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On-line and off-line solid–liquid extraction and liquid chromatographic analysis at trace levels, for monitoring of herbicides and their degradation products in river and fluvio–estuarine freshwater–seawater interfaces

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Abstract

Monitoring of trace levels of phenylurea and chlorotriazine herbicides and their metabolites deisopropylatrazine (DIA) and deethylatrazine (DEA) was performed on river, estuarine and coastal seawater by off-line (*n*-octadecyl silica, C_{18}) and on-line (styrene–divinylbenzene copolymer-based, PRP1) preconcentration techniques using reversed-phase chromatography and UV and electrochemical detection. It is shown that off-line and on-line technology fit monitoring of trace-level phenylurea and triazine analysis (detection limit 10–50 ng/l) in freshwater as well as seawater and in natural water with high dissolved organic carbon (DOC) content. Clean-up was unnecessary for most of the surface water sample for both off-line and one-line techniques. Samples of surface water originating from various rivers (Seine, Charente, Garonne), canals (Marennes–Oléron) and estuaries (Charente, Seudre salinity gradient up to 30‰) were analysed. Dissolved organic carbon (DOC) contents varied from <1 to 15 mg/l and provided numerous interferents and a major 'hump' whose intensity is correlated with the DOC content, suggesting that a major part of the organic matter, namely humic substances, is retained on the solid phase and eluted as polar compounds.

Keywords: Environmental analysis; Water analysis; Sample preparation; Pesticides

1. Introduction

The occurrence and distribution of pesticides in river water from the continental section to the ocean through the gradient of salinity of estuaries and non-point source contamination of surface water as well as groundwater has arisen as an urgent and imperative issue in terms of analytical challenge. In France, rivers drain extensive agricultural regions where large amounts of a growing variety of herbicides are applied as weed control agents on plants. Pesticide contamination of surface waters from agricultural soils has been well documented [1–4]. Important factors that determine analytical strategies in multiresidues monitoring in surface water at trace levels have been highlighted: runtime and easy automatisation [5–8]. However, most of the standard methods for pesticide analysis use liquid–liquid extraction (LLE) because it is a straightforward and fully developed technique of pesticide preconcentration prior to GC or LC analysis. Solid-phase extraction (SPE) has gained in popularity over the last ten years and some procedures have been validated by social institutions, e.g., the US En-

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vironmental Protection Agency (EPA) [9]. LLE techniques have been extensively used in the monitoring of pesticides at trace levels [10,11] but SPE is being increasingly applied with the development of modern solid phases (*n*-alkyl silicas, copolymers, graphitised carbon) and provides an attractive alternative to LLE. Advantages and drawbacks have been explained in comprehensive articles [5,6,12–14].

In particular, phenylureas and triazines can be simultaneously analysed on the same sample by SPE–LC and in the case of on-line procedures with reduced handling and no risk of sample contamination. However, the detection limit is sometimes seriously disturbed by interferent compounds issuing from the biogenic organic matrix and in some cases clean-up must be set up to achieve identification and quantification of herbicides.

This report deals with on-line and off-line SPE–LC analysis of herbicides in fresh and saltwater in continental and fluvio-estuarine zones exhibiting varied dissolved organic matrices.

2. Experimental

2.1. Apparatus

2.1.1. On-line

Percolation of water samples was performed with a LC-6A pump (Shimadzu). Precolumn elutions and analyses were carried out with a Model 680 automated gradient controller equipped with a 486 tunable absorbance detector (Waters, Milford, MA, USA) and a Coulochem model 5100A electrochemical detector (ESA, Bedford, MA, USA). Precolumn and analytical column switching was done by using a Rheodyne valve (Cotati, CA, USA). Quantitative measurements of peak areas were provided by an Apex Chromatography Workstation (Autochrom, Milford, MA, USA).

2.1.2. Off-line

Procedure analyses were carried out with an Sp8800 ternary LC pump and a Spectra Focus detector. Injections of the samples were performed by means of a Spectra AS 3000 autosampler. Quantitative measurements of peaks were provided by PC1000 software (the whole apparatus is from Thermo Separation Products, Les Ulis, France).

2.1.3. DOC analysis

DOC were analysed with a Shimadzu TOC 5000 analyser (catalyst: SiO_2 with 1.2% Pt, at 680°C).

2.2. Stationary phases and columns

2.2.1. On-line

Water samples were preconcentrated on a 2.3 cm×3 mm I.D. stainless-steel precolumn packed with 10 μm styren–divinylbenzene copolymer PRP1 from Hamilton (Reno, NV, USA). The precolumn was cleaned with pure acetonitrile. The analytical column was first a 15 cm×4.6 mm I.D. stainless-steel column packed with 5 μm Nucleosil C_{18} octadecyl silica, and then a 25 cm×4.6 mm I.D. stainless-steel column packed with 5 μm Spherisorb ODS2 octadecyl silica, both from Interchim (Montluçon, France).

