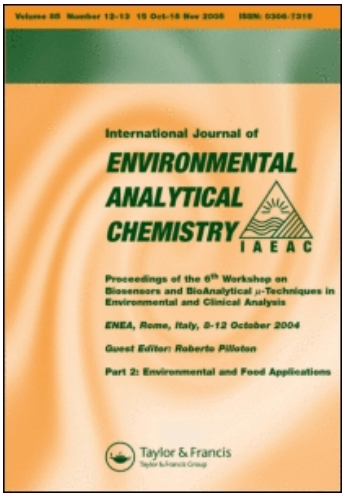

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Use of Extraction Disks for Trace Enrichment of Various Pesticides from River and Sea Water Samples

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To cite this Article Durand, G. , Chiron, S. , Bouvot, V. and Barceló, D.(1992) 'Use of Extraction Disks for Trace Enrichment of Various Pesticides from River and Sea Water Samples', International Journal of Environmental Analytical Chemistry, 49: 1, 31 — 42
To link to this Article: DOI: 10.1080/03067319208028124
URL: http://dx.doi.org/10.1080/03067319208028124

Intern. J. Environ. Anal. Chem., Vol. 49, pp. 31-42
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USE OF EXTRACTION DISKS FOR TRACE ENRICHMENT OF VARIOUS PESTICIDES FROM RIVER AND SEA WATER SAMPLES

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(Received, 26 June 1992; in final form, 23 September 1992)

C-18 Empore extraction disks were used for the isolation and trace enrichment of different groups of pesticides from river water and artificial sea water at concentration levels of 0.2, 5 and 20 μg/l [chlorotriazines, (atrazine and simazine), their dealkylated metabolites, (deethyl- and deisopropylatrazine), organophosphorus (parathion-ethyl), phenylurea (linuron), anilide (propanil), carbamate (aldicarb and carbofuran) and carbamate transformation products (aldicarb sulfoxide, aldicarb sulfone and 3-hydroxy-7-phenol carbofuran]. The extraction disks allowed high flow rates thus 5 l samples could be processed within 2h. 30 min.

For most of the pesticides the recoveries, as determined by liquid chromatography with diode array detection (LC-DAD), varied from 74 up to 125% with coefficients of variations (CV) of 5–10%, whereas for the carbamate transformation products the recoveries were in the range of 30–35% having a CV of 17–21%. At spiking level of 0.2 μg/l the dealkylated triazine metabolites and the carbamate transformation products were not detected at all.

KEY WORDS: Extraction disks, pesticides, water, liquid chromatography, diode array detection

INTRODUCTION

The identification and quantitation of pesticides in water matrices, such as surface and sea-water is required for measuring environmental regulations. Various pre-concentration methods based on different physico-chemical principles can be used for this purpose. Among them, liquid-liquid extraction (LLE), dynamic and static head-space analysis, solid-phase extraction (SPE) and membrane processes are quite commonly used and were recently described in several review articles[1-4].

A variety of extracting solvents is currently used for LLE. Thus, concentration of organophosphorus pesticides from water samples can be accomplished by using organic solvents such as n-hexane[5], dichloromethane with[6] or without[7] prior acidification to avoid hydrolysis of the pesticides[6] and chloroform[8]. The use of these and other extracting solvents such as ethyl acetate and acetonitrile was discussed in a book on the analysis of pesticides in environmental matrices[9].

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Other pesticides such as triazine herbicides have been extracted into dichloromethane[9–12], ethyl acetate[9] and mixtures of dichloromethane plus ethyl acetate and ammonium formate[13]. Screening methods for different pesticide groups have been developed using generally dichloromethane and washing with NaOH[14–16] adding NaCl[17] or adjusting to pH neutral and acidic for separation of two fractions[18,19]. In these methods the analysis of a variety of *N*-herbicides, including carbamates, triazines and phenylurea,[14–19], organophosphorus[17,19] and acidic herbicides[18,19] has been reported.

Although most official methods for pesticide analysis in water still use LLE extraction[5,10,11], some disadvantages have been noticed: they are laborious, time-consuming and expensive and are subject to problems arising from the formation of emulsions, the evaporation of large solvent volumes and the disposal of toxic or inflammable solvents. As a consequence, SPE techniques have gained popularity and some are already being used by the US Environmental Protection Agency (EPA)[17,20–22]

In SPE, the water sample is passed through a short bed of packing material which may contain functional groups of different polarity such as C-8 or C-18 bonded phase, graphitized carbon black or Amberlite XAD resins. C-8 and C-18 bonded phase cartridges have been used for the analysis of various organophosphorus pesticides in sea-[23] and surface[24,17,19] waters. Screening methods using these cartridges have been developed for the analysis of a variety of pesticides, including triazine, phenylurea, carbamate and others such as molinate, trifluralin, alachlor and carbofuran [14–17, 25]. Other type of SPE systems include the use of Amberlite XAD resins (XAD-2, XAD-4)[1,21,26] and graphitized carbon black[27] which have been employed for the analysis of a variety of pesticides.

