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Determination of organophosphorus and triazine pesticides in ground- and drinking water by solid-phase extraction and gas chromatography with nitrogen–phosphorus or mass spectrometric detection

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Abstract

Trace enrichement and determination of ethoprophos, fenamiphos, fenthion, isophenphos, mevinphos, monocrotophos, atrazine and simazine were performed by solid-phase extraction on XAD-2 columns and Sep-Pak C_{18} cartridges, subsequent elution with an organic solvent and determination by GC with nitrogen–phosphorus detection (NPD) and mass spectrometry in the selected-ion monitoring mode (MS-SIM). Ground- and drinking water volumes of 1–2.5 l at concentrations levels of 0.1–5 μg/l were used for application of the method. Both adsorbents provided recoveries of 75–95%. The limits of detection were 0.08–0.60 μg/l with NPD and 0.03–0.13 μg/l with MS-SIM.

1. Introduction

Natural waters are contaminated with various pesticides because of their widespread use. Herbicides and nematicides are potential contaminants of natural waters because they are directly applied to soil and are transported into groundwater or leached to surface water [1,2]. A large proportion of foliar sprays that do not reach their target also contribute greatly to soil residues. Another source of pesticides in soil is the residues of these chemicals (such as various insecticides) in the atmosphere, either in dust or rain water, which are washed out by precipitation and fall on to the soil. Therefore, insecticides are transported into groundwater [1]. During the last decade at least 46 pesticides have been reported to be leached into ground waters of the USA [2].

Screening methods for various pesticide groups, in various water matrices, generally consist of an appropriate extraction and isolation technique by which compound enrichement is achieved, followed by clean-up and chromatographic determination. Enrichement methods have been developed using liquid–liquid extraction (LLE) [3] and solid-phase extraction (SPE) with short Amberlite XAD-2 and XAD-4 resin columns [4,5], C_{18} cartridges [6–11] or membrane extraction discs [12].

LLE is an effective method of extracting organic compounds from water samples. Al-

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though LLE, because of its simplicity and because it is a fully developed technique, is used in most official methods for pesticide analysis [3], it has some disadvantages, such as evaporation of large solvent volumes [8], emulsification, contact of laboratory personnel with hazardous organic solvents [12], time consuming, laborious and expensive [13]. Comparisons between LLE and SPE have been well documented [14]. Because of these disadvantages the use of solid-phase preconcentration techniques has expanded substantially. Among them the extraction of analytes on bonded-phase silica is preferred to preconcentration on XAD, because the latter has the disadvantage of requiring extensive clean-up, On the other hand, XAD resins can generally be reused several times, making them an economical choice, especially if one takes into consideration the cost of bonded-phase cartridges and membranes.

We present here a comparative study in which triazine and organophosphorus pesticides were simultaneously determined in ground and drinking water, by using a preconcentration step on an XAD-2 column or a C_{18} bonded-phase cartridge, and determination by capillary gas chromatography with nitrogen–phosphorus detector (NPD) or mass spectrometric detection in the selected-ion monitoring mode (MS-SIM) Emphasis is given to the use of MS–SIM. The compounds studied were chosen on the basis of the following criteria: (a) their use as pesticides locally, (b) their water solubility (>20 mg/l), (c) their hydrolysis half-life (>20 weeks) and (d) their toxicity (oral acute $LD_{50} < 50$ mg/kg). With the exception of triazines the other compounds satisfy these criteria [15].

2. Experimental

2.1. Materials

All solvents of Pestanal grade were purchased from Mallinckrodt (St. Louis, MO, USA). Standard organophosphorus pesticides were purchased form Ehrenstorfer (Augsburg, Germany) and triazines were provided by the US Environmental Protection Agency (EPA). Amberlite XAD-2 (20–50 mesh, surface area 330 m^2/g) was purchased from Fluka (Buchs, Switzerland) and Sep-Pak C_{18} cartridges (0.3 g) from Waters (Milford, MA, USA). All materials used (glass and cotton-wool, paper filters, anhydrous sodium sulphate, etc.) were Soxhlet extracted, overnight and kept dry until use.

Groundwater samples were collected at three locations in the Heraclion area (Crete, Greece). The ground- and well water samples had pH values of 7.50–8.09, conductivities of 325–435 μS/cm and anion concentrations of Cl^- 25.0–28.0, NO_3^- 0 and SO_4^{2-} 11.0–30.0 mg/l. Tap water was obtained from the laboratory.

2.2. Solid-phase extraction

The standard compounds, dissolved in acetone, were added to 1 l of Nanopure-grade water and to 1 l of pre-analysed groundwater or tap water. The compounds were added at levels of 0.1, 0.5 and 5 μg in order to obtain concentrations of 0.1, 0.5 and 5 μg/l.

