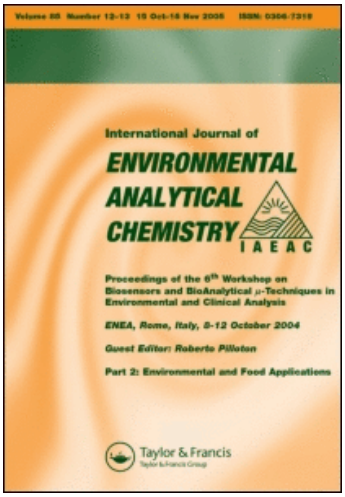

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SOLID PHASE EXTRACTION OF ORGANOPHOSPHORUS PESTICIDES FROM WATER USING CAPILLARY GAS CHROMATOGRAPHY WITH THERMIONIC SPECIFIC DETECTION

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The extraction and enrichment of sixteen organophosphorus pesticides (OPPs) have been studied in Tunisian surface and tap waters as a part of fast and reliable method for monitoring these pesticides. This extraction was performed using C-18 bonded silica cartridges. Capillary column (CC) gas chromatography with thermionic specific detection permitted the determination of the studied pesticides. Recovery depends on (i) the polarity of elution solvent (ii) pesticide levels (iii) the treated water volume. For a 250 mL volume of spiked water at 0.4 µg/L, the recovery of the OPPs studied lays between 70 to 98% but dimethoate was recovered at 52–60%. The limits of quantification (LOQ) are comprised between 0.007 and 0.03 µg/L. The chromatographic behaviour (resolution, relative retention ...) of these pesticides on non polar CC (HP-101), slightly polar CC (SPB-5) and intermediate polar CC (SPB-608 and HP-1701) is discussed. Applications are reported for the determination of parathion-ethyl and parathion-methyl in water samples from Medjerda river (the longest Tunisian river).

KEY WORDS: Organophosphorus pesticides, capillary gas chromatography, water (tap and surface), solid phase extraction.

INTRODUCTION

Organophosphorus pesticides (OPPs) are currently used in agricultural and animal husbandry for crop protection and control of ectoparasites. OPPs are non-persistent but their widespread use may create contamination risks for aquatic environments.

In the southern countries of EU, various OPPs such as fenthion, malathion, diazinon—which are widely used—have been found in surface water. The detected concentrations vary from 0.01 to 11 µg/L in Italian[1,2] and French[3] rivers, in Greek lakes and rivers[4] and in Spanish rivers[5,7].

The US National Pesticide Survey (NPS), in a joint project between EPA's Office of Drinking Water and the Office of Pesticide Programs, has included many OPPs in their monitoring surveys[8,9].

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To the best of our knowledge, no pesticide monitoring of Tunisia's waters has been done despite an average annual consumption of 600 tons of organophosphorus insecticides[10].

Determinations of OPP are currently carried out by gas chromatography (GC)[11-16], gas chromatography-mass spectrometry (GC-MS) [17-19] and high performance liquid chromatography (HPLC)[20-24]. A major problem in using HPLC for residues analysis has been the lack of highly selective or sensitive detector. As regards to the isolation of OPP from water samples liquid-liquid extraction (LLE) methods using dichloromethane (DCM)[18-25], chloroform[26] and n-hexane[27] have been reported. LLE is seen by many analysts as cumbersome. Moreover, it needs long analysis times and uses great quantities of expensive or even harmful solvents. These shortcomings led to new solid phase extraction techniques (SPE). Several workers have described SPE uses for determination of OPP in aqueous samples using various adsorbents such as graphitized carbon black[22], synthetic polymers such as XAD-4[28] and commercially available cartridges packed with C-8 or C-18 bonded-phase silica sorbents[7,11,14,15,29-32].

The objectives of this study were to evaluate and improve upon methods used for the extraction of 16 OPPs from tap and surface waters by using C-18 bonded-phase silica cartridge followed by capillary GC analysis as a part of a fast and reliable method for monitoring pesticides in Tunisian natural water. The parameters investigated included the type of analytical column, the influence of the elution solvent and the dependence of the recovery on the sample volume.