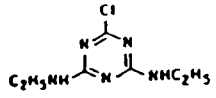
SPE methods can be easily converted into fully automated on-line systems coupled to LC[4,28–30]. Such systems also referred to as "precolumn technology", show additional advantages such as lower detection limits (analysis of eluate instead of aliquot), no evaporation losses, no contamination and easy automation.

In the last two years another alternative has appeared for the trace enrichment of organic compounds, including pesticides, from water samples. This is based also in the SPE principle and concerns the use of membrane extraction disks, which are available in a similar diameter and size as HPLC solvent filters. Their main advantage over SPE cartridges is the high sampling flow rate which facilitates sampling in the field. At present such disks have been tested for different groups of compounds, including pesticides, organotin and phthalates[31–33]. The system has also been applied on-line with LC for the concentration of triazine herbicides and chlorophenols[34]. Since the Empore extraction disks appear as a clear alternative to conventional C-18 cartridges, it is of analytical interest to carry out a systematic work to assess the performance of such disks for the trace enrichment of a variety of pesticides of different chemical groups spiked at various concentration levels using different water types. The results of this study are reported in the present paper. We have used liquid chromatography with diode array detection (LC-DAD) for identification thus avoiding false positives.

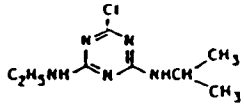
EXPERIMENTAL

Chemicals

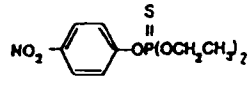
HPLC-grade water, acetonitrile and methanol from Merck (Darmstadt, Germany) were passed through a 0.45 μm filter before use. Propanil and simazine were obtained through Polyscience (Miles, IL, USA); carbaryl, atrazine, fenamiphos, aldicarb, aldicarb sulfoxide, aldicarb sulfone, carbofuran and 3-hydroxy-7-phenol carbofuran were purchased from



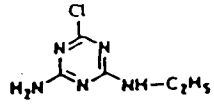
SIMAZINE



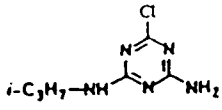
ATRAZINE



PARATHION-ETHYL



DEISOPROPYLATRAZINE



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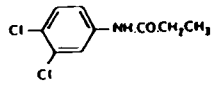
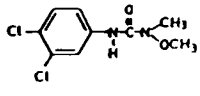
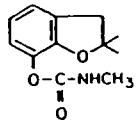


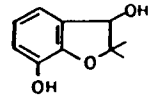
PROPANIL



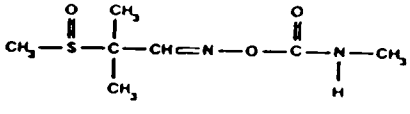
LINURON



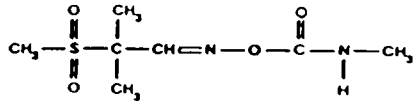
CARBOFURAN



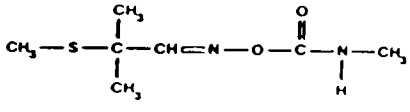
3-HYDROXY-7-PHENOL CARBOFURAN



ALDICARB SULFOXIDE



ALDICARB SULFONE



ALDICARB

Figure 1 Chemical structures of the model compounds used.

Promochem (Wesel, Germany) and parathion-ethyl and linuron were obtained from Riedel-de-Haën (Seelze-Hannover, Germany). Deethylatrazine and deisopropilatrazine were gifts from Ciba-Geigy (Basel, Switzerland). The names and structures of the pesticides are given in Figure 1.

Chromatographic conditions

Eluent delivery was provided by two model 64-high pressure pumps from Knauer (Bad-Homburg, Germany) coupled with a Chrom-A-scope rapid scanning UV/VIS detector from Barspec (Rehovot, Israel). Samples were injected via a 20 µl loop from Rheodyne (Cotati, California, USA). For the determination of the different pesticides, with the exception of the carbamates and their transformation products the following LC conditions were used: LiChrocart cartridge columns (12.5 × 4.0 mm i.d.) packed with 4 µm LiChrospher 100 RP-18 from Merck (Darmstad, Germany) were used. A gradient elution was used from an eluent containing methanol-acetonitrile-water (25:25:50) up to methanol-acetonitrile (50:50) in 12 min at a flow rate of 1 ml/min.

