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Multiresidue analysis of pesticides using new laminar extraction disks and liquid chromatography and application to the French priority list

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Abstract

The national French lists of priority pesticides to be monitored in drinking and/or surface water contain various pesticides with a wide range of physico-chemical properties and can be modified on a regional scale with the addition of other pesticides, depending on local agricultural usage. A multiresidue extraction method is presented using new disk formats engineered for high throughput that are particularly well adapted to the extraction of compounds from high volumes of dirty samples. However, because of the occurrence of very polar and very apolar compounds in the lists, two procedures are required for the extraction step. Divinylbenzene disks were used to extract the more polar compounds, as well as the moderately polar or acidic ones. For apolar pesticides, a C_{18} silica disk was used, and 10% methanol was added to the water sample before percolation in order to avoid adsorption on the flasks and connecting tubes. Since 1 l of surface water is extracted in less than 5 min without previous filtration using these new laminar disks, the percolation time is no longer a limiting factor in the analysis scheme of surface water samples containing suspended matter. The sample volume can be easily increased in order to reach lower detection limits, provided that the extraction conditions have been optimized in order to minimize the amount of co-extracted and interfering substances. A considerable decrease in the effect of the humic and fulvic substances was achieved using divinylbenzene disks, which allows the samples to be handled at pH 6, for the polar pesticides. Moreover, the necessary addition of 10% methanol in the samples for the extraction of the apolar ones also considerably decreases the amount of co-extracted analytes. The time of the whole sample preparation sequence, i.e., conditioning of the disks, sample extraction, sample clean-up and desorption, is achieved within 10 min for six simultaneous samples. Detection limits in the range 0.01–0.05 $\mu g\ l^{-1}$ are easily obtained for most pesticides contained in the national lists from 1 l of real surface water samples. The two procedures described in this work allow the handling of any compounds having a water–octanol constant, log K_{ow}, in the range 1–6. © 1998 Elsevier Science B.V.

Keywords: Extraction methods; Water analysis; Environmental analysis; Pesticides

1. Introduction

Pesticides are detected worldwide in surface and ground water in agricultural areas, especially in North America and Europe [1–6]. As a consequence, several countries have established national priority lists [7]. In France, in 1994, a National Committee, constituted of members belonging to the three ministries, Agriculture, Environment and Health, has provided priority lists of pesticides to orientate the survey of water quality on a national scale, depending on criteria based on the properties of pesticides,

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i.e., migration potential, toxicity, ecotoxicity, national usage, and water type. Two lists deal with pesticides to be monitored in drinking water, depending on whether this water comes from ground water or from surface water.

In order to decrease the price of the analyses and to keep the possibility of adding any compound after a regional decision without changing the analytical procedure, it was relevant to perform multiresidue analyses. The major difficulty is the wide range of physico-chemical properties (polarities, water solubilities, acido-basic properties), as shown in Table 1. A multiresidue procedure includes an extraction step of as many compounds as possible in one run and a minimum of separation–quantification steps using gas chromatography (GC) and/or liquid chromatography (LC). In these lists, some compounds cannot be directly analyzed by GC because they are thermolabile or require specific derivatization steps. Therefore, LC was obligatory for some of them and, therefore, it was selected as a multiresidue separation method for testing the multiresidue extraction.

Solid-phase extraction (SPE) was preferred over liquid–liquid extraction due to the actual trends in reducing the use of organic solvents in analytical laboratories and to its higher performance in extracting polar compounds using new polymeric sorbents [8–14]. Using disposable cartridges for off-line procedures, we have shown that a multiresidue extraction over a large polarity range is possible, provided that the list of compounds is divided into two groups, the polar to moderately polar in one run and the nonpolar compounds in another run [15]. The reason is that the extraction of very apolar compounds requires the addition of an organic solvent to the aqueous sample in order to avoid adsorption phenomena on flasks and connecting tubes, with the drawback of losing the more polar compounds.