EXPERIMENTAL

Chemicals and reagents

The solvents methanol, ethyl acetate and n-hexane (pesticide grade) were obtained from Merck (Darmstadt, Germany). Anhydrous sodium sulfate, 12–60 mesh (analytical-reagent grade) was purchased from Fluka (Buchs, Switzerland), heated at 450°C and stored in a 130°C oven. Sorbents: 3 mL Supelclean LC-18 SPE tubes (Supelco) containing 500 mg of C-18 bonded silica were used. The pesticide standards were purchased from several suppliers: parathion, parathion-methyl, paraoxon and azinphos-ethyl from Riedle de Haën (Seelz, Germany), azinphos-methyl, diazinon, ethion, coumaphos, disulfoton, phorate, dichlorvos and malathion from Supelco Inc (Bellefonte PA, USA). Phosmet, fenitrothion, fenthion and dimethoate are a gift from "Société Tunisienne des Engrais Chimiques" (Mégrine, Tunisia). Purities of individual standards ranged from 95 to 99.5%. Stock standard solution was prepared by dissolving a 10 mg portion of each pesticide in 100 mL of ethyl acetate to give a 0.1 mg/mL stock solution. The standard solutions for GC-TSD calibration were prepared by serial dilution from the stock pesticide solution. The standard solution then contained 0.05, 0.5, 1, 2, 4, 5 μg/mL of each pesticide. Spiked water samples were prepared by adding an appropriate amount of stock pesticide solution (diluted with methanol) to obtain a μg/L concentration level. Spiked water never contained more than 0.2% of methanol.

Samples

Surface water samples were obtained from Medjerda river water (the longest Tunisian river) used for irrigation in the North East of the country (Bizerta region). Unless they

contained large amounts of suspended sediments, river water samples were extracted unfiltered. When necessary, 0.45 μm PTFE fiber glass filters (Millipore Corp. Bedford, MA, USA) were used. Drinking water samples were collected from the municipal water supply in the authors' laboratories. 0.2 g/L sodium thiosulfate was added to municipal water samples to avoid oxidation of some pesticides by hypochlorite, which will be discussed later. Sodium thiosulfate was also added to surface water samples. The samples were collected in February–June 1994. The collection and analysis of each sample are made on the same day.

SPE procedure

The cartridge was connected to a 1–L separating funnel with appropriate fittings. The solid phase was sequentially prewashed with 5 mL of methanol and distilled water (10 mL) at a flow rate of 1–2 mL/min. The sample was allowed to flow through the cartridge at 10–12 mL/min under water aspirator vacuum. After the sample had been applied, the solid phase cartridge was duly dried by flowing air for another 5 min. The analytes were eluted with ethyl acetate (2 × 2.5 mL) and the combined eluate was then dried with approximately 0.5 g of anhydrous sodium sulfate and concentrated to 0.2 mL in a micro Kaderna-Danish evaporator and nitrogen stream.

Apparatus

Varian model 3700 gas chromatograph equipped with thermionic specific detector (TSD). Column I: SPB-5 fused silica capillary column, 30 m × 0.25 mm I. D., coated with 0.25 μm film (Supelco). Column II: HP-101 fused silica capillary column, 25 m × 0.2 mm I. D., coated with 0.2 μm film (Hewlett-Packard, Palo Alto, CA, USA). Column III: SPB-608 fused silica capillary column, 15 m × 0.53 I. D., coated with 0.5 μm film (Supelco). Column IV: HP-1701 fused silica capillary column 25 m × 0.32 mm I. D., coated with 0.25 μm film (Hewlett-Packard). Operating conditions: The injector and detector temperatures were 240° and 280°C, respectively; column temperature for column I, II and IV—initial 50°C for 1 min, programmed to 280°C at 10°C/min, final 280°C for 15 min; for column III—initial 130°C for 2 min, programmed to 250°C at 10°C/min, final 250°C for 10 min. Carrier gas (nitrogen) at an inlet pressure of 80 KPa for columns I, II and IV, at an inlet pressure of 40 KPa for column III. Detector make up gas flow: 20 mL/min. The detector source was operated at 4 volts. The flow rates of air and hydrogen were set at 175 and 4.5 mL, respectively. Amounts of 2 μL of sample were injected in a splitless mode with the split closed for 40 s.

