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Journal of Chromatography A, 857 (1999) 157–166

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Ultra-trace-level determination of polar pesticides and their transformation products in surface and estuarine water samples using column liquid chromatography–electrospray tandem mass spectrometry

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Received 26 April 1999; received in revised form 24 June 1999; accepted 25 June 1999

Abstract

A method is developed for the determination of polar pesticides and their transformation products [atrazine, de-ethylatrazine, deisopropylatrazine, hydroxyatrazine, diuron, 3,4-dichlorophenylmethylurea, 3,4-dichlorophenylurea (DPU), monuron, bentazone, anthranil-isopropylamide, chloridazon, metolachlor] in surface, estuarine and sea water samples at the low ng/l level. Solid-phase extraction is combined off-line with column liquid chromatography–electrospray ionization tandem mass spectrometric detection (LC–ESI-MS–MS). The applicability of two solid-phase materials, i.e., LiChrolut EN cartridges and graphitized carbon black extraction disks, is evaluated. The influence of the organic solvent used in gradient LC, as well as the amount of co-extracted humic material on the ESI process is studied. The eluotropic strength of the organic solvent was found to have a distinct effect on the sensitivity of ESI-MS if coupled with LC gradient separations. Methanol gave much better results than acetonitrile and phenylurea compounds are more susceptible to solvent changes than triazines. Co-extracted humic material causes signal suppression in ESI-MS–MS detection. The degree of suppression depends upon the sample pH and the nature of the samples, i.e., surface or estuarine water. Detection limits in LC–ESI-MS–MS ranged from 0.2 to 2 ng/l, with the exception of DPU (8 ng/l). The applicability of the procedure was demonstrated by analyzing surface and estuarine water.

Keywords: Water analysis; Environmental analysis; Pesticides

1. Introduction

In earlier studies we have shown that considerable amounts of pesticides are being transported by rivers from their catchment area into the marine environment [1]. Next to parent compounds such as atrazine, simazine, alachlor and metolachlor, relatively large

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0021-9673/99/$ – see front matter
PII: S0021-9673(99)00772-4

amounts of the atrazine transformation product (TP), deethylatrazine, were found to be transported into estuaries of the rivers Louros (Greece), Ebro (Spain), Rhone (France) and Scheldt (The Netherlands). To assess the overall risk of pesticides, it is important, therefore, to include TPs in environmental monitoring programmes. This is even more true because over 50% of the TPs of triazines, carbamates and phenoxypropionic acids seem to pose a similar or even higher risk than their parent pesticides [2]. Whereas deethylatrazine is thermally stable, i.e., amenable to gas chromatographic analysis, the majority of the TPs are much more polar than their parent pesticides, much less volatile, and often also thermolabile, which makes liquid chromatography (LC) the preferred analytical separation technique. Electrospray ionization (ESI) has proven to be a reliable, robust and sensitive ionization interface in combination with single mass spectrometry (MS) [3–7] or tandem MS (MS–MS) detection [8–10] for the determination of polar pesticides in aqueous samples. Absolute detection limits of polar pesticides in LC–ESI-MS are reported to be strongly compound dependent and range from 0.003–0.5 ng for standard injections of ioxynil and 2,4-dichlorophenol, respectively, to 0.01–2 ng for propazine and coumaphos, respectively, for tap water in the single ion monitoring (SIM) mode [8,9]. An increase in selectivity was reported for tandem mass spectrometry, however, at the cost of a 3–10-fold loss of absolute sensitivity [9].

The aim of the present study was to develop a method for the determination of a series of polar pesticides and their TPs in estuarine water samples. The selection of compounds was based on their occurrence in the estuary of the river Scheldt. Monuron was studied as a transformation product of diuron rather than as a parent compound because its use is banned since several years [11]. For the low-salinity samples the dissolved organic carbon (DOC) content, mainly in the form of humic acids, will be relatively high. This may cause a serious suppression of the ESI efficiency of analyte molecules [12,13]. For the high-salinity samples, analyte concentrations are expected to be very low, i.e., at or below the 1 ng/l level. To attain the necessary detection limits, relatively large sample volumes and, consequently, solid-phase extraction (SPE) sorbents with a high retention power will be required. Both aspects, the reduced ESI ionization efficiency and the retention power of different SPE sorbents, will be considered in this study.