For the carbamates and their transformation products the following LC conditions were used: A Serva LC column (Heidelberg, Germany) of 25 cm × 4.6 mm i.d. packed with 4 µm dactosil 100-octadecyl was used. A gradient elution was used from an eluent containing 5% of A [acetonitrile-water (90:10)] /95% of B [acetonitrile-water(10:90)] up to 25% of A/ 75% of B in 15 min. From 25% of A/75% of B up to 100% of A in 15 min. Back to initial conditions: 10 min; post-run time of 5 min at a flow rate of 0.8 mL/min. Quantitation by LC-DAD was performed using UV absorption at 220 nm with external standard calibration methods over the concentration range studied.

Water samples

Surface river water and artificial sea-water from Instant Ocean-Aquarium systems (Sarresbourg, France) from which composition of salts was reported elsewhere [13] were used. The artificial sea-water was used to simulate waters from the natural oceans environment. Water samples (1 and 5l) were spiked with the different pesticides with final concentrations of 20, 5 and 0.2 µg/l. To obtain a better approach of real environment situations, such as estuarine waters, humic acids from Fluka (Buchs Switzerland) at levels of 1 mg/ 600 ml were added to the synthetic sea-water, in a similar way as reported elsewhere[13].

Extraction and concentration of samples

A standard Millipore 47-mmm filtration apparatus was used. The membrane extraction disks were manufactured from 3M (St. Paul, MN, USA) under the trademark Empore and are distributed by J.T. Baker and Analytichem International. The disks used in these experiments were 47 mm diameter and 0.5 mm thick. Each disk contains about 500 mg of C-18 material.

The extraction procedure used is the following: After spiking 5l of water with different

