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Part-per-trillion level determination of antifouling pesticides and their byproducts in seawater samples by off-line solid-phase extraction followed by high-performance liquid chromatography–atmospheric pressure chemical ionization mass spectrometry

Karell Martínez, Imma Ferrer, Damiá Barceló*

Department of Environmental Chemistry, IIQAB-CSIC, c/Jordi Girona 18–26, 08034 Barcelona, Spain

Abstract

A new method for the simultaneous determination of antifouling pesticides and some of their byproducts such as dichlofluanid, diuron and its byproducts [demethyldiuron and 1-(3,4-dichlorophenyl)urea], (2-thiocyanomethylthio)benzothiazole, chlorothalonil, Sea-nine 211, Irgarol 1051 and one of its byproducts (2-methylthio-4-*tert*.-butylamino-*s*-triazine) in seawater was developed. The extraction of these compounds from the filtered seawater samples was performed off-line with different solid-phase extraction sorbents using (I) a 500 mg graphitized carbon black cartridge (ENVI-Carb) and (II) 200 mg polymeric cartridges (LiChrolut EN and Isolute ENV+) and passing 500 ml of the sample through these cartridges. The detection was carried out by reversed-phase high-performance liquid chromatography coupled with atmospheric pressure chemical ionization mass spectrometry both in the negative and positive ion modes. The recovery ranged from 76 to 96% for the whole antifouling group with the ENVI-Carb cartridges and the detection limit was at the part-per-trillion level except for TCMTB. The method utilizing the polymeric cartridge proved to be very useful, time saving and with good recoveries when only Irgarol and its byproduct, Sea-nine 211 and diuron and its byproducts, have to be analyzed. The different cartridges were applied to the analysis of these pesticides in different marinas of the Catalan coast; diuron, dichlofluanid, Sea-nine 211, Irgarol as well as demethyldiuron and the Irgarol byproduct being the must ubiquitous pollutants. Maximum concentration levels were 2–3.5 μg/l of diuron and Sea-nine 211, respectively.

Keywords: Water analysis; Environmental analysis; Solid-phase extraction; Pesticides

1. Introduction

The use of antifouling agents in boat paints has originated an organotin seawater contamination in European seas causing deleterious effects in non target organisms. These compounds avoid primary colonization of hull surfaces by microalgae as well as the attachment and growth of seaweeds and animals [1]. Tributyltin (TBT), one of the most used antifouling biocides, was found to severely damage populations of bivalves and gastropods in the sea at extremely low concentrations [2] and in Arcachon Bay (France) alone, caused a loss of US$150 million through reduced oyster production [3].

At the end of the 1980s, TBT and other organotin-copper-based antifoulings were banned by the European Union in small vessels (<25 m) [4], leading to a decrease of TBT concentrations in seawater. Be-

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*Corresponding author. Tel.: +34-93-4006-118; fax: +34-93-2045-904.

E-mail address: dbcqam@cid.csic.es (D. Barceló)

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cause of the restrictions, new biocides and well-known pesticides were introduced for substituting the TBT congeners, such as Irgarol 1051, diuron, (2-thiocyanomethylthio)benzothiazole (TCMTB), dichlofuanid, chlorothalonil, Sea-nine 211 (Kathon 5287), (2,3,5,6-tetrachloro-4-methylsulphonyl)pyridine (TCMS) pyridine, zinc pyrithione and Zineb [5]. Due to the fact that these chemicals are also toxic to aquatic life there is a need to develop a reliable analytical methodology to determine their concentrations in the marine environment. In fact, Irgarol 1051 and diuron have been found by our group in enclosed areas of the Mediterranean coasts in the last few years [6,7].

Several methods for analyzing these compounds can be found in the literature. They are mainly based on liquid–liquid extraction (LLE) or solid-phase extraction (SPE) followed by gas chromatography (GC) or high-performance liquid chromatography coupled to mass spectrometry (HPLC–MS) [5–12]. In the last few years SPE cartridges with C_{18} or polymeric adsorbents have been used for the determination of antifoulings in natural waters. Recently, an on-line SPE method using PRLP-s and HPLC–atmospheric pressure chemical ionization (APCI) MS for diuron, Irgarol 1051, chlorothalonil and TCMTB was developed by our group [6]. In the same way, four of the above mentioned antifoulings were determined in aqueous samples but using a C_{18} cartridge [5]. However these methods showed poor recovery values for dichlofluanid ($<10\%$) and for this reason it is of interest to test other SPE materials for the extraction of this group of antifoulings agents and some of their byproducts. In addition, recoveries for Sea-nine 211 have not yet been reported in the literature.

