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Determination of a variety of chemical classes of pesticides in surface and ground waters by off-line solid-phase extraction, gas chromatography with electron-capture and nitrogen–phosphorus detection, and high-performance liquid chromatography with post-column derivatization and fluorescence detection

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Abstract

Octadecyl (C₁₈)-bonded porous silica was evaluated for the extraction of triazines, organochlorine, carbamates and acidic pesticides from surface and ground water. Gas chromatography with selected detection methods (electron-capture detection, nitrogen–phosphorus detection, mass spectrometry) and liquid chromatography–post-column derivatization fluorescence detection was employed for the determination of 32 pesticides. Recoveries varied from 52 to 102%. The recoveries of triazines obtained using C₁₈ extraction cartridges and conventional liquid–liquid extraction (LLE) are compared. The limit of detection for seventeen organochlorine compounds was better than 0.003 µg/l and the limit of detection for other 15 analytes was better than 0.06 µg/l. The proposed analytical methodology was applied to analyze pesticides in surface and ground-water samples of the Lassithi Plateau, Crete, Greece. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Environmental analysis; Pesticides; Triazines; Organochlorine compounds; Carbamates

1. Introduction

The presence of pesticides in aquatic system as a result of their common use, persistence in the environment and toxicity, is one of the main hazards to life and health not only to humans but also to animals and plants. Because many pesticides are partially water soluble, they may leach into surface and ground water at greater than ppb levels [1]. Conventional water-treatment practices do not remove these soluble pesticides which then may affect drinking-water quality [2]. Monitoring studies in European countries have shown widespread detection

of pesticides in ground and surface water [3–5]. The levels of pesticides detected in water depend largely on the intensity of agricultural production in a given region. As the council directive 80/778 of the European Union (EU) limits the concentration of individual pesticide and toxic transformation products in drinking water to 0.1 µg/l and the total concentration to 0.5 µg/l, many methods have been developed for both sample preparation and chromatographic separation and detection.

The most common methods of preconcentration of various classes of pesticides from water samples are liquid–liquid extraction (LLE) and solid-phase extraction (SPE) [6]. Nowadays solid-phase extraction methods are routinely used for monitoring pesticides

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in the aquatic environment due to simplicity, reduced processing time and substantial solvent saving, in relation to liquid–liquid extraction [7,8]. Depending on the organic group bonded to the surface the modified sorbent can be used for the isolation of selected classes of analytes. Among the sorbents available for the isolation of pesticides from water phase, octadecyl-bonded porous silica has become the most popular [9–11].

The aim of this work was to study analytical procedures for the determination of the 32 target compounds of 4 different chemical classes using C_{18} solid-phase extraction cartridges at levels below the values fixed by EU to 0.1 $\mu\text{g}/\text{l}$ in drinking water. Various solvents were used for conditioning of microcolumns and for extraction of target compounds as appropriate, according to chemical class of adsorbed pesticides. Organochlorine and triazines were determined using capillary gas chromatography with specific detection methods [electron-capture detection (ECD), nitrogen–phosphorus detection (NPD)]. Confirmation was achieved using at least two GC columns of different polarity; or by HPLC–diode array UV spectra. Gas chromatography–mass spectrometry (GC–MS), with electron impact selected ion monitoring (SIM) mode, was used for the detection and determination of the acidic herbicides after derivatization with pentafluorobenzyl bromide. High-performance liquid chromatography with fluorescence detection (HPLC–FLD) was applied for the determination of the carbamate pesticides by post-column derivatization [*o*-phthalaldehyde (OPA) derivatives]. The analytical methodology was applied to spiked and real samples from the ground and surface waters of the Lassithi Plateau (Crete, Greece) which after treatment are going to be used for the water supply for the cities of Heraklion and Agios Nikolaos, in order to partly solve the problem of water demand of these cities.

