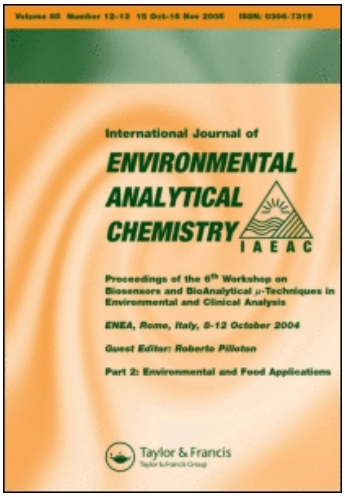

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Gas chromatographic-mass spectrometric methodology using solid-phase microextraction for the multiresidue determination of pesticides in surface waters

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GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC METHODOLOGY USING SOLID-PHASE MICROEXTRACTION FOR THE MULTIRESIDUE DETERMINATION OF PESTICIDES IN SURFACE WATERS

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Solid-phase microextraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS) and selected ion monitoring (SIM) was used for the analytical determination of priority pesticide residues. Fibers coated with a 65-μm film thickness of polydimethylsiloxane divinylbenzene (PDMS-DVB) were used to extract 31 pesticides of different chemical groups. The quality parameters of the method demonstrated a good precision with detection limits of 1–56 ng/L. Linearity was controlled in the range of 0.1–50 μg/L. The proposed method was applied for the trace-level determination of the target pesticides in surface water samples including three rivers and one lake at the Epirus region (north-west Greece) for a period of one year. The results demonstrate the suitability of the SPME–GC–MS approach for the analysis of multi-residue pesticides in environmental water samples.

Keywords: Water analysis; SPME; Pesticides; Greece

INTRODUCTION

Over the years there has been an increasing interest in water-quality preservation and improvement. Among the various water pollutants, pesticides constitute a significant category. The widespread use of pesticides for agricultural and non-agricultural purposes has resulted in the presence of their residues in the aquatic environment. Pesticide contamination of surface and ground waters has been well documented around the world [1–4]. The determination of pesticide residues in water samples is necessary for solving various environmental and biological problems [5]. Several pesticides are included in the European Union list for priority organic compounds to be

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monitored from discharges (European Union Directive EC/76/464), while some of them and their transformation products are classified by the IARC (International Agency for Research on Cancer) as possibly carcinogenic to humans [6].

In addition, EU regulations for drinking-water quality set a limit in concentration at 0.5 μg/L for the sum of all pesticides and 0.1 μg/L for each individual compound in order to limit human risks and environmental pollution [7]. To study the fate and transport of pesticides in natural waters, such low detection limits must be reached. The trace determination of pesticides requires both high-performance analytical instruments and efficient sample preparation. The applied methodologies using solvents are time-consuming, labour-intensive and multi-stage operations. Each step, especially concentration, can introduce errors and losses especially when analysing volatile compounds. Waste disposal of solvents is an additional problem, adding extra costs to the analytical procedure and the environment, and creating health hazards to laboratory personnel. Surveys show that more than 80% of analysis time is spent on sample collection and sample preparation. This is necessary because in most cases, analytical instruments cannot handle the sample matrices directly. The whole analytical process can be wasted if an unsuitable sample preparation method has been employed before the sample reaches the chromatograph and the analyser [8].

Several authors have indicated the need for a major simplification in the sample preparation accounting for a miniaturization in scale, which will also result in a reduction in time and solvent consumption [9,10]. Moreover, multiresidue methods to cover all the main groups of pesticides are desired and require the universality of sample pretreatment procedure and the same conditions for the chromatographic separation [11].

Solid-phase microextraction (SPME), a recent sample-preparation technique, is proving increasingly useful for the isolation of organic micropollutants from water. The method eliminates the use of organic solvents, has the advantage of simplicity and integrates sampling, extraction, concentration and sample introduction into a single solvent-free step [12]. SPME has been reported for the analysis of pesticides in different matrices such as wine [13] fruits [14], soils [15], honey [16,17], biological fluids [18] as well as in aqueous samples [19].

Mass spectrometry (MS) is recognized as a highly sensitive and specific technique suitable for use in environmental organic analysis. GC–MS is the most common technique used by the laboratories involved in pesticides analysis for the analysis of volatile and thermally stable compounds, as it allows their identification and determination in several matrices [20,21]. Recently, there has been a tendency towards the use of GC–MS in the selected ion-monitoring mode in which a few selected and characteristic ions for each compound are used, thus improving the sensitivity of the technique to the ng/L level [22].

The present work presents the combination of SPME and GC–MS as an analytical tool for the screening of 31 pesticide residues in environmental waters. The objectives of this study were: (1) to establish a single extraction procedure using SPME that will allow the multiresidue determination of selected compounds belonging to different chemical groups in surface waters; (2) to combine this sample preparation step with the use of GC–MS using the selected ion-monitoring mode (SIM) for the qualification and quantification of the target analytes; and (3) to apply the developed methodology for the routine analysis of natural water samples in the framework of an extended water-quality monitoring survey that included 18 different sampling points in three rivers and one lake in Epirus region (north-west Greece), during a period of one

year. The method takes into account pesticides that are included in the EU list of priority compounds for control of their residues in water and in the list of priority for the Mediterranean countries; moreover, they are common in the area of study for agricultural or other uses. To our knowledge, only a few authors have explored the excellent selectivity and sensitivity that is recognizable to both SPME and GC–MS-SIM combined in a single technique.