Graphitized carbon black (GCB) cartridges have been used for the extraction and concentration of pesticides from natural water samples in the last few years [13]. This material has been demonstrated to recover polar compounds from water samples such as phenols and chloroanilines [14,15] due to a specific adsorption mechanism involving ion pair and dipole–dipole interactions. A similar interaction can be observed by using polymeric adsorbents such as ethylvinylbenzne–divinylbenzene copolymer (LiChrolut EN) and styrene–divinylbenzene polymers (Isolute ENV+) with reported applications for the isolation of organophosphorous pesticides and benzene- and naphthalenesulfonates from water [16–18].

In order to analyze the whole group of antifouling pesticides LC–MS techniques are preferred because they allow the simultaneous determination of all pesticides, as we have shown earlier [6,7]. Moreover, in the present work we decided to include Sea-nine 211 and three polar byproducts: two of them from diuron and one from Irgarol 1051. Such byproducts are likely to be formed under environmental conditions.

The aim of this work is to compare different materials like GCB and two different polymeric sorbents (LiChrolut EN and Isolute ENV+) for the simultaneous extraction of dichlofluanid, diuron, Irgarol 1051, chlorothalonil, TCMTB, demethyldiuron, 1-(3,4-dichlorophenyl)urea, Sea-nine 211 and one of the Irgarol byproducts from seawater using HPLC–APCI-MS for the detection of these analytes. These methods were used to determine the previous cited antifouling pesticides and their byproducts in several marinas of Catalonia such as El Masnou marina, Blanes port, the Olympic port of Barcelona and the Sant Carles de la Ràpita marina (close to the Ebre Delta) which have an important yachting activity.

The present work follows previous work by our group [6,7]. In this work we have improved the previous analytical method for antifouling pesticides by analyzing a larger range of these compounds including Sea-nine 211, three byproducts and solving the problem of dichlofluanid determination. We will also show for the first time the presence of the antifouling agent Sea-nine 211 in the Catalan coast. To our knowledge this compound had not been found in any water samples before and this is also the first report of important levels of Sea-nine 211 in seawater samples.

2. Experimental

2.1. Reagents and chemicals

Pesticide analytical standards such as dichlofluanid, diuron, TCMTB and chlorothalonil, as well as, acetonitrile, methanol, water and dichloromethane HPLC-grade solvents were purchased from Promochem (Wesel, Germany) and Merck (Darmstadt, Germany), respectively. Irgarol 1051 and one of its Irgarol byproducts were a gift from Ciba Geigy (Barcelona, Spain). Demethyldiuron and 3,4-dichlorophenylurea were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Sea-nine 211 (4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one) was obtained from Rohm & Haas (Philadelphia, PA, USA). The structures of the different antifouling pesticides and their byproducts are shown in Fig. 1.

SPE cartridges ENVI-Carb (500 mg, 100 m^2/g surface area), Isolute ENV+ (200 mg, 1200 m^2/g surface area) and LiChrolut EN (200 mg, 1200 m^2/g surface area) were obtained from Supelco (Bellefonte, PA, USA), International Sorbent Technology (Cambridge, UK) and Merck, respectively.

1 mg/ml stock solutions of each compound were prepared in methanol. They were used to prepare the corresponding solutions for the calibration graphs and to spike the seawater.

