

# Multi-residue pesticide analysis in environmental water samples using solid-phase extraction discs and gas chromatography with flame thermionic and mass-selective detection

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## Abstract

A multi-residue analysis for 25 pesticides was developed as a rapid screening method for organic contaminants in river, lake and sea water samples. Gas chromatography with flame thermionic detection (GC-FTD) and mass selective detection (GC-MSD) using two different capillary columns, DB-1 and HP-5, was employed for the identification of 25 selected pesticides belonging to triazines, organophosphorus compounds and substituted ureas, carbamates, anilides, anilines and amides. The extraction of various natural waters spiked with pesticide mixtures was effected with  $C_{18}$  Empore solid-phase extraction discs and filter-aid glass beads. The triazine compounds (atrazine, simazine, propazine, prometryne and cyanazine) were recovered from distilled and underground water samples at relative high levels (73.5–105%) compared with the river waters (39.9–80.5%), lake water (54.6–81.8%) and marine water (38.6–79.9%). The organophosphorus compounds studied (monocrotophos, terbufos, diazinon, methyl parathion, ethyl parathion, malathion and ethion) were also recovered from distilled and underground water samples at relatively high levels (62.4–118%) compared with river waters (27.3–98.9%), lake water (41.0–85.2%) and marine water (33.4–81.3%). The substituted ureas (monuron, diuron and linuron), substituted anilines and anilides (trifluralin, propanil, propachlor and alachor), carbamates (EPTC and carbofuran) and other compounds (molinate, picloram, captan and MCPA isooctyl ester) were recovered at the same level as triazines. Confirmation of pesticide identity was performed by using GC-MS in the selected-ion monitoring mode.

## 1. Introduction

Pesticides of different chemical nature are widely used for agricultural and non-agricultural purposes throughout the World. Some of the modern pesticides have replaced the organochlorine pesticides, which were banned after evidence of their toxicity, persistence and bioaccumulation in the environment [1]. Because of their widespread use, pesticides are currently

detected by determination of their residues in various environmental matrices, such as soil, water and air [2,3].

The determination of pesticide residues in water samples is necessary for solving various environmental and biological problems [3]. The chromatographic techniques used for pesticide analysis require efficient isolation and concentration procedures such as liquid-liquid supercritical fluid and solid-phase extraction [4–6]. Although single-residue methods are often used in the analyses required by legislation or in

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results confirmations, in the case of environmental water sample analysis where nothing is known about the nature of possible contaminants, universal and reliable analytical methods are required. These methods enable one to analyse in a single run and within the shortest possible time as many pesticides as possible from the bulk of those which may occur in a sample of unknown origin. It is then an advantage to use methods that permit the determination of pesticide residues of different chemical classes in the same extract.

The chromatographic stage of a method for pesticides determination at low levels in drinking and surface waters requires previous efficient solvent extraction and concentration procedures [5,6], which can make pesticide determination a time-consuming and laborious process involving consumption of organic solvents in large volumes. To overcome these problems, solid-phase extraction has been extensively applied to the extraction of pesticides present in water samples. The adsorbed compounds are then eluted from the solid phase with an organic solvent [7].

C<sub>8</sub>- and C<sub>18</sub>-bonded-phase cartridges [8,9], XAD resins [10–12], activated charcoal [13,14], graphitized carbon blank and Tenax GC [15,16] have all been employed for the analysis of a variety of pesticides. In the last 3 years, solid-phase extraction discs have been employed as an alternative method for the trace enrichment of organic compounds, including pesticides, in water. The solid-phase extraction discs are available in a diameter of 47 and 90 mm, similar to LC solvent filters. Such discs have been tested for different groups of compounds, including pesticides, organotin and phthalates [17]. The system has also been applied on-line with LC for the concentration of triazine herbicides and chlorophenols from river and sea-water [18].

The purpose of this work was to carry out a systematic study to select certain of the most commonly used and important pesticides in the European Community [19] and especially in the Mediterranean region [20], belonging to triazines, organophosphorus compounds and substituted ureas, carbamates, anilides anilines and amides, and study their retention times in two

different columns, DB-1 and HP-5, to characterize these compounds by the use of GC-MS, to develop an extraction method for various environmental waters by the use of solid-phase extraction with Empore C<sub>18</sub> discs and to apply the analytical methodology developed to analyse spiked and natural water samples of different origin (underground water of Ioannina, Louros river, Pamvotis lake and Ionian sea in N.W. Greece and Nestos river and Thermaikos gulf in N. Greece).