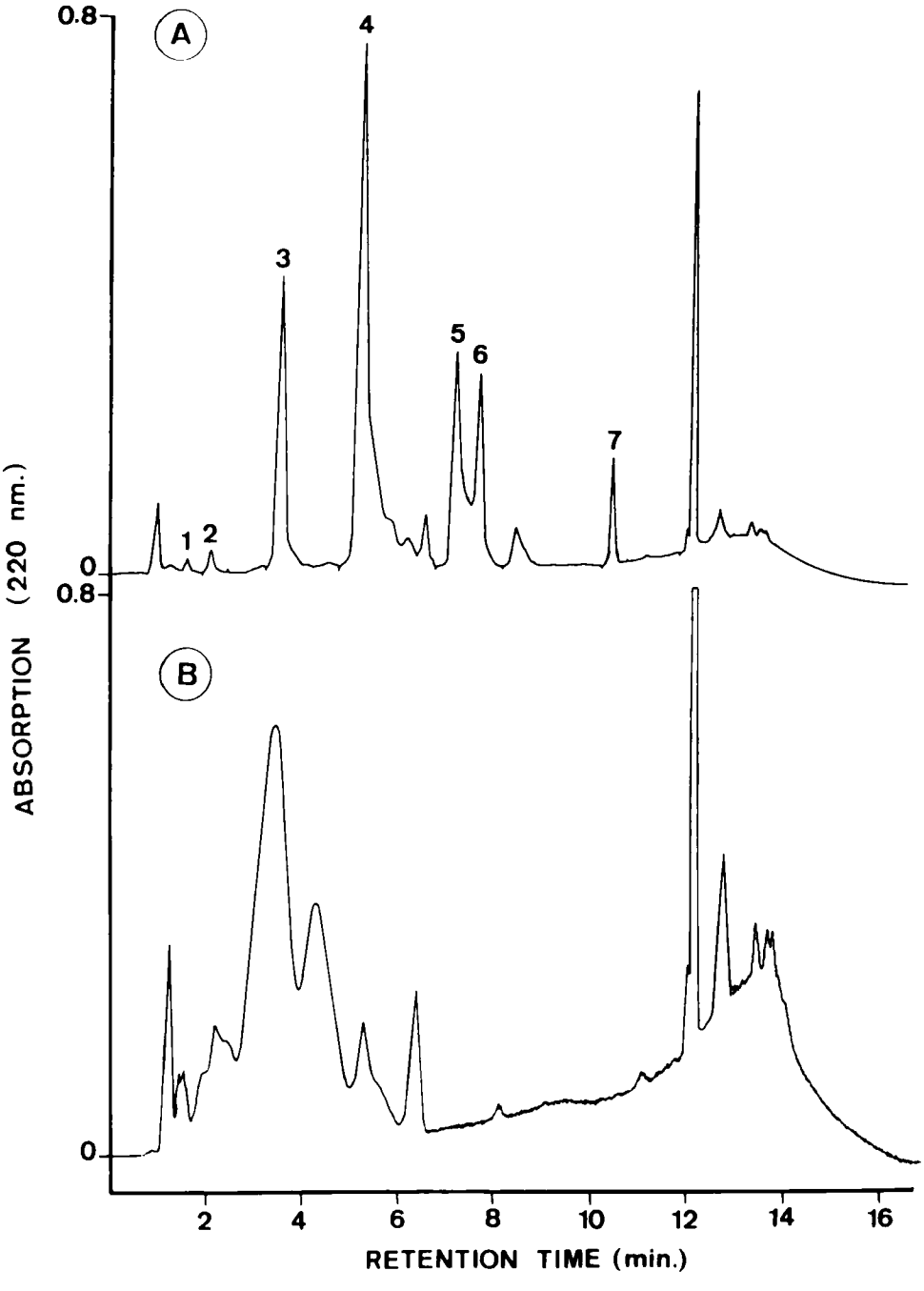


Figure 2 LC-DAD chromatogram at 220 nm obtained on: (A) the extract of 5 l of artificial sea-water containing 20 μg/l of (1) deisopropylatrazine, (2) deethylatrazine, (3) simazine, (4) atrazine, (5) propanil, (6) linuron and (7) parathion-ethyl; (B) the extract from 5 l of artifical sea-water blank sample containing humic acis.

pesticides with a resulting analyte concentration of 20 μg/l, 5 μg/l and 0.2 μg/l, the solution was prefiltered to eliminate particulate matter[23,31,33] and subsequently passed through the Empore extraction disk. The disks, placed in the conventional Millipore apparatus, were washed with 2 × 10 ml of methanol with the vacuum on avoiding to become dry, as recommended[31–33]. Immediately after 5 l of water were extracted with the vacuum adjusted to yield 2h 30 min extraction time. After this operation, the pesticides trapped into the disk were collected with the following volumes of methanol: 2× 10ml. The solvent was vacuum evaporated and the residue re-dissolved in 100–400 μl of methanol.

RESULTS AND DISCUSSION

General considerations

The main advantage of using SPE membrane disks such as Empore, instead of SPE cartridges, is the increased productivity caused by the relatively high flow rates permitted. In this study, only 2h 30 min sampling time was needed for the trace enrichment of 5 l water samples. These results were in good agreement with other studies[31,32]. It should be noted that SPE cartridges would have cost at least 5 hours for our samples[27,32].

In general, the combined use of SPE disks and LC is very beneficial. Contrary to GC applications [31–33], it will not be necessary to remove all the residual water from the disks, and the elution solvent, e.g., methanol, is compatible with the final separation method.

Prefiltration of water samples through 0.45 μm PTFE filters has been recommended before when using C-8 cartridges [23] or Empore extraction disks[31,33]. Prefiltering will not affect the determination of the polar pesticides used in this study, since they exhibit log Koc (partition coefficient between soil organic carbon and water) of 2, and consequently are distributed in the dissolved and not in the suspended phase of the water. According to ref. 35 the distribution between the dissolved and particulate phases is 99.5% to 0.5%, respectively. In contrast, when the same experiments are carried out with hydrophobic organochlorinated pesticides (log Koc ca. 6), there should be a strong tendency to adsorb onto the particulate matter on the filter[36]; so in that sense, prefiltering would yield much lower recoveries.

Blank levels

Figure 2 shows two chromatograms obtained after trace enrichment of 5 l of artificial sea-water sample spiked with seven pesticides at 20 μg/l level (Figure 2A) and a blank sample of 5 l of artificial sea-water (Figure 2B). An important background absorption up to 0.5 A.U., from the blank samples can be noticed in the LC-DAD chromatogram which will lead to interferences when analyzing low concentration values of pesticides in sea-water samples. Due to this fact, it was impossible to spike the pesticides at lower concentration levels in the sea-water samples.

Table 1 Mean % Recovery and coefficient of variation (CV) of pesticides in water using C-18 Empore extraction disks. Spiking level: 5 μg/l and 0.2 μg/l for surface river water and 20 μg/l for sea-water samples (n=6 for each pesticide). Water volume: 5 l. Elution solvent: Methanol.