2.2. Sampling

Seawater samples were taken in 2.5-l amber

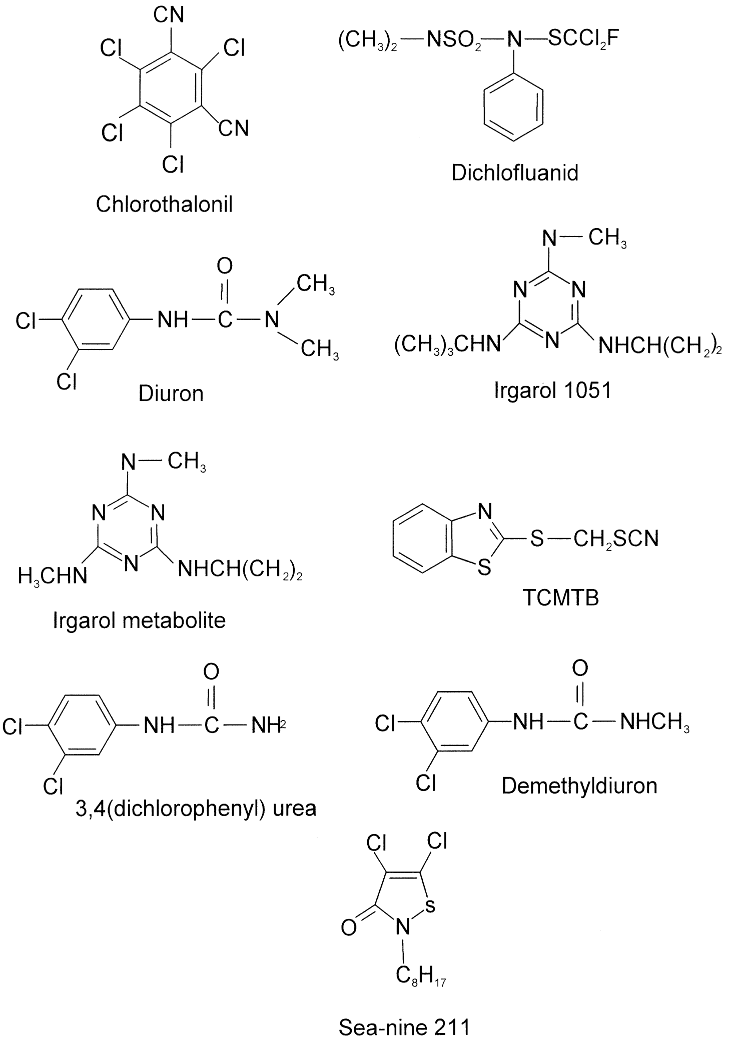


Fig. 1. Chemical structures of the different antifouling pesticides and their byproducts analyzed in this paper.

Fig. 2. Sampling points: 1=Sant Carles de la Ràpita; 2=Olympic port of Barcelona; 3=El Masnou port and 4=Blanes port.

bottles from four marinas of Catalonia (Fig. 2), at a depth of 1 m from the surface, by means of a water sampler. Blank samples for the recovery studies were taken from open sea. Sampling was carried out between October 1998 and August 1999 and all samples were stored in the dark at 4°C until analysis when they were not immediately extracted after arriving to the laboratory.

2.3. Extraction

A 1-l volume of the seawater sample was filtered through a 0.45-μm filter (Millipore, Bedford, MA, USA). Isolation of the antifouling compounds and their byproducts from the filtered water samples were performed off-line using an automated SPE system ASPEC XL (Gilson, Villiviers-le-Bel, France).

2.3.1. ENVI-Carb cartridge

The cartridge was conditioned with 6 ml of dichloromethane–methanol (8:2) mixture followed by 9 ml of methanol and 9 ml of HPLC-grade water. Then, 500 ml of the samples was passed through the GCB cartridge at a flow-rate of 10 ml/min. Afterwards, the cartridge was washed with 9 ml of HPLC-grade water and dried under vacuum for 2 min. To ensure that the cartridge was completely dry 0.4 ml of methanol was applied to the cartridge followed by 1 min of vacuum. The antifoulings were eluted into a round bottom flask with 2 ml of methanol plus 18 ml of the above mentioned mixture.

The eluate was evaporated in a rotatory evaporator (Buchi, Switzerland) up to 1 ml and then under a gentle stream of nitrogen until dryness. The residues were dissolved in 1 ml of acetonitrile for the HPLC analysis.

2.3.2. Isolute ENV+ and LiChrolut EN cartridge

These cartridges were conditioned first with 6 ml of methanol followed by 6 ml of HPLC-grade water. Afterwards, 500 ml of the sample was passed through the cartridges at a 10 ml/min flow-rate. Then, the cartridges were washed with 6 ml of the same water and dried under vacuum for 10 min. The analytes were eluted with 6 ml of methanol and this solvent was evaporated until 2 ml under a nitrogen stream with the aid of a water bath at 40°C.

For the recovery studies, 2.5 l of seawater was spiked at 1 and 10 ppb and 500 ml of the spiked sample was processed in the same way as the real samples.

2.4. HPLC–APCI-MS analysis

Liquid chromatography was carried out with a HP 1090 system (Hewlett-Packard, CA, USA) equipped with a HP mass spectrometer (HP1100) with a APCI probe. In order to separate the antifouling pesticides, a LiChrosorb RP18, 4 μm, 75×4.6 mm I.D. column (Merck) with a guard column of the same material was used. The chromatographic separation was performed with a methanol (solvent A) and water (solvent B) gradient programmed as follows: from 30% A linearly to 100% A in 10 min and held for 2.5 min. The injection volume was 20 μl. The mass spectrometer parameters are shown in Table 1.