1.1. SPE procedure

In recent literature, graphitized carbon black (GCB) related materials [5,14–16] and styrene–divinylbenzene copolymers with high specific surface areas [17–19] have been used successfully for the extraction of polar pesticides and their TPs from environmental water samples. With the GCB materials rather large volumes of organic solvent are required to desorb the analytes [20]. In most studies, elution is performed in the backflush mode which results in a reduction of the required elution volume. Di Corcia et al. developed a drilled conical PTFE piston to backflush prepacked cartridges [21]. No extra instrumentation is needed, on the other hand, for the backflush elution of Empore extraction disks. The stryene–divinylbenzene copolymers, with high specific surface areas of ca. 1000 m^2/g for LiChrolut EN and SDB-1 instead of ca. 500 m^2/g for the conventional materials such as PRLP-S, PRP-1 and SDB, have been shown to give improved recoveries for a number of polar and moderately polar pesticides [14,18,19]. To retain acidic compounds, the sample pH is often adjusted to approx. 2. Crescenzi et al. reported that the LC–UV chromatograms of the acidified samples showed a huge peak for humic acids which was almost completely eliminated by omitting acidification of the sample. Pichon et al. showed that recoveries of a mixture of acid, neutral and basic pesticides on 200 mg of a SDB-1 sorbent with a specific surface area of 1060 m^2/g, were above 80% for a 500-ml drinking water sample at pH 7 [17]. In the present study, we decided to study two sorbents for the extraction of polar pesticides and their TPs from a 1-l water sample, i.e., an Empore extraction disk containing 500 mg of a GCB sorbent, and an extraction cartridge containing 200 mg of LiChrolut EN. For the GCB sorbent the disk configuration was selected because of its ease of use in the backflush-elution mode. An off-line sample preparation procedure was developed which could be performed on board the sampling vessel, to minimize the time between sampling and extraction, which

should allow us to distinguish between environmental degradation and degradation during transport to the laboratory.

1.2. Ionization suppression

A well-known phenomenon frequently observed in MS ionization techniques, is the reduced ionization efficiency of analyte molecules in the presence of large quantities of other compounds, e.g., sample matrix constituents. In ESI, ions are released from electrically charged droplets. The limited amount of charge per droplet is mainly used for the conversion of matrix molecules to free ions and is, therefore, no longer available for the formation of free ions of the analyte molecules [12,13]. We therefore studied the influence of the humic acid content on the ionization efficiency of pesticides and their TPs. The concentration of humic acids in the final extract was varied by adjusting the pH of the sample to pH 3 or 7 prior to extraction. Finally, a method to remove humic acids during the extraction of polycyclic aromatic hydrocarbons, based on the use of an aminopropyl/C_{18}-bonded silica SPE column with subsequent elution with dichloromethane to keep the humic acids retained [22], was studied for a set of polar pesticides and TPs.

2. Experimental

2.1. Reagents

Diuron, atrazine, deethylatrazine, deisopropylatrazine, hydroxyatrazine, anthranilisopropylamide (AIPA), chloridazon, metolachlor and bentazone were obtained from Riedel-de Haën (Seelze, Germany) and 3,4-dichlorophenylmethylurea (DMPU) and 3,4-dichlorophenylurea (DPU) from Dr. Ehrenstorfer (Augsburg, Germany). Standards were at least 98% pure and stock standard solutions were prepared by dissolving 10 mg in 10 ml of methanol and were stored in the dark at −20°C. In the case of hydroxyatrazine a few drops of concentrated formic acid (J.T. Baker, Deventer, The Netherlands) were added to promote dissolution. HPLC-gradient grade water, methanol, acetonitrile (ACN), tetrahydrofuran (THF), dichloromethane (DCM) and reagent-grade ascorbic acid were obtained from J.T. Baker. Nitrogen (99.999% purity) and argon (99.9995% purity) were from Praxair (Oevel, Belgium).

