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Simultaneous determination of antifouling herbicides in marina water samples by on-line solid-phase extraction followed by liquid chromatography–mass spectrometry

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Abstract

Solid-phase extraction (SPE) coupled on-line with either liquid chromatography–diode array detection (LC–DAD) or liquid chromatography–atmospheric pressure chemical ionization mass spectrometry was applied to the simultaneous analysis of several antifouling herbicides such as diuron, TCMTB (2-thiocyanomethylthiobenzothiazole), Irgarol and chlorothalonil in seawater samples. SPE was carried out on polymeric cartridges (PLRP-s) after the percolation of 100 ml of seawater sample, with recoveries ranging from 96 to 111% for the antifouling compounds. LC–MS detection was used in negative and positive ion mode. In positive ion mode, additional structural information for diuron and Irgarol was obtained by increasing the fragmentor voltage, thus permitting the unequivocal identification of these compounds in environmental waters. Method detection limits were in the range of 0.005 μg/l. This methodology was also compared to LC–DAD in terms of selectivity and sensitivity. Finally, the method was evaluated for the analysis of environmental seawater samples, from the Ebre Delta area and Masnou marina, in Catalonia (Spain).

Keywords: Environmental analysis; Water analysis; Pesticides

1. Introduction

In the last few years, antifouling herbicides have been widely used as alternative additives in paints in order to reduce primary colonization by algae and growth of seaweeds in boats [1]. Since the legislation, in many European countries, bans the use of tributyltin (TBT) as an antifouling agent for small boats up to 25 m, alternative additives which enhance antifouling properties of paints have been applied. In this sense, herbicides are generally used to supplement the more traditional biocides such as copper and tin based compounds. As an example, Irgarol 1051 has proven to be effective for this purpose [1]. This compound is used in tin-free antifouling paint formulations which are mainly based on copper and zinc metal oxides.

According to this, important coastal concentrations have been found in areas of high yachting activity, particularly in marinas and sportive harbors. This is the case of several surveys carried out in English and French coastal waters [1–3] and also in lake Geneva [4]. In all these studies concentrations of Irgarol in freshwater and seawater ranged from 0.0025 to 0.64 μg/l. In a previous work from our group, concentrations of Irgarol and diuron in the ppb level were reported for first time in the Mediterranean coastal waters [5].

Data concerning the usage, concentration, distribution and effects of most of these biocides are

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currently not available due to the fact that no sensitive analytical methodologies exist. At the same time, if such analytical methods are not available no monitoring can take place. So that, in order to assess the risk to the environment posed by antifouling agents, the development of a robust and sensitive methodology is of primary importance. Several analytical methods for the analysis of antifouling herbicides in environmental waters have been developed. In this way, many authors have reported the extraction of antifouling agents from water samples by means of liquid–liquid extraction using dichloromethane [3]. Nevertheless, the disadvantages of such extraction methodology have been pointed out in many reviews dealing with the trace enrichment of pesticides from aqueous samples [6]. For this reason, isolation of herbicides from water samples is commonly carried out by means of solid-phase extraction (SPE) using silica or polymeric phases, such as C_{18} or PLRP-s [poly(styrene–divinylbenzene)]. For example, C_{18} cartridges have been used extensively over the past decade for the isolation of many types of organic contaminants from water [7]. On the other hand, these methodologies include as a detection method the use of gas chromatography techniques such as gas chromatography with nitrogen–phosphorus detection (GC–NPD) or gas chromatography–mass spectrometry (GC–MS) [1–3]. Few applications using high-performance liquid chromatography (HPLC) techniques have been reported in the literature; furthermore, liquid chromatography–mass spectrometry (LC–MS) has scarcely been applied for the determination of antifouling agents in seawater samples [4]. Moreover, a sensitive methodology for the simultaneous determination of several antifoulings have not yet been described in the literature. There are analytical methodologies available for each specific compound but not for the total range of antifouling compounds. In a recent work, four antifouling agents were identified by liquid chromatography–atmospheric pressure chemical ionization mass spectrometry (LC–APCI-MS), after SPE using C_{18}, in marina waters from the UK [8].