RESULTS

GC—TSD analysis

The pesticides studied in this work (Figure 1) have been selected due to their persistence, toxicity and mobility in the aquatic environment and because of their wide use in Tunisia in agriculture and in public health. These pesticides cover a wide range of polarity, as indicated by their octanol-water partition coefficient, K_{ow}; log K_{ow} ranges from 0.77 for

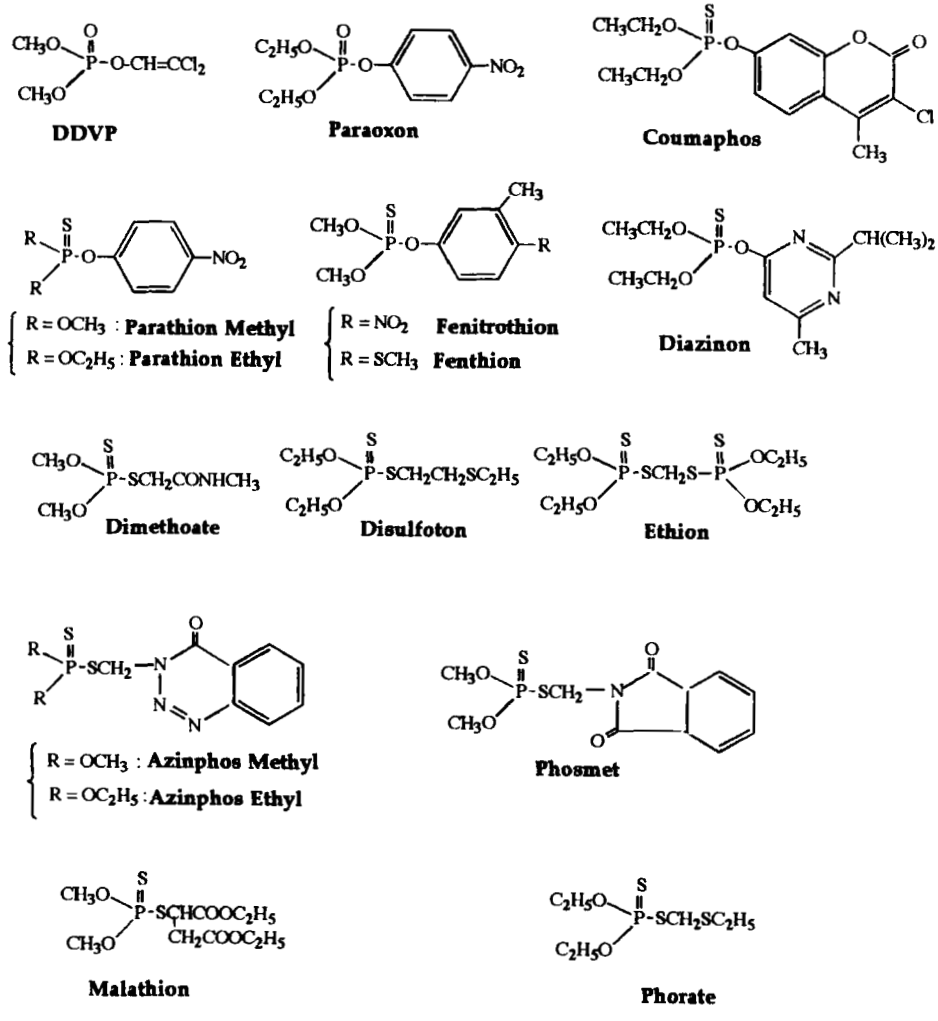

Figure 1 Chemical structures of pesticides studied.