Mass spectra for six of the compounds were obtained in selected ion monitoring (SIM) and full scan mode under the operation conditions previously reported [6]. Flow injection analysis (FIA) was performed to determine the optimum detection param-

Table 1
Mass spectrometer operational parameters used for the analysis of the antifouling compounds and their byproducts

Compound	Positive ionization	Negative ionization
Drying gas temperature	350°C	350°C
Vaporizer temperature	400°C	400°C
Drying gas flow	4.0 l/min	4.0 l/min
Nebulizer gas pressure	310.26 KPa	310.26 KPa
Capillary voltage	2000 V	2000 V
Corona current	8.0 μA	60 μA
Gain	5.0	5.0

eters for demethyldiuron, 1-(3,4-dichlorophenyl)-urea and Sea-nine 211.

Diuron, Sea-nine 211, the Irgarol 1051 byproduct and Irgarol 1051 were detected in the positive ionization (PI) mode and chlorothalonil, dichlofluanid, demethyldiuron, 1-(3,4-dichlorophenyl)urea and TCMTB in the negative ionization (NI) mode. In general, poor fragmentation was observed for the different compounds with distinct fragmentor voltages (70 and 120 V). Thus, the fragmentor was set at 110 V to carry out all the antifouling determinations (Table 2).

2.5. Quantitation

The quantitative determination was done by means of calibration curves constructed with standards under SIM conditions. The linearity range was checked from 0.025 up to 2 μg/ml. The calibration data and the limits of detection (LODs) are shown in Table 3. LODs were calculated using a signal-to-noise ratio of 3.

3. Results and discussion

3.1. HPLC

The use of a short analytical column allowed us to diminish the chromatographic time without losing efficiency in the separation as well as to analyze a large number of samples without changing the column because of the overpressure of the system. In fact, with this column we reduced the chromatographic time almost two-fold compared to previous work (from 35 min to 20 min) and used methanol in our gradient which is better than acetonitrile for the separation of these antifoulings due to its lower elution power.

3.2. Solid-phase extraction

ENVI-Carb cartridge behavior was satisfactory for extracting the five antifoulings from the seawater samples as can be seen in Table 4. Another important advantage of this type of cartridge is that it is able to trap dichlofluanid, which could not be

Table 2
Main *m/z* ions observed in APCI-MS for the different antifouling pesticides[a]

Compound	*M*	Ionization mode	*m/z*	Fragment ion
Dichlofluanid	332	Negative	199 (100%)	[M−SCCl2F]−
Diuron	232	Positive	233 (100%)	[M+H]+
TCMTB	238	Negative	166 (100%)	$[M-CH_2SCN]^-$
Chlorothalonil	264	Negative	245 (100%)	$[M+H_2O-HCl]^-$
Irgarol 1051	253	Positive	254 (100%)	[M+H]+
Demethyldiuron	218	Negative	160 (100%)	$[M-CONHCH_3]^-$
1-(3,4-Dichlorophenyl)urea	204	Negative	160 (100%)	$[M-CONH_2]^-$
Irgarol byproduct	213	Positive	214 (100%)	[M+H]+
Sea-nine 211	281	Positive	282 (100%)	[M+H]+

[a] Fragmentor voltage at 110 V.

Table 3
HPLC–APCI-MS calibration data and LODs of the analyzed antifouling agents in seawater samples[a]

Compound	Calibration equation	R^2	LOD (ng/l)
1-(3,4-Dichlorophenyl)urea	$y=194\,659x-1933$	0.9998	2.0
Chlorothalonil	$y=467\,260x-27\,268$	0.9875	1.0
Demethyldiuron	$y=567\,728x+11\,681$	0.9995	1.0
Dichlofluanid	$y=51\,248x+6907.9$	0.9912	4.0
Diuron	$y=2.106x-19\,216$	0.9994	1.0
Irgarol	$y=68\,078x-6917.6$	0.9918	4.0
Irgarol byproduct	$y=97\,395x-1776.8$	0.9996	2.0
Sea-nine 211	$y=3.106x+21\,870$	0.9977	1.0
TCMTB	$y=23\,617x-1961$	0.9983	20.0

[a] SPE was carried out passing 500 ml of seawater sample through the carbon cartridges. Calibration range from 25 to 2000 μg/l.

trapped in earlier works [6] and the two more polar degradation products of diuron [demethyldiuron, 1-(3,4-dichlorophenyl)urea and Irgarol 1051 (2-methylthio-4-*tert*.-butylamino-*s*-triazine)].