Up to now, two SPE formats were available, mainly disposable cartridges and membrane extraction disks. The percolation of surface water containing suspended matter through cartridges is difficult without previous filtration (which is necessary to avoid a clogging effect), and can take a long time for a typical volume of 500 ml. The main advantage of using SPE membrane disks rather than SPE cartridges is usually reported to be the increased productivity permitted by the relatively high flow-rates. In general, the time required for the extraction

Table 1
Physicochemical parameters (water solubility, water–octanol partition coefficient, K_{ow}, and ionization constant, pK_a) of the pesticides to be monitored in drinking water coming from ground- or surface water and included in the national French priority list

Pesticides	M_w (g mol^{-1})	Solubility (mg/l)	Log K_{ow}	pK_A
Alachlor	269.8	242 (25°C)	2.8[a]	
Aldicarb	190.3	4930 (20°C)	1.15[a]	
Aminotriazole	84.1	280 000	−0.8[a]	
Atrazine	215.7	33 (20°C)	2.5	1.7
Chlorpyrifos	350.6	1.4 (25°C)	4.7	
Dinoterb	240.2	4.5 (25°C)		5.0
Diuron	233.1	42 (25°C)	2.85	
Endosulfan α	406.9	0.3 (22°C)	4.74	
Endosulfan β		0.33 (22°C)	4.79	
Fenpropimorph	303.5	4.3 (pH 7, 20°C)	4.1 (pH 7)	7.0
Fluzilazole	315.4	45 (pH 7.8)	3.7 (pH 7)	
Ioxynil	370.9	50 (25°C)		4.0
Isoproturon	206.3	65 (22°C)	2.5	
Lindane	290.8	7.3 (25°C)	3.8	
Linuron	249.1	81 (25°C)	3.0	
Oxydemeton-methyl	246.3	Very high	0.18	
Simazine	201.7	6.2 (20°C)	2.1	1.7
Terbuthylazine	229.7	8.5 20°C)	3.05	2.0
Trifluraline	335.3	0.2 (20°C)	5.3	7.0
Triallate	304.7	4 (25°C)		

Data from ref. [17,18][a].

of various pesticides using disks is half of that using cartridges, typically 30 vs. 60 min for 1 l of water [16]. Therefore, when using cartridges, the time required for sample percolation is important, and it was worthwhile to lower the sample volumes as much as possible. New laminar disks, known as Speedisk, consist of a thin bed of microparticles supported in a laminar structure in a pre-assembled disk. This thin bed and the inlet structure allow high throughput rates, even when samples contain suspended solids, without clogging and previous filtration. Therefore, since 1 l of surface water can be percolated within 3–5 min, with possible automation, it is easy to increase the sample volume in order to enhance the sensitivity of the detection. However, increasing the sample volume has the drawback of increasing co-extracted interfering substances, so that, often, the increase in sensitivity is not really obtained.

In this paper, we describe a multiresidue extraction procedure for compounds with a wide range of polarities and acido-basic properties. The sorbents have been selected on the basis of their polarity in order to have good recoveries of extraction using 1 l of samples for neutral and acidic compounds. The procedures were optimized to lower (as much as possible) the effect of interfering substances. The objective is to obtain detection limits to the low 0.1 $\mu g\ l^{-1}$ level in real surface water samples. The French national priority lists have been selected as reference list of pesticides.

2. Experimental

2.1. Apparatus

LC analyses were performed with a Varian LC System Workstation including a Varian Star 9010 solvent delivery system and a 9065 Polychrom diode array detector (Varian France, les Ulis, France). The analytical column was connected to a Rheodyne (Cotati, CA, USA) valve. The simultaneous extraction of six samples was performed using a six-port vacuum manifold (Speedisk compact extraction station, Mallinckrodt Baker France, Noisy-le-Sec, France).

2.2. Stationary phases and columns

A 25 cm×4.6 mm I.D. analytical column, prepacked with Bakerbond Narrow Pore 5 μm octadecylsilica, was used for the separation of the two mixtures. The extraction of the polar and moderately polar neutral and acidic compounds was performed using a Bakerbond Speedisk divinylbenzene (DVB) disk containing 300 mg of DVB polymers, characterized by a 50-mm diameter and 0.5-mm high bed height. For the extraction of the nonpolar pesticides, disks containing 750 mg of C_{18} silica (Bakerbond Speedisk C_{18}), characterized by a 50-mm diameter and 1 mm high bed height, were used.