2. Experimental

2.1. Chemicals

All solvents used (*n*-hexane, dichloromethane, methanol, acetonitrile, toluene, ethyl acetate and acetone) were of pesticide residue grade and were

products of Lab Scan (Dublin, Ireland). High-purity water was the product of Reidel-de Haen (pestanal) (Seelze, Germany). The mixture of organochlorine pesticides were purchased from Alltech (Deerfield, IL, USA) as solution of 2000 $\mu\text{g}/\text{ml}$ in toluene. Analytical standards of triazines (atrazine, simazine, terbuthylazine, prometryn and metribuzine) were purchased from Riedel-de Haen, Ciba Geigy (Basel, Switzerland) and Dr. Ehrenstorfer (Augsburg, Germany) with a purity range of 98.4–99.8%. Analytical reagent grade standards of acidic herbicides (bromoxynil, bentazone, mecoprop, MCPA, 2,4-D and dichlorprop) were purchased from Chem Service (West Chester PA, USA) and Pesticide Analytical Standard Institute of Organic Industrial Chemistry (Warsaw, Poland) with a purity range of 99–99.7%. Carbamate pesticides (aldicarb, carbofuran, carbaryl, methomyl) were obtained from Riedel-de Haen, Chem Service and Dr. Ehrenstorfer with a purity range of 99–99.7%. Pentafluorobenzyl bromide (PFBBBr) and triethylamine were obtained from Sigma (St. Louis USA). C_{18} Bond Elute extraction cartridges (3 ml/500 mg) were from Varian (Harbor City, CA, USA).

2.2. Sample preparation

Clean-up with disposable C_{18} extraction cartridges. The extraction methods employed in this study were based on the procedures reported previously [12–14]. In all instances high-purity water was used as a blank. Water samples at pH 2 were filtered through a 0.45- μm filter (Millipore) to remove particulate material.

(a) Organochlorine and triazines compounds. A portion of 1 l was introduced by suction onto the C_{18} cartridge first conditioned with 10 ml methanol and 10 ml water. Organochlorine pesticides were eluted from the column by passing 10 ml of *n*-hexane. The extracts were evaporated just to dryness on a rotary evaporator and the final organochlorine extract was dissolved in 2 ml of hexane prior to injection into the gas chromatograph equipped with an ECD system. After this step the triazines were extracted from C_{18} cartridge using 20 ml acetonitrile. The triazines extracts were dissolved in 2 ml of methanol prior to injection into the gas chromatograph equipped with an NPD system.

In order to evaluate the performance of the SPE

system, fortified (triazine mixture at level of 0.1 µg/l) water samples (500 ml) were also extracted by LLE with dichloromethane. The dichloromethane extracts that had been dried over anhydrous sodium sulfate and concentrated to 1 ml, were analyzed using GC–NPD.

(b) *Acidic herbicides*. One litre portion of filtered-water sample was percolated through a C₁₈ cartridge, at a maximum flow-rate of approximately 8 ml/min applying a low vacuum, first conditioned with 10 ml acetone, 10 ml methanol and finally 10 ml water. After drying the cartridge for 2–3 h under a gentle stream of nitrogen, the acidic herbicides were eluted with 2.5 ml of methanol. The eluate from the SPE-cartridge was mixed with 50 µl of an internal standard (2,4-dichlorobenzoic acid solution in methanol, 2 ng/µl) and dried under a stream of nitrogen. The sample eluate was derivatized by adding 200 µl of pentafluorobenzyl bromide (2%, m/v, in toluene) and 5 µl triethylamine in a sample vial that was sealed with caps containing Teflon lined septa and at 110°C in a drying cabinet for 1 h. Finally, the eluate was dried under a stream of nitrogen and dissolved in 100 µl toluene for GC–MS injection.

(c) *Carbamate pesticides*. An aliquot of 500 ml acidified filtered-water sample were passed through a C₁₈ cartridge first conditioned with 5 ml ethyl acetate, 5 ml methanol and 10 ml water. Carbamate pesticides were eluted from the column by passing 1 ml of ethyl acetate ready for HPLC–post-column derivatization fluorescence detection.

2.3. Apparatus

2.3.1. Gas chromatography

2.3.1.1. GC–ECD

(a) A Carlo Erba Model Mega 2 gas chromatograph with ECD system, split/splitless injection port, a DB-1 fused-silica capillary column by J&W Scientific (30 m×0.32 mm I.D., 0.25 µm film thickness) and autosampler Model A200S, with a program for the evaluation of GC runs (Chrom-Card, Fisons Instruments, Rodano, Italy). The temperature program applied in GC–ECD was as follows: 80°C for 1 min, 80–218°C at 8°C/min, 218 for 18 min, 218–250°C at 4°C/min and 250°C for 10 min. The

injection was carried out splitless at 250°C and the injection volume was 1 µl.