2.2.2. Off line

Water samples were preconcentrated on a 6 ml SPE encapped cartridge packed with 1000 mg of octadecyl silica from Supelco (Bellefonte, PA, USA). The analytical column was a 2 cm×4 mm I.D. stainless-steel column packed with 5 μm Ultrasep octadecyl silica followed by a 25 cm×4 mm I.D. stainless-steel column packed with 3 μm Spherisorb ODSII octadecyl silica from Bischoff supplied by ICS (Lapeyrouse–Fossat, France).

2.3. Chemicals

2.3.1. On-line

The LC-grade acetonitrile was from Rathburn (Walkerburn, UK) and the methanol from Prolabo (Paris, France). LC-quality water was prepared by purifying water in an Alpha-Q filtration system (Millipore, Bedford, MA, USA). The phenylureas and triazines were supplied by Cluzeau (Sainte Foy, France).

2.3.2. Off-line

The LC grade acetonitrile was from Scharlau supplied by ICS (Lapeyrouse–Fossat, France), the

methanol from Carlo Erba and the LC-quality water from Biochrom (Vindelles, France). The phenylureas and triazines were supplied by Cluzeau (Sainte Foy la Grande, France).

2.4. Procedures

2.4.1. On-line

The sample was filtered through a glass microfiber filter (Whatman GF/F) and from 100 to 500 ml depending on the sample origin. The experimental set-up is shown in Fig. 1 according to [5]. The water was percolated through the PRP1 precolumn by switching a valve and backflush-eluted by an acetonitrile–water gradient via the LC pump. The initial mobile-phase composition was: with the Nudeosil C_{18} column, 5% acetonitrile and 75% water solution of potassium acetate–acetic acid (0.1 *M*, pH 4.7), elution to analytical column was performed by an acetonitrile–water gradient from 15:75 to 24:76 in 40 min, 33:67 at 60 min and 100:0 at 80 min at a flow-rate of 1.5 ml/min; and with the Spherisorb ODS2, 20% acetonitrile–80% aqeous solution of potassium acetate–acetic acid (0.1 *M*, pH 4.7), elution to analytical column was performed by an acetonitrile–water gradient rising from 20:80 to 80:20 in 45 min and 100:0 at 55 min. The herbicides were monitored with the UV-detector set at 254 nm and the electrochemical detector at 0.7 and 0.8 V.

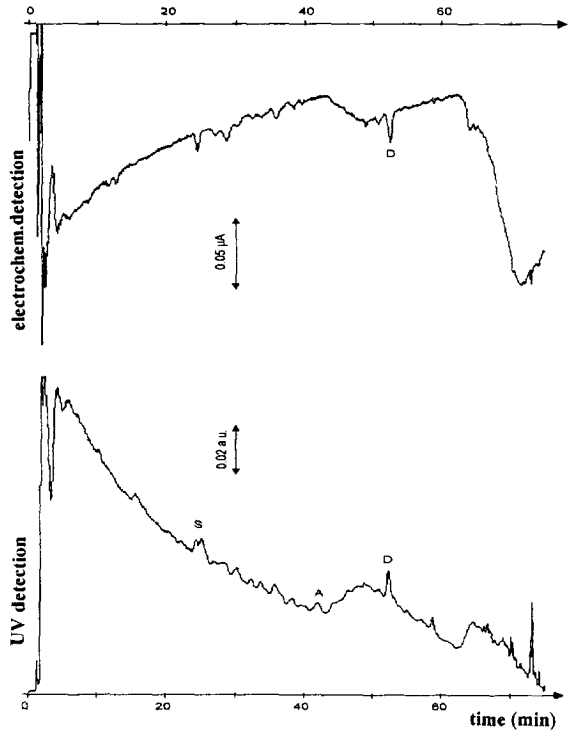

Fig. 1. On-line SPE–LC-UV-electrochemical detection chromatogram: S=simazine, A=atrazine, D=diuron. Preconcentration of 500 ml of the Charente River water on PRP1 cartridge. Analytical column: Nucleosil C_{18}, 5 µm, 150×4.6 mm. Gradient elution of acetonitrile–water (15:85) up to (24:76) in 40 min, (33:67) at 60 min and (100:0) at 80 min, with the use of a buffer containing potassium acetate–acetic acid 0.1 *M* (pH 4.7). Flow-rate, 1 ml/min. UV detection at 254 nm and electrochemical detection at 0.8 V.

2.4.2. Off-line

The sample was filtered through a glass microfiber filter (Whatman GF/F, porosity 0.7 µm). The pH of the filtrate was adjusted to 7. An aliquot, 100 or 200 ml, depending on the sample origin, was concentrated on an SPE cartridge (C_{18}) which was then eluted by 3 ml of acetonitrile, evaporated to dryness and dissolved in 1 ml of acetonitrile–water (20:80). 50 µl were injected. The initial phase composition was acetonitrile–water (20:80) in order to reach 45:55 in 70 min at a rate of 0.4 ml/min. The triazines and their metabolites were monitored at 220 nm and phenylureas at 240 nm.