The GCB cartridges showed its great adsorbing properties as reported in the literature [19,20]. Therefore, it was necessary to use 20 ml of the eluting mixture to desorb all the analytes from the sorbent, which is not usual when other types of SPE cartridges are used in environmental analysis. Dichlofluanid, the most polar compound analyzed in this study, eluted in the first 9-ml fraction of the eluent but, for instance, chlorothalonil was desorbed with a larger volume. In former studies dichlofluanid was not trapped by C_{18} or PLRP-s sorbents. Recently a method for dichlofluanid in which the authors use LLE for its extraction from water has been published [12].

The well-known great adsorption power of the GCB material is due to its mechanism for trapping the analytes. This mechanism is based on anion-exchange and hydrophobic properties. The graphite structure and the positively charged oxonium groups are responsible for the hydrophobic interactions and the anion-exchange capacity of this sorbent, respectively. For that reason, at least three adsorption mechanisms are involved in the adsorption process of this sorbent: anion-exchange due to oxonium groups, hydrophobic interaction between the graphite surface and the aromatic structure of the solutes, and hydrogen bonds between protonated functional groups of the analytes and the carbonyl groups of the GCB or vice versa [21]. On the other hand, the presence of some other oxygen-containing groups contaminating the surface of this adsorbent such as quinones, semiquinones and hydroquinones was

Table 4
Recoveries from 500 ml of seawater spiked with 10 ppb of the antifoulings agents using ENVI-Carb, LiChrolut EN and Isolute ENV+ cartridges[a]

Compound	Mean recovery (%) ($n=5$)		
	LiChrolut EN	Isolute ENV+	ENVI-Carb
Dichofluanid	20.4	52.0	95.0
Diuron	91.8	105.3	89.4
TCMTB	8.1	16.2	87.7
Chlorothalonil	9.8	12.1	76.3
Irgarol 1051	77.7	96.7	81.7
Demethyldiuron	89.2	96.4	92.0
1-(3,4-Dichlorophenyl)urea	85.6	94.3	88.1
Irgarol byproduct	75.4	92.1	80.2
Sea-nine 211	95.8	98.0	96.4

[a] Experimental procedure as in Section 2.3.

confirmed through polarographic measurements [22]. For example, the very reactive quinone groups caused partial irreversible adsorption of particular compounds such as metribuzin and metamitron [22]; it was necessary to reduce the quinone group to the less reactive hydroquinone one with an ascorbic acid aqueous solution. Another phenomenon originated by the quinone group is the chemisorption probably via addition reactions.

The LiChrolut EN and Isolute ENV+ cartridges exhibited good performance for extracting diuron and Irgarol 1051 and their byproducts as well as Sea-nine 211 from the seawater samples (Table 4). These polymeric adsorbents contain a lot of binding sites and exhibit different adsorption mechanisms like ion-exchange, dispersion, hydrophobic interactions and hydrogen bonding. These properties and their high specific surface areas are responsible for the adsorbing capacity of these materials. Moreover, using these polymeric cartridges it is possible to save time and to avoid the use of a highly toxic chlorinated solvent like dichloromethane. Dichlofluanid was not well retained with this kind of sorbent material under our experimental conditions similarly as observed previously with on-line SPE [6]. On the other hand, there were loses of chlorothalonil when the eluate was evaporated in a heated water bath and under a nitrogen stream. The use of a heated water bath at 40°C was very useful to evaporate the methanol in a few minutes, otherwise almost 2 h were needed to concentrate the eluate to 2 ml under nitrogen.

3.3. Antifouling pesticide determination in different marinas of the Catalan coasts

Fig. 3 shows the levels of the antifoulings found in the four marinas of Catalonia and in Fig. 4 a chromatogram of a real sample is also shown. As can be observed in Fig. 3 there is a considerable diminution in Irgarol concentration with respect to the former year (see Ref. [6]). This compound has been found only during the first months of the year and its main byproduct appeared in June and July in three of the four sampled marinas. It is likely that Irgarol was not used in this year as the major antifouling agent of the yacht paints. In the case of diuron, similar concentrations have been detected with respect to 1998. The principal byproduct of diuron (demethyldiuron) was detected for the first time in this work, although at very low concentrations.

On the other hand new compounds have appeared in the Catalan coast such as: Sea-nine 211, dichlofluanid and the above-mentioned demethyldiuron. Dichlofluanid has been detected in the last 4 months of the sampling period at a concentration of 0.3 μg/l in Blanes Port and at 0.6 μg/l in the Masnou Marina. The major antifouling concentrations found belong to Sea-nine 211, with values of about 2.7 μg/l in Blanes and Masnou Marinas and above 3.3 μg/l in the Olympic Port of Barcelona and in Sant Carles de la Ràpita. It should be pointed out that high levels of Sea-nine 211 were detected in the four sampling points only in 1 month. It could be due to the fact that this compound degrades rapidly. In fact it has been recognized as an ecological advance for marine antifoulings by the US Environmental Protection Agency (EPA) as compared to other half-life time antifouling agents.