(b) A Varian Model 3400 gas chromatograph equipped with an ECD system, split/splitless injection port, a methyl–phenyl 5% fused-silica capillary column by Quadrex (25 m×0.20 mm I.D., 0.1 µm film thickness) and autosampler Model 8200 CX, with a program for the evaluation of GC runs (DAPA Scientific, Kalamunda, Australia). The temperature program applied in GC–ECD was as follows: 80°C for 1 min, 80–218°C at 8°C/min, 218°C for 18 min, 218–250°C at 4°C/min and 250°C for 10 min. The injection was carried out splitless at 250°C and the injection volume was 1 µl.

2.3.1.2. GC–NPD

A Hewlett-Packard Model 5890 II gas chromatograph, with an NPD system, split/splitless injection port, a CP-SIL 13CB fused-silica capillary column by Chrompack (50 m×0.32 mm I.D., 0.4 µm film thickness) and autosampler Model 7673, with a program for the evaluation of GC runs (HP CHEM, Hewlett-Packard, Little Falls, USA). The temperature program applied in GC–NPD was as follows: 100°C for 1 min, 100–150°C at 30°C/min, 150°C for 2 min, 150–205°C at 3°C/min, 205–260°C at 2°C/min and 260°C for 1 min. The injection was carried out splitless at 250°C and the injection volume was 1 µl.

2.3.1.3. GC–MS

All MS measurements were performed with an Hewlett-Packard HP 5971 mass-selective detector combined with an HP 5890 gas chromatograph fitted with a 25 m×0.20 mm I.D., 0.33 µm HP-5 capillary column. The oven temperature was held at 100°C for 1 min following injection, then programmed at 30°C/min to 150°C, which is held for 1 min, then at 3°C/min to 205°C followed by 10°C/min to 260°C and finally held for 23 min. Injection port and transfer line temperatures were set to 250°C. 3 µl quantities of sample were injected using hot splitless injection with the split closed for 0.9 min.

MS measurements were performed with electron impact (EI) ionization at 70 eV. Solvent delay was set to 6 min. For SIM three characteristic ions were selected for each compound and scanned using corresponding time windows with dwell times between 100 and 200 ms per ion. Mass spectrometer

tuning was performed weekly using the autotuning macro. The insert liner was exchanged at least after 50 injections.

2.3.2. Liquid chromatography

LC analysis was performed with: (a) a Hewlett Packard (HP) 1050 solvent delivery unit with a 20 μ l injection loop and a post-column derivatization fluorescence system. The analytical column used was a 25 cm \times 4.6 mm I.D. packed with 5 μ m octadecylsilica gel. The LC column eluent was delivered by a Model HP-1050 LC quaternary pump coupled to a PCX 5100 carbamate post-column analysis module from Pickering Labs. (Mountain View, CA, USA). Post-column reaction was carried out as described elsewhere [15], using OPA and thiofluor, instead of 2-mercaptoethanol, at pH 9–10. A Model HP-1050 fluorescence detector was used at excitation and emission wavelengths of 330 nm and 465 nm, respectively. A HP-ChemStation data system was used for data collection. (b) A HPLC apparatus consisted of a Waters (Milford, MA, USA) Model 600E pump associated with a Waters Model 600 gradient controller, a Rheodyne (Cotati, CA, USA) Model 7725i sample injector equipped with a 20 μ l sample loop, a reversed-phase (RP) C₁₈ analytical column by Novapak (25 cm \times 4.6 mm I.D., 5 μ m), a Waters Model 996 photodiode array detector controlled by the Millenium (Waters) software operated

on an IBM compatible computer. The photodiode array detector was operated in the range 200–400 nm. The mobile phase of the HPLC system consisted of acetonitrile (solvent A)–phosphate buffer at pH=7 (solvent B) gradient that follows: time 0 min, 30:70, time 10 min, 40:60, time 20 min, 55:45, time 30 min, 60:40, time 42 min, 70:30, time 55 min, 70:30, time 65 min, 30:70. Detection at 220 nm. The mobile phase flow-rate was 1 ml/min and the volume injected 20 μ l.

