2. Chromatographic conditions as explained in the text. Peaks: 1 = dichlorvos; 2 = TiBP; 3 = TBP; 4 = sulfotep; 5 = diazinon; 6 = monocrotophos; 7 = methylchlorpyrifos; 8 = dimethoate; 9 = chlorpyrifos; 10 = parathion-methyl; 11 = malathion; 12 = fenitrothion; 13 = parathion-ethyl; 14 = chlorthion; 15 = tetrachlorvinphos; 16 = methidathion; 17 = ethion; 18 = tris(2-ethylhexyl)phosphate; 19 = tributoxiethylphosphate; 20 = leptophos; 21 = EPN; 22 = azinphos-methyl; 23 = azinphos-ethyl; 24 = coumaphos.

ferences, however, were not as apparent with the more selective FPD detector.

As shown in Fig. 3, recoveries using Amberlite are not as dependent on K_{ow} of the compound and, in comparison, all compounds with a log K_{ow} lower than 2 were not quantitatively recovered on the octadecyl-silica bonded phase (and SDB disks). This might relate to the larger quantity of adsorbent used in the resin columns compared to the thin film of adsorbent present in the disks. It is possible that the poor reproducibility of recovery for some compounds from

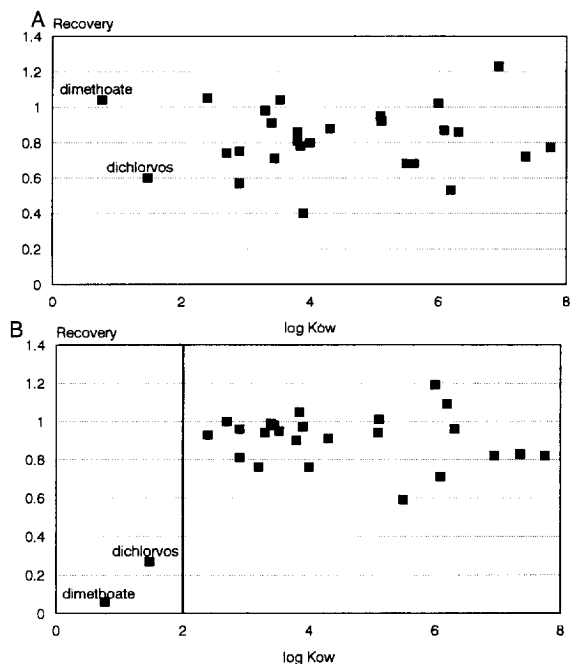


Fig. 3. Recoveries of organophosphorus and organochlorine compounds versus log K_{ow} : (A) using XAD-2, with acetone as extracting solvent; (B) using C_{18} with acetonitrile as wetting agent. The following compounds are not shown because of the lack of reported K_{ow} values: monocrotophos, TiBP, TBP, tris-(2-ethylhexyl)phosphate, tributoxiphosphate, coumaphos, α -endosulfan, β -endosulfan and endosulfan sulphate.

the Amberlite columns, compared to the SDB disks could be attributed to the larger quantities (and hence surface areas) of resin particles and the associated higher π - π interactions. More data is, however, required to clarify this suggestion.

According to our results, hydrophobicity of organochlorine and organophosphorus compounds is a more relevant factor for their adsorption onto the C_{18} silica bonded phase and SDB disks than onto the Amberlite resins. Nevertheless, C_{18} and SDB disks seem to be more reliable than Amberlite columns because of their uniform behaviour for compounds with a log K_{ow} higher than 2. In addition, the C_{18} and SDB disks do not, apparently, suffer from the irreversible adsorption or degradation observed for some compounds on the Amberlite resins.

4. Conclusions

It is clear that the use of macroreticular resins for the determination of some organophosphorus and organochlorine compounds is not completely satisfactory, probably owing to irreversible adsorption or chemical degradation. Recovery efficiencies of analytes from C_{18} bonded-silica and styrene–divinylbenzene disks, however, depends on the polarity of the compounds and good recoveries are only achieved for compounds with a water solubility below 300 mg/l or with a log K_{ow} higher than 2.

This study provides a sound basis for analyses of water samples using these solid-phase extractants, although the influence of biogenic dissolved organic compounds (such as humic and fulvic acids) on the recoveries of pesticides needs to be investigated to further evaluate the performance of these protocols with environmental water samples.

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