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Application of solid-phase microextraction in the monitoring of priority pesticides in the Kalamas River (N.W. Greece)

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Abstract

A solid-phase microextraction (SPME) method was applied to an extended monitoring survey of priority pesticides for the European Union for a period of 12 months in water of the Kalamas River (Epirus region of northwestern Greece) in order to determine their concentrations and seasonal variations. Polydimethylsiloxane-coated fiber (100 μm) was used. The samples were screened using gas chromatography with flame thermionic detection. Detection was confirmed by gas chromatography–mass spectroscopy. The most frequently detected pesticides were some of the more commonly used herbicides, such as *S*-ethyl-*N*,*N*-di-*n*-propylthiol carbamate (EPTC), trifluralin, atrazine, deethylatrazine, terbuthylazine and alachlor, and insecticides, such as carbofuran, diazinon, disulfoton, parathion methyl, parathion ethyl, fenthion and ethion. Concentrations of individual compounds ranged from 0.020 to 0.3 μg/L. Greater pesticide concentrations occurred during the seasons of application. A comparison with a well-established solid-phase extraction (C_{18} disks) procedure was performed for samples of high-season application (May–September) in order to confirm the effectiveness of the SPME technique. The results demonstrate the suitability of the SPME method for routine screening multiresidue analysis in natural waters.

Keywords: Water analysis; Environmental analysis; Pesticides

1. Introduction

Pesticide contamination of surface and ground water resulting from agricultural use has been well documented around the world. The widespread use of pesticides for agricultural and non-agricultural purposes has resulted in the presence of their residues in various environmental matrices. Thus, pesticide residue analysis in environmental samples has received increasing attention in the last few decades, resulting in many environmental monitoring programs for a broad range of pesticides [1].

Studies involving the determination of pesticides in environmental matrices often deal with samples with low analyte concentrations containing a large number of interfering compounds. Thus, simple and highly sensitive analytical techniques are required to detect and quantify pollutants in water at trace levels [2].

The determination of pesticides by chromatographic techniques requires extensive and time-consuming sample preparation, prior to final concentration. This usually includes an extraction step [liquid–liquid extraction (LLE), supercritical fluid

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extraction (SFE) or solid-phase extraction (SPE)] as well as a clean-up procedure in order to obtain a final extract fully compatible with the chromatographic determination [3–6].

In the last few years, several authors have reported the requirement for a major simplification of sample preparation, with a miniaturization of scale, which will result in a reduction in analysis time and solvent consumption [7,8].

Solid-phase microextraction (SPME), developed by Pawliszyn and co-workers [9,10], is a recent sample preparation technique that is proving increasingly useful in analytical chemistry and that presents some of the characteristics outlined above for a new sample preparation strategy. 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 [9].

SPME has been employed successfully in the analysis of a wide range of pollutants, such as BTEX (benzene, toluene, ethylbenzene and xylenes) [11], polycyclic aromatic hydrocarbons (PAHs) [12] and polycyclic biphenyls [13]. Pesticides have also been determined by SPME in different matrices, such as wine [14], fruits [15], soils [16], honey [17,18], biological fluids [19] and aqueous samples [8,20].

This work presents the results of an extensive monitoring survey that was carried out for a period of one year in the Kalamas River (Epirus region, northwestern Greece) using SPME coupled to GC.

The main objectives of this study were: (1) to demonstrate the applicability of the proposed method for rapid and accurate screening multiresidue pesticide analysis in environmental water samples, (2) to monitor the occurrence of a wide range of pesticides belonging to different chemical groups, routinely applied in the basin of the Kalamas River, and to determine their temporal and spatial variations in river water samples, and (3) to assess the surface water quality of the Kalamas River with respect to potential pesticide contamination at selected sites.

2. Area description

The pesticide survey was conducted in 2000 at six different stations (K1–K6) along the course of the Kalamas River. The Kalamas River (96 km long), with a few tributaries, a catchment area of ca. 1800 km^2, and with a mean annual flow-rate of 54 m^3/s, discharges into the Ionian Sea (Fig. 1). Agriculture and mixed farming are the major economic activities in the area of study and the main cultivation includes maize, sorghum, cereals, alfalfa, vegetables, potatoes, citrus fruits and olives.