In the present work, on-line SPE coupled with LC–APCI-MS was applied for the first simultaneous analysis of several antifouling herbicides in seawater samples. The efficiency of extraction was tested on polymeric cartridges (PLRP-s) showing a good performance of the sorbent material for most of the antifouling compounds. Additional structural information was obtained by using the APCI interface at different fragmentor settings, in positive mode of ionization, thus permitting the unequivocal identification of these compounds in environmental waters. Finally, the method was tested for the analysis of seawater samples from two marina areas, Ebre Delta and Masnou, containing the compounds under study. To our knowledge, this work represents the first identification of these compounds in seawater from the Mediterranean coast by on-line SPE–LC–MS and it follows the previous work carried out regarding the monitoring of Irgarol and diuron in seawater samples [5].

2. Experimental

2.1. Chemicals

HPLC-grade solvents acetonitrile, methanol and water were purchased from Merck (Darmstadt, Germany). Pesticide standards: dichlofluanid, diuron, TCMTB (2-thiocyanomethylthiobenzothiazole) and chlorothalonil were obtained from Promochem (Wesel, Germany). Irgarol 1051 was a gift from Ciba Geigy (Barcelona, Spain). Stock standard solutions of 500 μg/ml were prepared by weighing the solutes and dissolving them in methanol.

A stock solution of 1 μg/ml was used to spike groundwater at the μg/l level for the preconcentration through the cartridges and further determination of recoveries and construction of the calibration graphs. The final standard solutions did not contain more than 0.5% of methanol.

The SPE cartridges used (Spark Holland, The Netherlands) consisted of 10 mm×2 mm I.D. disposable pre-columns that contained 20 mg of either 40-μm C_{18}-bonded silica or polymeric material (PLRP-s).

2.2. Chromatographic conditions

2.2.1. (a) LC–DAD

The eluent was delivered by a gradient system Waters 600-MS with a 20-μl injection loop and a Waters 996 photodiode array detector (Waters, Milli-

pore, MA, USA). The gradient elution was performed as follows: from A (acetonitrile)–B (LC-grade water) (30:70) to A–B (100:0) in 25 min. The analytical column used was of 25 cm×4.6 mm I.D. packed with 5 μm octylsilica gel from Shandon (Cheshire, UK). Quantification was carried out with UV detection at 220 nm for all the compounds.

2.2.2. (b) LC–APCI-MS

LC–APCI-MS in both positive and negative modes of operation was used for the determination of the compounds at low levels of concentration. The eluent was delivered by a liquid chromatograph Model HP 1090 (Hewlett-Packard, CA, USA). The mobile phases used for the elution of the analytes consisted of acetonitrile–water at a flow-rate of 0.8 ml/min. The gradient elution and the analytical column was the same as that used in the LC–DAD analyses. This HPLC system was connected to a HP mass spectrometer, Model HP 1100, system equipped with an APCI probe. The design of the APCI consists of a coaxial flow probe. After the HPLC separation, the sample is introduced into the APCI source together with a nebulizing gas, which flows directly through the probe tip, maximizing the efficiency of the nebulization. A drying gas is added to flush out any solvent that may have entered the gas line by capillary action.

The different operating parameters included a drying gas (N_2), a nebulizing gas, a capillary voltage, a corona current and a fragmentor voltage setting. The experimental conditions and operational parameters used for the characterization of the analytes are summarized in Table 1. These values were optimized for the compounds under study in both ion modes of operation. The fragmentor voltage was varied between 50 and 200 V in order to study the fragmentation of the three compounds. Generally, a fragmentor voltage of 70 V was used in the analysis of the seawater samples. The instrument control and data processing utilities included the use of the HP application software installed in a Digital Pentium personal computer. Chromatograms were recorded under selected ion monitoring (SIM) and full scan (from m/z=100 to 400) conditions.

2.3. Sampling

Sampling of the seawater samples was carried out at a depth of 1 m from the surface layer of the Ebre Delta and Masnou marinas. The samples (taken between April 1996 and January 1999) were collected in 2.5-l precleaned amber glass bottles and kept at 4°C in the dark until analysis. Water sample pH varied from 7.9 to 8.3. Before analysis, samples were filtered through a glass fiber filter (0.45 μm pore size) in order to remove the suspended particles. Blanks of seawater samples were also taken from open sea in order to spike them with known amounts of the antifouling herbicides and to prepare the calibration curves.