Pesticide	*Recovery (%)*			*CV*
	River water		*Sea-water*	
	5 μg/l	*0.2 μg/l*	*20 μg/l*	
Aldicarb	83	70	n.i.	7
Aldicarb sulfoxide	35	n.d.	n.i.	21
Aldicarb sulfone	30	n.d.	n.i.	20
Atrazine	100	125[a]	132[a]	5
Carbofuran	74	60	n.i.	7
Deethylatrazine	9	n.d.	10	25
Deisopropylatrazine	3	n.d.	4	30
3-Hydroxy-7-phenol-carbofuran	31	n.d.	n.i.	17
Linuron	96	94	100	6
Parathion-ethyl	97	106	91	6
Propanil	95	90	103	7
Simazine	80	80	85	10

[a] High recovery values due to interferences in the chromatograms (see Fig. 2A and 3C, peak 4)
n.d.: not determined. (Values below the limit of detection)
n.i.: not investigated

Although similar recoveries were obtained either using surface river water and sea-water samples at 20 μg/l level of spiking, the atrazine peak (Nr. 4) exhibits tailing caused by the interferences from the sea-water matrix containing humic acid. The higher blanks obtained in artificial sea-water samples have been also observed when using LLE[13]. The main advantage of using LC-DAD is that the inferences can be easily detected by their differentiated UV spectra thus avoiding false positives[13-15].

The interferences noticed in the LC-DAD chromatogram at high retention times were also noticed, and even more pronounced[32,33] when analysing water blank samples after passage through C-18 cartridges. In the case of the cartridges, the interferences obtained in the LC-DAD chromatogram were attributed to the higher polarity of methanol that can elute more polar compounds than other solvents, e.g. ethyl acetate[37]. However, we still prefer the use of methanol as the elution solvent since the extracts can be directly injected onto the LC-DAD system and there is no need of extra manipulation of the extract.

Recovery studies

For the pesticides studied, Table 1 shows the different recovery values obtained at different spiking levels into 5 l of surface river water and sea-water samples containing humic acids. Figure 3 shows the LC-DAD chromatogram of a solution of 5 l of a surface river water sample extract with a resulting pesticide concentration of carbamates and their transformation products of 5 μg/l (Figure 3A) and 0.2 μg/l (Figure 3B). Figure 3C shows the LC-DAD