EXPERIMENTAL

Chemicals and Materials

Pesticide standards of 99% purity or more (Promochem, Wesel, Germany), pesti-grade solvents (Pestiscan Labscan Ltd, Dublin, Ireland) and analytical-grade reagents (Merck Darmstadt, Germany) were used throughout the analysis.

SPME holder and fiber assemblies for manual sampling were obtained from Supelco (Bellefonte, PA) and used without modification. Polydimethylsiloxane divinylbenzene 65 μm (PDMS-DVB 65 μm) was used as the stationary phase in SPME. Prior analysis the fiber was conditioned in the injector for 3 h at 240°C, with the split vent open, to fully remove any contaminant which might have caused very high baseline noise and large ghost peaks. Then, the fiber was repeatedly injected into the GC until interfering peaks disappeared. During this desorption process, the GC column oven temperature was maintained at 250°C.

Area Description

The province of Epirus is located in the north-west part of Greece and spreads out in an area of 9203 km^2, the greatest part of which is mountainous and with plains covering only the 15%. Agriculture and mixed farming are the major economic activities in the area and the main cultivation includes corn, alfalfa, potatoes, citrus fruits, olives and winter gardening. The major surface water systems are the Arachthos, Louros and Kalamas Rivers, and Pamvotis Lake. Arachthos River is the greatest river of Epirus, 115 km long with a catchment area of 2240 km^2. The mean annual flow rate is estimated at 68 m^3/s, and its flow is regulated by a dam for electric-power production. Louros River is 75 km long, drains a basin of *c*. 925 km^2 and has a mean annual flow of 19 m^3/s. The deltas of the Arachthos and Louros Rivers form extended wetland areas that are protected by the Ramsar Convention. The Kalamas River (96 km long) discharges into the Ionian Sea with an estimated flow rate of 54 m^3/s; it has few tributaries and has a catchment area of 1800 km^2. Pamvotis Lake is a moderately sized (22 km^2) shallow (average depth of 4 m), eutrophic lake. The city of Ioannina lies along its south-western shoreline. The lake is utilized for recreation (rowing, water skiing and fishing), tourism (island ferries, lakeside cafés), commercial fishing (netting), and irrigation (outflow and pumped lake water). The watershed of the lake has undergone substantial agricultural, industrial and urban development. The hydrology of the basin is poorly understood because of its karstic nature. The basin has no naturally occurring surface outflows. Drainage from the basin occurs through a system of sink holes that drain to the Arachthos, Louros and Kalamas Rivers. The estimated application rates of pesticides are 19, 25, 15 and 2.5 tonnes per year for the Arachthos, Louros and

TABLE I Estimated pesticide application rates (tonnes/year)

	Kalamas River basin	*Louros River basin*	*Arachthos River basin*	*Pamvotis Lake basin*
Herbicides	8.0	15.5	9.0	1.0
Insecticides	5.0	6.5	16.0	0.5
Fungicides	1.5	3.0	4.0	1.0

Kalamas Rivers, and Pamvotis Lake, respectively. The distribution for the different pesticide categories is given in Table I.

Sampling

Sampling was performed on a monthly basis, from September 1998 to September 1999, at a maximum of four or five sample stations in the rivers. Sample sites were selected to cover all the possible pollution sources on the river courses (Fig. 1). Five sample stations were established in Lake Pamvotis, and samples were collected monthly from September 1998 to September 1999 at the medium depth layer.

Sampling Preparation Procedure

Water samples (5 mL) were placed into 8 mL vials, sealed with hole-caps and PTFE-line septa. The samples were stirred before and during extraction. After the addition of 15% w/v NaCl, the fiber was exposed to the aqueous phase for an appropriate time period of 50 min, with a stirring rate of 960 rpm at room temperature ($25 \pm 2^{\circ}C$). After extraction, the fiber was directly exposed to the hot injector of the GC systems for analysis. Thermal desorption of pesticides was carried out for 5 min. After this period, no significant blank values were observed. The overall methanol concentration during these experiments was less than 0.1% (v/v) in all cases.

GC–MS Determination

A Shimadzu GC 17A gas chromatograph, coupled to a Shimadzu QP-5000 mass spectrometer, was used for analysis. Chromatographic separation of the 31 pesticides was accomplished with a DB-5MS (J & W, Folsom, CA) fused-silica capillary column (30 m, 0.32 mm i.d., 0.25 mm) coated with a 5% biphenyl–95% dimethylsiloxane stationary phase. Helium was the carrier gas at a flow rate of 1.0 mL/min. Sample injection was in the splitless mode at 240°C. The GC oven temperature programme was as follows: initial temperature 55°C ramped at 5°C/min to 200°C followed by another ramp of 1°C/min to 210°C, held for 1 min and finally to 270°C at 20°C/min (held for 3 min). The temperatures of the ion source and the interface were set at 240°C and 290°C, respectively. The mass spectrometer was operated in the electron impact (70 eV), selected ion monitoring (SIM) mode at 1.75 kV. For each analyte, the most abundant and characteristic mass fragment was chosen for quantification and two others for confirmation (Table II). Pesticides analytes were subsequently identified by their relative retention time and by the ratios of their respective confirmation ions to their quantitation ion.