2.3. Chemicals

LC-grade acetonitrile was obtained from Baker–Mallinckrodt and methanol was from Prolabo (Paris, France). LC-grade water was obtained from Baker–Mallinckrodt or was prepared by purifying demineralized water in a Milli-Q filtration system (Millipore, Bedford, MA, USA). Other chemicals were purchased from Baker–Mallinckrodt, Prolabo, Merck or Fluka.

The various pesticides were supplied by Riedel-de Haën (Seelze, Germany), Promochem (Wesel, Germany) or Cluzeau (Sainte Foi La Grande, France). Stock solutions of selected solutes were prepared by weighing and dissolving them in methanol and these were stored at 4°C. They were used for the preparation of diluted standard solutions and for spiking water samples. No change in the chromatograms of the standard solution was observed during the three months of this study. The final spiked samples did not contain more than 0.5% methanol, except for the samples containing the nonpolar pesticides, which contained 10% methanol.

Surface waters from the rivers Seine and Marne were taken from around Paris (dissolved organic content, DOC around 3 $mg\ l^{-1}$).

2.4. Procedure

2.4.1. LC conditions

Gradient 1, which was used for the separation of polar and moderately polar compounds, is as fol-

lows: Acetonitrile (ACN) gradient with $5 \cdot 10^{-3}$ *M* phosphate buffer, acidified at pH 3 with perchloric acid, from 20–43% ACN from 0 to 30 min, 77% ACN at 48 min and 100% at 55 min. Gradient 2, which was used for the separation of the nonpolar compounds is as follows: ACN gradient with $5 \cdot 10^{-3}$ *M* phosphate buffer, pH 7; from 40–70% ACN from 0 to 30 min, 75% ACN at 45 min and 100% at 60 min. The flow-rate of the mobile phase was 1 ml min^{-1}.

2.4.2. Extraction of polar and moderately polar compounds

Off-line extraction steps with Speedisks were performed using a six-port vacuum manifold. The procedure used for the extraction step was as follows:

The DVB disks were conditioned with 10 ml of acetonitrile, 10 ml of methanol and 10 ml of LC-grade water. The sample was percolated at 200 ml/min, and the disk was dried by air flow (aspiration) for a few seconds. This was followed by desorption with 9 ml of acetonitrile. A 120-μl volume of a mixture of methanol and ammonia (4:1, v/v) was then added and evaporation was commenced at 40°C using a rotary evaporator and was stopped when 1 ml remained, the volume of which was reduced to 80 μl using a gentle stream of nitrogen. The initial mobile phase (acetonitrile–phosphate buffer. pH 3, 20:80, v/v) was then added up to 200 μl and 50 μl were injected into the analytical column.

2.4.3. Extraction of nonpolar compounds

The C_{18} disks were conditioned using 10 ml of acetonitrile, 10 ml of methanol and 10 ml of LC-grade water. Methanol (10%) was added to the sample, which was percolated at a flow-rate of 200 ml/min. The disk was then dried by air flow (aspiration) for a few seconds, which was followed by desorption with 10 ml of methylene chloride–methanol (4:1, v/v). Evaporation was performed at 40°C using a rotary evaporator and was stopped when 1 ml remained, the volume of which was reduced to 80 μl using a stream of nitrogen. Methanol was then added to bring the volume up to 200 μl and 50 μl were injected into the analytical column.

3. Results and discussion

3.1. Selection of the disk sorbents for the multiresidue extraction

As can be seen in Table 1, the priority lists contain very polar analytes with high water solubility, such as aminotriazole and oxydemeton-methyl (log K_{ow} −0.8 and 0.18, respectively), but also very apolar analytes with log K_{ow}>4 and water solubility below 0.5 mg l^{-1}, such as endosulfan and trifluraline. Moreover, some compounds have acidic properties, such as dinoterb, ioxynil and are ionized in natural water.

In a multiresidue approach, a single extraction procedure should ideally be applied and all the compounds should be separated and quantified at the same time. Looking at the properties of the compounds and from our experience, it clearly appeared that aminotriazole would never be included in a multiresidue approach. This compound is very difficult to extract from water because of its high water solubility, and its separation without derivatization can only be performed by ion-exchange- or ion-pair LC with electrochemical detection [19,20]. Although oxydemeton-methyl can be included in a multiresidue chromatogram by simple reversed-phase chromatography, in a first attempt, it was removed from our study because the separation time was doubled when it was included in the mixture. Therefore, as it is eluted quickly, it is better to analyze it separately.