2.2. Sample preparation

Surface water samples (1 l) were taken from the Amsterdam–Rhine Canal or the River Scheldt and filtered though a 0.45-μm ME-25 filter from Schleicher and Schuell (Dassel, Germany) to remove particulate matter. The contribution of the particulate pesticide concentration is generally considered to be less than 1% of the total [23]. GCB Empore extraction disks were obtained from Varian (Walnut Creek, CA, USA). LiChrolut EN (200 mg) and aminopropyl (1000 mg) cartridges were obtained from Merck (Darmstadt, Germany). The GCB disks were conditioned with 5 ml of THF, 5 ml of a DCM–methanol (80:20, v/v) solution, 2 ml of methanol and 15 ml of a 10 g/l ascorbic acid solution adjusted to pH 2 with hydrochloric acid. The LiChrolut EN and aminopropyl cartridges were conditioned with 5 ml of methanol and, next, 5 ml of HPLC-grade water. The LiChrolut EN cartridges were used either in the tandem mode, with an aminopropyl cartridge placed on top, or as a single column. After conditioning, the sample was added and the disks or cartridges were not allowed to run dry in between the conditioning steps and the addition of the sample. The GCB disks were eluted in the backflush mode with 2×5 ml of DCM–methanol (80:20, v/v), and the LiChrolut EN cartridges with 3×3 ml of methanol. The aminopropyl cartridges were eluted separately with 3×3 ml of DCM. The extracts were evaporated to a volume of approx. 200 μl under a gentle stream of nitrogen and 20 μl were injected onto the LC column.

2.3. LC–ESI-MS–MS

A HP 1090 LC system equipped with a ternary solvent delivery unit (Hewlett-Packard, Waldbronn, Germany) was used. Separations were performed on a 250 mm×4.6 mm I.D. Vydac (Hesperia, CA, USA) column packed with 5 μm C_{18}-bonded silica. The column was operated at a flow-rate of 1 ml/min, 70 μl/min being directed to the ESI interface via a post-column splitter. Tandem MS was performed on

a VG Quattro II triple-stage quadrupole equipped with a dual electrospray/atmospheric pressure chemical ionization (ESI/APCI) source (Micromass, Altrincham, UK). The source temperature was set at 80°C, the ESI capillary voltage at 3.5 kV and the skimmer lens offset at 5 V. The standard dwell time was 1.5 s; it was adjusted to lower values depending on the number of multiple reaction monitoring (MRM) scans per segment. Nitrogen was used as drying and nebulizing gas at flow-rates of 350 l/h and 15 l/h, respectively. The argon pressure in the collision cell was 2.5 μbar.

3. Results and discussion

3.1. Optimization of LC–ESI-MS–MS parameters

For every compound the intensity of the (de)protonated molecule was optimized in the positive and negative ionization mode by varying the cone voltage (CV). Product-ion spectra of these protonated molecules were generated at different collision energies (CEs) and the CE which revealed the highest intensity for the major product ion was used to set up the MRM scans. The presence of co-extracted humic acids in, especially, the low-salinity samples requires the increased selectivity of MS–MS detection. The optimized parameters and product ions are summarized in Table 1. Calibration plots were linear (r^2 values ranged from 0.996 to 0.999, five data points) in the range tested (sample concentrations, 0.025–1.5 μg/l).

We also studied the influence of two organic modifiers commonly used in reversed-phase LC, methanol and acetonitrile. For each solvent the signal intensity of all but one test analyte (monuron was not included) was recorded after a gradient LC separation with a 10 m*M* ammonium acetate buffer (pH 4.5) as the aqueous LC component. The signal intensities using an acetonitrile gradient relative to the methanol gradient are given in Table 2. For all compounds lower signals were observed for acetonitrile. ESI is attained by a gas-phase reaction and, especially in the case of small molecules, by ion evaporation [12,24]. A thorough discussion of the different mechanisms involved is outside the scope of the present study. One should note, however, that a low surface tension and dielectric constant of the solvent promote ion evaporation. With respect to ionization in the gas phase, the gas-phase basicity or proton affinity and gas-phase acidity are important solvent properties in the positive and negative ionization mode, respectively [24]. Each of these properties favors the use of methanol over that of acetonitrile. In addition, the eluotropic strength of the solvent will