## 2. Experimental

### 2.1. Chemicals

HPLC-grade water, methanol, dichloromethane from Pestiscan (Labscan, Dublin, Ireland) were passed through a 0.45- $\mu$ m filter before use. Alachlor, atrazine, captan, carbofuran, cyanazine, diazinon, diuron, EPTC, ethion, linuron, malathion, MCPA is. ester, molinate, monocrotophos, monuron, parathion ethyl, parathion methyl, picloram, prometryne, propachlor, propanil, propazine, simazine, terbufos and trifluralin were purchased from Promochem (Wesel, Germany). Empore extraction discs were manufactured by 3M and distributed by Varian (Harbor City, CA, USA). The discs used were 47 mm in diameter and 0.5 mm thick. Each disc contained about 500 mg of C<sub>18</sub>-bonded silica (92  $\pm$  2%) and 10  $\pm$  2% PTFE. The particle characteristics were particle size 8  $\mu$ m, pore size 60 Å and shape irregular. Empore (St. Paul, MN, USA) filter-aid 400 glass beads were used as a filtration aid when extracting samples with high particulate content using extraction discs.

### 2.2. Waters used

Water samples were collected, in summer 1993, from Louros and Nestos rivers, Pamvotis lake (Ioannina) Amvrakikos gulf and Ionian sea; underground water from the Ioannina area and distilled water were also used. Their characteristics are given in Table 1.

Table 1  
Characteristics of selected environmental waters

Origin of water sample	pH	Conductivity ( $\mu\text{s}/\text{cm}$ )	Total suspended matter ( $\text{mg}/\text{l}$ ) <sup>a</sup>	TOC <sup>b</sup> ( $\text{mg}/\text{l}$ )	Salinity (%)
Distilled water	5.95	5	–	b.d.l. <sup>c</sup>	– <sup>d</sup>
Underground water	7.93	450	15	0.03	– <sup>d</sup>
Pamvotis lake	8.25	350	385	9.65	0.55
Louros river	8.72	350	115	4.16	0.36
Nestos river	7.76	300	56	3.20	0.21
Thermaikos gulf	8.01	15,240	310	5.25	16.54
Ionian sea	8.02	14,400	240	1.32	34.40

<sup>a</sup> TSM (total suspended matter) was measured by filtration through a 0.45- $\mu\text{m}$  PTFE filter (Millipore).

<sup>b</sup> TOC = total organic carbon.

<sup>c</sup> b.d.l. = below detection limit (0.01  $\text{mg}/\text{l}$ ).

<sup>d</sup> Not determined.

### 2.3. Sample extraction and concentration

Empore extraction discs were conditioned with 10 ml of acetone for 3 h. Environmental water samples ( $n = 3$ ) of 1 l each were spiked with a mixture of the 25 selected pesticides at final concentrations of 0.1, 0.25, 1.0, 2.5, 5, 10, 20 and 50  $\mu\text{g}/\text{l}$ . Methanol modifier (5 ml) was added to 1-l water samples to allow a better extraction [21,22]. The sample pH was adjusted to <3 with 1:1 (v/v) sulfuric acid.

Twelve grams (1 cm) of glass beads were poured on the disc already placed in the conventional Millipore apparatus, and both were washed with 10 ml of dichloromethane with the vacuum on and with 10 ml of methanol for 3 min with the vacuum off. The disc was not allowed to become dry, as recommended [23,24]. The sample was mixed well and allowed to percolate through the discs at a flow-rate of 50 ml/min under vacuum. After sample extraction, the pesticides trapped in the disc were collected by using 2  $\times$  5 ml of solvent mixture [dichloromethane–ethyl acetate (1:1, v/v)] as eluting solvent. The fractions were evaporated to 4 ml on a rotary evaporator (35°C). After careful evaporation of the solvent to 0.5 ml in a gentle stream of nitrogen, the residue was dissolved in 2 ml of *n*-hexane and the solution was evaporated to a final volume of 1 ml for GC injection.