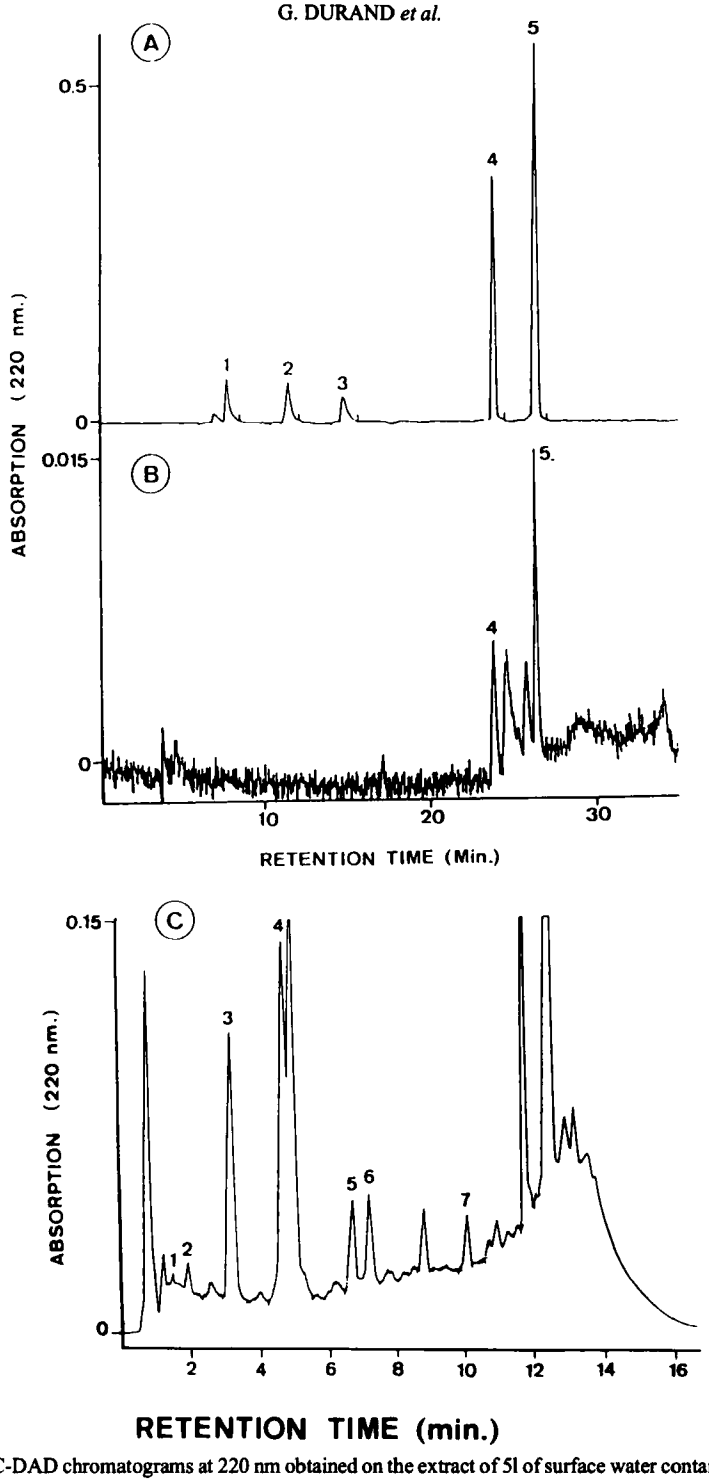


Figure 3 LC-DAD chromatograms at 220 nm obtained on the extract of 5l of surface water containing: (A) 5 µg/l of (1) aldicarb sulfoxide, (2) aldicarb sulfone, (3) 3-hydroxy-7-phenol carbofuran, (4) aldicarb and (5) carbofuran; (B) 0.2 µg/l of the same pesticide mixture as A and (C) 0.2 µg/l of the pesticide mixture indicated in Fig. 2.

chromatogram obtained on the extract of 5 l a surface river water extract spiked at 0.2 μg/l level with the non-carbamate pesticides.

The recovery values obtained for the pesticides do not differ considerably with the spiking level, but they are much lower for the different pesticide metabolites such as aldicarb sulfoxide, aldicarb sulfone and 3-hydroxy-7-phenol carbofuran, deethylatrazine and deisopropylatrazine. At 5 μg/l spiking level the carbamate transformation products showed low recoveries of 30%, with a CV of 20%, i.e. ca. 3 times lower than those of most of the pesticides studied, with the exception of triazine metabolites, that were practically not recovered. At the spiking level of 0.2 μg/l all the metabolites are not recovered at all (see Table 1) and it can be ascribed to the fact that the breakthrough volume was exceeded (5 liters of water was preconcentrated). This is quite commonplace when atrazine metabolites are pre-concentrated in C-18 bonded silica materials, which usually require low sample volumes for optimal recovery, i.e., a recovery of 50% is obtained for deisopropylatrazine at 1 μg/l level using 100 ml of water[38]. For the carbamate transformation products, lowering the concentration precluded detection since in addition to breakthrough volume being exceeded, the compounds occurred at concentration levels below their L.O.D. This is apparent from the LC-DAD chromatogram in Figure 3B where compound 4 (aldicarb) at the concentration level of 0.2 μg/l has a L.O.D. of ca. 0.1 μg/l (S/N=3) whereas the carbamate transformation products are not detected at all.

In the LC-DAD chromatogram of Fig. 3C only atrazine (peak 4) exhibits an interference due to the surface water sample. However, the use of LC-DAD offers the possibility of detecting false positives and still allows the identification of atrazine at a low level of 0.2 μg/l.

Limits of detection

Table 2 lists the L.O.D. for the different pesticides and metabolites and compares them with literature data obtained by using Carbopack[27] and C-18 cartridges[15]. The better L.O.D. reported in ref. 15 and 27 for some of the pesticides can be ascribed to: (i) the use of Carbopack cartridges[27] (they need much lower sample volumes for similar L.O.D.) which exhibit an increased trapping capacity of the Carbopack surface and absorb many different pesticides (e.g., those listed in Table 2) as compared to C-18 bonded silica phase. Unfortunately the authors of ref. 27 did not pre-concentrate the carbamate transformation products as they could have tested the much higher adsorption capacity of this material, (ii) the use of a real diode array detector[15], based on a different principle as compared to the rapid scanning UV detector used in this study, and of a UV detector[27], which are more sensitive; (iii) the injection of 50 μl in both studies rather than 20 μl water extract in the present study and (iv) the fact that the authors of ref. 15 and 27 used groundwater samples, which produce less interferences in the whole analytical procedure. It is estimated that the L.O.D. are lowered by a factor of 3 as compared when using surface river water samples.