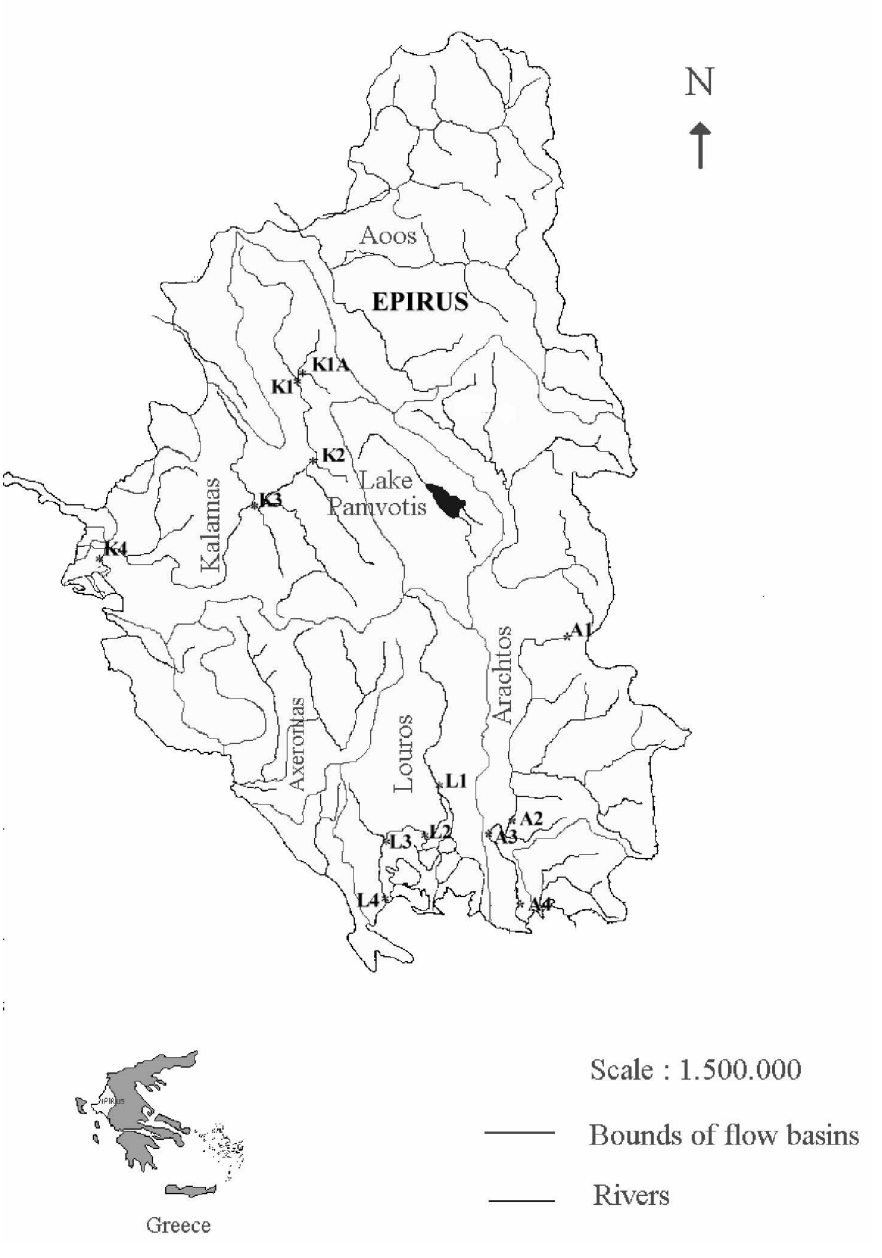

FIGURE 1 Locations of sampling stations.

A calibration curve was obtained with pesticides standards in the range of 0.05–10 μg/L, extracted in the same conditions as the real samples. Because the presence of organic solvents in the aqueous samples influences the extraction process, the same methanol content (0.1%) was added to the real samples to normalize the influence of methanol concentration between spiked (calibration curves) and real water samples.