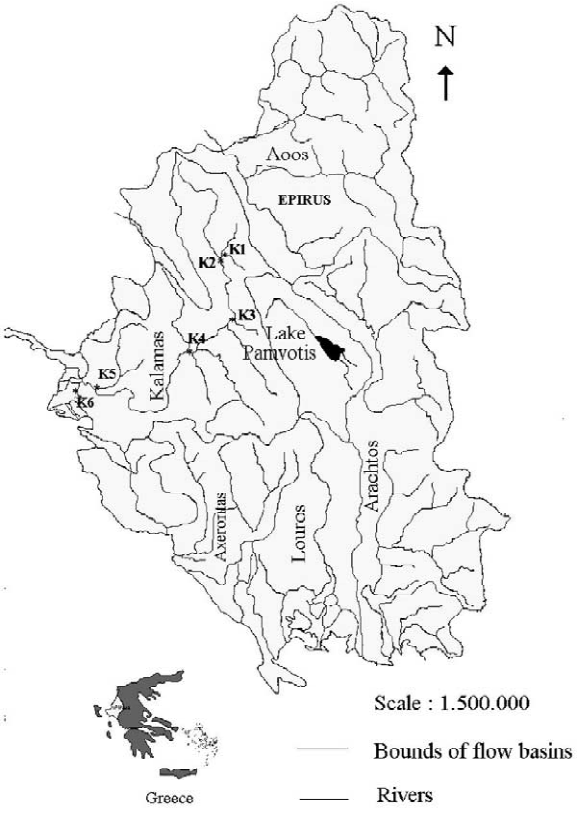

Fig. 1. Sampling stations along the course of the Kalamas River.

3. Experimental

3.1. Sampling

Water samples were collected monthly from the main flow of the Kalamas River between January and December 2000. Six sampling stations were selected in order to cover all the possible pollution sources of the Kalamas River (Fig. 1), located near points where tributaries meet the main river course.

A 2.5 L volume of water was collected in glass bottles from each sampling site at medium depth. After being filled with water, the bottles were sealed with screw caps lined with aluminum foil. The bottles were stored in an ice-cooler at 4 °C, reaching the laboratory on the same day, and were normally extracted within 48 h.

3.2. Reagents and standards

Pesticide analytical standard materials were purchased from Riedel-de Haën (Seelze, Germany). Stock standard solutions of 50 mg/L of each compound were prepared in methanol and were used for the preparation of a mixture solution of the selected compounds at the required concentration. Methanol, dichloromethane and ethyl acetate were purchased from Pestiscan (Labscan, Dublin, Ireland). Sodium chloride was purchased from Merck (Darmstadt, Germany). Empore extraction C_{18} disks (47 mm I.D.×0.5 mm) were purchased from Varian (Harbor City, CA, USA).

3.3. SPME fibres

SPME holder and fibre assemblies for manual sampling were provided by Supelco (Bellefonte, PA, USA) and used without modification. The fibre coating assayed was polydimethylsiloxane (PDMS, 100 μm). Before measurements the PDMS fibre was conditioned in the injector for 3 h at 240 °C, with the split vent open to fully remove any contaminant that might have caused very high baseline noise and large ghost peaks. The fibre was then repeatedly injected into the GC system until interfering peaks disappeared. During this desorption process the GC column oven temperature was maintained at 240 °C.

3.4. Analytical method

Water samples were screened for 22 pesticides [herbicides: *S*-ethyl-*N*,*N*-di-*n*-propylthiol carbamate (EPTC), propachlor, metolachlor, alachlor, trifluralin, simazine, atrazine, terbuthylazine and prometryne; insecticides: diazinon, disulfoton, parathion methyl, parathion ethyl, fenthion, fenitrothion, ethion, bromophos ethyl, bromophos methyl, terbufos and carboruran; fungicides: chlorothalonil and vichlozolin] (Table 1). These pesticides were chosen as target analytes on the basis of being included in the priority list of the European Union (EU), because of their application in the studied area, and their previously reported detection [24]. Thirteen of the 22 analyzed pesticides were detected in the Kalamas River during the 12 month sampling survey.