2.4.3. DOC analysis

The samples were filtered on glass fiber filters (Whatman GF/F, precombusted), in a glass filter holder. The filtrates (10 ml) are poisoned with mercury chloride (10 mg/l and collected in glass tubes, with PTFE lined screw caps. DOC was measured from acidified and bubbled samples. Each value reported is the average of three injections. The areas of peaks are compared to a calibration curve (0–350 µ*M*) obtained with potassium hydrogenophtalate standards. The blank of the instrument, measured with the internal blank check system is subtracted from the measured value to give real concentration. The precision of the measurement is usually lower than 5% [22,23].

3. Results and discussion

3.1.1. On-line method

With the on-line method, the SPE is packed in a precolumn coupled to a reversed-phase analytical column via a switching valve. This technique has many advantages: no contamination, no evaporation and no handling. But it requires a short-size precolumn in order to avoid band broadening of analytes during their transfer from the precolumn to the analytical column. So, the set-up of an on-line SPE–LC method for herbicides in surface water depends on the concentration levels to be determined, the detection limit and the retention volume of the precolumn.

3.2. Detection limits and experimental recoveries

For budget assessments of phenylurea and triazine herbicide exportation from drainage basins to oceans and for geochemical behavior studies, effective quantitative measurements are most frequently >100 ng/l. This value can be considered as acceptable, owing to the inaccuracy of the other environmental parameters, in particular water discharge and rate of the degradation processes. This means, for accurate measurements, a detection limit of about 10 ng/l. For UV detection used at 254 nm, the average detection limit was 5 ng injected (Nucleosil C_{18} column) or 2 ng injected (Spherisorb ODS2 column). The detection wavelength (254 nm) was experimentally selected as the best compromise for phenylurea and triazine detection owing to the mono wavelength tunable absorbance detector used in this work. At present, better detection limit can be reached by using a diode array detector (DAD), with a 0.005 *M* phosphate buffer solution at two different detection wavelengths: 240 nm for phenylureas and 220 nm for triazines (Fig. 6). To reach a concentration level of 100 ng/l with an average detection limit of 2–5 ng injected, a sample volume of 200–500 ml and a 100% recovery of each compound are necessary. Phenylureas and triazines are mild-polar compounds and moderately soluble in water (Table 1). In order to reach complete recovery, PRP1 styrene–divinylbenzene copolymer was preferred as the stationary phase rather than octadecylsilica (C_{18}). It has been shown that the breakthrough volumes of the herbicides listed in Table 1 are about 10-times higher on PRP1 than on C_{18} [15,20]. In Milli-Q water, the average detection limit was >10 ng/l. Several determinations of detection limits in freshwater (Charente River, $S=0.3$) and saltwater (Garrigue Chanel, $S=32.3$) have been done on spiked samples. The average detection limits were observed between 20 and 30 ng/l for the herbicides listed on Table 1 and at 50 ng/l for DEA. Most of the time, DIA could not be quantified because interferents frequently occurred in natural water. Experimental recoveries were calculated by the ratio between peak areas obtained by percolation of 10 ml of Milli-Q water with a known amount of phenylureas and triazines for which 'theoretical' 100% recovery should be observed and peak areas obtained by percolation of successively 200 and 500 ml of solutions containing the same herbicide amounts as the former ones (10 ml) (Table 1). Complete recoveries are obtained for herbicides listed in Table 1, except for the atrazine metabolites DEA and DEA due to the percolation volumes exceeding their breakthrough volumes.

SPE applied on natural water leads simultaneously to preconcentration of pesticides and interferents originating from the dissolved organic matter which appear on chromatograms as an early 'hump' and also frequently as superimposed peaks at the end of the chromatogram (Fig. 1). When superimposed peaks arise, these co-elutions result in poor resolution of the peaks corresponding to the pesticides, in particular the more polar compounds (DIA and DEA). By using a longer analytical column, a 25 cm×4.6 mm packed with Spherisorb ODS2 instead of a 15 cm×4.6 mm packed with Nucleosil C_{18}, the detection limit was perceptibly lowered from 5 to 2 ng injected. The volume of percolation can be reduced from 500 ml to 200 ml which then substantially decrease the matrix interferences (Fig. 2).

3.3. Clean-up for on-line SPE–LC

Analysing pesticide residues at trace level in natural water by off-line LLE or SPE often involves isolation and clean-up of the extract. In such cases, gel permeation (GPC) or Fluorisil low-pressure chromatography applied as a molecular size discrimination mechanism or partioning are often preferred [5]. When on-line SLE–LC was used, two pro-

Table 1
Solubility in water (mg/l), octanol–water partition coefficients ($\log P_{oct}$) of phenylureas and triazines herbicides, recoveries (%) and standard deviation (%) for on-line and off-line SPE–LC methods