Table 1
Optimization of ESI-MS–MS parameters

Analyte	$[M+H]^+$ ESI+	$[M-H]^-$ ESI−	Cone voltage (V)	Collision energy (V)	Main product ion (*m*/*z*)[a]	Other product ions (*m*/*z*)
Bentazone		239	40	20	132 (100)	196 (71), 175 (60), 133 (49)
Deisopropylatrazine	174		35	15	132 (100)	146 (23), 138 (15), 110 (15), 104 (82), 96 (75), 79 (62), 68 (29)
Chloridazon	222		50	20	104 (60)	92 (51), 77 (11), 65 (5)
AIPA	179		30	10	120 (100)	92 (6), 65 (4)
Hydroxyatrazine	198		35	20	156 (100)	128 (10), 114 (32), 97 (21), 86 (72)
Deethylatrazine	188		35	15	146 (100)	110 (29), 104 (31), 79 (10), 68 (10)
Monuron	199		40	15	72 (100)	154 (5), 126 (6), 46 (52)
DPU	205		40	15	127 (100)	162 (9), 160 (12)
		203	30	10	160 (100)	42 (42)
Atrazine	216		35	15	174 (100)	146 (14), 132 (21), 110 (5), 104 (15), 96 (28), 79 (11), 68 (5)
DPMU	219		30	15	127 (100)	162 (30), 160 (7), 58 (11)
		217	30	10	160 (100)	124 (4)
Diuron	233		40	15	72 (100)	188 (16), 160 (9), 46 (42)
		231	40	20	186 (100)	150 (18), 122 (5)
Metolachlor	284		30	15	252 (100)	176 (28), 73 (5)

[a] Numbers in parentheses give relative abundance.

Table 2
Retention data and signal reduction of protonated molecules in LC–ESI-MS

Analyte	Retention time (t_R) (min)		% Organic modifier in eluting solvent at t_R		% Signal intensity with ACN relative to MeOH gradient	
	MeOH	ACN	MeOH	ACN	ESI+	ESI−
Bentazone	7.60	5.86	45	27		67
Deisopropylatrazine	7.78	5.58	51	32	36	
Chloridazon	8.57	6.55	77	40	88	
AIPA	8.68	7.43	78	48	80	
Hydroxyatrazine	8.88	5.95	61	35	58	
Deethylatrazine	8.97	6.57	62	40	40	
DPU	10.73	8.00	76	53	<1	67
Atrazine	10.97	8.94	78	61	57	
DPMU	11.06	8.53	79	58	15	74
Diuron	11.19	9.05	80	62	21	86
Metolachlor	12.18	10.99	90	78	58	

be important when combining gradient LC with ESI-MS. This is illustrated in Fig. 1 where the signal intensities of $[M+H]^+$ for four selected compounds are depicted as a function of the percentage of organic solvent added to a 10 m*M* ammonium acetate solution. The intensities for methanol are higher than for acetonitrile due to the more favorable ionization properties and, for both methanol and acetonitrile, the intensities are seen to increase at higher percentages of organic solvent. From Table 2 it is clear that, due to the lower eluotropic strength of methanol, compounds are eluted at a higher percentage of methanol than acetonitrile. This, in addition to the more favorable ionization properties, explains the overall higher signal intensities for the methanol gradient. Distinct differences in the reduction of signal intensity are found between the compound classes. The reduction is strongest for the phenylureas in the positive ionization mode.

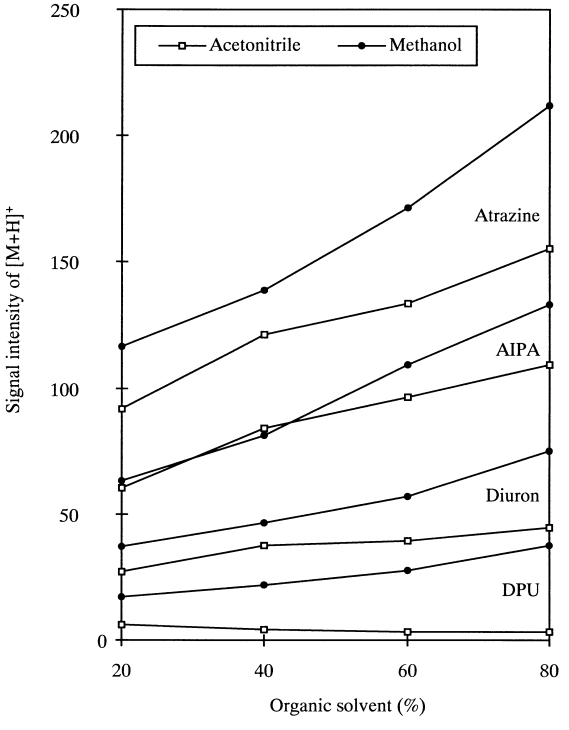

Fig. 1. Dependence of signal intensity of $[M+H]^+$ on percentage of organic modifier for four test compounds.