The analysis of pesticides was based on the SPME procedures described for each pesticide chemical group in previous works [25–28]. However, in the present study the parameters of the direct SPME multiresidue analysis were optimized as follows, in order to obtain the best extraction performance for all groups of target analytes: salt 15%, methanol <0.1%, stirring rate 960 rpm, pH 7, and an equilibrium time of 45 min. A 5 mL volume of a water sample was placed in a 10 mL vial, which was sealed with a hole-cap and a PTFE-lined septum. The samples were stirred before and during extraction. The fibre was then immersed in the aqueous phase for 45 min with stirring at room temperature (25±2 °C). After extraction, the fibre was exposed directly to the hot injector of the GC system for analysis. Thermal desorption of pesticides was carried out for 10 min. After this period, no significant blank values were observed.

The analysis of water samples using SPE C_{18} disks was performed according to the methodology described by Albanis and Hela [4].

3.5. Quantification

Quantification of the samples was carried out by peak area using the external standard calibration. A calibration curve was obtained with pesticide standards in the range from 0.05 to 10 μg/L, extracted under the same conditions as the real samples. The concentrations of the detected pesticides were the average values of three measurements. 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 in order to normalize the influence of the methanol concentration between spiked (calibration curves) and real water samples.

GC–MS confirmation in both the full-scan and selected ion monitoring modes was performed on the selected samples in order to determine the presence

Table 1
Molecular structure, molecular mass, water solubility, octanol–water coefficients and soil sorption of target compounds

Pesticide	Molecular mass	Water solubility[a] (mg/L)	Log K_{ow}[b]	Soil sorption K_{oc}[a]
Herbicides				
EPTC	189.32	344	3.20	200
Trifluralin	335.28	0.3	3.97	8000
Propachlor	211.69	613	2.41	80
Simazine	201.66	6.2	2.20	130
Atrazine	215.69	33	2.48	100
Deethylatrazine (DEA)	188.60	3200[c]	–	48
Terbuthylazine	229.72	8.5	3.06	170
Alachlor	269.77	240	2.63	170
Prometryne	241.37	33	3.34	400
Metolachlor	283.80	530	3.28	200
Insecticides				
Terbufos	288.43	5	4.48	500
Diazinon	304.35	60	3.30	1000
Disulfoton	274.40	25	4.02	600
Parathion methyl	263.21	60	2.94	5100
Fenitrothion	277.24	30	3.40	2000
Fenthion	278.33	34	4.09	1500
Parathion ethyl	291.27	24	3.76	5000
Bromophos methyl	366.00	40	4.88	–
Bromophos ethyl	394.00	2	5.68	–
Ethion	384.48	1	5.07	10 000
Carbofuran	221.25	351	1.63	22
Fungicides				
Chlorothalonil	265.92		2.88	4000
Vichlozolin	286.11	1000	3.00	100

[a] OSU Extension Pesticide Properties [21].
[b] Log K_{ow}, octanol–water partition coefficients from Ref. [22].
[c] From Ref. [23].

of pollutants. Pesticides in river water samples are identified when the following criteria are met: the chromatographic peaks of both ions for the unknown and the standard sample must coincide at the same retention time and the ratio between the two selected ions (Table 2) must be the same with a tolerance of ±15%.

3.6. Gas chromatographic conditions

3.6.1. GC–flame thermionic detection

Chromatographic analysis was performed using a Shimadzu 14A capillary gas chromatograph equipped with a flame thermionic detector (FTD). The DB-5 column used, 30 m×0.32 mm I.D., contained 5% phenyl–methylpolysiloxane (J & W Scientific, Folsom, CA, USA). The temperature program used was as follows: 55 °C (2 min) to 210 °C (21 min) at 5 °C/min; then 210 °C to 270 °C (0 min) at 10 °C/min. The injection temperature was 240 °C. Helium was used as the carrier gas (1.5 mL/min) and make-up gas (40 mL/min). The detector gases were hydrogen and air, and their flow-rates were regulated at 120 and 4.0 mL/min, respectively. The FTD ion source was an alkali metallic salt (Rb_2SO_4) bonded to a 0.2 mm spiral of platinum wire.