Compound	M_r	Water solubility (mg/l)	$\log P_{oct}$	Recovery					
				On-line PRP1[i]				Off-line C_{18}[j]	
				500 ml		200 ml		200 ml	
				%	RSD	%	RSD	%	RSD
DEA	188	3200[a]		47	6	71	9	50	3
DIA	174	670[a]		7	12	25	5	40	2
Metoxuron	229	660[b]	1.60[c]	102	4	96	3	72	2
Simazine	202	6.2[d]	1.96[e]	103	3	97	3	80	3
Isoproturon	206	70[d]	2.25[e]	105	5	98	3	81	2
Chlortoluron	213	70[d]	2.29[e]	104	4	98	3	89	2
Atrazine	216	30[d]	2.34[e]	103	4	98	3	84	4
Diuron	233	42[f]	2.77[g]	104	4	99	2	83	3
Terbutylazine	230	8.5[d]	3.04[e]	106	4	97	2	86	3
Linuron	249	75[h]	3.00[e]	109	3	96	4	80	4
Néburon	275	4.8[d]		114	5	98	4	-	-

[a] At 22°C, data from Ref. [18].
[b] At 22°C, data from Ref. [16].
[c] At 28°C, data from Ref. [17].
[d] At 20°C, data from Ref. [16].
[e] Data from Ref. [17].
[f] At 27°C, data from Ref. [16].
[g] Data from Ref. [19].
[h] At 25°C, data from Ref. [16].
[i] 2.3 cm×3 mm I.D. stainless-steel precolumn from Hamilton.
[j] SPE cartridge packed with 1 g of octadecylsilica from Supelco.

cedures were employed: (i) two precolumns (C_{18} and PRP1) are coupled in series for the preconcentration step. The set-up is described in Ref. [15]. When the percolated volume is 500 ml, the pesticides are selectively retained on the first C_{18} precolumn according to their polarity, and the more polar ones leak but are retained by the second PRP1 precolumn. The result of this sample pretreatment is that the organic compounds from the matrix are partially trapped into the first precolumn acting as a filter [20] and as far as the triazines and phenylureas listed in Table 1 are concerned, this transfer is beneficial to their analysis since a substantial number of organic matrix interferents are retained on the first precolumn (C_{18}). (ii) faster clean-up procedure was used, consisting in flushing 1 ml of acetonitrile–water (5:95) into the PRPl precolumn prior to the elution gradient. The elution of the more polar compounds considerably lowers the top of the 'hump' where DEA becomes measurable but of course with unknown losses (Fig. 3). However, no losses of phenylureas and triazines were observed.

3.4. Effect of co-elution of organic matter on SPE–LC of pesticides in surface water

Few things are known about the dissolved organic matrices of surface water and ground water, their physico-chemical interactions with pesticides and possible interference on multiresidues analysis. The dissolved organic carbon (DOC) content in natural waters, as a measurement to quantify organic matter, varies by a factor of almost 60 according to the water origin (from 0.5 mg/l in seawater to 30 mg/l in marsh) [21]. The DOC content of river waters varies on a narrower scale but commonly between 3 and 15 mg/l [22]. Fig. 4 shows typical 'humps' obtained for different fresh and saltwater from different canals located on the estuarian zone of the Charente River (France). Absorbance at 254 nm measured on the top

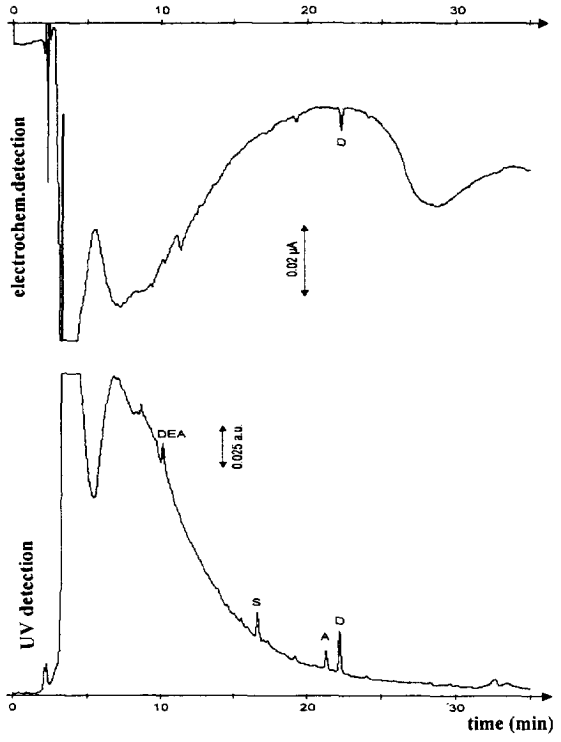

Fig. 2. On-line SPE–LC-UV chromatogram: DEA= deethylatrazine, S=simazine, A=atrazine, D=diuron. Preconcentration of 200 ml of the Charente River water (30 April 1991, salinity=6. 0) on PRP1 cartridges. Analytical column: Spherisorb ODS2, 5 μm, 250×4.6 mm. Gradient elution of acetonitrile–water (20:80) up to (80:20) in 45 min and (100:0) at 55 min with the use of a buffer containing potassium acetate–acetic acid 0.1 *M* (pH 4.7). Flow-rate: 1 ml/min. UV detection at 254 nm.