By using the whole analytical protocol indicated in this paper a limit of detection (L.O.D.) of 0.01 μg/l (for atrazine and simazine), 0.02 μg/l (for linuron, propanil and parathion-ethyl) 0.05 μg/l (for carbofuran), 0.1 μg/l (for aldicarb) and 2–3 μgl for the carbamate metabolites was estimated. For the analysis of the chlorotriazine metabolites the method is not adequate since poor recoveries are obtained.

Table 2 L.O.D. (μg/l) with different SPE techniques using LC- with UV (ref. 27), diode array (ref. 15) and rapid scanning UV detection (this study).

Pesticide	*This paper*	*ref.27*	*ref.15*
Water Vol.	*5 l*	*1.5 l*	*0.5 l*
SPE type	*C-18 disks*	*Carbopack*	*C-18 Cartridge*
Aldicarb	0.1	0.016	n.i.
Aldicarb sulfoxide	2	n.i.	n.i.
Aldicarb sulfone	2	n.i.	n.i.
Atrazine	0.01	0.001	0.03
Carbofuran	0.05	0.012	n.i.
Deethylatrazine	> 25	n.i.	0.03
Deisopropylatrazine	> 25	n.i.	0.06
3-Hydroxy-7-phenol-carbofuran	3	n.i.	n.i.
Linuron	0.02	0.003	0.03
Parathion-ethyl	0.02	0.016	n.i.
Propanil	0.02	0.004	n.i.
Simazine	0.01	0.001	0.03

n.i.: not investigated

CONCLUSIONS

Although extraction efficiency of LLE can be higher than SPE using Empore disks for extracting certain polar pesticide metabolites, e.g., deethylatrazine and deisopropylatrazine, from water samples, the use of SPE is preferred since: it avoids emulsifications, the solvent consumption and potentially hazardous solvents are reduced, manpower can be saved (higher productivity) and because of its easy handling. Main advantages of using Empore SPE disks in combination with LC-DAD analysis are: (i) the possibility of preconcentration up to 5l of water samples spiked with pesticide at levels of 20, 5 and 0.2 μg/l, (ii) less extraction time than using C-18 cartridges, (5 l of water is extracted in 2h. 30 min, whereas the cartridges require 5 h), (iii) ease of use, so they can be employed in remote places for preconcentration of different types of water, including sea-water (iv) no need to eliminate the water from the disks by careful air drying, as it is the case when GC determinations are done following the SPE, (v) since the solvent used to desorbe the samples (methanol) is similar with the LC eluent it is very unlikely that the sample extract contains any substance which can be irreversible adsorbed on the stationary phase of the column, (vi) LC-DAD allows the identification of the polar pesticides from interferences and it is of help in avoiding false positives.

The use of SPE with Empore disks and LC-DAD method described here is recommended for screening polar pesticides in surface river water samples at levels below 5 μ/1, whereas in the case of seawater water samples, the method is limited to a concentration level in the range of 20 μg/l.

Acknowledgements

One of us (S. Chiron) acknowledges financial support from the Commission of the European Communities (B/STEP-913011. CEC grant ref. 910212). This work was supported by the Environment R & D Programme 1991-94 (Commission of the European Communities) on the Analysis and Fate of Organic Pollutants in Water (Contract No. EV5V-CT92-0114).