dimethoate to 5.08 for ethion[33,34]. Table 1 gives the relative retention time (RTT) obtained for 16 OPPs studied with four columns. Two of the columns used namely SPB-5 and HP-1701 are similar to DB-5 and DB-1701, respectively. These latter columns are recommended by the US EPA when monitoring organophosphorus and organonitrogenous pesticides[25]. However, only three of the OPPs studied—namely diazinon, dichlorvos, and disulfoton—are on the EPA 507 method. Columns I (SPB-5) and II (HP-101) are non polar and have the same phase ratio β ($\beta = 250$). They separate all the analyzed pesticides in the same elution order. However, for column II (100% dimethylpolysiloxane) which is less polar than column I (5% phenyl 94% dimethyl and 1% vinylpolysiloxane), many peaks of the chromatogram show important tailings which make qualitative as well as quantitative analysis more difficult. Similar results have been

Table 1 Relative retention time and limits of detection (LOD) of organophosphorus pesticides.

Compound	*No.*[a]	*Relative retention time*[b]				*LOD*
		I[c]	*II*[c]	*III*[c]	*IV*[c]	*(pg)*
Dichlorvos	1	0.56	0.55	0.53	0.16	13
Phorate	2	0.84	0.84	0.75	0.68	15
Dimethoate	3	0.86	0.86	0.87	0.82	18
Diazinon	4	0.89	0.90	0.80	0.79	16
Disulfoton	5	0.90	0.91	0.85	0.81	8
Parathion-methyl	6	0.95	0.95	0.91	0.93	17
Paraoxon	7	0.96	0.96	0.96	0.95	16
Fenitrothion	8	0.97	0.97	0.98	0.99	10
Malathion	9	0.98	0.98	0.98	1.00	20
Fenthion	10	0.99	0.99	0.94	1.03	10
Parathion-ethyl	11	1.00	1.00	1.00	1.00	12
Ethion	12	1.14	1.14	1.12	1.26	6
Phosmet	13	1.26	1.23	1.25	1.53	32
Azinphos-methyl	14	1.30	1.28	1.30	1.67	40
Azinphos-ethyl	15	1.36	1.33	1.34	1.75	16
Coumaphos	16	1.43	1.39	1.39	1.40	32

[a] The pesticides are numbered to coincide with those in Figure 2.
[b] Relative to parathion-ethyl. Retention times of parathion are 23.33, 22.4, 7.77, and 21.6 min on column I, II, III and IV respectively.
[c] Column I (SPB-5); Column II (HP-101); Column III (SPB-608); Column IV (HP-1701). For operating conditions, see text.

achieved with wide bore columns of polarity comparable to those of HP-101 (column I) or of SPB-5 (column II) and reported in the literature[16,35]. According to these authors, slightly polar capillary columns such as SPB-5 yield the best results regarding OPPs multiresidual analysis. Moreover, coelution have been observed with column III (SPB-608) and IV (HP-1701) of intermediate polarity. Fenitrothion and malathion peaks overlap on column III; parathion ethyl and malathion peaks overlap too on column IV. When comparing the elution order of the resolved pesticides on the four column set, some observations can be made:

(i) The three insecticides dimethoate, diazinon and disulfoton are eluted in the said order on columns I and II. On columns III and IV the elution is rather: diazinon, disulfoton and dimethoate.

(ii) For column IV: the fenitrotion and fenthion elutions are inverted comparatively to columns I and II.

(iii) For column III: the fenitrothion and parathion ethyl elutions are inverted comparatively to columns I and II.

(iv) The last four peaks of the chromatogram are eluted in the same order whatever the column may be.

Throughout the study that follows, column I was used for the quantitative analysis and column III as a confirmation tool.