TABLE II Retention time, linearity data, recoveries, LODs, RSD values and typical fragment ions (m/z) of the target pesticides in GC–MS–SIM using an SPME PDMS-DVB 65 μm fiber

	Compounds	t_R (min)	*Linearity*	*Quantitation ions* (m/z)	*Confirmation ions* (m/z)	*Recoveries* (*Arachthos River water*)[c]	*LODs*[a] (ng/L)	*R.S.D.*[b]	*Ion set*
1	EPTC	17.64	0.998	86	128,132	97	1	5	
2	Molinate	22.56	0.995	126	187,98	75	1	8	
3	Propachlor	24.20	0.996	120	196,176	74	2	6	*1*
4	DEA	25.65	0.991	172	187,145	89			
5	Trifluralin	25.71	0.990	306	264,172	86	3		
6	Dicloran	27.14	0.990	124	206,176	86	15	15	
7	Carbofuran	27.50	0.992	164	149,131	84	8	12	
8	Simazine	27.68	0.997	201	186,173	94	13	15	
9	Atrazine	27.80	0.999	200	215,173	102	10	7	*2*
10	Terbuthylazine	28.38	0.998	214	229,100	103	3	7	
11	Diazinon	28.65	0.999	137	304,179	99	1	5	
12	Chlorothalonil	28.78	0.995	266	268,264	72	9	11	
13	Dichlofenthion	30.34	0.990	97	279,223	87	1	6	
14	Vinclozolin	30.91	0.995	285	212,198	76	3	8	
15	Alachlor	31.02	0.994	160	263,188	104	3	8	*3*
16	M. Parathion	31.18	0.992	263	125,109	91	6	7	
17	Prometryne	31.72	0.993	241	226,184	92	4	10	
18	Fenitrothion	32.34	0.999	277	260,109	96	20	14	
19	Dichlofluanid	32.64	0.997	123	224,167	94	3	7	
20	Malathion	32.90	0.990	125	173,158	98	32	14	
21	Metolachlor	33.06	0.996	162	238,146	89	3	9	*4*
22	Fenthion	33.49	0.997	278	125,109	99	2	6	
23	E. Parathion	33.72	0.995	109	291,139	90	4	9	
24	M. Bromophos	34.49	0.993	331	329,125	89	4	8	
25	Sea Nine 211	35.74	0.997	169	246,184	62	6	9	
26	Irgarol 1051	36.47	0.999	182	253,238	79	2	6	
27	E. Bromophos	37.43	0.997	97	359,301	88	3	10	
28	α-Endosulfan	38.27	0.995	195	237,207	96	7	11	*5*
29	Fenamiphos	39.43	0.991	303	217,154	84	56	14	
30	β-Endosulfan	42.60	0.993	195	237,207	95	4	9	
31	Ethion	43.04	0.991	97	231,153	91	4	9	

[a]LODs: limits of detection. [b]RSD: Relative standard deviation. [C]Spiking level: 1 μg/L.

RESULTS AND DISCUSSION

Significance of SPME in Monitoring Study

It is clear that low cost and neat sample preparation methods are imperative in pesticide field analysis. Advantages of the SPME approach over traditional sampling include complete elimination of solvent, simplification of sampling procedure, reduction in analysis time and cost, and regeneration of the fiber for immediate reuse. In addition to these advantages, SPME overcomes problems related to matrix effects and elution of impurities generated by extraction materials.

In a previous study by our group, effective analytical protocols were established, based on SPME extraction and coupled to electron-capture detection and flame thermionic detection (ECD–FTD) for pesticides belonging to different chemical groups, such as triazines, organophosphates, acetamides and carbamates [23–26]. A similar extraction protocol was adopted here in association with GC–MS detection in the SIM mode, which should give the equivalent sensitivity but also allow unequivocal confirmation of the identity of the pesticides. As a result of the different relative sensitivities between detectors towards the groups of pesticides studied, the extraction conditions were checked with this detection system. However, no relevant discrepancies were found to justify the use of a different set of SPME conditions. Moreover, a few more compounds (carbofuran, DEA, α-endosulfan, β-endosulfan, metolachlor) were included in this study compared with previous for the multi-residue determination of 31 pesticides. Briefly, a PDMS–DVB fibre was chosen with regard to its intermediate polarity properties that proved to be especially suited for the simultaneous analysis of the target analytes.

Performance of the SPME

The linearity of the method was investigated over a range between 0.1 and 50 μg/L. Series of seven concentration levels were obtained by spiking distilled water with the calibration mixture to generate the calibration curves. Each solution was run in triplicate. Square regression coefficients (R^2) were higher than 0.990 for all target compounds, and RSD values less than 15% were observed. The linearity was also checked with uncontaminated natural water samples using the same concentration levels as for distilled water.

The limits of detection (LODs) were determined according to published guidelines by comparing the signal-to-noise ratio (S/N) of the lowest concentration to a S/N = 3. The limits of detection were at the ng/L level for all analytes and are characterized as very low for the detection of pesticides in surface water. Except for fenamiphos and malathion, for which LODs of 0.056 and 0.032 μg/L were obtained, all the other pesticides had LODs less than 0.025 μg/L that express the 25% of the EU maximum acceptable concentration for drinking water (0.1 μg/L).

The recoveries generally ranged from 52 to 110% depending on the matrix of the water sample and especially on the presence of dissolved organic matter (the lowest recovery was observed in the case of sea nine 211 in lake water sample). The analytical characteristics of the method are summarized in Table II.

Application of SPME to Surface Waters

The proposed SPME method was applied for the determination of pesticide residues in three rivers and lake waters in north-west Greece during a one-year survey. The occurrence of pesticides in the different surface reservoirs of Epirus region is summarized in Table III. The mean and range concentrations of the detected pesticides for all stations at the three rivers and the lake during the 12-month period along with the frequency of detection in the water samples are given also. Figure 2 shows a TIC of a spiked sample and a real sample representative of Louros water samples collected in the summer period (July 1999).