With the exceptions of lindane and endosulfan, all other compounds can be analyzed by reversed-phase LC and detected by UV diode array detection (UV DAD) or mass spectrometry (MS) without derivatization [21]. LC with UV DAD was therefore preferred as the method for measuring the recoveries. The conditions for the multiresidue extraction have been discussed previously using disposable cartridges and off-line extraction procedures [15]. The net advantage of using apolar divinylbenzene copolymers with high specific surface areas of ca. 700–1200 m^2 g^{-1} (HSA DVB) for the extraction of polar and moderately polar compounds has been demonstrated [10–13,15]. However, when apolar compounds are in the mixture, low recoveries were obtained for some of them, especially those with

very low water solubilities and high hydrophobicities, such as chlorpyrifos, trifluralin, triallate and fenpropimorph. The low recoveries were explained by adsorption on the flasks and connecting tubes. Recoveries of between 70 and 130%, as accepted in any Environmental Protection Agency (EPA) method, were obtained after the addition of 10% organic solvent to the samples before extraction [15]. However, the use of 10% organic solvent, which increases the recovery of the nonpolar analytes, has the drawback of decreasing the recoveries of the more polar compounds, because this addition decreases the breakthrough volume of the analytes. The only solution to this incompatibility was to divide the lists of compounds. One extraction procedure was optimized for the extraction of the polar and moderately polar compounds and a second procedure was optimized for the extraction of the nonpolar analytes. Therefore, any compound added to the list can be extracted using one of the two procedures. The guidelines for the selection of procedures are that any compounds with a log K_{ow} value <4 or a water solubility >5 mg l^{-1} can be extracted using the procedure optimized for polar–moderately polar compounds, whereas those characterized by a water solubility <5 mg l^{-1} and a log K_{ow} value >3.5 should be extracted using the second procedure, which was optimized for the nonpolar pesticides. Only very polar analytes may still be difficult to extract with these sorbents, and graphitized carbon has been shown to solve this problem for some analytes [11,12,22,23].

New disks under study are available with both HSA, DVB and C_{18} silica packing. Therefore, the two extraction procedures were investigated with 1 l of sample, in terms of recoveries and interfering compounds.

3.2. Decrease in the interferences with sample pH for polar and moderately polar compounds

New apolar polymers with high specific surface areas provide very high retention for neutral compounds. As a comparison, we have shown that retention factors of compounds in water were 100–1000-times higher than those observed with C_{18} silicas [10]. Using disposable commercial cartridges containing 200 mg of DVB (specific surface area of 1060 m^2 g^{-1}), acidic pesticides such as dicamba, bentazone, ioxynil, dinoterb, mecoprop (MCPP) and other phenoxyacetic acids could be extracted in their ionic form in natural samples at pH 7 with good recovery from sample volumes as high as 500 ml. It was therefore possible to handle the samples at pH 7, with the advantage of removing many fulvic and humic acids that are co-extracted when the samples