### 2.4. Chromatographic conditions

#### GC–FTD

Single pesticide standards and 1.5  $\mu\text{l}$  of extracts from the Empore disc preconcentration step were injected in the splitless mode into a Shimadzu 14A capillary gas chromatograph equipped with an instrument for flame thermionic detection (FTD) at 250°C. The DB-1 column (30 m  $\times$  0.32 mm I.D.) used contained 5% methylsilicone (J&W Scientific, Folsom, CA, USA). The column was programmed from 55°C (2 min) to 210°C (20 min) at 5°C/min and to 270°C (4 min) at 20°C/min. The injection temperature was 220°C.

Helium was used as the carrier and nitrogen as make-up gas. The detector gases were hydrogen and air, and their flow-rates were regulated according to results obtained through simplex optimization of the analytical variables, in this instance air and hydrogen flow-rates in the detector. The FTD ion source was an alkali metal salt ( $\text{Rb}_2\text{SO}_4$ ) bonded to a 0.2-mm spiral of platinum wire.

#### GC–MS

A Hewlett-Packard (Palo Alto, CA, USA) Model 5890B instrument with an HP autosampler model and 5971A mass-selective detector interfaced to a Model 59970C instrument for

data acquisition and processing were used. A HP-5 fused-silica capillary column coated with 5% phenyl–95% methyl-polysiloxane (25 m × 0.25 mm I.D.) (Hewlett-Packard) was used. Helium was used as the carrier gas at 83 kPa. The injection temperature was 240°C. The column was programmed from 55°C (2 min) to 210°C at 5°C/min and to 270°C at 20°C/min (4 min). The ion source were maintained at 200°C and electron impact (EI) mass spectra were obtained at 70 eV. The spitless mode was used for injection of 1.5- $\mu$ l volumes with the valve opened for 30 s.

Two ions for each pesticide were chosen for screening analysis in selected-ion monitoring (SIM). The ion traces were divided into five groups that were recorded sequentially during the injection, on the basis of the retention times of the single substances; the first group was from 17.1 to 27.2 min, the second from 27.2 to 29.0 min, the third from 29.0 to 31.3 min, the fourth from 31.3 to 34.0 min and the fifth from 34.0 to 50.2 min.

### 3. Results and discussion

#### 3.1. General considerations

The main advantage of using Empore extraction discs over liquid–solid extraction cartridges is the increased productivity resulting from the high extraction flow-rate, which facilitates sampling in the field water. In this study, only a 20-min extraction time was needed for the trace enrichment of 1-l water samples. These results are in good agreement with those of other studies [17,25,26]. Generally, prefiltration of (sea and lake) surface water samples through 0.45- $\mu$ m PTFE filters has been recommended when Empore discs [17,25,27] are used and it would not affect the determination of the polar pesticides used in this study. The polar pesticides (Table 2) exhibit a  $\log K_{oc}$  (partition coefficient between organic carbon and water) of 2 and consequently are widely distributed in the dissolved (>99%) and not in the suspended phase of water [17,28] (Table 2). In contrast, for non

polar pesticides,  $\log K_{oc} > 3$ , prefiltration would yield much lower recoveries. Therefore, for our multi-residue analytical method in this study, which included compounds with a wide level of  $\log K_{oc}$ , we decided to use Empore filter aid 400. Filter aid 400 is a high-density glass bead product intended for use as a filtration aid when Empore discs are used for the extraction of samples with high particulate content. The non-polar compounds adsorbed strongly on particulate matter are eluted simultaneously by the extraction solvent along with the compounds trapped in the extraction discs.

The eluent volume effect (1–15 ml) was investigated. The maximum recovery was obtained with 8 ml for all the pesticides; 2 × 5 ml was adopted because it was found that the relative standard deviation was slightly lower.

#### 3.2. Gas chromatographic techniques

Table 3 gives the retention times and the detection limits obtained for the 25 selected pesticides by GC–FTD using a DB-1 column and by GC–MS using an HP-5 column. Figs. 1 and 2 show the simultaneous determination of typical chromatograms, obtained after extraction of 1 l of Nestos river and Amvrakikos gulf water samples spiked with pesticides at the 0.25–5  $\mu$ g/l level. Owing to the selectivity of the detector, no interferences were noticed in the GC–FTD retention time data of these compounds. When comparing the elution order obtained with the two columns used, the elution order is the same for both the DB-1 and HP-5 columns with different stationary phases for seventeen of the selected compounds. Monuron, monocrotophos and carbofuran do not elute from the HP-5, similarly to their retention order on DB-1, and four compounds, picloram, diuron, prometryne and cyanazine, cannot be determined by GC–MS under conditions described for the HP-5 column. Finally, the resolution by column DB-1 permits, in two cases, overlappings between carbofuran and simazine and between atrazine and diuron to be observed. Similar problems appearing with the HP-5 column in GC–MS could be attributed to overlapping between