Pamvotis Lake

Two herbicides (simazine and atrazine), the triazine metabolite desethylatrazine (DEA) and four insecticides (diazinon, carbofuran, malathion and ethion) were detected in water samples from the five sampling stations in Pamvotis Lake. DEA and diazinon were detected in more than 50% of samples. Atrazine and diazinon were detected at higher concentrations throughout the sampling period, with a more constant horizontal distribution. The maximum detected concentrations were 0.79 μg/L and 2.1 μg/L, respectively. Pesticides with the lower occurrence (carboruran, simazine and malathion) were determined in the samples from the summer period, whereas ethion was detected only in the samples collected from January to March. The presence of the pesticide residues in the lake is primarily due to the runoff from the agricultural area of Kastritsa in the south-western part of the lake, which is reflected in the relatively higher concentrations at the neighboring stations. The biocides Sea Nine 211 and Irgarol 1051 (used as antifouling agents in boat paints) were not detected in any of the water samples.

Arachthos River

The occurrence of pesticides in the Arachthos River was lower than the other rivers both in the frequency of detections and in the levels of concentrations of the determined pesticides. Atrazine, simazine, propachlor, triffluralin, EPTC, diazinon and carbofuran were detected at four sampling sites along the river course with mean concentrations that did not exceed 0.05 μg/L. The herbicide EPTC and the insecticide diazinon were present more frequently, while the highest concentrations were for propachlor (0.74 μg/L) and carbofuran (0.55 μg/L). An integration of concentrations from the river sources to the estuaries was evident for all the identified pesticides. The sampling stations after the dam were more polluted, with the higher values being detected during the summer and fall (Fig. 3A and B).

Kalamas River

Six herbicides, the *s*-triazines simazine and atrazine, the metabolite DEA, the chloroacetanilides alachlor and propachlor, the anilide trifluralin and the carbamide EPTC as well as the organophosphorus insecticides diazinon, ethyl and methyl parathion and the carbamate carbofuran were present in Kalamas River water. The mean detected concentrations ranged from 0.004 μg/L for ethyl parathion to 0.263 μg/L for propachlor. The compound that occurred most frequently was diazinon (54% of samples), and

TABLE III Mean concentrations of the detected pesticides in the surface waters of Epirus in 1998–1999

	Kalamas River			*Louros River*			*Arachthos River*			*Pamvotis Lake*		
	Detection (%)	*Mean conc.* (μg/L)	*Range* ($n=50$)	*Detection* (%)	*Mean conc.* (μg/L)	*Range* ($n=55$)	*Detection* (%)	*Mean conc.* (μg/L)	*Range* ($n=40$)	*Detection* (%)	*Mean conc.* (μg/L)	*Range* ($n=60$)
Herbicides												
EPTC	34.0	0.118	bdl[a]-1.851	21.8	0.024	bdl-0.897	22.7	0.018	bdl-0.120		bdl	bdl
Simazine	38.0	0.036	bdl-0.486	25.0	0.018	bdl-0.222	13.6	0.003	bdl-0.098	10.0	0.002	bdl-0.028
Atrazine	36.0	0.313	bdl-3.866	40.0	0.032	bdl-0.204	11.4	0.003	bdl-0.022	35.0	0.056	bdl-0.792
DEA	50.0	0.035	bdl-0.090	25.5	0.007	bdl-0.128		bdl	bdl	53.3	0.012	bdl-0.120
Alachlor	16	0.027	bdl-0.939	38.2	0.039	bdl-1.026		bdl	bdl		bdl	bdl
Propachlor	38	0.263	bdl-3.754	25.5	0.031	bdl-0.745	11.4	0.040	bdl-0.739		bdl	bdl
Trifluralin	34	0.023	bdl-0.325	23.6	0.020	bdl-0.201	20.5	0.007	bdl-0.015		bdl	bdl
Insecticides												
Diazinon	54	0.037	bdl-0.775	40	0.010	bdl-0.234	27.3	0.048	bdl-0.057	50.0	0.163	bdl-2.105
Carbofuran	16	0.019	bdl-0.160	12.7	0.006	bdl-0.111	6.8	0.016	bdl-0.553	10.0	0.009	bdl-0.158
Parathion ethyl	14	0.004	bdl-0.040	3.6	bdl	bdl	-	bdl	bdl	-	bdl	bdl
Parathion methyl	14	0.009	bdl-0.271	30.9	0.005	bdl-0.070	-	bdl	bdl	-	bdl	bdl
Malathion		bdl	bdl		bdl	bdl		bdl	bdl	21.7	0.038	bdl-1.227
Ethion		bdl	bdl		bdl	bdl		bdl	bdl	8.3	0.021	bdl-0.993

[a]bdl: below detection limit.