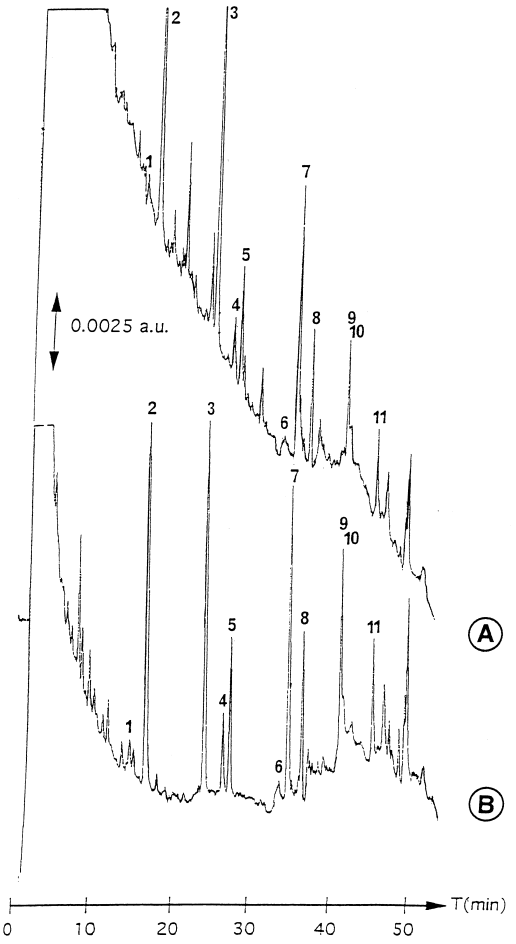

Fig. 1. Effect of the sample pH on the co-extraction of humic and fulvic acids. Preconcentration of 250 ml of drinking water spiked with 0.5 μg l^{-1} of each pesticide using the procedure for the polar and moderately polar pesticides (neutral and acidic); sample adjusted to pH 3 (A) and sample adjusted to pH 6 (B). Preconcentration using DVB Speedisks; Analytical conditions: See Section 2. Peaks: (1) Aldicarb, (2) simazine, (3) atrazine, (4) isoproturon, (5) diuron, (6) ioxynil, (7) terbuthylazine, (8) linuron, (9) flusilazole, (10) alachlor and (11) dinoterb. Detection was at 220 nm.

Table 2
Recoveries (%) of extraction obtained for polar and moderately polar pesticides in drinking and surface water using DVB laminar extraction disks and sample volumes of 250 ml and 1 l

Pesticides	Drinking water (250 ml)				Surface water, pH 6	
	pH 3	pH 6			Recovery (%)	
	Recovery (%)	Recovery (%)	R.S..D (%)	LOD ($\mu g\ l^{-1}$)	250 ml	1 l
Aldicarb	84	90	1	0.05	89	98
Simazine	95	94	2	0.005	95	95
Atrazine	96	91	3	0.005	95	90
Isoproturon	85	95	2	0.005	91	100
Diuron	87	93	5	0.005	90	98
Ioxynil	95	89	8	0.05	88	25
Terbuthylazine	88	92	3	0.005	88	75
Linuron	86	92	10	0.005	89	90
Flusilazole	90	89	2	0.01	87	66
Alachlor	78	83	5	0.01	88	nd
Dinoterb	93	87	7	0.01	89	77

Spiking level: 0.5 $\mu g\ l^{-1}$ in samples of 250 ml and 0.1 $\mu g\ l^{-1}$ in the 1 l sample.
Surface water samples were from the River Seine (250 ml) and the River Marne (1 l).
Each recovery value is based on the mean value of three experiments.
nd, not determined, LOD, defined as a signal-to-noise ratio of three.