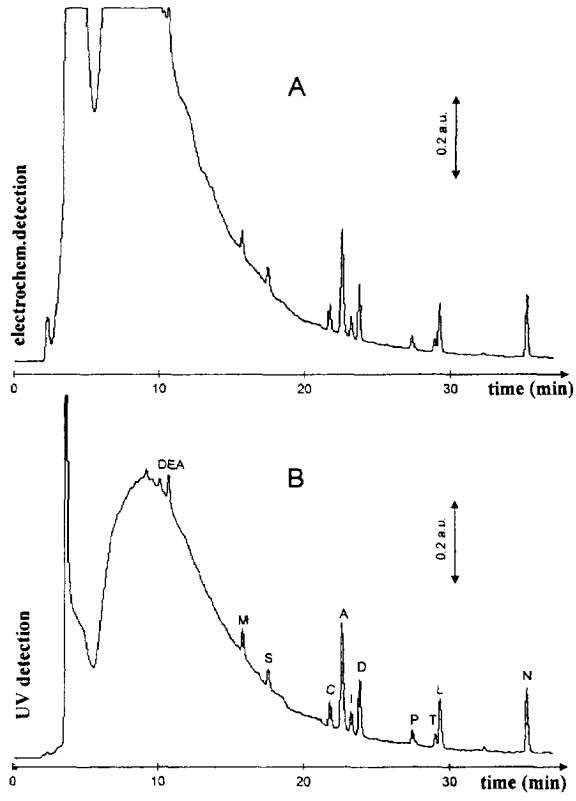

Fig. 3. On-line SPE–LC-UV chromatogram: DEA= deethylatrazine, S=simazine, A=atrazine, D=diuron. (A) after preconcentration of 200 ml of the Brouage canal water (24 May 1993, salinity=5.3) on PRP1 cartridges; (B) and clean-up by flushing 1 ml of Milli-Q water–acetonitrile (95:5). Analytical column: Spherisorb ODS2, 5 μm, 250×4.6 mm. Gradient elution of acetonitrile–water (20:80) up to (80:20) in 45 min and (100:0) at 55 min with the use of a buffer containing potassium acetate–acetic acid 0.1 *M* (pH 4.7). Flow-rate, 1 ml/min. UV detection at 254 nm.

of the second 'hump' appears to be positively correlated to the DOC content (mg/l) (Fig. 5). In addition, several peaks of various intensities that could interfere with the analytes are superimposed on the 'hump'. This organic matter very probably originates in biogenic compounds but these are completely unknown and we can only speculate on what types of compounds are present: acidic and/or hydroxylated aromatic and/or aliphatic compounds on a large scale of polarity (lipids, nitrogen compounds, fulvic moieties). Interesting questions about their molecular mass arise, for example, what is the mechanism of their elution: exclusion, desorption, partioning?

3.4.1. Off-line method

In off-line SPE, the water sample percolates through a bed of packed C_{18}-bonded phase silica. To prevent breakthrough of the phenylureas and triazines, 1000 mg of Ultrasep *n*-C_{18} bonded phase cartridges were employed.

3.5. Detection limits and experimental recoveries

The detection limits were from 0.2 to 1 ng injected. In Milli-Q water, the detection limits were