2.4. Sample preparation

Preconcentration of the samples was performed on-line with an automated sample preparation system. The automated SPE device used (Prospekt, Spark Holland) was connected on-line with the gradient pumps. The general scheme of this system was previously described [9]. The C_{18} and the PLRP-s cartridges were washed sequentially with 6 ml acetonitrile and 4 ml LC-grade water. Afterwards,

Table 1
LC–APCI-MS operational parameters used in the analysis of the seawater samples[a]

Operational parameters	Positive ionization (PI) mode	Negative ionization (NI) mode
Drying gas flow	4 l/min	4 l/min
Drying gas temperature	350°C	350°C
Nebulizer gas pressure	60 p.s.i.	60 p.s.i.
Vaporizer temperature	400°C	400°C
Capillary voltage	2000 V	3000 V
Corona current	8 μA	50 μA
Gain	3	3

[a] Carrier stream: acetonitrile–water (50:50) at a flow-rate of 0.8 ml/min. 1 p.s.i.=6894.76 Pa.

a 100-ml aliquot of seawater sample was passed through the cartridge at a flow-rate of 2 ml/min. The compounds trapped on the sorbent were eluted with the chromatographic mobile phase by switching the valve into the elute position.

For recovery studies, 100 ml of groundwater sample spiked at 1 μg/l were percolated through the C_{18} and the PLRP-s cartridges and analyzed by LC–DAD. This experiment was performed in replicate ($n=5$) for all the pesticides studied.

The calibration curves were obtained by LC–MS after the percolation of 100 ml of seawater sample spiked in the trace level range of 0.005–1 μg/l in order to have the same matrix as in the environmental water samples.

3. Results and discussion

3.1. Solid-phase extraction

The retention of five antifouling herbicides (see Fig. 1) was investigated on two different types of sorbents in order to assess the best conditions for the extraction of these compounds in environmental seawater samples. Table 2 presents the recoveries of extraction obtained for these compounds analyzed after their extraction from 100 ml of seawater, spiked at 1 μg/l, onto C_{18} and PLRP-s cartridges. High recoveries of extraction were obtained for all the compounds except for dichlofluanide which was poorly recovered in both C_{18} or PLRP-s cartridges. On the other hand, chlorothalonil exhibited higher recovery in the polymeric cartridges as compared to the silica ones. The main drawbacks of the C_{18} sorbents are their limited breakthrough volumes for polar analytes and the narrow pH stability range. For this reason, reversed-phase polymeric sorbents are frequently used in environmental applications for the trace enrichment of soluble molecules that are not effectively isolated by C_{18} sorbents; these kinds of sorbents have a greater surface area per gram, so that they can retain the most water soluble analytes. In this sense, polymeric materials are known to be more suitable for those compounds presenting a high polarity, such is the case of herbicide metabolites [10]. In this work, polymeric cartridges were chosen according to the high recoveries obtained for the

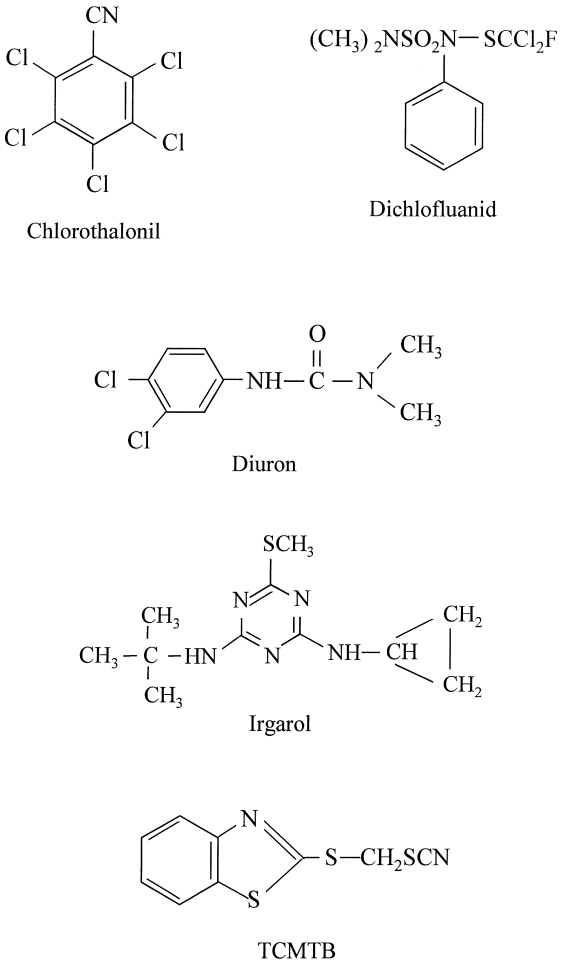

Fig. 1. Chemical structures of the compounds studied.