3.2. Graphitized carbon black vs. LiChrolut EN

Table 3 lists the recoveries of the test analytes for the two types of sorbent studied. Analytes were extracted from 1 l of demineralized water at pH 7. Demineralized water was used to avoid signal suppression by co-extracted humic material. The acidic bentazone ($pK_a=3.3$) was also studied at pH 7 because, as will be shown below, at this pH substantially less humic material is co-extracted. The analytes were measured in the positive ionization mode except for bentazon which was only detectable in the negative ionization mode. High recoveries of some 80–100% and good standard deviations of 5% ($n=4$) in all but one case were found when using LiChrolut EN. The rather satisfactory recovery of 66% for bentazone demonstrates the high retention power of

Table 3
Percent recoveries of test analytes from 1 l of demineralized water (pH 7) spiked at 200 ng/l

Analyte	Recovery±SD for	
	LiChrolut EN (n=4)	GCB disk (n=3)
Bentazone	66±3	9±4
Deisopropylatrazine	92±2	70±2
Chloridazon	96±5	26±5
AIPA	79±3	55±3
Hydroxyatrazine	91±9	46±8
Desethylatrazine	96±5	76±2
Monuron	102±4	55±4
DPU	84±3	21±3
Atrazine	96±2	80±5
DPMU	85±2	11±2
Diuron	91±5	26±1
Metolachlor	96±2	78±15

LiChrolut EN, even for the largely ionized bentazone. On the other hand, rather low recoveries were found for the GCB disks. Earlier studies suggest that this is most likely caused by very strong interaction between analytes and sorbent which hampers their quantitative elution and not by a low retention power of GCB [15,21].

3.3. Signal suppression by humic substances

The signal suppression by co-extracted humic acids was studied by varying the amount of humic acids present in the final extract. Two surface water samples taken from the Amsterdam–Rhine Canal and adjusted to pH 3 and 7, respectively, were extracted with LiChrolut EN. A third sample (pH 7) was extracted with the tandem aminopropyl/LiChrolut EN SPE set-up. With this device, the humic acids should be retained on the aminopropyl column, while the polar analytes are expected to break through and be retained on the LiChrolut EN column. Indeed, (part of) the humic material was retained on the aminopropyl column as was indicated by the top of the column becoming brown-colored. When the two columns were eluted separately, the DCM extract of the aminopropyl column was virtually colorless which indicates that the interaction between the humic acids and the sorbent was maintained. In the methanol extract of the LiChrolut EN column, however, humic acids were clearly present as indicated by the yellow color of the extract. Apparently, part of the humic acids which were not retained on the aminopropyl column, were trapped on the LiChrolut EN column and subsequently eluted with methanol. The presence of humic acids was even more evident for the extract obtained from a sample adjusted to pH 3.

The separate methanol and DCM extracts of the tandem aminopropyl/LiChrolut EN run were combined and evaporated to approx. 200 μl in order to determine the analyte concentrations in a single run, in order to ensure a higher sensitivity compared to a method in which the extracts are analyzed separately. Next, 20-μl aliquots of this and all other extracts were analyzed by LC–ESI-MS–MS to determine the concentration of the pesticides. The extracts were then spiked with 20 μl of the standard analyte mixture which resulted in a final concentration of approx. 5 ng/ml. Fig. 2 shows the signal intensities of the spiked extracts relative to those of a standard solution The results were compared with an extract that was measured after direct infusion (5 μl/min), i.e., without an LC separation (procedure 1). From the infusion experiments it is clear that the signal is strongly suppressed when compounds are not separated from the co-extracted humic material by an LC gradient. However, signal suppression is still present after an LC separation and, apart from metolachlor and AIPA, only a small increase in signal intensity is observed with the sample adjusted to pH 7 compared to the sample at pH 3. Although a substantial amount of humic material was removed, the tandem SPE procedure did not effect an improvement with respect to signal suppression and from the data in Table 4 it is clear that the procedure had a detrimental effect on the overall recovery and precision of