In previous works our group has detected the presence of diuron, Irgarol 1051 and the byproduct of Irgarol in the Catalan coast and no other antifouling pesticide was found [6,7]. In the present work we have expanded the list of antifouling pesticides present in marina waters that should be monitored and we have pointed out new antifouling compounds, like Sea-nine 211, were introduced in the last year.

4. Conclusions

The use of the GCB cartridge (ENVI-Carb) followed by LC–APCI-MS allowed us to unequivocally determine five antifouling pesticides and two of their degradation products as well as Sea-nine 211 and dichlofluanid for which to our knowledge there was no SPE method reported until now in the literature. Due to the great adsorbing properties of the ENVI-Carb cartridge this method could be used for the monitoring of other types of polar compounds in environmental waters.

Polymeric cartridges can only be recommended for the monitoring of Irgarol 1051 and diuron and their respective byproducts and Sea-nine 211.

The LODs of these methods are appropriate to

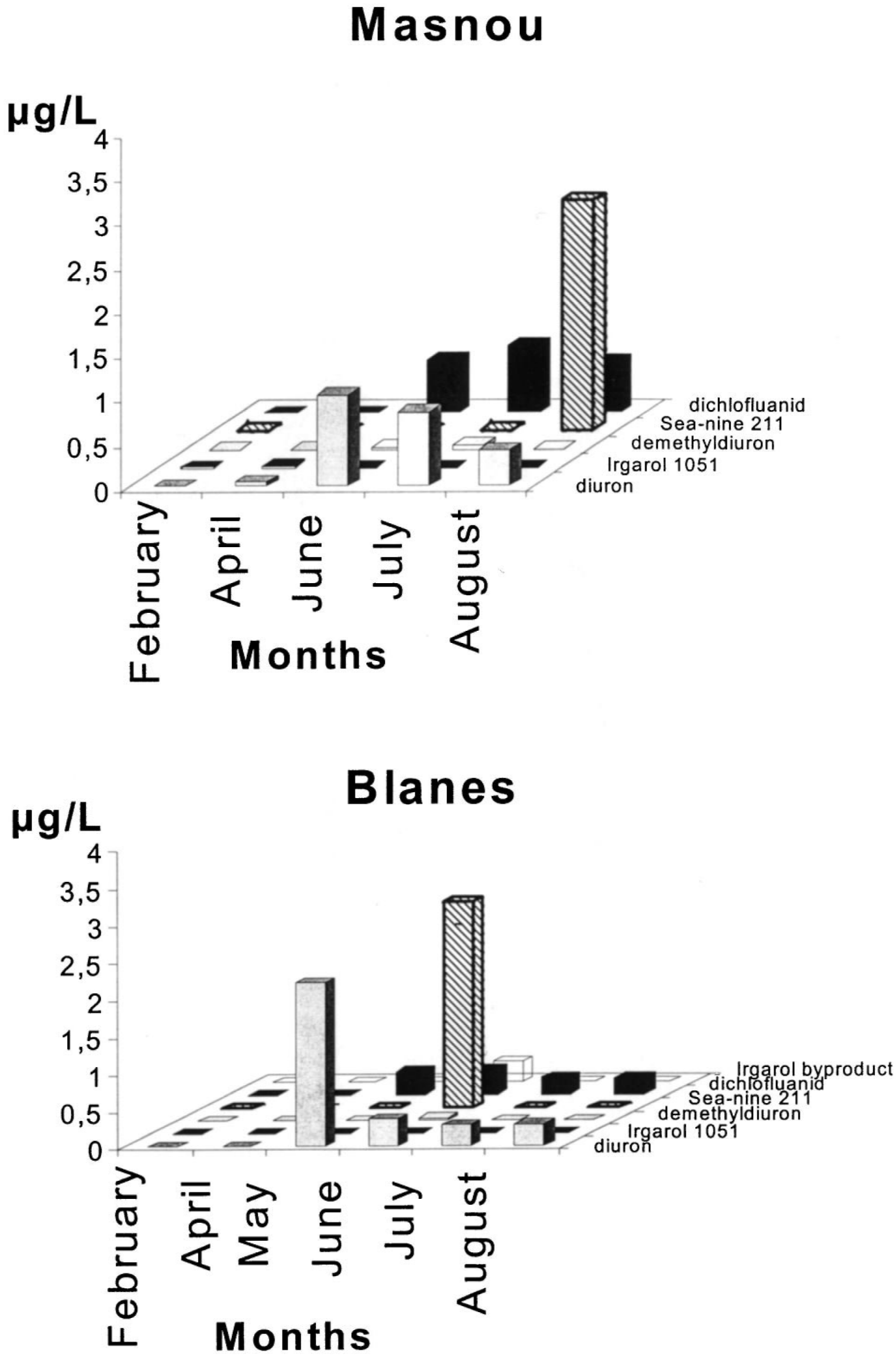
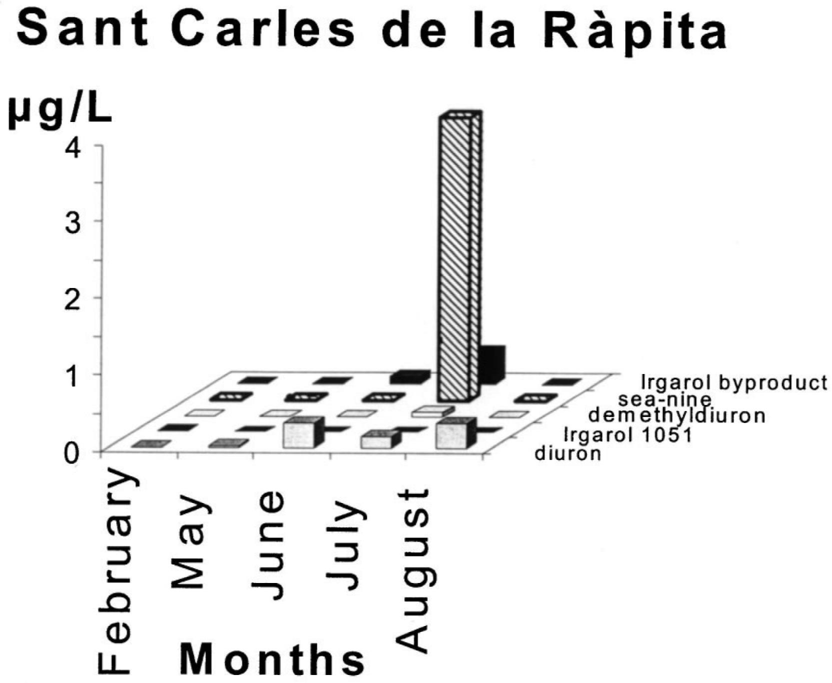