3. Results and discussion

3.1. General considerations

The selection of target compounds was based to their intensive use in the agricultural area of Crete island (Greece) and on the consideration to be of environmental pollution concern in Mediterranean locations. The target compounds, which were studied in this work are given in Table 1.

Triazine herbicides are the pesticides most frequently reported in recent studies of ground and surface waters [16]. They are widely used to pre- and post-emergence weed control and are flushed, after rainfall events, from cropland during the May and June application period. According to recent studies in Greece, herbicides have been detected in rivers

Table 1
List of common names of the target compounds

Subgroups	Target compounds			
<i>Organochlorine pesticides</i>				
HCH-isomers	α -HCH	β -HCH	Lindane	δ -HCH
DDT and related compounds	4,4-DDT	4,4-DDE	4,4-DDD	Methoxychlor
Cyclodiens	Aldrin, dieldrin	Endrin, endrin aldehyde	Heptachlor, heptachlor epoxide	α -Endosulfan, β -Endosulfan and endosulfan sulfate
<i>Triazine herbicides</i>				
2-Chlorotriazines	Simazine	Atrazine	Terbutylazine	
2-Thiomethylatrazines	Prometryne			
Miscellaneous triazines	Metribuzin			
<i>Acidic herbicides</i>				
	Mecoprop	MCPA	Dichlorprop	2,4-D
	Bromoxynil	Bentazone		
<i>Carbamates</i>				
	Methomyl	Aldicarb	Carbofuran	Carbaryl

HCH=Benzene hexachloride, MCPA=(4-chloro-2-methylphenoxy) acetic acid.

draining agricultural areas [17,18]. Less frequently reported, although widely used, are the phenoxyacids (2,4-D, MCPA) and acidic herbicides which, are more rapidly degraded in soil than triazines [19,20]. Carbamate insecticides are also detected infrequently, due to their rapid degradation, in combination with the fact that are used in smaller quantities in comparison to herbicides [21,22]. Organochlorine pesticides have been banned in most countries. As lindane (γ -HCH) and endosulfan are still used in Greece and as some of the organochlorine compounds are still manufactured in other Balkan coun-

tries, residues of these compounds have been found in aquatic systems [5,12,14].

3.2. Extraction on C_{18} cartridges

Table 2 shows the data on retention times of target analytes, the chromatographic technique used for their quantitative analysis, the limits of detection (LODs) and the recoveries obtained from spiking surface-water samples at 0.1 $\mu\text{g/l}$ level using different eluents for solid-phase extraction. In previous works [12–14] several pesticides were extracted and

Table 2
Retention times (t_R , $\text{min} \pm 0.1$), LODs ($\mu\text{g/l}$) and mean recovery [0.1 $\mu\text{g/l}$ fortification level ($\text{R}\% \pm \text{R.S.D.}$)] of the target pesticides