3.6.2. GC–MS

A QP 5000 GC–MS system from Shimadzu, equipped with a capillary column DB-5-MS, 30× 0.25 mm, 0.25 μm, containing 5% phenyl–methyl-

Table 2
Typical fragment ions (m/z) of the target pesticides in GC–MS-SIM

Compound	t_R (min)	m/z
EPTC	17.84	128, 86
Propachlor	24.07	176, 120
DEA	25.26	187, 172
Trifluralin	25.90	306, 264
Carbofuran	27.40	164, 149
Simazine	27.68	201, 173
Atrazine	27.90	200, 215
Terbuthylazine	28.49	229, 214
Terbufos	28.51	288, 97
Diazinon	28.76	304, 137
Chlorothalonil	28.89	266, 264
Disulfoton	29.16	274, 88
Vinclozolin	31.03	285, 212
Alachlor	31.16	188, 160
Parathion methyl	31.26	263, 109
Prometryne	31.70	226, 184
Fenitrothion	32.57	277, 109
Metolachlor	33.37	238, 162
Fenthion	33.76	278, 125
Parathion ethyl	33.97	291, 109
Bromophos methyl	34.80	329, 125
Bromophos ethyl	37.80	357, 97
Ethion	45.56	97, 231

polysiloxane (J & W Scientific), was used under the following chromatographic conditions: injector temperature 240 °C, oven temperature programme 55 °C (2 min) to 210 °C (20 min) at 5 °C/min and to 270 °C at 10 °C/min. Helium was used as the carrier gas at 1.0 mL/min. The interface was maintained at 290 °C and the spectra were obtained at 70 eV.

4. Results and discussion

4.1. Overview of pesticide detection

Table 3 contains a summary of the occurrence and concentrations of the pesticides detected in samples collected during the 12-month study on the Kalamas River. Six herbicides of the chemical groups triazines (DEA, atrazine, terbuthylazine), acetamides (alachlor), dinitroanilines (trifluralin) and carbamates (EPTC) were detected. The SPME method used allows the determination of these compounds at very low concentrations [limits of detection (LODs) ranged from 0.003 to 0.080 μg/L depending on the compound] and the obtained recoveries were above 85% for all pesticides in this type of water (Table 4).

Table 3
Mean detected pesticide concentrations (μg/L) and range at six stations on the Kalamas River (K1–K6) in the period from January to December 2000

Pesticide	Detection (%) ($n=72$)	Concentration (μg/L)	
		Mean detected	Detected range
Herbicides			
EPTC	21	0.06	0.04–0.12
DEA	44	0.03	0.03–0.09
Trifluralin	56	0.10	0.02–0.30
Atrazine	46	0.05	0.02–0.23
Terbuthylazine	4	0.02	0.01–0.02
Alachlor	3	0.08	0.04–0.13
Insecticides			
Carbofuran	21	0.05	0.03–0.15
Diazinon	47	0.11	0.04–0.25
Disulfoton	53	0.03	0.01–0.07
Parathion methyl	8	0.08	0.05–0.09
Parathion ethyl	13	0.02	0.02–0.04
Fenthion	4	0.02	0.01–0.03
Ethion	18	0.02	0.01–0.03

These pesticides are recommended for use on multiple crops in the Epirus area according to our market survey and they are reported to be relatively persistent with half-lives of up to 3 months [29]. For these reasons it is not surprising that multiple detections of these compounds were observed and their concentrations were the highest during the application season and low-rainfall events.

Trifluralin was the most frequently detected herbicide with a maximum concentration of 0.30 μg/L. Its occurrence was observed throughout the whole survey period with the exception of the winter months when dilution effects and degradation reduced concentrations to below the detection limit (Table 5).

The maximum concentrations for atrazine were observed in the period of May to June with a decreasing tendency during the months after field application (Table 5). The atrazine metabolite DEA was found in 85% of the samples that contained atrazine and also in five samples where atrazine was below the limit of detection. The mean ratio of DEA to atrazine, DAR, was estimated to be 0.4 to 0.7 at each station during April–September 2000 (Table 5).

Table 4
Limits of detection (LODs) and relative standard deviations (RSDs) for the GC–FTD and GC–MS systems and recoveries for the GC–FTD system for the selected pesticides using a PDMS 100 μm fiber