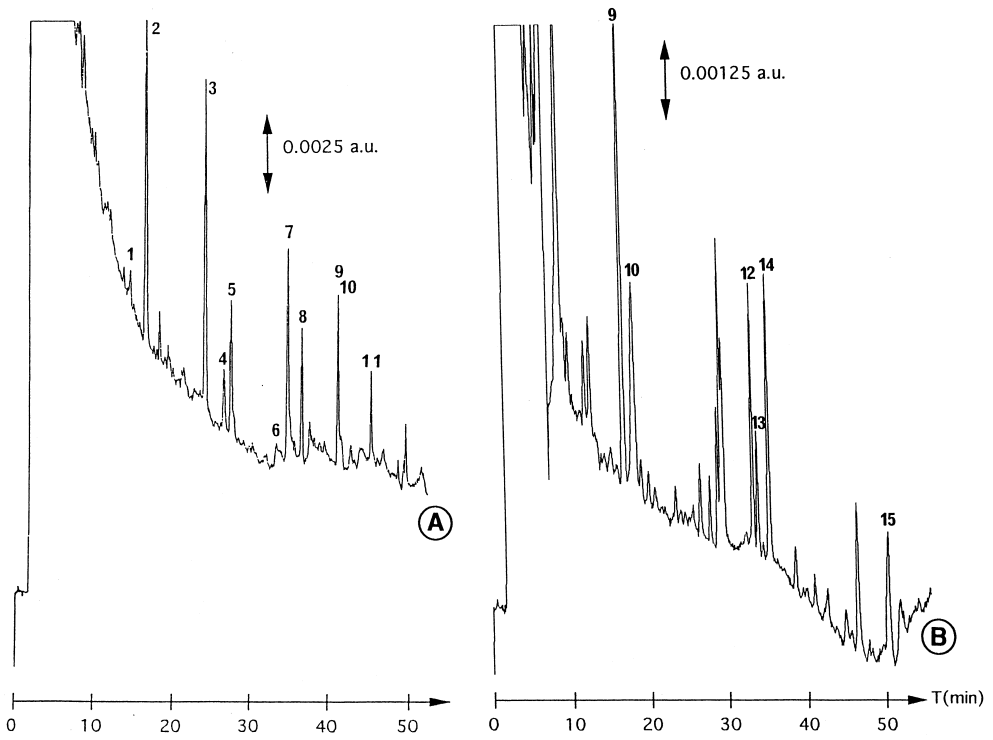

Fig. 2. Preconcentration of 250 ml of River Seine water spiked with 0.5 $\mu g\ l^{-1}$ of each pesticide using (A) the procedure for the polar and moderately polar pesticides (neutral and acidic) and (B) the procedure for the nonpolar pesticides; sample was collected in January 1997 and adjusted to pH 6; 25 ml of methanol was added to the sample for (B). Analytical conditions: See Section 2. Peaks: (1) Aldicarb, (2) simazine, (3) atrazine, (4) isoproturon, (5) diuron, (6) ioxynil, (7) terbuthylazine, (8) linuron, (9) flusilazole, (10) alachlor, (11) dinoterb, (12) chlorpyriphos, (13) trifluarine, (14) triallate and (15) fenpropimorphe. Detection was at 220 nm.

are adjusted at pH 3. This effect is shown in Fig. 1, with the handling of 250 ml of drinking water using DVB laminar disks. The effect of sample pH is clear when comparing the interfering pattern at different pH values; interference is much higher at pH 3 than at pH 6 and it can be seen that drinking water contained less interfering compounds than surface water. The chromatogram is shown at 220 nm, which is not the optimum wavelength for each compound, but is very common, since almost all of the compounds can be detected. The separation of fluzilazole and alachlor has not been achieved because these two compounds are at the border between nonpolar and polar compounds according to our criteria. Their separation was optimized in the nonpolar procedure. Because some compounds can be linked to humic and fulvic substances, the recoveries were compared at the two pH values after the samples has been agitated and equilibrated overnight. Table 2 shows that recoveries are similar for drinking water samples at pH values of 3 and 6. At pH 6, the acidic compounds, dinoterb and ioxynil, are extracted with recoveries above 85%. In surface water samples, the recoveries measured at pH 6 are similar to those obtained with drinking water samples. These results indicate that no link is observed between polar and moderately polar pesticides and humic and fulvic substances. For acidic pesticides, this could have been predicted, since both humic and fulvic substances and pesticides have negative charges at pH 6.

Fig. 2A shows the chromatograms corresponding to a sample volume of 250 ml of surface water (pH 6) spiked at 0.5 $\mu g\ l^{-1}$ with the mixture of polar and moderately polar pesticides. Compared with the same volume of drinking water, higher amounts of interfering substances can be observed with surface water (Fig. 2A) than with drinking water at pH 6 (Fig. 1B), which can be easily explained by the higher amount of fulvic and humic substances generally encountered in surface water. However, determination of the target pesticides in the range of concentration 0.1–0.5 $\mu g\ l^{-1}$ is possible from this volume. No pesticide was detected in the non-spiked water.