	Detector and column	t_R ($\text{min} \pm 0.1$)	LOD ($\mu\text{g/l}$)	$\text{R}\% \pm \text{R.S.D.}$ SPE, C_{18}
<i>Organochlorine pesticides (n-hexane)*</i>				
α -HCH	GC–ECD capillary methyl-phenyl 5%	12.8	0.002	53.8 \pm 10.2
Lindane (+ β -HCH)		13.6	0.003	81.4 \pm 8.9
δ -HCH		14.7	0.002	82.2 \pm 7.1
Heptachlor		15.4	0.001	74.6 \pm 8.2
Aldrin		16.3	0.001	59.7 \pm 4.5
Heptachlor epoxide		17.3	0.001	93.4 \pm 3.9
α -Endosulfan		18.2	0.001	93.8 \pm 3.8
4,4-DDE		19.0	0.001	92.9 \pm 3.9
Dieldrin		19.1	0.001	91.5 \pm 4.1
Endrin		19.7	0.001	52.9 \pm 9.9
β -Endosulfan		20.0	0.001	94.7 \pm 4.1
4,4-DDD+endrin aldehyde		20.6+20.7	0.002	51.5 \pm 4.8
Endosulfan sulfate		21.7	0.002	96.3 \pm 7.2
4,4-DDT		22.1	0.002	93.6 \pm 3.9
Methoxychlor		23.8	0.002	78.7 \pm 6.3
<i>Triazine herbicides (acetonitrile)*</i>				
Simazine	GC–NPD capillary CP-Sil-13CB	13.9	0.005	85.7 \pm 3.8
Atrazine		14.0	0.001	90.7 \pm 2.4
Terbutylazine		14.6	0.01	90.4 \pm 1.9
Metribuzin		18.1	0.02	58.3 \pm 4.3
Prometryne		19.2	0.01	61.9 \pm 1.9
<i>Acidic herbicides (methanol)*</i>				
Mecoprop	GC–MS of derivatives capillary HP-5	20.7	0.010	79.6 \pm 14.5
MCPA		22.4	0.010	85.8 \pm 18.4
Dichlorprop		22.8	0.010	88.1 \pm 18.9
2,4-D		24.2	0.050	102.1 \pm 26.6
Bromoxynil		24.5	0.050	80.8 \pm 21.1
Bentazone		26.7	0.010	88.8 \pm 23.2
<i>Carbamates (ethyl acetate)*</i>				
Methomyl	HPLC post-column FLD	7.5	0.030	62.6 \pm 6.0
Aldicarb		14.2	0.060	92.2 \pm 2.5
Carbofuran		17.8	0.060	89.2 \pm 2.2
Carbaryl		20.4	0.030	94.0 \pm 2.5

* Eluting solvent.

concentrated from water samples using C_{18} cartridges. Several additional herbicides and insecticides were included in the present study, in order to examine further the recovery efficiency and the limits of detection. The limit of detection of each pesticide was determined after extraction of spiked water samples that produced a chromatographic peak having a height equal to three times the standard deviation of the baseline noise [23]. Quantitation of the pesticides in the sample extracts was performed by use external standard calibration curves. The calibration curves were linear in the working range and the correlation coefficients were usually higher than 0.999, for all the used detectors.

The organochlorine pesticides were detected using the GC–ECD system on a Quadrex (methyl–phenyl 5%) capillary column. The resolution of lindane/ β -

HCH and 4,4-DDD/endrin aldehyde pairs was poor under the conditions employed in this study. Therefore, the identification of peak identity was performed on a DB-1 column (t_r values=15.15/15.30, 23.70/23.81, respectively). The mean recoveries reported here, for organochlorine compounds, ranged from 51.5 to 96.3%, were slightly lower than those obtained in previous work after solid-phase (C_{18}) extraction of spiking drinking-water samples. This result indicated that the use of surface water had no significant effect on the method performance.

The triazine herbicides were quantified by GC–NPD due to its highest sensitivity in comparison with that obtained by HPLC–diode array detection (DAD) system. The resolution between simazine and atrazine on a CP-Sil-13CB capillary column was quite poor under the chromatographic conditions employed