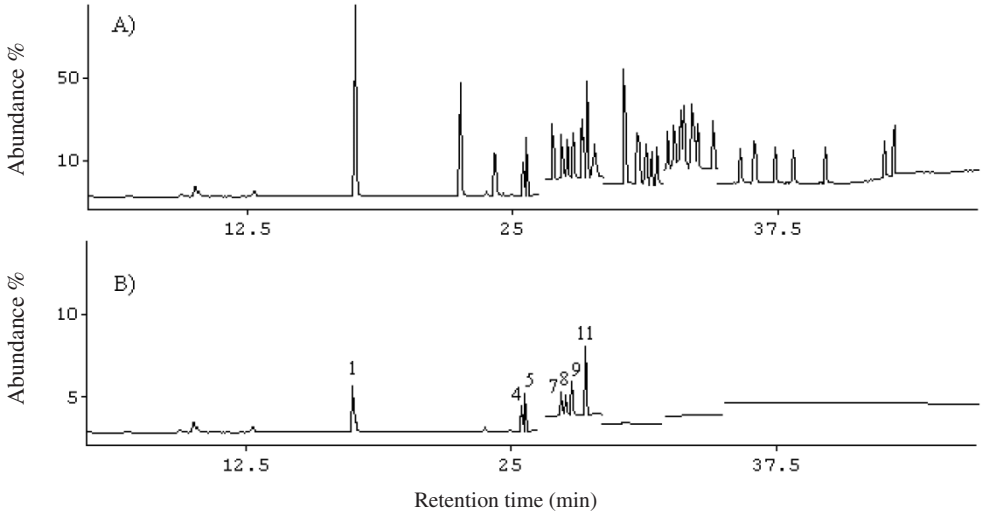

FIGURE 2 GC–MS–SIM chromatogram of Louros river water sample using PDMS-DVB 65 μm fiber: (A) in spiked river water; (B) real water sample (July 1999, peak number corresponding to Table II).

the triazine metabolite DEA followed (50% of samples). The maximum concentration levels for all the compounds were observed from June to September, a period that comes after the spring application for most pesticides, and with a decreasing tendency through the other months. The variation of the pesticide contamination does not follow the pattern of integration from the sources to the estuaries as was observed in the cases of Arachthos and Louros Rivers and also reported in previous studies for those river basins of Epirus [27]. This is probably because the main contributions to pesticide pollution are located in the upper river, while dilution effects occur along the river course (Fig. 3C and D).

Louros River

The pesticides that were detected in Louros River were the same as those in Kalamas River, though the mean concentrations were generally lower, ranging from 0.005 μg/L for parathion methyl to 0.039 μg/L for alachlor. The most frequently occurred compounds were diazinon (40% of the samples), atrazine (40% of the samples) and alachlor (38.2% of samples). The concentrations were higher for the period from May to July and from October to November (Fig. 3E and F). The first period is after the application season, and the second after rainfall in the fall. The fact that the size of the Louros basin is smaller than that of Kalamas River and the agricultural areas are located close to the river banks may explain why the transport of compounds was faster with the runoff water in the fall.

Comparisons of Pesticide Detections Between Surface Waters

Six herbicides of the chemical groups of triazines and acetanilides, six organophosphorus and carbamate insecticides and the metabolite desethylatrazine were detected in the surface waters of Epirus at μg/L levels. The total herbicide concentrations