Table 2  
Molecular mass solubility in water and log  $K_{oc}$  (ml/g) of selected pesticides

No.	Compound	Activity <sup>a</sup>	Molecular mass	Solubility in water (mg/l)	Log $K_{oc}$ [19,29]
1	EPTC	H	189.4	370–375	2.44
2	Monuron	H	198.7	230	2.25
3	Molinate	H	187.3	800–912	2.62
4	Propachlor	H	211.7	700	2.62
5	Monocrotophos	I	223.2	1 (kg/l)	–
6	Trifluralin	H	335.3	0.05	3.86
7	Picloram	H	241.5	430	1.68
8	Carbofuran	I	221.3	700	1.44
9	Simazine	H	201.7	5	2.10
10	Atrazine	H	215.7	35	2.20
11	Diuron	H	233.1	42	2.50
12	Propazine	H	230.0	4.8	2.20
13	Terbufos	I	288.4	4.5	3.60
14	Diazinon	I	304.4	40	1.92
15	Propanil	H	218.1	500	2.15
16	Methyl parathion	I	263.2	50	3.70
17	Prometryne	H	241.4	40	2.78
18	Alachlor	H	269.8	148	2.07
19	Cyanazine	H	240.7	171	2.20
20	Linuron	H	249.1	75	2.93
21	Malathion	I	330.4	145	3.25
22	Ethyl parathion	I	291.3	24	4.04
23	Captan	F	300.6	3.3	2.50
24	MCPA is. ester	H	312.8	550	1.69
25	Ethion	I	384.5	1	3.64

<sup>a</sup> I = insecticide; H = herbicide; F = fungicide.

prometryne and alachlor and between cyanazine and linuron. In this last case the problem seems also to come from the lower detector sensitivity for propachlor, picloram, diuron, prometryne and cyanazine.

In Table 3 the selected typical fragment ions of the selected pesticides studied are listed. It is possible that two compounds have an ion with the same  $m/z$  value but with different structures and belonging to different retention time groups.

### 3.3. Recovery studies

The mean recoveries of three analyses, obtained for the 25 selected pesticides spiked into seven different types of water (see Table 1), are given in Table 4. It should be noted that the recoveries obtained for distilled and underground water samples were higher than 80% for

twenty and fifteen compounds, respectively, indicating that the use of the disc does not pose any problem to the analysis of such a type of water.

The recoveries of all the pesticides were higher in distilled and underground water than those from surface waters (rivers, lake and marine waters). The main differences among the studied surface waters are the high salinity and conductivity of Thermaikos gulf and Ionian sea water and the higher concentration of the total organic carbon in Pamvotis lake water samples. Chromatograms for two types of spiked samples of Nestos river and Amvrakikos gulf water are shown in Figs. 1 and 2. It is clearly seen that the lake and marine waters pose more problems to the analysis, with high interferences. All the studied pesticides show lower levels of recovery in marine waters (Themaikos gulf and Ionian sea

Table 3  
Analysed pesticides, retention times and selected ions

No.	Compound	DB-1 and FTD			HP-5 and GC-MS		
		$t_R$ (min)	RRF <sup>a</sup> (diazinon)	LOD <sup>b</sup> ( $\mu\text{g/l}$ )	$t_R$ (min)	Selected ions ( $m/z$ )	LOD ( $\mu\text{g/l}$ )
1	EPTC	23.04	5.41	0.005	18.30	190, 192	0.0008
2	Monuron	27.64	338.1	0.08	23.13	198, 200	0.010
3	Molinate	27.77	5.79	0.003	22.94	187, 189	0.001
4	Propachlor	29.65	10.94	0.005	24.88	211, 213	0.010
5	Monocrotophos	30.56	1.77	0.001	26.82	223, 225	0.010
6	Trifluralin	31.61	8.41	0.001	26.56	335, 337	0.005
7	Picloram	32.13	166.6	0.05			
8	Carbofuran	32.32	0.92	0.001	28.02	221, 223	0.010
9	Simazine	32.44	4.29	0.005	27.35	201, 203	0.010
10	Atrazine	32.75	3.27	0.002	28.22	215, 217	0.005
11	Diuron	32.77	36.79	0.05			
12	Propazine	33.05	3.23	0.002	28.44	229, 231	0.004
13	Terbufos	33.93	1.59	0.001	28.66	231, 233	0.010
14	Diazinon	34.40	1.00	0.001	29.28	304, 306	0.015
15	Propanil	35.96	20.28	0.010	30.97	217, 219	0.010
16	Methyl parathion	36.80	1.04	0.0005	31.16	263, 265	0.015
17	Prometryne	37.76	62.49	0.005			
18	Alachlor	37.84	3.87	0.002	31.52	269, 271	0.010
19	Cyanazine	39.19	5.24	0.005			
20	Linuron	39.30	1.98	0.002	32.47	248, 250	0.005
21	Malathion	39.54	1.16	0.001	32.79	127, 173	0.010
22	Ethyl parathion	40.74	0.68	0.0005	33.20	291, 293	0.005
23	Captan	43.57	135.2	0.05	34.97	264, 266	0.020
24	MCPA is. ester				36.43	312, 314	0.0005
25	Ethion	60.06	0.58	0.0008	41.61	384, 386	0.008