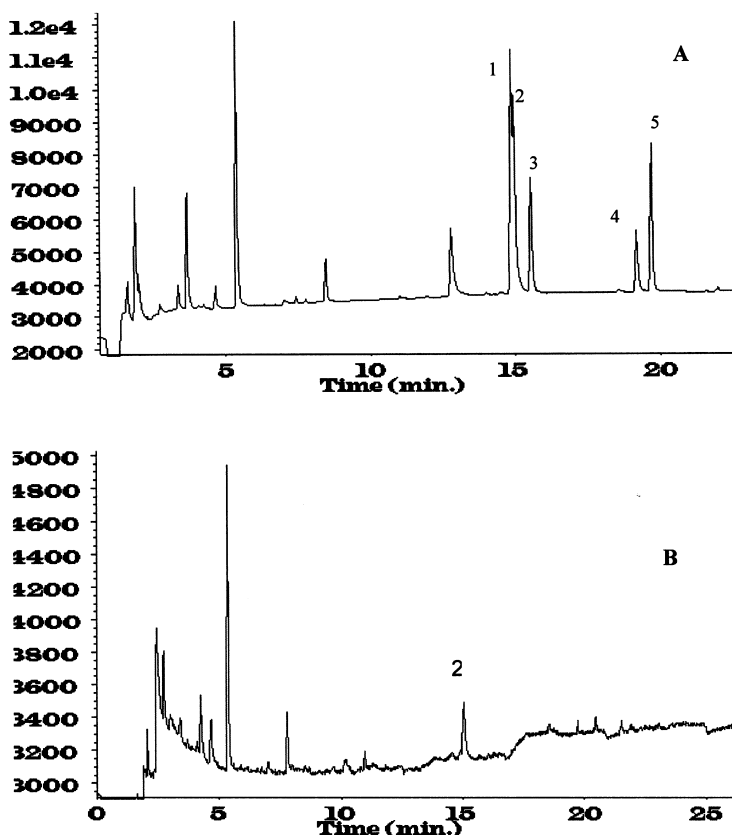


Fig. 1. (A) Chromatogram of a spiked surface water sample (0.1 $\mu\text{g}/\text{l}$) obtained by liquid–liquid extraction and GC–NPD: (1) simazine, (2) atrazine, (3) terbuthylazine, (4) metrybuzine, (5) prometryn. (B) Sample chromatogram from the analysis by LLE–GC–NPD of a field water sample. Atrazine was found at 0.010 $\mu\text{g}/\text{l}$ level.

here. Therefore, during analysis of natural-water samples identification of these analytes was always confirmed by the HPLC–DAD system (t_R simazine/atrazine=24.99/26.42). The recovery values of triazines were not affected by previous elution of the cartridge with *n*-hexane, used for the extraction of organochlorine pesticides. Other researchers [9] have reported recovery rates of 6.9% and 2.2% for prometryne and simazine, respectively, when *n*-hexane was used as the eluting solvent.

In order to evaluate the performance of the selected SPE system the recoveries of triazine herbicides when fortified (0.1 $\mu\text{g}/\text{l}$) water samples (500 ml) were extracted by LLE with dichloromethane were also determined ($79.3 \pm 9.2\%$ – $95.5 \pm 5.5\%$). The mean recovery values (%) and the respective R.S.D. values were approximately the same in both ex-

traction methods. The mean recovery of the more polar compound metribuzine ($\log P_{\text{oct.}}$, 1.65), compared with atrazine ($\log P_{\text{oct.}}$, 2.7), was higher when samples extracted by LLE (96.4%) than by SPE (58.3%). Fig. 1 shows the chromatogram of a water sample extracted by LLE and analyzed by GC–NPD. Fig. 2 shows the chromatogram of the same water sample extracted by SPE and analyzed by GC–NPD. The SPE technique was found to be generally more selective than the LLE one.

The average recoveries (79.6–102.1%) for all acidic herbicides were better than those reported in previous work [13] which might be explained by the better conditions of derivatization step (triethylamine, 5 μl instant of 2 μl and oven temperature, 110 instant of 90°C).