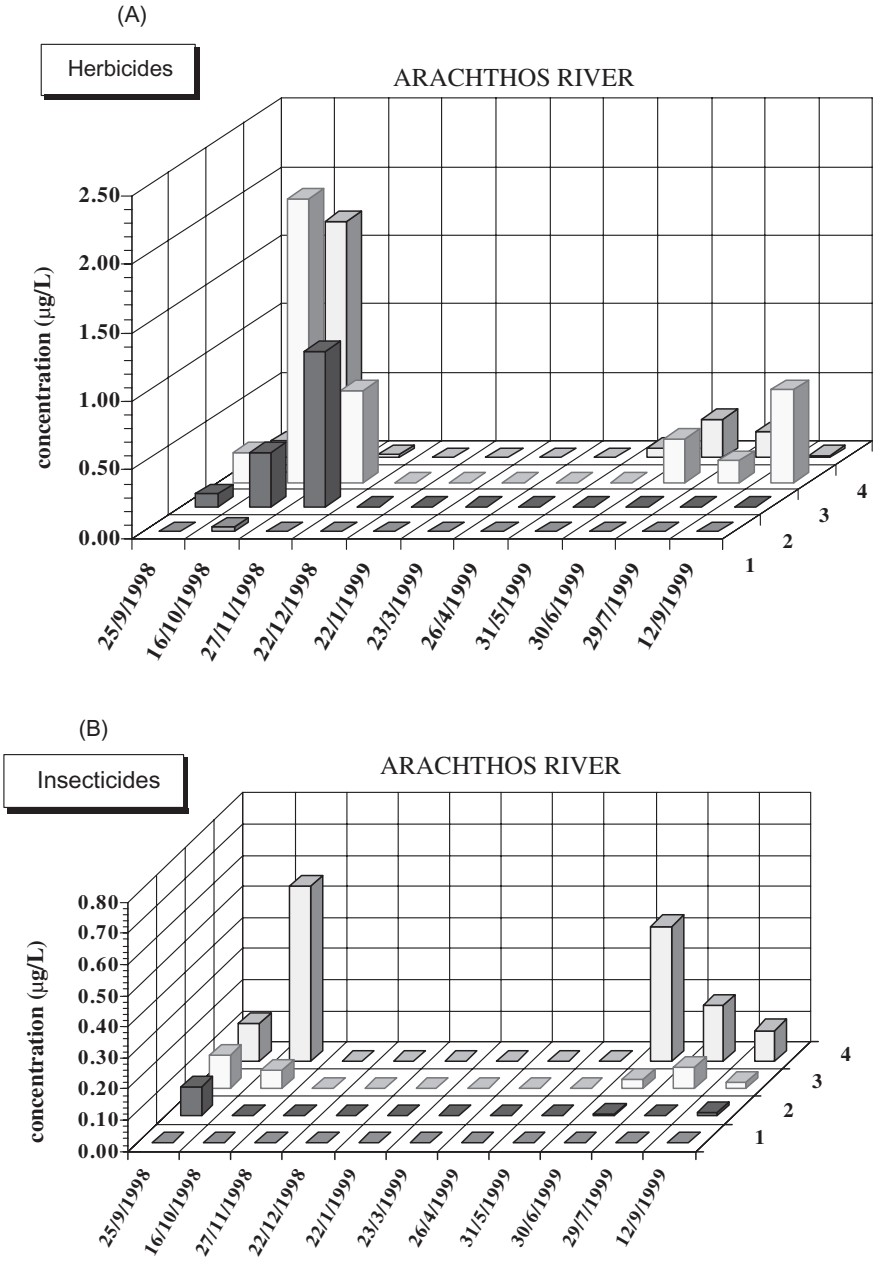

FIGURE 3 Seasonal variations of: (A) herbicide and (B) insecticide concentrations in Arachtos; (C) herbicide and (D) insecticide concentrations in Kalamas; (E) herbicide and (F) insecticide concentrations in Louros.

were higher than the total insecticide concentrations in all rivers and the lake. More compounds and higher concentration levels were determined in the Kalamas River than in the other surface reservoirs. The lowest concentration levels were detected in the Arachthos River. In the Louros and Arachthos Rivers, an increase in the