The quantification of peaks was carried out by an external standard method, using measurements of peak areas and calibration curve for each pesticide. The linearity of the

detector response was tested by the drawing of the calibration curve for various pesticides in a concentration interval 0.05 to 5 μg/mL. The correlation coefficients are R > 0.998 for all the solutes but fenthion R = 0.985, parathion ehtyl R = 0.996 and coumaphos R = 0.979. The limit of detection (LOD) was calculated by using a signal-to-noise ratio (S/N = 3). The obtained values 6 to 40 pg (Table 1) are within the frame of 3 to 100 pg reported in the references previously cited.

The choice of the elution solvent and the recovery efficiency

The solute recovery by SPE is function of both the retention on the solid phase and the elution efficiency by a solvent. In order to reach the optimum conditions of the elution, the choice of the elution solvent is a parameter to consider. Given their wide range polarity, the three solvents tested in this study—i.e. n-hexane, methanol and ethyl acetate—have been selected among the various solvents found in the literature. The OPPs recovery was determined using 250 mL of spiked distilled water up to 10 μg/L. These results obtained lead to two remarks: (i) The recoveries by n-hexane are, for all the solutes, lesser than when one uses methanol or ethyl acetate. The latter two solvents achieve, on the whole, similar results. Ethyl acetate was chosen in our case because of the OPPs' stability it confers. (ii) With ethyl acetate or methanol, dichlorvos and dimethoate are the only among the OPPs studied which show a recovery less than 70%. In this instance, there is a slight retention on C-18 bonded silica. For dimethoate, since its structure displays an N amide polar function, it may give hydrogen bondings with water reducing thus the interactions with the C-18 ligate on the silica surface. This matches the results given by Mallet *et al.*,[28]. These workers compared the LLE of 14 OPPs with n-hexane, DCM and ethylacetate. Dimethoate has been extracted only with DCM and ethyl acetate (polar solvents) with a mean recovery of 57%. For the other OPPs such as disulfoton and malathion, the extraction was performed by n-hexane with a recovery higher than 90%. The little recovery shown by dichlorvos may be explained by the 1, 1 dichlorovinyl radical polarity bound to oxygen. Generally speaking, the recovery efficiency of an OPP on a non polar reversed-phase silica varies conversely to the radical polarity bound to the heteroatom.

Optimization of the treated water volume

In order to asses the effect of the treated water volume and the solutes concentration on recovery yied, distilled water samples (250 mL and 1000 mL), spiked with the studied pesticides with final concentration of 0.4 and 4 μg/L, were analyzed. The results achieved with a 250 mL of water for the two levels of spiking dealt with show no significant discrepancy. However, the recovery levels for dimethoate and dichlorvos decrease when the treated water volume increases from 250 mL to 1000 mL. The breakthrough volume for the latter two pesticides on the C-18 cartridge used is then less then 250 mL. This is a common feature when polar analytes are preconcentrated on C-18 bonded-silica materials that require lower volume samples in order to achieve an optimum recovery. Otherwise, a decrease of the recovery rate for all the pesticides studied is observed when the treated water volume is one liter spiked at the level of 4 μg/L. In this case, the C-18 cartridge load is 4 μg for each compound. Thus, it is easy to overload its active sites and to exceed its retention capacity even towards the more hydrophobic analytes.

The treatment of a 250 mL water volume for a concentrated extract of a final volume of 0.2 mL leads to an enrichment factor of 3000 for dimethoate recovered at 60% and 5000 for the pesticides recovered at more than 90%. These operating conditions—which were adapted for this work—decrease the analysis time length and the sampling troubles comparatively to the use of water volumes going from 1 to ten liters[7,11,31].

Method performance

This method was assessed on real spiked water samples with the aim of studying the effect of the matrix in recoveries, separation and interfering peaks. Moreover, in order to avoid recovery and reproducibility problems related to OPP decay in water[36,37], this phenomenon was studied at room temperature over a 24 h period. OPP degradation was recently the focus of many workers e.g.[8,38–41]. Table 2 shows some transformation outcomes from selected representative compounds. In the case of spiked tap water all the compounds studied—except dichlorvos and paraoxon—undergo within two hours some transformation, the yield of which lays between 50 to 100%. However, in the same conditions, no significant decay is shown by paraoxon or dichlorvos. Also, by adding sodium thiosulfate to tap water any significant breakdown is avoided[22]. This may be explained by the fact that the degradation rate of the instable OPPs in water is increased when oxidizing reactants such as hypochlorite ions are present. Moreover, it was

Table 2 Degradation of selected OPP in drinking and surface water[a].