The carbamate pesticides were detected by the

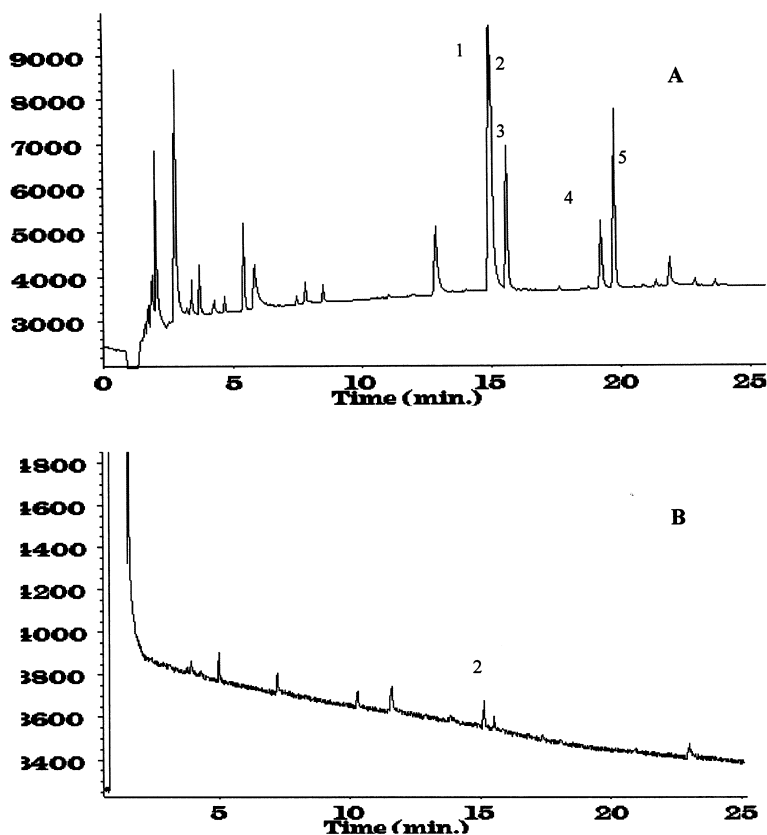


Fig. 2. (A) Chromatogram of a spiked surface water sample (0.1 $\mu\text{g}/\text{l}$) obtained by solid-phase extraction and GC–NPD: (1) simazine, (2) atrazine, (3) terbuthylazine, (4) metribuzine, (5) prometryn. (B) Sample chromatogram from the analysis by SPE–GC–NPD of a field water sample. Atrazine was found at 0.010 $\mu\text{g}/\text{l}$ level.

HPLC–post-column derivatization system. The recovery values for carbamate pesticides were found between 62.6–94.0%. The LODs ranged between 0.03 and 0.06 $\mu\text{g}/\text{l}$.

As the recovery results demonstrate, the water sample matrix does not influence the recovery values of pesticides significantly. The chromatograms of blank water samples were very clean and no interference compounds were present in the extracts.

3.3. Pesticide monitoring studies in the Lassithi's Plateau, Crete, Greece

The proposed analytical scheme was used for the analysis of field-water samples collected from the

Plateau of Lassithi, Crete. The Crete island, located in the south-eastern Mediterranean, is the largest one in Greece, with a population greater than 500 000 and an area of 8 500 000 km^2 . A series of environmental pressures have been exerted on the island: unsustainable agricultural practices (mainly potato, cereal and vegetable cultivations) and rapid demographic expansion and tourism, particularly in the coastal areas, have resulted in a considerable increase in water demand. A dam, built in the Aposelemis river area, is going to concentrate the waters of the Lassithi's Plateau, which, after treatment, are going to be used for the water supply of the cities of Heraklion and Agios Nikolaos, in order to partially solve the water demand of these cities.

Table 3

List of the concentration ranges in $\mu\text{g}/\text{l}$ (no. of samples with positive pesticide detection) of the target pesticides detected in surface and ground water samples of Lassithi plateau