Table 2
Recoveries of extraction (%) and repeatability (relative standard deviation among replicates, $n=5$) obtained after the percolation of 100 ml of seawater spiked at 1 μg/l with the antifouling herbicides studied, through C_{18} and PLRP-s cartridges

	Recovery, % (RSD, %)	
	C_{18}	PLRP-s
Dichlofluanid	<10	<10
Diuron	89 (8)	99 (5)
TCMTB	98 (9)	111 (3)
Irgarol	95 (2)	106 (3)
Chlorothalonil	63 (2)	96 (4)

majority of compounds and in order to retain the most polar metabolites of Irgarol [11].

Repeatability of the method was calculated from five independent extractions of the compounds from seawater samples upon both type of sorbents. The repeatability ranged from 2 to 8% indicating good performance of the method developed in this work. One advantage of automation in an on-line preconcentration is that more reproducible results are expected, provided that the manipulation of the samples is avoided as compared with an off-line methodology. So that, a great accuracy on the analysis of water samples can be achieved with this kind of methodology.

3.2. APCI characteristics

The different operational parameters of the APCI interface were optimized for the five compounds under study and those presenting the maximum sensitivity were chosen for further analysis. In Table 1 the operational parameters used in the analysis of the groundwater samples are summarized. The most relevant parameters were the capillary voltage and the corona current. The capillary voltage is applied to the entrance of the capillary and it is relative to the nebulizer and spray chamber which are at ground potential. On the other hand, the corona current parameter controls the current (in μA) from the corona discharge needle to the end plate The field of free electrons that make up this current ionizes the mobile phase molecules. The ionized mobile phase molecules in turn react with, and ionize, the sample molecules. These two values were observed to be different in positive and in negative ionization mode according to the specifications of the mass spectrometer system. A value of 2000 V for the capillary voltage and a value of 8 μA for the corona current were chosen for the analysis under positive ion (PI) conditions. On the other hand, a value of 3000 V and a value of 50 μA were chosen for the analysis under negative ion (NI) conditions.

A comparison of the use of APCI under positive and negative ion mode of operation was also carried out. In this way, the difference in response of the five analytes studied under both positive and negative mode of operation was assessed. Whereas for dichlofluanid, diuron, TCMTB and chlorothalonil the sensitivity obtained in negative ion mode of operation was higher, for Irgarol was lower. The triazine compound accepts easily a proton in the nitrogen position of the chemical structure, so that, this compound exhibits a higher sensitivity under positive ion mode of operation than under negative ion mode when performing the analysis by LC–APCI-MS.

3.3. APCI fragmentation

The fragmentor voltage affects the transmission and fragmentation of sample ions. In general, the higher the fragmentor voltage, the more fragmentation will occur. In compounds that do not fragment readily, higher fragmentor voltages often result in better ion transmission. The fragmentor voltage gives the ions a ''push'' that helps them traverse the relatively high pressure region between the exit of the capillary and the skimmer. Thus, at higher values of voltage the maximum structural information is obtained [12]. However, optimum fragmentor voltage is compound dependent and, for this reason, an accurate evaluation of a wide range of fragmentor values for each one of the compounds studied in this work was performed. In Fig. 2 the different patterns in fragmentation for Irgarol and diuron are shown as a function of the fragmentor voltage. A monitoring of the signal produced by the molecular ion and the main fragment ion was carried out for both compounds at different values of fragmentor voltage. The main fragment ions of Irgarol and diuron are reported in Table 3 and correspond to typical fragmentation of triazines and phenylureas, respectively. In both cases, the molecular ion presents its maximum sensitivity at a fragmentor value of 70 V. At higher fragmentor values the sensitivity for the molecular ion decreases and the sensitivity for the fragment ion increases. For the rest of the compounds studied, dichlofluanid, TCMTB and chlorothalonil, total fragmentation was observed even at low values of voltage.

Tables 3 and 4 report the typical fragment ions of the compounds studied in this work in both positive and negative mode of operation, respectively. Fragmentor voltages of 70 V and 120 V were chosen in order to study the main fragment ions formed under LC–APCI-MS at a low and at a high voltage value. A fragmentor voltage of 70 V was chosen as the