Pesticide	GC–FTD			GC–MS	
	LOD (μg/L)	RSD (%)	Recovery Kalamas River (%)	LOD (μg/L)	RSD (%)
Herbicides					
EPTC	0.010	7	96	0.020	9
Propachlor	0.030	9	97	0.040	14
Trifluralin	0.005	10	105	0.010	12
Simazine	0.030	8	97	0.040	9
DEA	0.010	9	95	0.020	12
Atrazine	0.005	7	110	0.015	8
Terbuthylazine	0.005	8	98	0.010	7
Alachlor	0.020	8	89	0.025	11
Prometryne	0.005	12	95	0.010	7
Metolachlor	0.010	6	92	0.015	7
Insecticides					
Carbofuran	0.030	9	87	0.050	11
Terbufos	0.020	8	97	0.025	10
Diazinon	0.015	3	98	0.020	6
Disulfoton	0.005	4	93	0.015	6
Parathion methyl	0.080	10	92	0.090	12
Fenitrothion	0.025	8	97	0.035	7
Fenthion	0.010	6	95	0.015	8
Parathion ethyl	0.015	5	97	0.030	7
Bromophos methyl	0.005	8	94	0.010	8
Bromophos ethyl	0.003	6	90	0.010	8
Ethion	0.005	10	92	0.015	12
Fungicides					
Chlorothalonil	0.025	11	102	0.030	13
Vinchlozolin	0.015	6	104	0.020	9

These results agree with those reported in other studies [30,31], suggesting that DEA is a very common detectable metabolite of atrazine. In addition, the presence of DEA in some water samples could be attributed to microbial degradation of the *s*-triazine herbicides in soil being transported in the dissolved phase by the river [32].

Terbuthylazine was only detected during the application period (March) at stations K2 and K3 at trace concentrations, showing that this triazine is also being applied preferentially to atrazine and simazine. This preferential use has been reported for other regions with similar cultivations [33].

EPTC was detected in the period of the first rainfall events from late August to October with a mean concentration of 0.60 μg/L. This compound is applied as a pre-planting herbicide with soil incorporation and its residues can be detected in runoff waters with the first rainfall events after the dry season [34].

Alachlor was determined at station K4 in the middle of the river course during its application period in April with concentrations above 0.1 μg/L, while a low concentration of 0.040 μg/L was found in late August with the first rainfall events. Traces of alachlor were found during these periods at stations K5 and K6, probably due to dilution effects, reflecting a regional application of the pesticide close to the sampling station (K4).

With respect to insecticides, diazinon was found at the highest levels (maximum concentration 0.25 μg/L) compared to other insecticides at all stations

Table 5
Mean detected concentrations (μg/L) of pesticides in Kalamas River water samples (K1–K6) in the period from May to September 2000 using SPME (PDMS, 100 μm) and SPE (C_{18} disks)

Pesticide	Mean detected concentration (μg/L)±RSD (%)				
	May	June	July	Aug.	Sep.
SPME					
Herbicides					
EPTC	–	–	–	0.060±6	0.075±8
DEA	0.070±7	0.040±6	0.028±8	0.017±7	0.020±8
Trifluralin	0.093±4	0.060±6	0.183±4	0.100±5	0.117±5
Atrazine	0.110±5	0.062±6	0.056±6	0.035±6	0.117±5
Insecticides					
Diazinon	0.080±7	0.138±6	0.168±6	0.093±6	0.047±6
Disulfoton	0.023±7	0.028±7	0.032±6	0.020±7	0.023±6
Carbofuran	0.045±9	–	–	–	–
SPE					
Herbicides					
EPTC	–	–	–	0.050±7	0.05±8
DEA	0.070±6	0.038±6	0.030±7	0.021±7	0.017±9
Trifluralin	0.088±7	0.046±8	0.169±7	0.085±9	0.111±8
Atrazine	0.080±8	0.050±8	0.040±9	0.030±9	0.090±8
Insecticides					
Diazinon	0.075±9	0.120±8	0.145±8	0.086±9	0.035±9
Disulfoton	0.020±8	0.020±8	0.025±8	0.015±9	0.020±9
Carbofuran	0.060±10	–	–	–	–

(Table 5). Diazinon is one of the most widely used insecticides in the area around the Kalamas River according to the unofficial reported usage by local farmers. It is used for the control of insects in a wide range of cultivations as well as a seed treatment for maize and for insects and pests in animal houses.

Disulfoton was the most frequently detected insecticide throughout almost the whole period with the exception of the winter months at a mean detected concentration of 0.03 μg/L (Table 5).

Ethion and parathion methyl were detected during the Spring period with mean concentrations of 0.02 and 0.08 μg/L, respectively, while parathion ethyl was also detected in the Summer months at a mean concentration of 0.01 μg/L.

Fenthion was detected only twice at stations K1 and K4 at trace levels. This was an expected result due to the fact that fenthion is readily degraded in aqueous solutions. Its instability in water solution has already been reported [5] and its exclusion from the National Pesticide Survey (USA) list demonstrates that it is unstable in well water over a period of 14 days.