Fig. 3. Levels of the antifoulings in the four Catalan marinas sampled between January and August 1999.



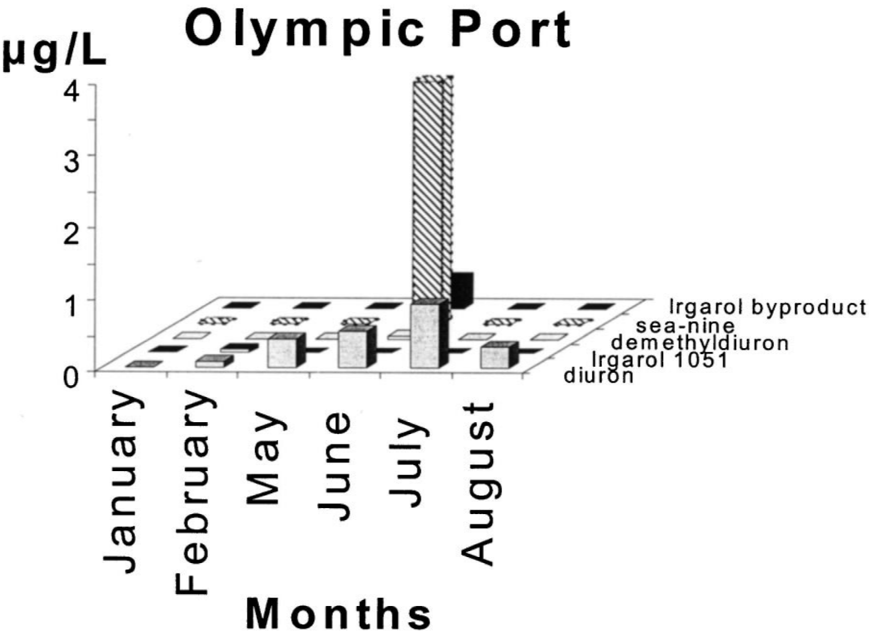
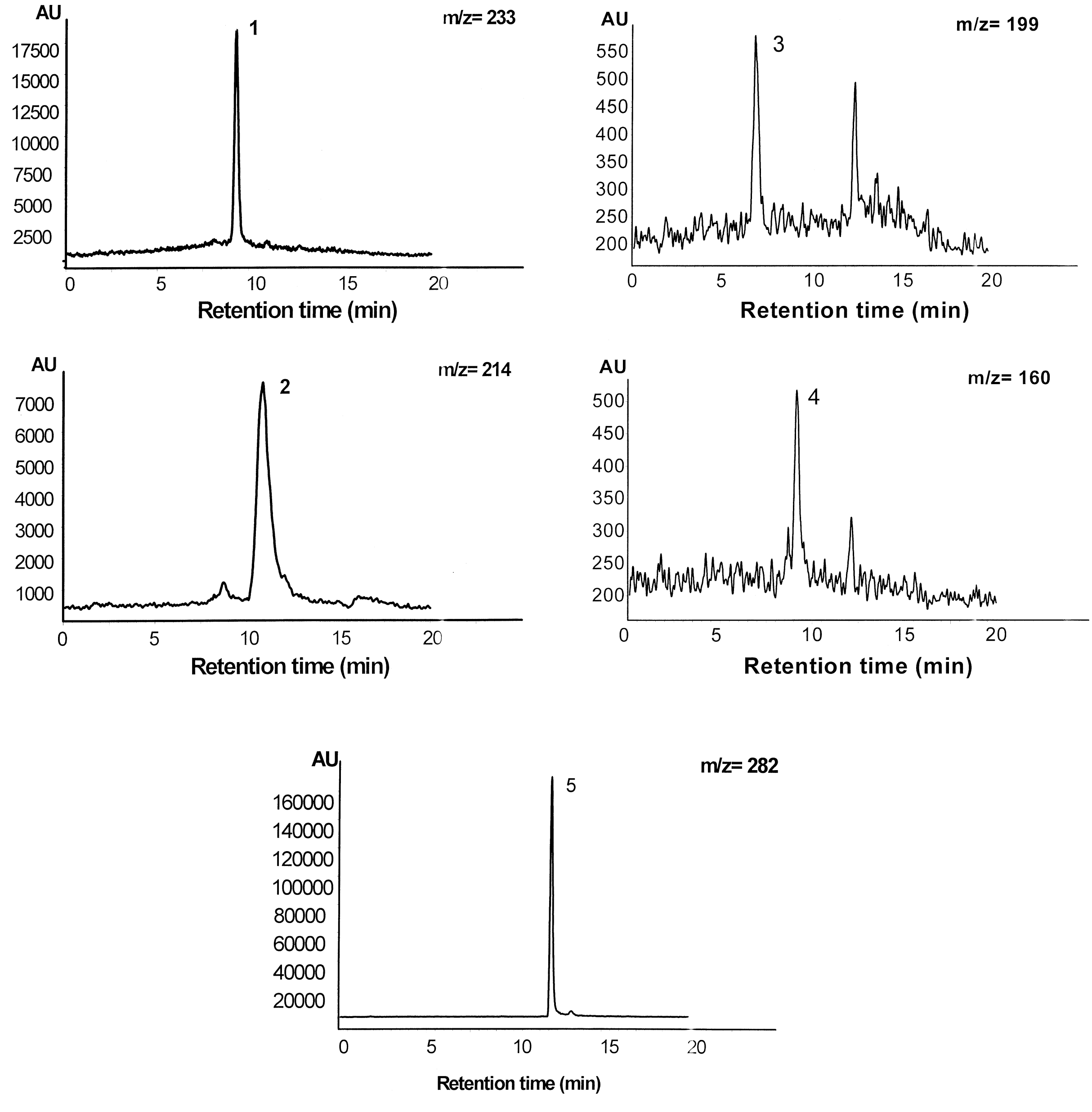


Fig. 3. (*continued*).



AU: Arbitrary Intensity Units

Fig. 4. HPLC–APCI-MS (SIM) chromatograms obtained after SPE with ENVI-Carb cartridge of a water sample collected from Blanes port in August 1999. Peak numbers: (1) diuron; (2) Irgarol byproduct; (3) dichlofluanid; (4) demethyldiuron and (5) Sea-nine 211. Concentration levels are shown in Fig. 3.

determine these compounds in environmental waters since part-per-trillion levels are achieved. If needed lower concentrations can be determined, but then much higher sample volume should be extracted through these cartridges and this should not be a problem with this carbon black cartridge. The method reported in this paper is being routinely applied in our laboratory in the monitoring of priority antifouling pesticides and their byproducts in marine samples.

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