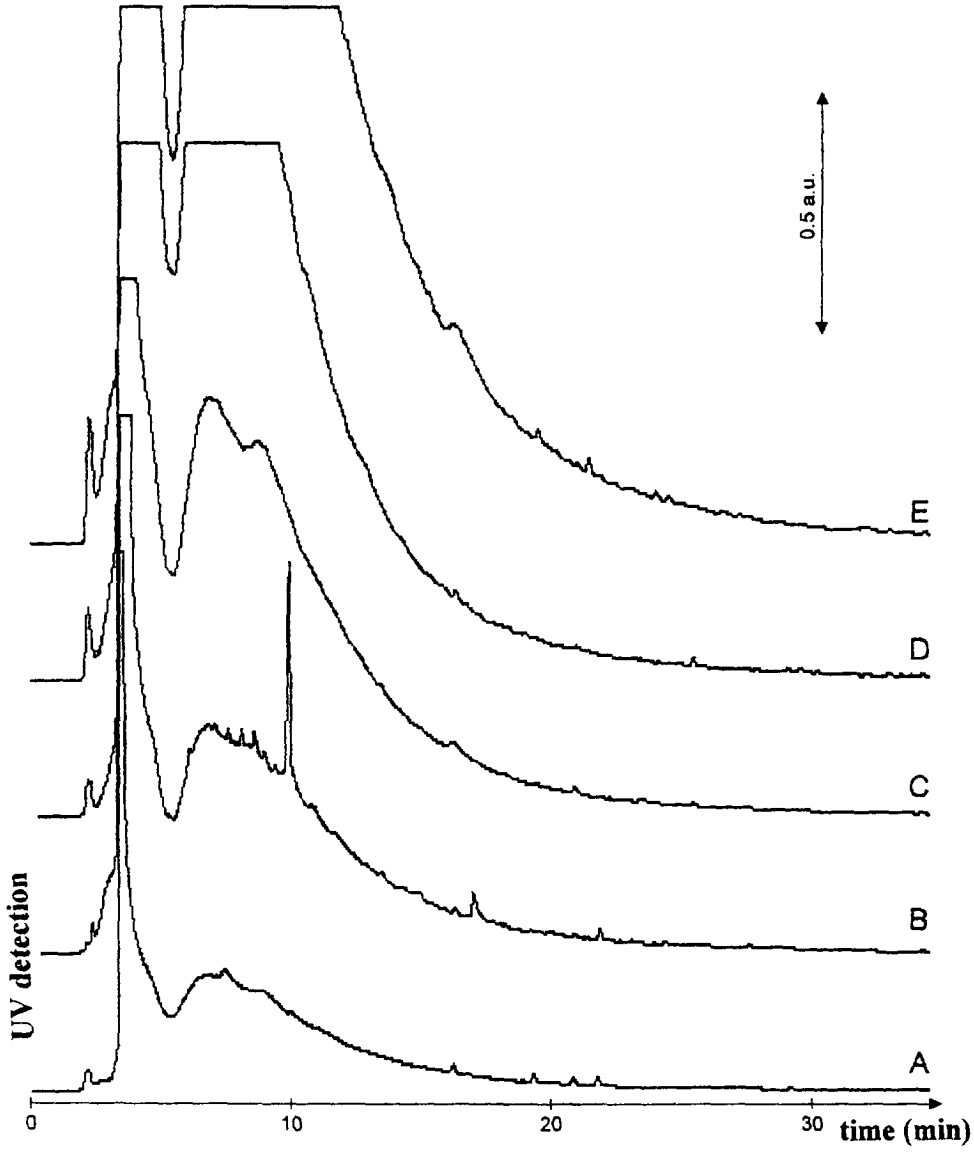

Fig. 4. On-line SPE–LC-UV chromatograms: Preconcentration of 200 ml of water. (A and E) Brouage canal, COD=3.3 and 15.1 mg/l; (B) Merignac canal, COD=4.4 mg/l; (C) Grand Garçon canal, COD=7.3 mg/l; (D) Marennes canal, COD=10.1 mg/l. Analytical column: Spherisorb ODS2, 5 μm, 250×4.6 mm. Gradient elution of acetonitrile–water (20:80) up to (80:20) in 45 min and (100:0) at 55 min with the use of a buffer containing potassium acetate–acetic acid 0.1 *M* (pH 4.7). Flow-rate: 1 ml/min. UV detection at 254 nm.

15–25 ng/l for herbicides and 30 and 50 ng/l for atrazine metabolites DEA and DIA, respectively. The experimental recoveries of herbicides listed on Table 1 were determined, by the ratio between peak areas obtained by injecting 50 μl of the concentrate from 200 ml of tap water spiked with a known amount of the listed herbicides and a peak obtained by direct injection of 10 μl of a standard solution. Table 1 shows that average recoveries were 80–89% for phenylureas and triazines and 40 and 50% for

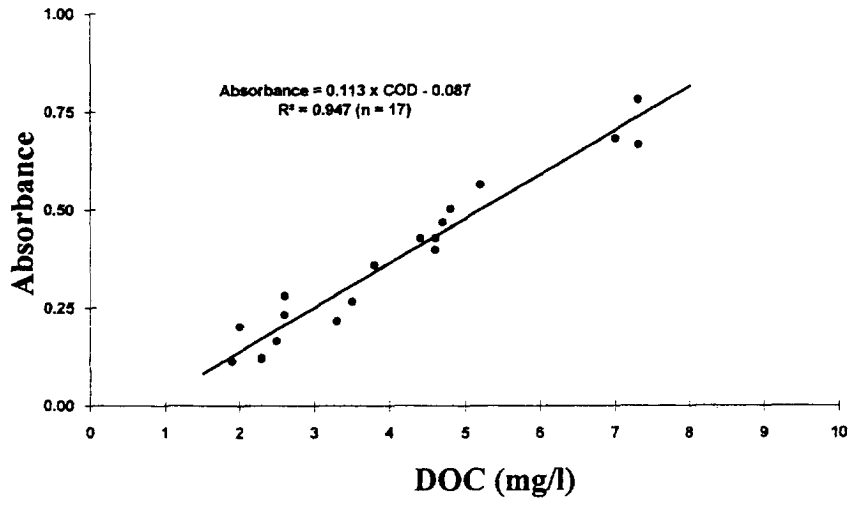

Fig. 5. Correlation between absorbance of the hump (peak maxima) and the dissolved organic content (DOC, mg/l): Fresh and salted water samples originated from canals (estuarian zone of the Charente, France).