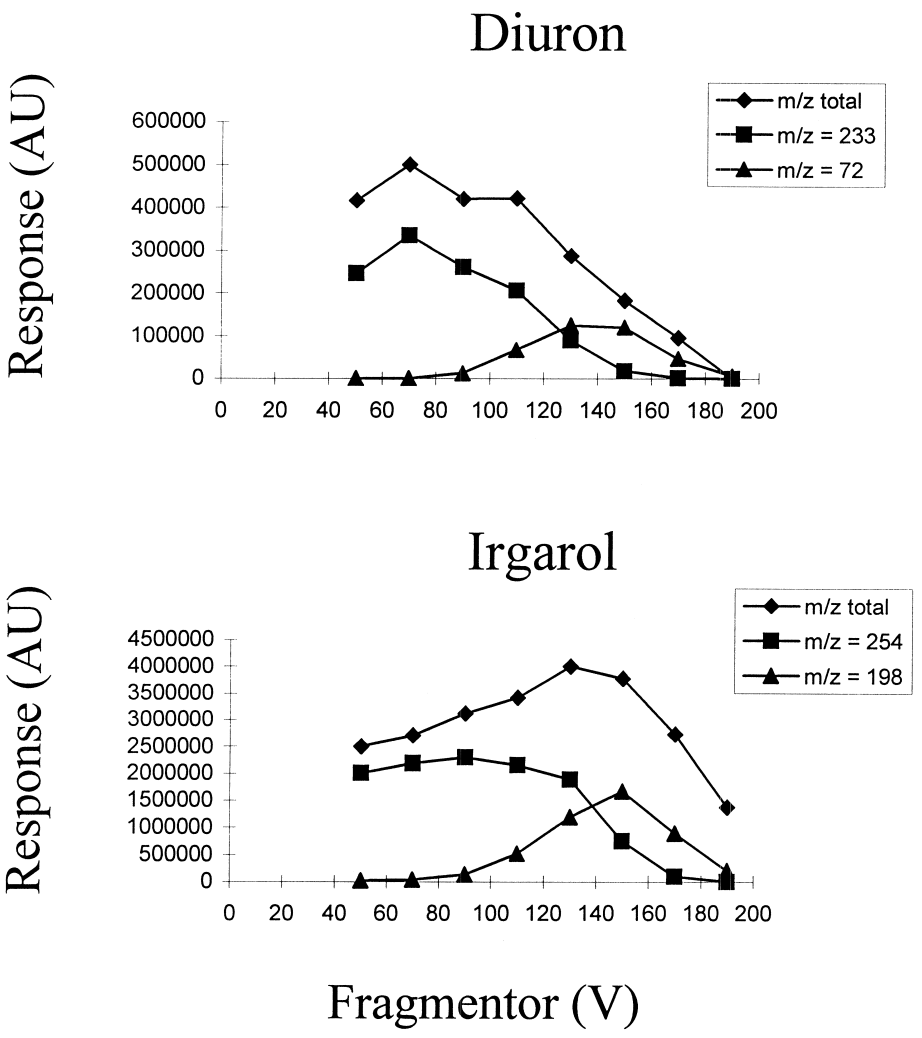

Fig. 2. Fragmentation pattern of diuron and Irgarol under LC–APCI-MS in positive mode of operation. Carrier stream: acetonitrile–water (50:50).

lowest voltage at which no fragmentation occurred (only the molecular ion is present). On the other hand, a fragmentor voltage of 120 V was chosen since this was a representative voltage at which fragmentation occurred without loss of sensitivity for the molecular ion at the same time. In this sense, the best structural information (molecular ion plus main fragment ion) is obtained (see Fig. 2). As shown in Table 3, at the low fragmentor value of 70 V, diuron and Irgarol gave only the molecular ion plus a proton as a base peak under positive mode of operation. This result is in agreement with the typical response obtained when analyzing phenylureas and triazines by LC–APCI-MS [12]. Both families of compounds tend to accept a proton under positive ion mode of ionization. So that, this fragmentor value does not give us useful structural information. However, it was observed that, under positive ion conditions, both compounds presented a major fragmentation at 120 V, which gave both good structural information and enough sensitivity for them. In negative mode of ionization, chlorothalonil, dichlofluanid and TCMTB suffered an appreciable fragmentation even at a low voltage value (see Table 4). Chlorothalonil is known

Table 3
Typical fragment ions and relative abundances (RAs) of the herbicides in LC–MS using an APCI interface in positive ion mode of operation[a]

Compound	M_n	APCI in PI			
		70 V		120 V	
		m/z	RA	m/z	RA
Diuron	232	233 $[M+H]^+$	100	233 $[M+H]^+$	70
				72 $[MH-C_6H_5Cl_2N]^+$	100
Irgarol	253	254 $[M+H]^+$	100	254 $[M+H]^+$	70
				198 $[MH-C_4H_8]^+$	100

[a] Fragmentor set at 70 V and 120 V. Carrier stream: acetonitrile–water (50:50) at a flow-rate of 1 ml/min. Concentration of analytes: 10 μg/ml. M_n=Number-average molecular mass.