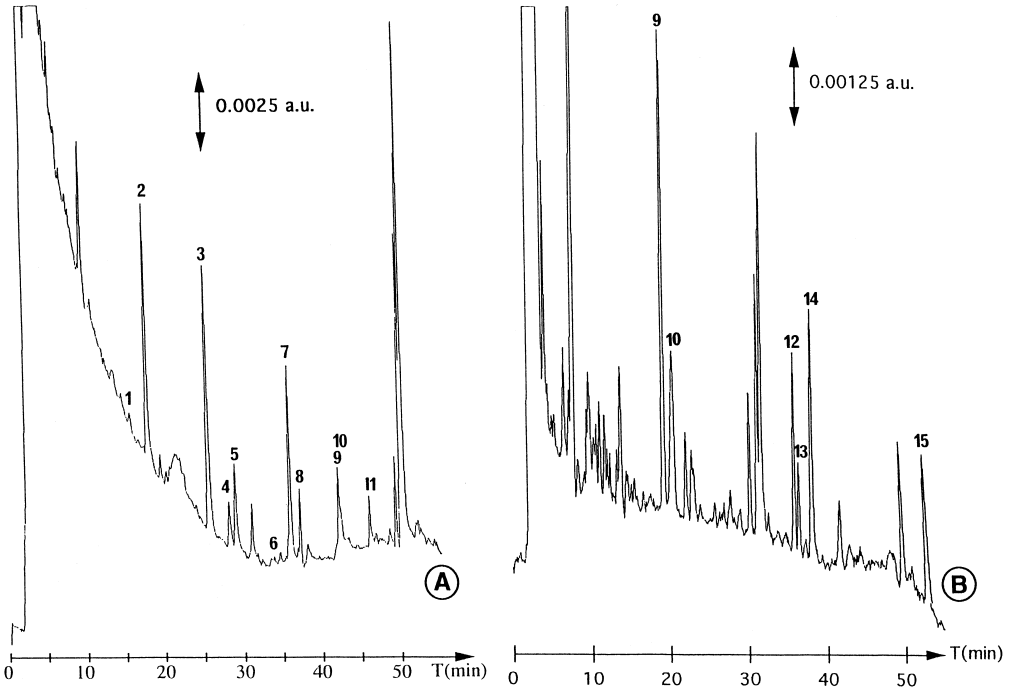

Fig. 3. Preconcentration of 1 l of drinking water spiked with 0.1 $\mu g\ l^{-1}$ of each pesticide using (A) the procedure for the polar and moderately polar pesticides (neutral and acidic) and (B) the procedure for the nonpolar pesticides; sample were adjusted to pH 6 and 100 ml of methanol were added to the sample for (B). Analytical conditions: See Section 2. Peaks: See Fig. 2. Detection was at 220 nm.

The sample volume was increased to 1 l. Recoveries in the range 85–105% were measured, except for ioxynil, as shown in Table 2. Fig. 3A Fig. 4B represent the chromatograms obtained for 1 l of drinking water and surface water, respectively, both spiked with 0.1 μg l^{-1} of each pesticide and at pH 6. We can see the advantage of increasing the sample to 1 l while minimizing the amount of interfering compounds by controlling the pH. Detection limits, defined as a signal-to-noise ratio of three are between 0.005 and 0.05 μg l^{-1} for most compounds in drinking water, depending on the UV properties of the compounds (see Table 2). In the non-spiked surface water (Fig. 4A), simazine, terbutylazine and diuron were found at concentrations of 0.09, 0.12 and 1.19 μg l^{-1}, respectively. Their presence in this non-spiked water was confirmed by their retention time and their UV characteristics, which were compared to a library of spectra. In the chromatogram corresponding to the spiked surface water (Fig. 4B), the peak of atrazine co-eluted with the peak of an interfering compound that was detected alone in the blank (Fig. 4A). The chromatogram at 220 nm shows that, in surface water, a little higher amount of interfering compounds is extracted than in drinking water, but most of the compounds can be easily detected at the 0.1 μg l^{-1} level, which is a very good result for the monitoring of surface water quality.

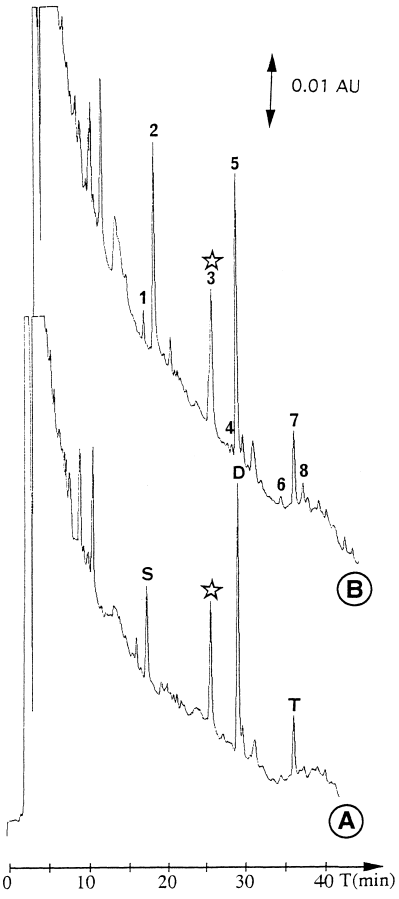

Fig. 4. Preconcentration of 1 l of River Marne water, non-spiked (A) and spiked with 0.1 μg l^{-1} of each pesticide (B) using the procedure for the polar and moderately polar pesticides (neutral and acidic). The sample was collected in May 1997 and adjusted to pH 6. Analytical conditions: See Section 2. Peaks: See Fig. 1. Detection was at 220 nm.