References

1. J. Namiesnik, T. Górecki, M. Biziuk and L. Torres, *Anal. Chim. Acta* **237**, 1–60 (1990).
2. S.K. Poole, T.A. Dean, J.W. Ondegema and C.F. Poole, *Anal. Chim. Acta*, **236**, 3–42 (1990).
3. D. Barceló, *Analyst* **116**, 681–689 (1991).
4. D. Barceló, *Chromatographia* **25**, 928–936 (1988).
5. Organophosphorus pesticides in river and drinking water 1980. Tentative method. (Her Majesty's Stationery Office, London, 1983), pp 1–17.
6. T.C. Wang, R.A. Lenahan and J.W. Tucker, Jr, *Bull. Emviron. Contam. Toxicol.* **38**, 226–231 (1987).
7. D. Barceló, C. Porte, J. Cid and J. Albaigés, J. *Intern. J. Environ. Anal. Chem.* **38**, 199–209 (1990).
8. A. Neicheva, E. Kovacheva and G. Marudov, *J. Chromatogr.* **437**, 249–253 (1988).
9. A.S.Y. Chau and B.K. Afghan, *Analysis of pesticides in water. Vol. I, II and III.* (CRC Press, Boca Raton, Fl, 1982).
10. C.D. Watts, L. Clark, S. Hennings, K. Moore and C. Parker, In *Pesticides: analytical requirements for compliance with EEC directives*, (Water Pollution Research Report 11. Commission of the European Communities, Brussels, Belgium, 1989) pp 16–34.
11. Chlorophenoxy acid herbicides, trichlorobenzoic acid, chlorophenols, triazines and glyphosate in water 1985. (Her Majesty's Stationery Office, London , 1986) pp 1–150.
12. W. Schüssler, *Chromatographia*, **27**, 431–435 (1989).
13. G. Durand and D. Barceló, *Toxicol. Environ. Chem.*, **25**, 1–11 (1989).
14. R. Reupert and E. Plöger, *Vom Wasser*, **72**, 211–233 (1989).
15. R. Reupert and E. Plöger, In *Pesticides: analytical requirements for compliance with EEC directives*, (Water Pollution research report 11, Commission of the European Communities, Brussels, Belgium 1989) pp 100–114.
16. R.G. Nash, *J. Assoc. Off. Anal. Chem.*, **73**, 438–442 (1990).
17. T.A. Bellar and W.L. Budde, *Anal. Chem.*, **60**, 2076–2083 (1988).
18. W. Schüssler, *Chromatographia*, **29**, 24–30 (1990).
19. M. Fielding, S. Gibby and K. Moore, In *Organic micropollutants in the aquatic environment, Lisbon symposium*, (A. Bjørseth and G. Angeletti Eds., Kluwer, Dordrecht, NL, 1991) pp 142–162.
20. Y. Lopez Avila, J. Milanes, N.S. Dodhiwala and W.F. Beckert, *J. Chromatogr. Sci.*, **27**, 209–215 (1989).
21. G.A. Junk and J.J. Richard, *J. Res. Natl. Bur. Stand.* **93**, 274–276 (1988).
22. Determination of organic compounds in drinking water by liquid-solid extraction and capillary column gas chromatography-mass spectrometry. Method 525.1. (US Environmental Protection Agency, National Technical Information Service, Springfield, VA, May 1991).
23. D.A. Hinckley and T.F. Bidleman, *Environ. Sci. Technol.* **23**, 995–1000 (1989).
24. J. Mañes Vinuesa, J.C. Moltó Cortés, C. Igualada Cañas and G. Font Pérez, *J. Chromatogr.* **472**, 365–370 (1989).
25. R. Bagnati, E. Benfenati, E. Davoli and R. Fanelli, *Chemosphere* **17**, 59–65 (1988).
26. A. Verweij, M.A. Van Liempt and H.L. Boter, *Intern. J. Environ. Anal. Chem.* **21**, 63–77 (1985).
27. A. Di Corcia and M. Marchetti, *Environ. Sci. Technol.*, **26**, 66–74 (1992).
28. P. Subra, M.C. Hennion, M.C, R. Rosset and R.W. Frei, *J. Chromatogr.*, **456**, 121–141 (1988).
29. M.C. Hennion, P. Subra, R. Rosset, J. Lamarq, P. Scribe, P and A. Saliot, *Intern. J. Environ. Anal. Chem.*, **42**, 15–33 (1990).
30. M.W.F. Nielen, R.W. Frei and U.A.Th. Brinkman, In *Selective Sample Handling and Detection in HPLC, Part A*, (R.W. Frei and K. Zech Eds. Elsevier, Amsterdam, NL 1988) pp 5–80.
31. D.F. Hagen, C.G. Markell, G.A. Schmitt and D.D. Blevins, *Anal. Chim. Acta.* **236**, 157–164 (1990).
32. A. Kraut-Vass and J. Thoma, *J. Chromatogr.*, **538**, 233–240 (1991).

33. O. Evans, B.J. Jacobs and A.L. Cohen, *Analyst*, **116**, 15–19 (1991).
34. E.R. Brouwer, H. Lingeman and U.A.Th. Brinkman, *Chromatographia*, **29**, 415–418 (1990).
35. W.E. Pereira and C. Rostad, *Environ. Sci. Technol*, **24**, 1400–1406 (1990)
36. M. Valls, J.M. Bayona and J. Albaigés, *Intern. J. Environ. Anal. Chem.*, **39**, 329–348 (1990).
37. E. Reupert, E. Plöger, and G. Brausen. HPLC determination of 29 controlled herbicides in water supplies, Hewlett-Packard, Germany Application Note, pp 1–23 (1990).
38. E.M. Thurman, M. Meyer, M. Pomes, Ch.A. Perry and P. Schwab *Anal. Chem.*, **62**, 2043–2048 (1990).