Table 4
Typical fragment ions and relative abundances (RAs) of the herbicides in LC–MS using an APCI interface in negative ion mode of operation[a]

Compound	M_n	APCI in NI			
		70 V		120 V	
		m/z	RA	m/z	RA
Dichlofluanid	332	199 $[M-SCCl_2F]^-$	100	199 $[M-SCCl_2F]^-$	40
				155 $[M-SCCl_2FN(CH_3)_2]^-$	100
Diuron	232	231 $[M-H]^-$	100	231 $[M-H]^-$	100
				186 $[M-H-HN(CH_3)_2]^-$	65
TCMTB	238	166 $[M-CH_2SCN]^-$	100	166 $[M-CH_2SCN]^-$	100
Chlorothalonil	264	245 $[M+OH-HCl]^-$	100	245 $[M+OH-HCl]^-$	100

[a] Fragmentor set at 70 V and 120 V. Carrier stream: acetonitrile–water (50:50) at a flow-rate of 1 ml/min. Concentration of analytes: 10 μg/ml. M_n=Number-average molecular mass.

to degrade under high temperature conditions leading to the substitution of a Cl atom by a hydroxyl group in the aromatic ring. TCMTB presented a characteristic fragmentation at 70 V corresponding to the loss of the CH_2SCN group. On the other hand, diuron presents fragmentation only at a higher fragmentor voltage.

3.4. Calibration curves and limits of detection (LODs)

Calibration graphs were constructed by percolating 100 ml of seawater sample, spiked with the solution containing the antifouling herbicides, through a PLRP-s cartridge. Calibration data are summarized in Table 5. The curves were linear in the range studied from 0.005 to 1 μg/l and the correlation coefficients were higher than 0.98 for all the pes-

Table 5
Calibration data obtained with LC–APCI-MS in time-scheduled SIM-PI mode for the studied pesticides (spiked from 0.005 to 1 μg/l) after on-line preconcentration of 100 ml of seawater through a PLRP-s cartridge

Compound	Calibration equation[a]	R^2	LOD[b] (μg/l)
Diuron	$y=139\,926+7\cdot10^6x$	0.9933	0.01
TCMTB	$y=100\,388+2\cdot10^7x$	0.9974	0.008
Irgarol	$y=139\,926+7\cdot10^6x$	0.9933	0.005
Chlorothalonil	$y=406\,763+2\cdot10^7x$	0.9844	0.002

[a] Least-squares regression equation.
[b] LODs were calculated by using a signal-to-noise ratio of 3 (the ratio between the peak intensity and the noise).

ticides studied, thus indicating a good performance of the on-line methodology developed in this work.

The LODs were calculated using a signal-to-noise ratio of 3 (the ratio between the peak intensity under SIM conditions and the noise). Low detection limits in the ng/l level can be obtained due to the high selectivity and sensitivity encountered by the LC–MS system. On the other hand, LC–MS detection has been proved to be very selective for pesticides and their metabolites since any or few interferences are encountered under SIM conditions [13,14]. The combination of SPE together with MS detection has been demonstrated to be a powerful technique for the preconcentration and detection of not only pesticides but also traces of their main metabolites in environmental water samples [15].

3.5. Sample analysis

3.5.1. (a) LC–APCI-MS versus LC–DAD

Seawater samples were preconcentrated upon PLRP-s cartridges and analyzed by LC–APCI-MS, with positive and negative mode of ionization under SIM conditions, and by LC–DAD. Fig. 3 shows the