Pesticide	*Drinking water*			*Surface water*[d]
	Time (h)	*A*[b]	*B*[c]	
Disulfoton	2	10	100	100
	4	tr[e]	100	97
	24	ND[f]	90	80
Dichlorvos	2	98	100	97
	4	102	98	103
	24	97	98	100
Parathion-ethyl	2	50	99	103
	4	10	100	100
	24	ND	97	100
Phosmet	2	ND	100	101
	4	ND	96	99
	24	ND	ND	ND
Azinphos-ethyl	2	30	100	100
	4	tr	99	96
	24	ND	100	98

[a] The results shown are mean percent recovery (n = 2) of a water sample initially spiked by 10 mg/L. The treated water volume is 100 mL.
[b] and [d] Water without sodium thiosulfate.
[c] Water containing 200 mg/L of sodium thiosulfate.
[e] Traces. [f] not detected.

observed that in a sample of surface water, the pesticide stability is comparable to the one displayed by the pesticides present in the tap water containing sodium thiosulfate. However, the same conditions were thoroughly applied to both surface and tap water included in this work in order to avoid any OPP degradation risks by unknown oxidizing species[42]. Operating on tap and river water at a spiked level of 0.4 μg/L, the recoveries (Table 3) are, for all the studied compounds, better then 70% but dimethoate is recovered at 60% for tap water and 52% for river water. Figure 2 gives the chromatograms related to the analysis of a spiked surface water and of unspiked distilled, tap and surface water samples. The blank chromatograms of distilled and tap water samples (Figures 2A and B) display no big differences and peaks related to the extracted products of the preconcentration cartridge are seen. These interferents are however less important qualitatively and quantitatively as those reported by other workers with C-18 cartridges and using FID and ECD detectors which are less selective than TSD[43]. Moreover, the chromatogram of the river water sample (Figure 2 C) shows three more peaks than that of the unspiked samples of distilled and tap water. One of these three peaks may be attributed to parathion-ethyl thanks to the confirmation gained on column III (SPB-608). The remaining peak has not been identified.

The linearity of the whole procedure was tested with drinking water over the concentration range 0.1–2 μg/L (6 data points). The regression coefficients obtained were fully satisfactory. The limit of detection (LOD) of the pesticides dealt with in the course of this work using the described operating conditions are given in Table 3. These LODs were calculated by using a signal-to-noise ratio (S/N = 3) and assuming that 1 cm was the minimum peak height that could be measured with reasonable confidence. The obtained results show that the adopted operating conditions permit the studied OPPs determination at weaker concentration than the tolerance limits set by the EU countries regulations (0.1 μg/L)[9].

Table 3 Limits of detection (L.O.D.) and mean percent recovery (n = 5) of studied pesticides in drinking water and surface water samples.

Pesticide	*L.O.D.*	*Recovery* (%)*	
	ng/L	*Tap water*	*Surface water*
Dichlorvos	12.5	80 (5)	76 (6)
Phorate	14.5	83 (7)	75 (5)
Dimethoate	20.5	60 (8)	52 (9)
Diazinon	14	92 (3)	89 (5)
Disulfoton	7.2	88 (5)	90 (6)
Parathion-methyl	14.4	93 (5)	85 (7)
Paraoxon	14.8	85 (3)	77 (5)
Fenitrothion	8.4	95 (3)	90 (4)
Malathion	16.4	97 (5)	95 (7)
Fenthion	8.4	94 (10)	95 (8)
Parathion-ethyl	9.2	93 (8)	96 (10)
Ethion	20	97 (14)	90 (15)
Phosmet	27.9	91 (13)	85 (13)
Azinphos-methyl	32.6	98 (12)	85 (12)
Azinphos-ethyl	13.5	95 (11)	90 (12)
Coumaphos	27.1	94 (14)	91 (14)

* Water volume: 250 mL and spiking level: 0.4 μg/L. Number in parentheses is relative standard deviation (RSD).