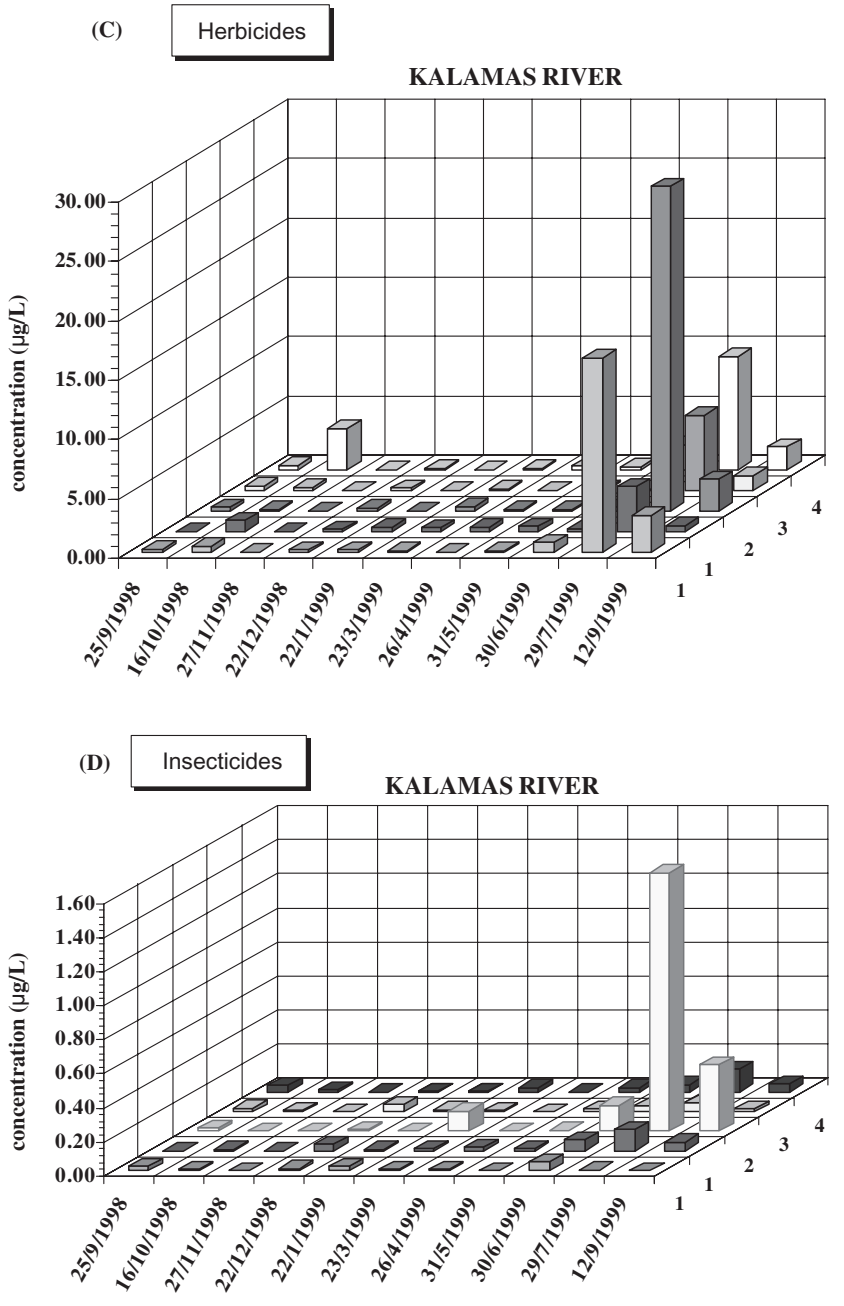

FIGURE 3 Continued.

concentration levels from the sources to the estuaries has been observed. The pesticide concentration levels in water show seasonal variations that follow the pesticide use at the corresponding basins. The highest levels occur in June and July, and a second peak is usually observed in October and November following the first rainfall events after the dry summer period.

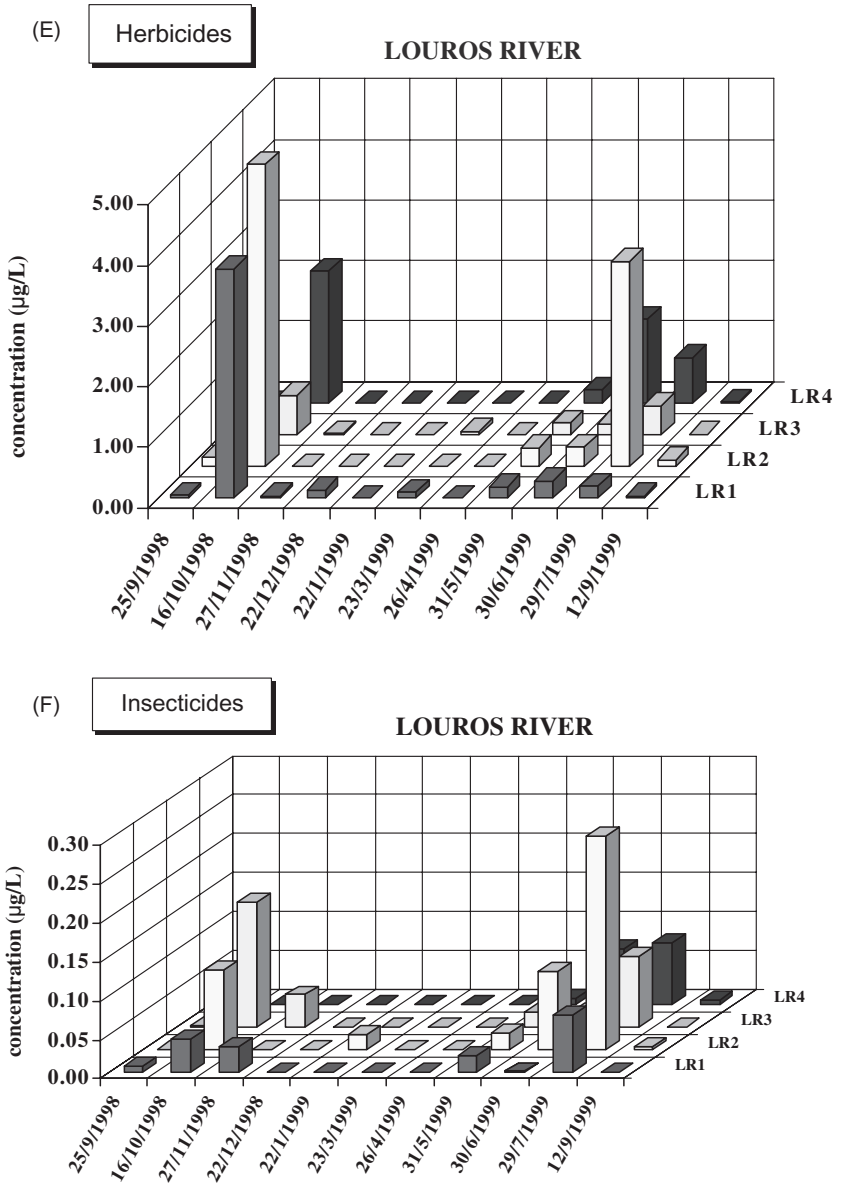

FIGURE 3 Continued.

CONCLUSIONS

SPME coupled to GC/MS-SIM was used to determine pesticides in surface waters. The PDMS-DVB 65 μm coating proved to be efficient on the extraction of 31 pesticides and thus suitable for multiresidue analysis. Subsequently, the GC/MS technique was selected due to its high selectivity, while the SIM mode showed an adequate sensitivity, selectivity and precisionm thus allowing the identification and quantification of low traces of pesticides regarding the 0.1 μg/L EU limit. The data obtained in this study

were useful for determining the occurrence and temporal distribution of 31 target compounds in the studied area.

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