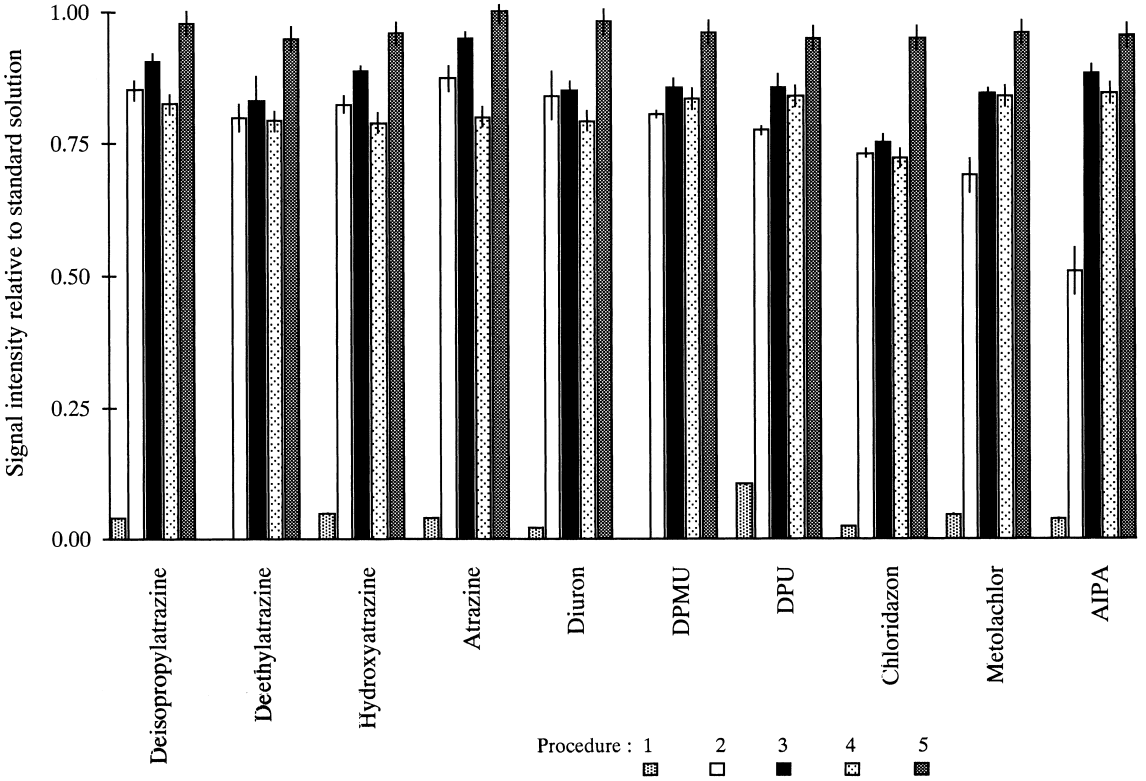

Fig. 2. Signal suppression in ESI-MS due to the presence of different amounts of humic material in the final extract. (1) Amsterdam–Rhine Canal sample; pH 7, direct infusion; (2) Amsterdam–Rhine Canal sample; pH 3, LC separation; (3) same as 2 but sample adjusted to pH 7; (4) same as 3, but with tandem SPE set-up; (5) Western Scheldt estuarine sample (salinity 1.5‰); pH 7, LC separation.

Table 4
Recoveries of test analytes from a 1-l canal water sample (pH 7) spiked at 200 ng/l (n=3)[a]

Analyte	Aminopropyl plus LiChrolut EN		LiChrolut EN	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Bentazone	–	–	71	13
Deisopropylatrazine	79	14	77	4
Chloridazon	92	19	63	4
AIPA	58	5	71	3
Hydroxyatrazine	78	10	82	5
Deethylatrazine	65	16	88	4
Monuron	78	21	76	6
DPU	82	13	93	8
Atrazine	70	10	88	3
DPMU	89	12	80	6
Diuron	74	13	75	3
Metolachlor	56	8	81	6

[a] For experimental conditions, see text.