FTD with DB-1 capillary column (30 m  $\times$  0.32 mm I.D.) and temperature programme 55°C (2 min), increased at 5°C/min to 210°C (30 min). GC-MS with HP-5 column (25 m  $\times$  0.25 mm I.D.) and temperature programme 55°C (2 min), 55–210°C at 5°C/min, 210°C (20 min), 210–270°C at 20°C/min, 270°C (4 min).

<sup>a</sup> RRF = relative response factor.

<sup>b</sup> LOD = limit of detection.

waters) with higher salinity values and, consequently, the interferences in the GC-FTD and GC-MS traces are higher when analysing samples of high salinity [18]. This negative influence of salinity on the pesticide levels obtained is stronger for monocrotophos, picloram, terbufos, prometryne and MCPA, where the recoveries are below 50% in marine water samples. The influence of salinity is greater for more polar compounds. This behaviour in the case of atrazine and simazine agrees with that reported in Chakespeare Bay and Ebro river estuaries [18,30]. In contrast, a positive salting-out effect

on adsorption on  $C_{18}$  silica has been observed for some herbicides and organophosphorus insecticides [31,32]. It is possible that the influence of negative salinity is stronger than the increase in extraction efficiency due to the ionic strength of aqueous samples.

The more hydrophobic compounds of the 25 pesticides studied ( $\log K_{oc} > 3$ : trifluralin, methyl and ethyl parathion and malathion) seem to show no significant decrease in their recoveries from lake and gulf water due to the higher organic carbon content. In the same way, experiments with hydrophobic organochlorine pesti-

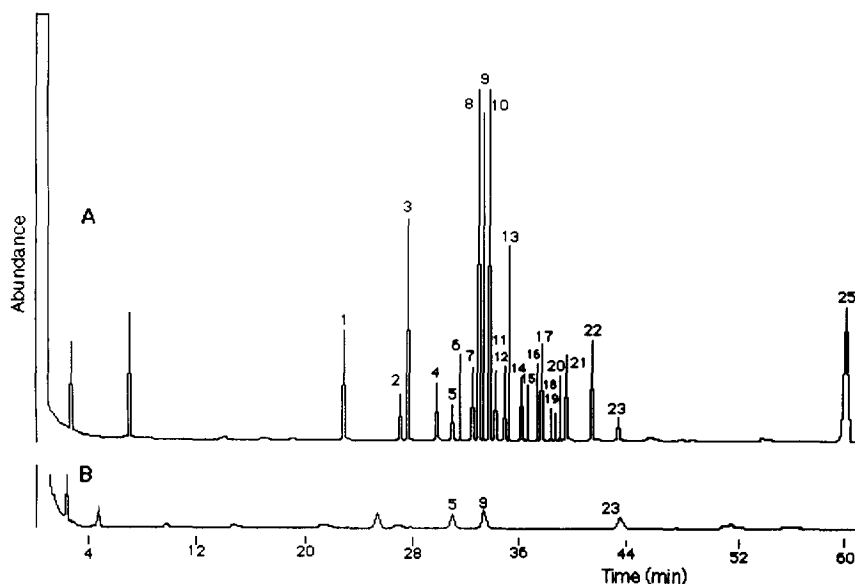


Fig. 1. GC-FTD for (A) ca. 0.25–5  $\mu\text{g/l}$  of 24 selected pesticides in spiked water and (B) water sample from Nestos river under the same conditions. A DB-1 column 30 m long containing 5% methylsilicone was programmed as follows: 55°C (2 min) to 215°C (20 min) at 5°C/min and from 210 to 270°C at 20°C/min, 270°C (4 min). For peak numbers, see Table 2.

cides ( $\log K_{oc} \approx 6$ ) have shown a strong tendency to adsorb on the particulate matter on the filter [18,33] and pre-filtration would give much lower recoveries.