Carbofuran was only detected at the Spring sampling during April–May, which coincides with the period of field application, and the respective concentrations ranged from 0.03 to 0.15 μg/L.

4.2. Seasonal pattern of pesticide detection

Seasonal trends were observed in the appearance of pesticides in river water samples. The seasonal variation of the sum of the detected pesticides for all sampling stations is shown in Fig. 2. The highest levels occur during the period of pesticide application and a seasonal peak is usually observed in late September following the first rainfall events after the dry Summer period. Low concentrations were observed during the winter months because of dilution effects due to high-rainfall events. The decrease in rainfall in Summer results in an increase in pesticide

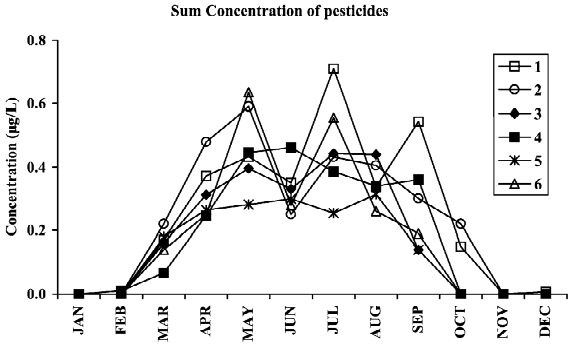

Fig. 2. Seasonal variation of the sum of concentrations of the detected pesticides in water samples of the Kalamas River at six sampling stations (K1–K6) for the period from January to December 2000.

concentrations at this time of year, in addition to the fact that the Summer period comes just after their application and most pesticides have soil half-lives of several weeks. The variation in pesticide contamination does not follow the pattern of integration from the sources to the estuaries as observed in previous reports for other river basins of the Epirus [35].

The concentration ranges of the pesticides do not show a large variation along the course of the river, indicating that new sources of pesticide residues contribute to their occurrence along the river course, competing with possible dilution effects from station to station.

5. Comparison between SPME and SPE

In order to check the effectiveness of the SPME technique, its performance was compared with that of a well-established conventional procedure based on extraction of river water samples, C_{18} SPE. The procedures were applied to samples collected in the Spring and Summer sampling at the stations along the Kalamas River and the pesticide concentrations obtained are given as the mean value for three replicates (Fig. 3). The mean concentrations determined by SPME and SPE are shown in Table 6. The obtained results demonstrate that both techniques can extract the detected pesticides successfully. Generally, SPE is a more expensive and time-consuming method, which makes the SPME method a more favorable technique for trace analysis work.

6. Conclusions

This study shows clearly that the combination of SPME with GC–FTD/MS can be used advantage-

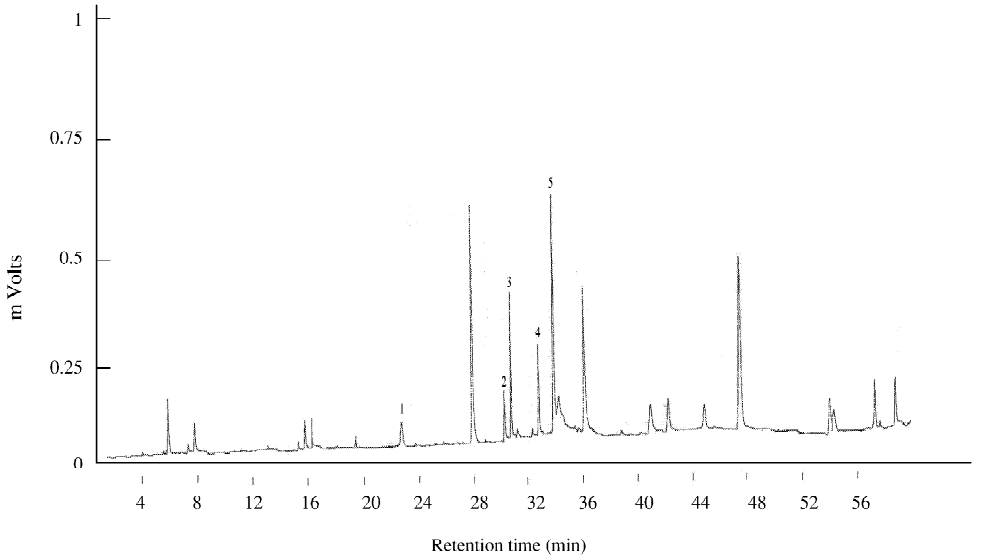

Fig. 3. GC–FTD chromatogram of Kalamas River water sample by PDMS 100 μm fiber (K1 station, June 2001). 1=EPTC, 2=DEA, 3=trifluralin, 4=atrazine, 5=diazinon.