metabolites of atrazine, DEA and DIA respectively. The recoveries of the C_{18} off-line procedure are 20–30% lower than these for the PRP1 on-line procedure. This loss is due to evaporation and transfer since retained analytes on the solid phase are eluted from the cartridge by 3 ml of acetonitrile, evaporated to dryness under a pure nitrogen stream and then solubilized in 1 ml of acetonitrile–water (20:80). The lower recoveries obtained for DEA and DIA suggest that in addition to these losses, breakthrough volumes might be <200 ml for these both compounds. However, if we compare chromatograms (Fig. 6) obtained with the off-line method with these obtained with the on-line protocol, the major part of the 'hump' is notably smaller in the former, in particular with the sample in June and makes DIA more accessible for quantification and better recoveries are obtained than with the on-line method (Table 1).

3.6. Intercomparison on-line C_{18} SPE–LC and PRP1 SPE–LC

In order to check the fluctuations in quantification of the mean herbicides (atrazine, simazine and DEA) in the Charente River by both off-line and on-line methods, we carried out comparisons between the two procedures. For 6 sites on the Charente River sampled at 3 periods (April, May and June 1993) and analysed in triplicate, the average deviations are 4% for atrazine, 6% for simazine and 9% for DEA. Among the whole 18 samples, artefacts occurred on 3 samples where DEA was not detected with the off-line protocol. This fact may be due to complete evaporation of the compound when the sample is evaporated to dryness.

4. Conclusion

In summary, we conclude that, in monitoring herbicides in fluvial, estuarian and coastal sea water, SPE is an attractive alternative to LLE methods suitable for geochemical studies and surface water quality assessment. The recoveries of the PRP1 on-line procedure are 20–30% higher than for the C_{18} off-line procedure except for DEA whose recoveries drop to <50% and are the same for both methods, and for DIA to 7 and 30%, respectively. The detection limit in Milli-Q water for all the phenylureas and triazines listed in this work is 20–30 ng/l and 50 ng/l for DEA and DIA. With natural water, the detection limit can vary sporadically on a large scale according to the organic carbon contents and the presence of specific and unforeseeable interferent peaks and make DIA determination chancy and