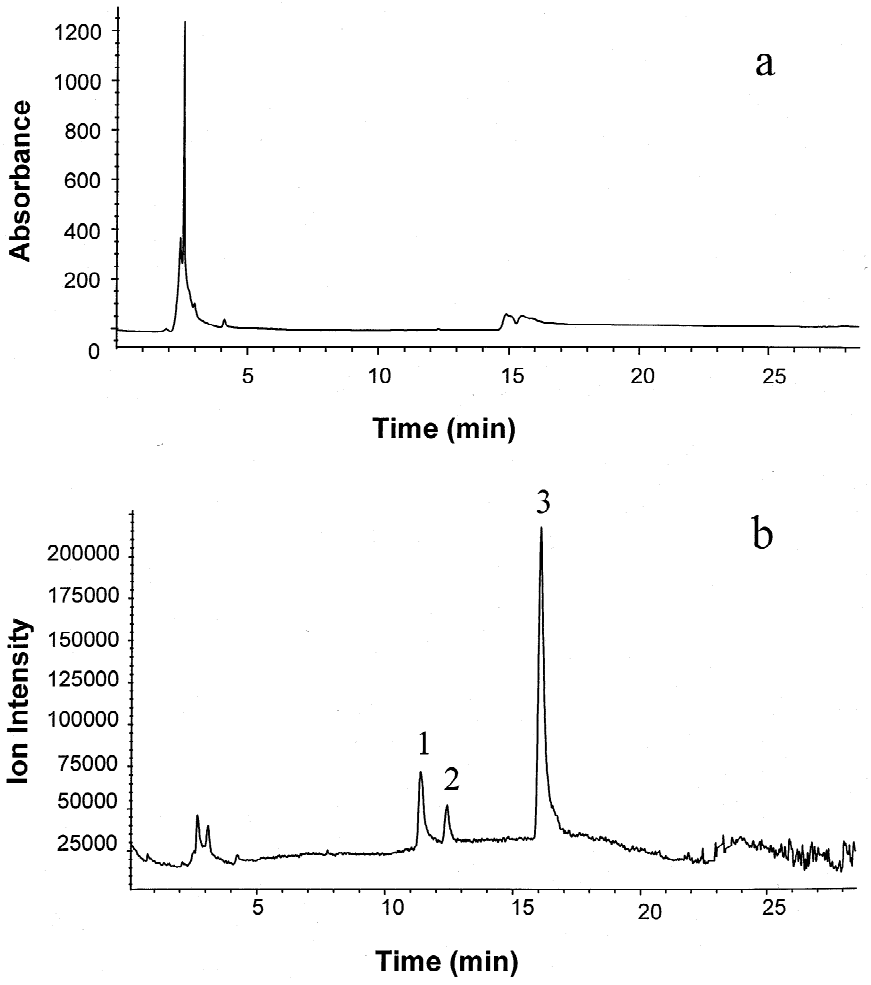

Fig. 3. Analysis of a seawater sample from the Masnou marina after its preconcentration through polymeric cartridges by (a) LC–DAD at 220 nm and (b) LC–APCI-MS with positive ion (PI) mode of operation under SIM conditions. Peak numbers: (1) Irgarol metabolite (m/z=214), (2) diuron and (3) Irgarol. LC conditions as described in Section 2.2.

comparison between the analysis of a seawater sample by LC–APCI-MS and LC–DAD after its preconcentration through polymeric cartridges. As it can be seen in this figure, the chromatogram obtained from the seawater sample analyzed by APCI-MS presented a clear baseline as compared with that corresponding to the analysis by LC–DAD. In this sense, the compounds could be easily identified and detected by using the LC–APCI-MS detection. One of the improvements achieved with LC–APCI-MS as compared to conventional LC–DAD is that a better sensitivity is obtained working under SIM conditions. Furthermore, the broad matrix peak corresponding to the humic and fulvic substances of natural waters is artificially avoided by the use of SIM conditions, which gives a clearer baseline. So that, the presence of the two major antifouling herbicides, Irgarol and diuron, was totally confirmed