The triazine compounds (atrazine, simazine, propazine, prometryne and cyanazine) were re-

covered from distilled and underground water samples at relative high levels (73.5–105%) compared with river waters (39.9–80.5%), lake water (54.6–81.8%) and marine water (38.6–79.9%). The decreased recoveries of prometryne from marine and lake waters is the main problem

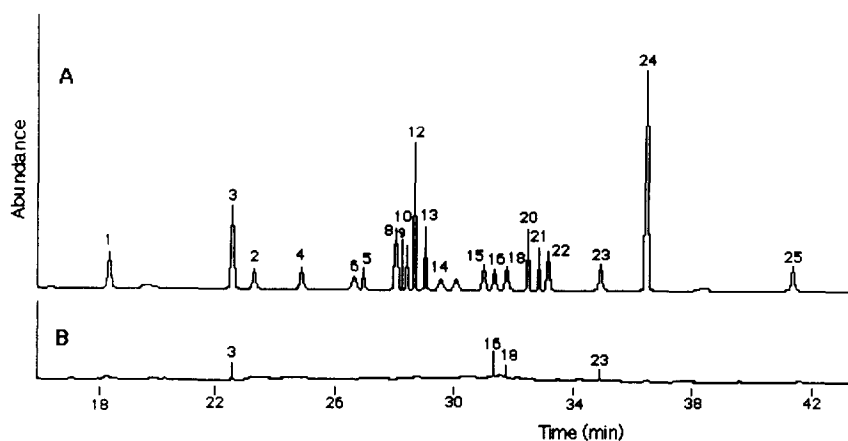


Fig. 2. GC-MS for (A) ca. 0.25–5  $\mu\text{g/l}$  of 19 selected pesticides in spiked water and (B) water sample from Thermaikos gulf under the same experimental conditions. A HP-5 column 25 m long containing 5% phenyl–95% methyl-polysiloxane was programmed as follows: 55°C (2 min) to 210°C at 5°C/min and 270°C at 20°C/min (4 min). For peak numbers, see Table 2.

Table 4  
Mean recoveries of 25 selected pesticides in environmental water samples by using C<sub>18</sub> Empore extraction discs

No.	Compound	Mean recovery (%)						
		Distilled water	Underground water	Pamvotis lake	Louros river	Nestos river	Thermaikos gulf	Ionian sea
1	EPTC	98.3	89.8	81.4	64.7	98.4	99.2	62.4
2	Monuron	87.6	80.3	76.2	92.7	64.3	50.7	48.3
3	Molinate	98.8	93.5	65.8	56.1	76.6	78.8	51.5
4	Propachlor	96.2	73.8	60.5	61.1	84.1	50.6	63.9
5	Monocrotophos	75.3	62.4	41.0	54.9	57.3	43.4	37.7
6	Trifluralin	106	96.7	48.9	82.8	76.5	55.7	61.8
7	Picloram	52.4	49.7	40.6	27.3	18.8	19.5	16.9
8	Carbofuran	85.4	80.1	87.4	60.7	49.8	54.3	54.8
9	Simazine	89.2	73.5	81.8	60.2	72.8	58.4	64.0
10	Atrazine	88.5	80.6	54.6	74.8	65.1	68.	58.4
11	Diuron	76.2	66.4	72.5	60.3	56.8	68.6	59.3
12	Propazine	105	87.7	62.2	78.1	78.6	79.8	72.2
13	Terbufos	81.6	87.8	53.4	27.3	48.7	33.4	40.2
14	Diazinon	112	104	84.1	77.8	76.1	81.4	70.1
15	Propanil	92.9	94.5	83.8	60.7	71.5	69.3	54.1
16	Methyl parathion	118	109	85.2	61.3	79.7	65.3	61.5
17	Prometryne	87.0	80.5	61.4	39.9	52.4	38.6	47.5
18	Alachlor	68.7	63.7	53.4	60.5	79.2	86.2	50.0
19	Cyanazine	82.3	78.6	61.3	70.4	80.5	61.8	59.4
20	Linuron	92.7	91.6	65.8	71.4	86.8	52.4	72.9
21	Malathion	89.6	95.4	64.3	75.3	70.4	55.2	67.5
22	Ethyl parathion	106	101	76.8	81.7	98.9	56.3	59.2
23	Captan	82.5	80.3	67.5	75.4	79.6	71.6	89.5
24	MCPA is. ester	56.3	62.6	57.3	58.2	65.2	43.2	34.8
25	Ethion	66	76.8	63.2	72.3	78.4	56.8	50.3