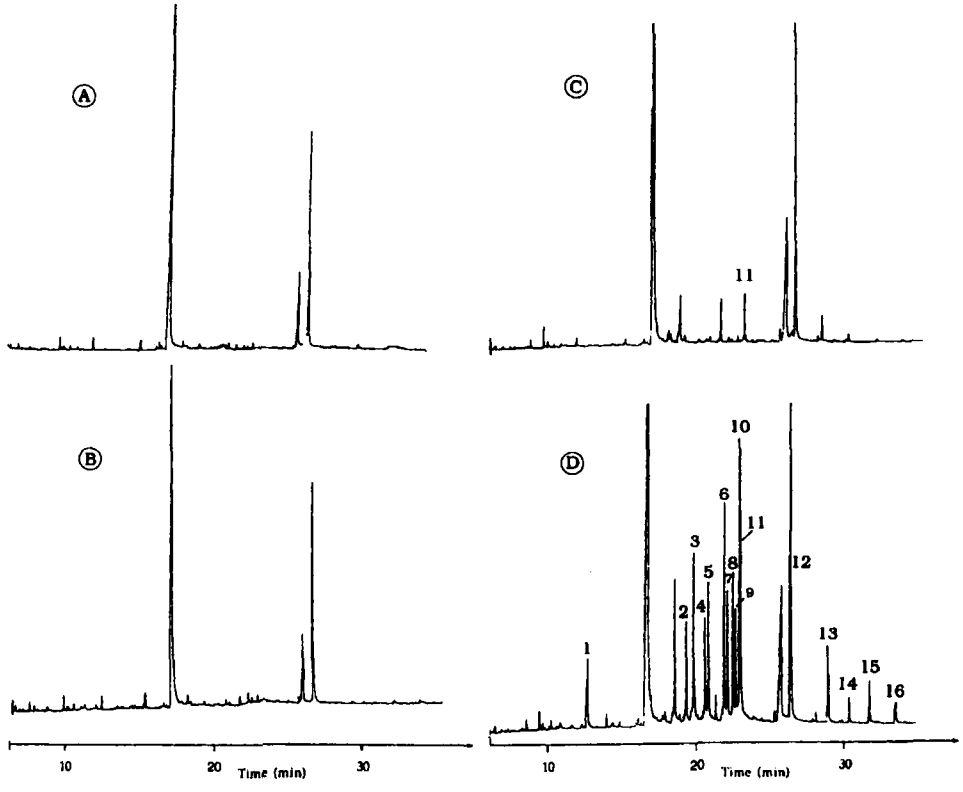

Figure 2 Capillary (SPB-5)-GC-TSD chromatograms of 250 ml water samples for: (A) distilled water, (B) tap water, (C) river water and (D) river water spiked with 16 OPPs at 0.4 µg/L. Chromatographic conditions are reported in the experimental section. Peak numbering corresponds to that given in Table 1.

Environmental levels

Using the above procedure, the 16 studied pesticides were analyzed in 20 samples of tap water and 10 samples of surface water. Four samples of tap water and two samples of surface water are collected monthly. The 16 OPPs were not found in the samples of tap water. For the surface water, parathion-ethyl and parathion-methyl are found with an average concentration of 0.3 and 0.09 µg/L respectively in the samples dating back to February and March 1994. The detected concentrations are comprised between 0.08 and 1.2 µg/L for parathion-ethyl and 0.03 and 0.5 µg/L for parathion-methyl. These findings are, to the best of our knowledge, the first ever reported for Tunisian surface water and may be related to heavy agricultural uses of OPPs in this country.

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