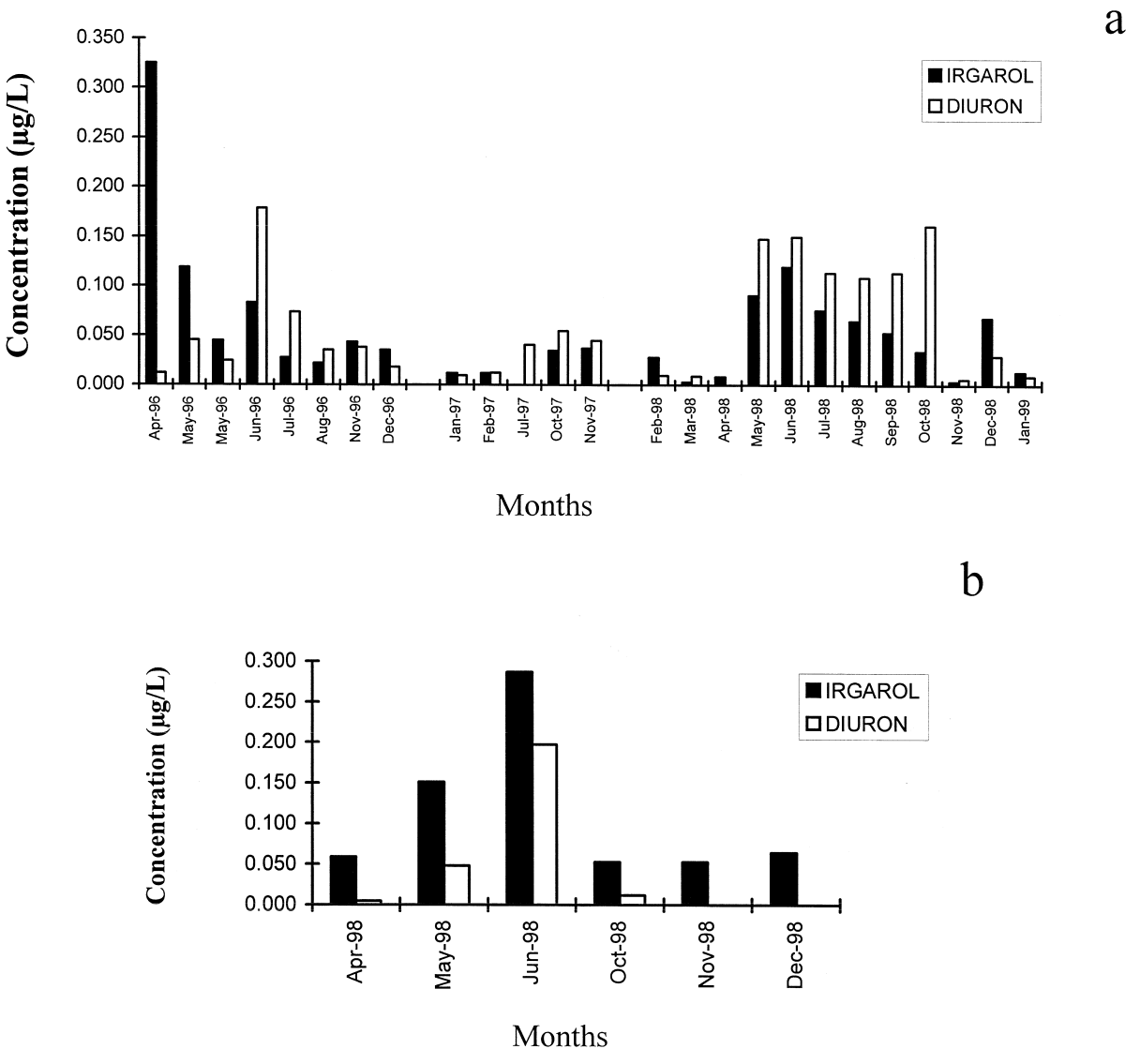

Fig. 4. Concentrations (µg/l) of Irgarol and diuron, in seawater samples from (a) the Masnou marina and (b) the Ebre Delta marina, after their analysis by LC–APCI-MS under PI mode of operation. Relative standard deviation ($n=3$) varied between 5–10%.

with the LC–APCI-MS technique. These compounds can be measured with great sensitivity, with detection levels of 0.005 μg/l for a 100 ml sample, which means a total mass detected of ~500 pg. When using only LC–DAD analysis, the humic and fulvic acids are a major huge interference peak in the chromatogram. With APCI using positive ion detection we can ''see-through'' the humic material and no interference occurs. This result enhances the detection limit of the method.

3.5.2. (b) Levels of concentration

Concentrations of Irgarol and diuron in the ng/l level (see Fig. 4) were found in all the samples collected. Moreover, the presence of one of the metabolites of Irgarol was assessed in all the samples analyzed with a molecular mass of 213 [11]. Fig. 3 shows the LC–MS chromatogram of an environmental seawater sample collected in the Masnou marina. As can be seen in this figure the presence of diuron, Irgarol and one of its metabolites was confirmed by LC–MS.

4. Conclusion

We have demonstrated in this work that the coupling of SPE using polymeric cartridges together with LC–APCI-MS detection is a powerful technique for the determination and quantitation of antifouling herbicides in environmental matrices at the low ng/l level without the need of additional clean-up steps. Very low detection limits can be reached due to the enhanced selectivity and high sensitivity obtained with this methodology. On the other hand, the good reproducibility obtained with an on-line methodology assess high quality of the whole analytical procedure and allows automation of the method to be used for routine monitoring.

Acknowledgements

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