Spiking levels 0.1, 0.25, 1.0, 5, 10, 20 and 50 µg/l (*n* = 3).

with the studied triazines. The organophosphorus compounds (monocrotophos, terbufos, diazinon, methyl parathion, ethyl parathion, malathion and ethion) were also recovered from distilled and underground water samples at relative high levels (62.4–118%) compared with river waters (27.3–98.9%), lake water (41.0–85.2%) and marine water (33.4–81.3%). The substituted ureas (monuron, diuron and linuron), substituted anilines and anilides (trifluralin, propanil, propachlor and alachlor), carbamates (EPTC and carbofuran) and the other compounds studied (molinate, picloram, captan and MCPA is. ester) were recovered at the same level as triazines.

### 3.4. Environmental levels

The water samples analysed were collected in Northern Greece during 1993–94 during periods of pesticide spraying. Screening analysis by GC-FTD showed the presence of monocrotophos, molinate, atrazine, simazine, methyl parathion, ethyl parathion alaclor and captan at low levels. Confirmatory analyses were made with GC-EI-MS. The first sampling was done in August 1993 and the second in June 1994. The concentrations of pesticides are given in Table 5. The levels of monocrotophos, captan and methyl parthion deleted are below the the limits set for drinking water (0.1 µg/l). The concentrations of moli-



Table 5  
Concentrations of pesticides found in natural waters of Northern Greece (GC-FTD)

Origin of water sample	Compound	Level ( $\mu\text{g/l}$ )	
		August 1993	June 1994
Underground water (Ioannina)	Atrazine	0.009	b.d.l. <sup>a</sup>
Pamvotis lake (Ioannina)	Monocrotophos	0.024	0.015
	Atarazine	0.140	0.085
Louros river	Molinate	0.055	0.050
	Monocrotophos	0.016	b.d.l.
	Simazine	0.135	0.070
Nestos river	Monocrotophos	0.082	– <sup>b</sup>
	Simazine	0.120	– <sup>b</sup>
	Captan	0.080	– <sup>b</sup>
Thermaikos gulf	Molinate	0.150	0.126
	Methyl parathion	0.021	0.034
	Atachlor	0.043	0.065
	Captan	b.d.l.	0.060

<sup>a</sup> b.d.l. = below detection limit.

<sup>b</sup> No sampling.

nate, atrazine and simazine were at the same levels as reported for surface waters in the Mediterranean region [20].

#### 4. Conclusions

In conclusion, the use of Empore extraction discs of  $C_{18}$ -bonded silica provides a rapid, efficient and reproducible method for the simultaneous determination of various pesticides in waters. The identification of 25 selected and first priority pesticides for the Mediterranean region was achieved by their retention times obtained with two GC columns, DB-1 and HP-5, using GC-FTD and from complementary structural information achieved by GC-MS. The use of  $C_{18}$  Empore discs was found to be an effective means for the trace determination of these pesticides in natural waters at detection limit at least ten times below the drinking water limit ( $0.1 \mu\text{g/l}$ ) for individual pesticides. GC-FTD is the best choice for the confirmation of organophosphorus pesticides from natural water samples, being a very selective means of detecting

levels as low as  $0.001 \mu\text{g/l}$ . All the pesticides studied showed lower recoveries from surface natural waters (rivers, lake and sea) than distilled and underground water. The salinity and the total organic compound content increase the interferences in the GC-FTD and GC-MS traces, reaching higher values when analysing surface water samples.

The combination of solid-phase extraction with GC-FTD and GC-MS permits the application of the method to the detection of compounds belonging to different chemical classes. This method can be easily extended to additional compounds, while simpler temperature and SIM programs could be developed for larger numbers of pesticides.

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