Table 6
Seasonal variation of the most frequently detected pesticides (trifluralin, atrazine, DEA, diazinon, disulfoton) in water samples of the Kalamas River at six sampling stations (K1–K6) for the period from January to December 2000

	Concentration (μg/L)											
	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.
Trifluralin												
1	–	–	0.07	0.10	0.06	0.08	0.30	0.05	0.30	0.10	–	0.02
2	–	–	0.06	0.16	0.12	0.03	0.15	0.17	0.12	0.10	–	–
3	–	–	0.03	0.10	0.10	0.07	0.20	0.15	bql	bql	–	–
4	–	–	bql[a]	0.05	0.10	0.08	0.10	0.05	0.18	bql	–	–
5	–	–	bql	0.04	0.06	0.05	0.10	0.10	bql	–	–	–
6	–	–	bql	0.02	0.12	0.05	0.25	0.08	0.10	–	–	–
Atrazine												
1	–	–	bql	0.07	0.12	0.09	0.07	0.04	0.03	–	–	–
2	–	–	bql	0.07	0.23	0.07	0.04	0.03	0.03	–	–	–
3	–	–	–	–	0.09	0.05	0.04	0.03	0.03	–	–	–
4	–	–	–	–	0.08	0.05	0.05	0.02	0.02	–	–	–
5	–	–	–	–	0.08	0.06	0.02	0.02	–	–	–	–
6	–	–	–	0.04	0.07	0.05	0.02	0.02	–	–	–	–
DEA												
1	–	–	–	0.03	0.06	0.03	0.04	–	–	–	–	–
2	–	–	–	0.03	0.04	0.04	0.03	0.03	–	–	–	–
3	–	–	–	0.03	0.05	0.03	0.03	0.03	–	–	–	–
4	–	–	–	0.03	0.07	0.05	0.03	0.03	–	–	–	–
5	–	–	–	0.04	0.09	0.03	0.03	0.03	0.03	–	–	–
6	–	–	–	0.03	0.09	0.04	0.03	0.03	0.03	–	–	–
Diazinon												
1	–	–	bql	0.06	0.08	0.13	0.25	0.08	0.08	bql	–	–
2	–	–	bql	0.13	0.14	0.08	0.17	0.10	0.05	0.04	–	–
3	–	–	–	0.10	0.01	0.15	0.14	0.15	bql	–	–	–
4	–	–	–	0.10	0.08	0.23	0.14	0.06	0.10	–	–	–
5	–	–	–	0.14	0.01	0.13	0.07	0.11	0.05	–	–	–
6	–	–	–	bql	0.16	0.11	0.23	0.06	bql	–	–	–
Disulfoton												
1	–	–	bql	0.04	0.02	0.02	0.05	0.02	bql	bql	–	–
2	–	–	0.02	0.02	0.03	0.02	0.04	0.02	bql	bql	–	–
3	–	–	bql	0.02	0.03	0.03	0.03	0.04	0.03	bql	–	–
4	–	–	bql	0.05	bql	0.05	0.03	bql	bql	–	–	–
5	–	–	bql	0.03	bql	0.03	0.02	0.02	bql	–	–	–
6	–	–	bql	0.07	0.04	0.02	0.02	bql	bql	–	–	–

[a] bql, below quantification limits.

ously for the rapid, routine, unequivocal and accurate determination of trace levels of pesticides in environmental water samples.

The pesticides detected in river water samples belong to different chemical or/and active groups. Six herbicides, EPTC, DEA, trifluralin, atrazine, terbuthylazine and alachlor, and seven insecticides, carbofuran, diazinon, disulfoton, parathion methyl, parathion ethyl, fenthion and ethion, were detected in Kalamas River samples throughout the period from January to December 2000.

Contamination by the detected pesticides showed a spatial variation that does not follow a clear pattern. Seasonal variations of pesticide detection in Kalamas River water samples, corresponding to pesticide application periods, were observed. Pesticide detection tended to be more frequent and levels more elevated during the late Spring and Summer months.

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