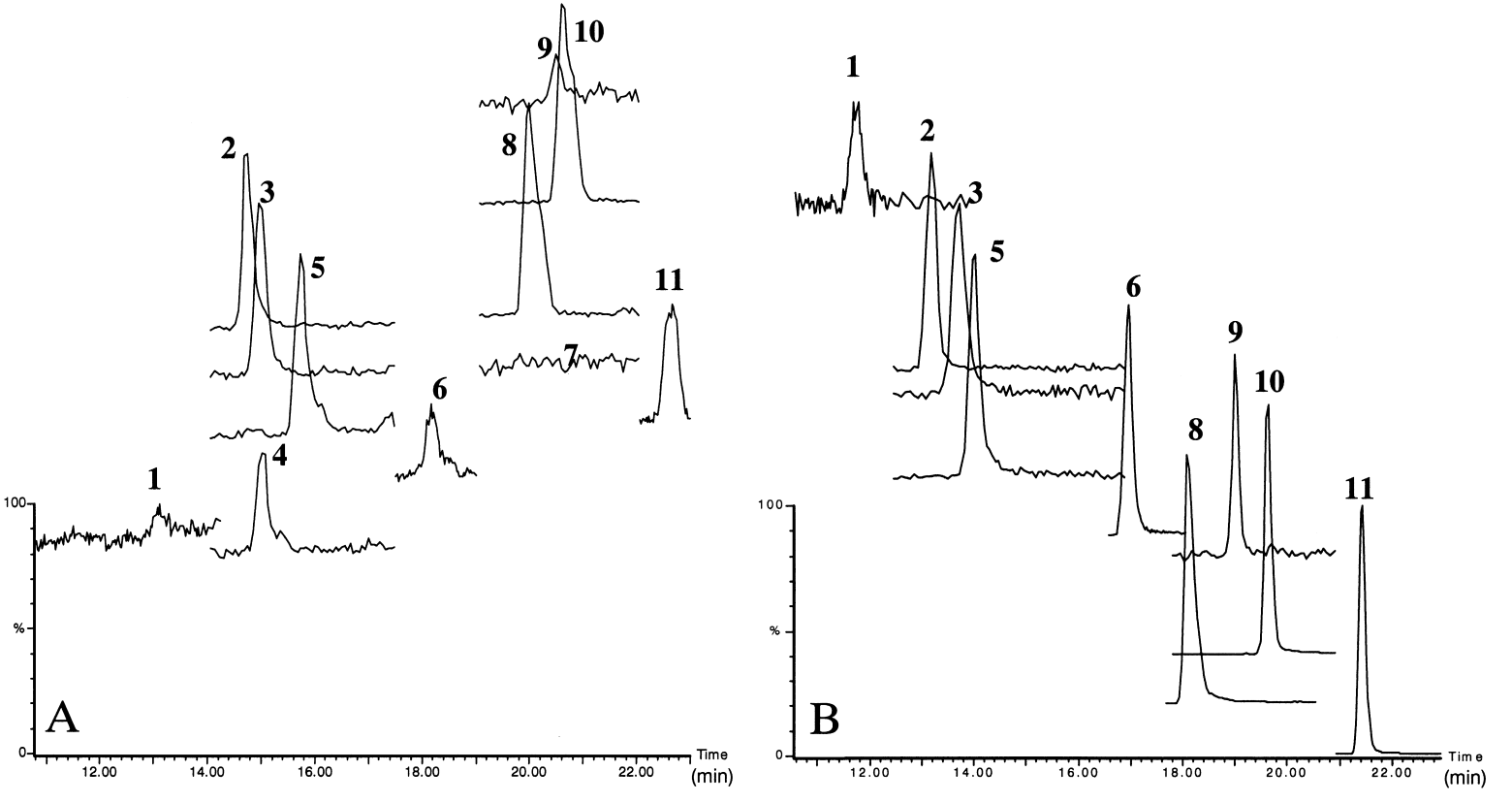

Fig. 3. LC–ESI-MS–MS determination of polar pesticides and their transformation products in (A) an Amsterdam–Rhine Canal surface water sample and (B) a Western Scheldt estuarine sample (salinity 1.5‰). Peak assignment and MRM transitions: 1, deisopropylatrazine, m/z 174→132; 2, chloridazon, m/z 222→104; 3, hydroxyatrazine, m/z 198→156; 4, AIPA, m/z 179→120; 5, deethylatrazine, m/z 188→146; 6, monuron, m/z 199→72; 7, DPU, m/z 205→127; 8, atrazine, m/z 216→174; 9, DPMU, m/z 174→146; 10, diuron, m/z 231→72; 11, metolachlor, m/z 284→252. For concentrations, see Table 5.

most of the analytes.

With the tandem SPE procedure, rather low recoveries were found for the less polar compounds, atrazine and metolachlor. Apparently both analytes are, to some extent, retained on the (end-capped) aminopropyl column and, subsequently, not eluted with DCM. This was confirmed by extracting a spiked demineralized water sample with the tandem SPE set-up and separately analyzing the DCM and methanol fractions. The DCM fraction did not contain detectable amounts of atrazine and metolachlor, whereas the amounts eluted from the LiChrolut EN column were only 87% and 66%, respectively. These values are considerably lower than the recovery of 96% for the single LiChrolut EN set-up reported in Table 3.