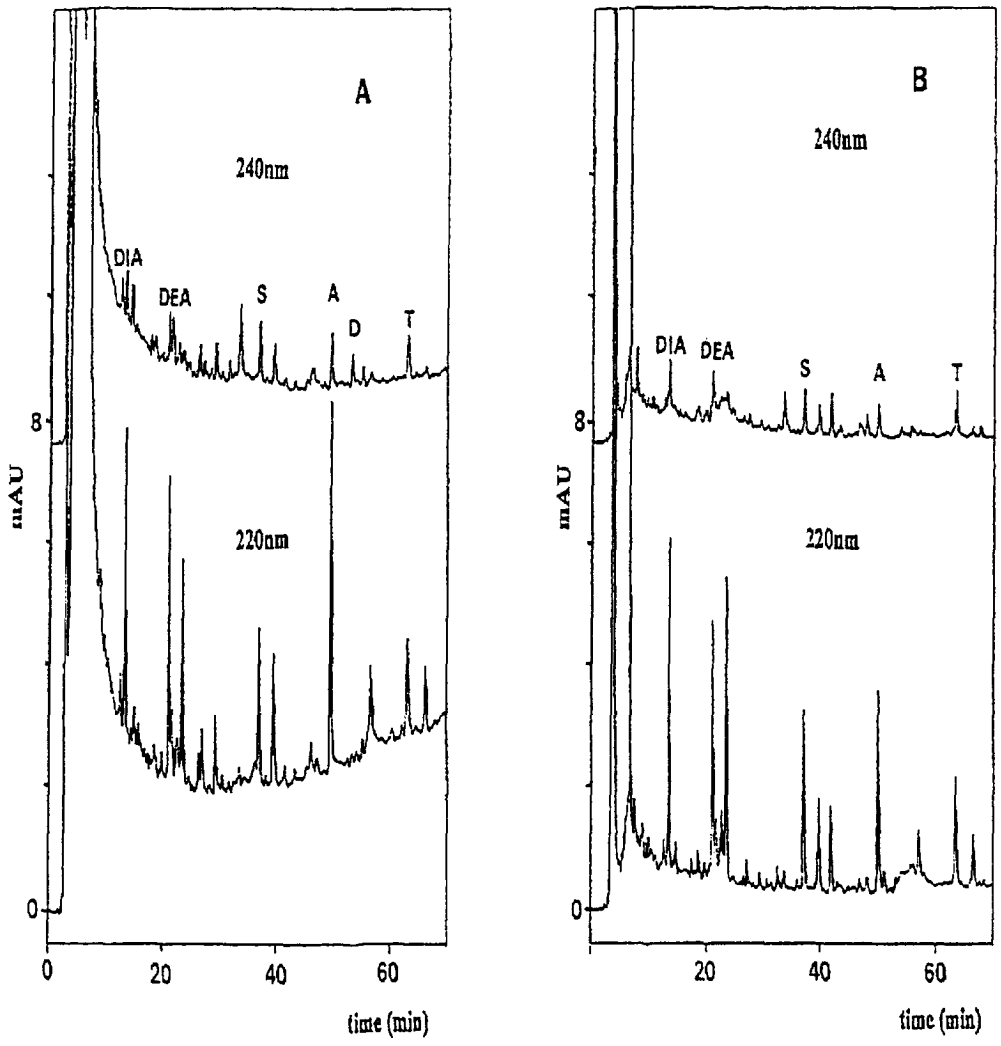

Fig. 6. Off-line SPE–LC-UV chromatograms: DEA=deethylatrazine, DIA=deisopropylatrazine, S=simazine, A=atrazine, T=terbutylazine, D=diuron. Preconcentration: (A) 200 ml of Ruiné River water during a low water period (June 1993); (B) 100 ml of Ruiné River water during a flood period (October 1993). Analytical column: Spherisorb ODS2, 5 μm, 250×4.6 mm. Gradient elution of acetonitrile–water (20:80) up to (55:45) in 70 min. Flow-rate: 0.4 ml/min. UV detection at 220 and 240 nm.

sometimes impossible with the on-line SPE–LC method. However, these methods have been used here on a broad pattern of surface water samples including fresh and saltwater up to salinity 35 and high organic matter content without clean-up. Off-line C_{18} and online PRPl procedures have been used and give satisfactory data on intercomparison exercises. The most valuable advantages of these techniques relative to the LLE, from the field-study point of view, are: low cost (less labour), small sample volumes, then less transport, less solvent, then increased safety, greater speed (2 h run).

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References

[1] L.P. Gianessi, A National Pesticide Usage Data Base, Resources for the Future, US Geological Survey, Washington, DC, 1986, p. 1.

[2] R.D. Wauchope, J. Environ. Qual., 7 (1978) 459.

[3] P. Bottoni and E. Funari, Sci. Total Environ. 123/124 (1992) 58.

[4] W.E. Pereira and C.E. Rostad, Environ. Sci. Technol., 24 (1990) 1400.

[5] D. Barcelo, Analyst, 116 (1991) 681.

[6] M.C. Hennion and P. Scribe, in D. Barceló (Editor) Environmental Analysis: Techniques, Applications and Quality Assurance, Elsevier, Amsterdam, 1993, p. 23.

[7] D. Barcelo, J. Chromatogr., 643 (1993) 117.

[8] M.W.F. Nielen, in R.W. Frei and K. Zech (Editors), Selective On-line Pre-column Sample Handling and Trace Enrichment in Liquid Chromatography, Part A (Journal of Chromatography Library, Vol. 39A), Elsevier, Amsterdam, 1988, p. 5.

[9] V. Lopez–Avilla, J. Milanes, N.S. Dodhiwala and W.F. Beckert, J. Chromatogr. Sci., 27 (1989) 209.

[10] W.E. Pereira, C.E. Rostad and T.J. Leiker, Anal. Chim. Acta, 228 (1990) 69.

[11] J. Troncczynski, C. Munschy, G. Durand and D. Barcelo, Sci. Total Environ., 132 (1993) 327.

[12] B.G. Olivier and K.D. Nicol, Int. J. Environ. Anal. Chem., 25 (1986) 275.

[13] W.R. Ming, J. Yman, G. Chun, B.S. Ming and Q.S. Jun, Int. J. Environ. Anal. Chem., 22 (1985) 115.

[14] R.L. Grob and M.A. Kaiser, Environmental Problem Solving Using Gas and Liquid Chromatography (Journal of Chromatography Library, Vol. 21), Elsevier, Amsterdam, 1982, p. 87.

[15] P. Subra, M.C. Hennion and R. Rosset, J. Chromatogr., 456 (1988) 121.

[16] Base de données AGRITOX. INRA Phytopharmacie, Versailles, 1994.

[17] C.R. Worthing and R.J. Hance, Editors, The Pesticide Manual, 9th Edition, The British Crop Protection Council, 1991.

[18] M.S. Mills and E.M. Thurman, Environ. Sci. Technol., 28 (1994) 73.

[19] P.H. Howard, In: Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Lewis, CITY???, 1991, p. 3

[20] M.C. Hennion, P. Subra, R. Rosset, J. Lamac P. Scribe and A. Saliot, Int. J. Environ. Anal. Chem., 42 (1990) 15.

[21] E.M. Thurman, Organic Geochemistry of Natural Waters. Dev. Biogeochem., 2 (1985) 8.

[22] E.T. Degens, Proceedings of a workshop arranged by Scientific Commitee on Problems of the Environment (SCOPE) and the United Nations Environment Programmme (UNEP) at Hamburg University, 1982, p..

[23] G. Cauwet, HTCO method for dissolved organic carbon analysis in seawater: influence of catalyst on blank estimation, Mar. Chem., 47 (1994) 55.