3.3. Effect of sample pH and the addition of organic solvent on the extraction of nonpolar analytes

Laminar disks containing 750 mg of C_{18} silica were used to concentrate the nonpolar pesticides. Although we could expect no breakthrough for nonpolar analytes using DVB disks, C_{18} silica was preferred because desorption is easier and requires a smaller volume of organic solvent. Table 3 shows that recoveries are in the range of 75–100% for each compound with 250 ml of drinking water or surface water, and with 1 l of drinking water.

Fig. 3B shows the chromatogram corresponding to the extraction of 1 l of drinking water spiked with 0.1 μg l^{-1} of each nonpolar analyte. This figure is to be compared to Fig. 3A, which was obtained with the procedure dedicated to the polar and moderately polar compounds. The amount of interfering substances is very low and one can see that the peak at the start of the chromatogram is absent. This is due to the combination of a pH value of 6 and the addition of 10% methanol to the sample, which prevents the extraction of the more polar interfering compounds. In surface water, the chromatogram corresponding to 250 ml of surface water spiked with 0.5 μg l^{-1} of each compound indicates a detection limit in the low 0.1 μg l^{-1} level (see Fig. 2B). When the sample volume was increased to 1 l, detection limits obtained in surface water are similar to those obtained in drinking water samples. No trace of these pesticides was detected in the non-spiked water.

Table 3
Recoveries (%) of extraction obtained for nonpolar pesticides in drinking and surface water (pH 6) using C_{18} laminar extraction disks and sample volumes of 250 ml and 1 l

Pesticides	Drinking water				River Seine water
	1 l	250 ml			250 ml
	Recovery (%)	Recovery (%)	R.S.D. (%)	LOD ($\mu g\ l^{-1}$)	Recovery (%)
Flusilazole	101	99	12	0.005	92
Alachlor	100	91	12	0.01	80
Chlorpyriphos	92	93	6	0.005	81
Trifluarine	93	79	9	0.05	77
Triallate	95	91	5	0.01	85
Fenpropimorphe	93	91	3	0.01	85

The sample volume used was 275 ml, containing 25 ml of methanol, or 1.1 l, containing 100 ml of methanol, and samples were spiked at 0.5 and 0.1 $\mu g\ l^{-1}$, respectively.
Each recovery value was based on the mean of three experiments.
LOD is defined as a signal-to-noise ratio of three.

3.4. Conclusion

To date, the sample preparation step has been optimized by the handling of a minimum sample volume because of the time required for the percolation of dirty samples. Moreover, minimizing the sample volume reduces the amount of co-extracted substances. The new laminar disks allow very rapid handling of the sample with a typical volume of 1 l, so that it is worthwhile to reconsider the optimization of the SPE process and to minimize the amount of co-extracted compounds by other methods. This was achieved here by the selection of the sorbent, in order to handle the acidic analytes at pH 6 and to get rid of the effect of co-extracted humic and fulvic substances, and/or by adding 10% methanol. These clean-up methods are included in the SPE sequence without any additional step.

Using the two procedures described above, it is possible to extract any compound, either polar or nonpolar, including acidic compounds, with detection limits in the range 0.01–0.05 $\mu g\ l^{-1}$ in drinking or ground water, whereas these detection limits are still in the low 0.1 $\mu g\ l^{-1}$ levels in 1 l of dirty surface water samples.

The problem of the extraction of very polar analytes still exists. One solution is to develop new extraction sorbents, such as immunoaffinity sorbents, which involve interactions which are specific to the compounds of interest and are not based on hydrophobicity or polarity. Such sorbents have been shown to be very selective and are now under investigation for application to very polar analytes [24].

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