	Sampling areas				
	Pinakiano well	Malia ground water	Honos river	Havgas river	Aposelemis river
α -HCH	0.002–0.011 (3)	0.002–0.043 (2)	0.002 (1)	0.002–0.018 (2)	0.002–0.091 (3)
Lindane+ (β -HCH)	0.003–0.007 (3)	0.003–0.008 (2)	0.003–0.006 (3)	0.003–0.006 (1)	0.003–0.080 (2)
δ -HCH	0.002 (1)	0.002 (1)	n.d.	0.002 (1)	n.d.
Heptachlor	0.001–0.005 (4)	0.001–0.047 (3)	0.001–0.020 (5)	0.001–0.050 (3)	0.001–0.051 (3)
Aldrin	0.001–0.005 (2)	0.001–0.023 (1)	0.001–0.004 (2)	n.d.	0.001–0.024 (2)
Heptachlor epoxide	0.001–0.003 (2)	0.001–0.003 (1)	0.001–0.013 (2)	0.001–0.006 (1)	n.d.
α -Endosulfan	0.001 (1)	n.d.	n.d.	n.d.	0.001 (1)
4,4-DDE	n.d.	0.001 (1)	0.001–0.010 (5)	0.001 (1)	0.001–0.037 (1)
Dieldrin	0.001 (1)	0.001 (1)	0.001–0.010 (3)	0.001 (1)	0.001–0.015 (1)
Endrin	0.001 (1)	0.001–0.002 (1)	0.001–0.002 (1)	n.d.	0.001–0.006 (1)
β -Endosulfan	0.001–0.004 (1)	n.d.	n.d.	n.d.	n.d.
4,4-DDD+endrin aldehyde	n.d.	n.d.	n.d.	n.d.	n.d.
Endosulfan sulfate	0.002 (1)	n.d.	n.d.	0.001–0.002 (1)	0.001–0.004 (1)
4,4-DDT	0.002–0.004 (1)	n.d.	0.002 (1)	0.002–0.004 (1)	0.002–0.003 (1)
Methoxychlor	n.d.	n.d.	n.d.	n.d.	n.d.
Atrazine	n.d.	n.d.	0.010–0.030 (4)	0.010–0.056 (2)	0.010–0.040 (2)
Simazine	n.d.	n.d.	0.010–0.036 (3)	0.010–0.039 (2)	0.010–0.028 (2)
Terbutylazine	0.04–0.046 (1)	n.d.	n.d.	n.d.	n.d.
Metribuzin	n.d.	n.d.	0.040–0.046 (2)	n.d.	n.d.
Prometryn	n.d.	n.d.	n.d.	n.d.	n.d.
Mecoprop	0.010–0.014 (3)	0.010 (1)	0.010–0.029 (1)	0.010–0.024 (3)	n.d.
MCPA	0.010–0.015 (1)	n.d.	0.010–0.052 (1)	n.d.	0.010–0.170 (1)
Dichlorprop	0.010–0.018 (1)	n.d.	0.010–0.084 (2)	0.010 (1)	n.d.
2,4-D	0.030 (1)	n.d.	0.040–0.194 (3)	n.d.	0.040–0.300 (1)
Bromoxynil	n.d.	n.d.	n.d.	n.d.	n.d.
Bentazone	0.010–0.021 (1)	n.d.	n.d.	0.010–0.024 (1)	n.d.
Methomyl	n.d.	n.d.	n.d.	n.d.	n.d.
Aldicarb	n.d.	n.d.	n.d.	n.d.	n.d.
Carbofuran	n.d.	n.d.	n.d.	n.d.	n.d.
Carbaryl	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected.

Thirty surface- and ground-water samples of the Plateau of Lassithi were collected each month from November 1995 to June 1996 from the Aposelemis, Havgas and Honos rivers and the Pinakiano and Malia wells. The levels of pesticides found in the waters are given in Table 3. The levels of pesticide residues found, ranged widely, from 0.001 $\mu\text{g/l}$ to 0.091 $\mu\text{g/l}$ for the organochlorine pesticides, from 0.010 $\mu\text{g/l}$ to 0.046 $\mu\text{g/l}$ for the triazines, and from 0.009 $\mu\text{g/l}$ to 0.300 $\mu\text{g/l}$ for the acidic pesticides. Carbamates pesticides were not detected in any sample.

The identification of organochlorine pesticides was based on their retention times using two capillary GC columns of different polarity (methyl-phenyl 5% and DB1). The confirmation of triazine herbicides was performed using HPLC–DAD UV detection at 220 nm and C_{18} column. The most commonly encountered pesticides in the region studied were α -HCH, lindane, 4,4-DDE, heptachlor, atrazine, simazine and mecoprop.

The concentration levels found are lower than the EU maximum acceptable concentration of 0.1 $\mu\text{g/l}$ for all compounds examined, except for 2,4-D in two samples (0.194 $\mu\text{g/l}$ in the Honos river and 0.300 $\mu\text{g/l}$ in the Aposelemis river) and MCPA in one sample (0.170 $\mu\text{g/l}$ in the Aposelemis river). The results of this survey show that the surface and ground waters in the Plateau of Lassithi have no particular problems with respect to pesticide residues, so they can be used for the production of drinking water.

4. Conclusions

Octadecyl (C_{18})-bonded porous silica was evaluated for the extraction of a wide chemical range of pesticides from surface- and ground-water samples. The selection of suitable solvents for each step of the procedure has permitted the isolation of selected classes of pesticides with low levels of interference from the water matrix. Recoveries varied from 52 to 102%. The recoveries of triazines obtained using C_{18} extraction cartridges and conventional LLE are compared, and C_{18} cartridges were found to be more selective for triazine analysis than the LLE tech-

nique. The limit of detection for seventeen organochlorine compounds was better than 0.003 $\mu\text{g/l}$ and the LOD for fifteen other analytes was better than 0.06 $\mu\text{g/l}$.

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