From Fig. 2 it is also clear that the degree of signal suppression is strongly sample-type dependent. The bars for procedure 5 of Fig. 2 represent the signal suppression in a low-salinity Western Scheldt estuarine water sample. Although the same procedures were followed as for the Amsterdam–Rhine Canal sample (procedure 3), much less signal suppression is observed. The humic acid content may vary substantially between surface waters from different origin and between samples taken at different seasons [25]. This implies that the extent of signal suppression will have to be determined for every sample type via a standard-addition experiment. In the case of estuarine water samples one may assume that, if signal suppression is absent in the low-salinity region of the estuary, it will be absent as well at higher salinity due to mixing with sea water which contains less humic material [25].

3.4. Applications

For further experiments we selected the single LiChrolut EN-based SPE set-up with adjustment of the sample to pH 7. The overall ''recoveries'', i.e., extraction recovery plus signal suppression compared to a standard injection, for all test analytes in a spiked Amsterdam–Rhine Canal water sample were already reported in Table 4 above. The results, with recoveries of over 70% in all but one case, and RSDs of ca. 4–8% ($n=3$) in, again, all but one case, can be called fully satisfactory. As a further illustration, Fig. 3A shows the results of the target analysis of six pesticides and five transformation products for a raw, i.e., non-spiked canal water sample using a 200 mg LiChrolut EN cartridge and LC–ESI-MS–MS. The concentrations of the microcontaminants, and their detection limits ($S/N=3$) are given in Table 5. The chromatogram was divided into five windows with a maximum of four MRM transitions per window. The dwell time for each MRM scan was adjusted so that the LC peak contained at least 12 data points. The use of LC to separate the compounds is, therefore,

Table 5
Detection limits of selected pesticides and TPs in LC–ESI-MS–MS and concentrations in real life samples[a]

Analyte	Analyte concentrations (ng/l) in:		Detection limit (ng/l)
	Amsterdam–Rhine canal (March 1998)	River Scheldt (July 1998)	
Bentazone	–	–	2
Deisopropylatrazine	<LOD	6	0.6
Chloridazon	4.3	70	0.6
AIPA	0.2	<LOD	0.2
Hydroxyatrazine	1.7	34	0.6
Deethylatrazine	1.7	19	0.3
Monuron	0.3	26	0.3
DPU	<LOD	<LOD	8
Atrazine	1.9	510	0.2
DPMU	<LOD	70	2
Diuron	4.1	860	0.3
Metolachlor	0.2	90	0.1

[a] For experimental conditions, see text.

advantageous because fewer target analytes are assigned to one window and the detectability is, consequently, improved. Fig. 3B shows the target analysis of a water sample from the Western Scheldt estuary. From the data included in Table 5 it is evident that the level of contamination is about 20–100-fold higher than in the canal water and that easily detectable amounts of several TPs are transported by the river into its estuary.

4. Conclusions

Off-line SPE combined with LC–ESI-MS–MS was successfully used for the determination of polar pesticides and their TPs in surface and estuarine water down to the low ng/l level. For all but one of the twelve test compounds, the detection limits ranged from 0.2 to 2 ng/l (DPU, 8 ng/l). With respect to the type of SPE sorbent used, LiChrolut EN cartridges gave much better results than GCB disks. Methanol is preferred over acetonitrile when MS with ESI is coupled to gradient LC. The lower eluotropic strength of methanol causes compounds to elute at a higher percentage of organic solvent through which the ESI sensitivity is increased. This study also demonstrates that co-extracted humic material causes signal suppression in ESI-MS detection. The extent of this suppression is determined by the sample pH and the nature of the samples, i.e., surface or estuarine water. Detectable amounts of TPs of diuron and atrazine were found to be transported into the Western Scheldt estuary. Concentrations in the low-salinity region were 6, 19 and 34 ng/l for deisopropylatrazine, deethylatrazine and hydroxyatrazine and 26 and 71 ng/l for monuron and DPMU, respectively. The developed methodology has already been used successfully in a study on the environmental behavior of these TPs and their parent pesticides in the estuarine environment. The results of this study will be presented in a forthcoming paper.

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