XAD-2 resin was sonicated three times (30 min each) with acetonitrile. The cleaned resin was kept in methanol. The purified XAD resin as a methanol slurry was placed in a 20×1 cm I.D. column until a resin bed 6 cm high was obtained. The methanol was drained and then the resin was washed with three 20-ml portions of Nanopure water. A 1-l reservoir, capped with a nitrogen pressure source, was attached to the top of the column. The nitrogen pressure was regulated in order to obtain a flow-rate 8–10 ml/min at the bottom of the column. When the sample had passed through the column, the nitrogen pressure was continued for 5–10 min. The pesticides were eluted from the XAD-2 column with 100 ml of acetone at a flow-rate of 1–2 ml/min. The acetone was evaporated to 1–2 ml with a Kuderna–Danish apparatus. The internal standard was added and the solvent was further evaporated to 50–100 μl with a gentle stream of nitrogen.

The C_{18} cartridges were connected at the bottom of the previously described apparatus. Prior to use, the cartridges were flushed with two

5-ml portions of dichloromethane, one 5-ml portion of methanol and one 3-ml portion of Nanopure water. The nitrogen pressure was regulated in order to obtain a 8–10 ml/min flow-rate of the water sample. After the cartridges had been purged with nitrogen for 30 min, the analytes were desorbed with 5 ml of dichloromethane on to a sodium sulphate microcolumn. The column was further washed with 2.5 ml of dichloromethane. After addition of internal standard the solution was concentrated to 100–200 μl for GC–MS analysis. The dichloromethane was evaporated using a gentle stream of nitrogen and replaced with 100–200 μl of hexane for GC–NPD.

2.3. GC–MS-SIM and GC–NPD

GC–MS analyses were carried out using a Hewlett-Packard mass-selective detector with the appropriate data system. A Hewlett-Packard Model 5890 gas chromatograph, equipped with a Grob-type split–splitless injector, was directly coupled with the fused-silica capillary column (SE-54, 25 m × 0.25 mm I.D.) to the ion source. Helium was used as the carrier gas with a back-pressure of 0.8 atm (1 atm = 101 325 Pa). The electron impact ionization conditions were as follows: ion energy, 70 eV; ion source temperature, 195°C; mass range, 45–450 m/z full scan; in the SIM mode for quantitative determinations the masses scanned were m/z 192, 224 and 162 (20–30 min), m/z 127, 158, 201, 215 and 223 (30–39 min) and m/z 213, 278, 303, 125, 109 and 154 (39–60 min); and electron multiplier voltage, 1680–1850 V. In Table 1 are shown the ions, with their tentative structures, selected for each compound.

GC–NPD analyses were performed on a Hewlett-Packard Model 5890 gas chromatograph with a Hewlett-Packard Chemstation data system, equipped with an SP 2100 (30 m × 0.25 mm I.D.) fused-silica capillary column (Supelco). Helium was used as the carrier gas with a back-pressure of 0.8 atm.

The chromatographic conditions for both techniques were as follows: injector temperature, 290°C; detector temperature (NPD), 290°C; temperature programme, 50°C (1 min), increased from 60 to 290°C at 4°C/min, held at 290°C for 10 min. Aliquots of 1–2 μl were injected in the splitless mode (split closed for 45 s) and the hot needle technique was applied.

The internal standard for GC–NPD was parathion ethyl [relative response factors (RRF) for triazines 2.5–3.1 and for organophosphorus pesticides 0.4–1.5] and for GC–MS-SIM it was hexamethylbenzene (m/z 162 in the SIM mode; for RRF see Table 1).

3. Results and discussion

Fig. 1A shows the GC–NPD trace obtained for a sample of groundwater containing 5 μg/l of each pesticide and extracted on the XAD-2, column and Fig. 1B shows the corresponding GC–NPD trace with extraction on the C_{18} cartridge. Fig. 1C shows the GC–MS-SIM trace for a drinking water sample containing 0.25–0.30 μg/l of each compound and extracted with a Sep-Pak C_{18} cartridge. Fig. 2 shows (A) the GC–NPD trace for a groundwater sample extracted with a C_{18} cartridge and (B) a coinjection trace for the same sample with reference compounds. Table 1 gives details of the ions selected for each compound for GC–MS analysis. Table 2 gives the mean recoveries for different spiking levels. Table 3 gives the limits of detection (LOD) for several analytes following extraction with C_{18} cartridges and determination by GC–NPD and GC–MS-SIM.

3.1. Blanks

The XAD-2 resin cleaned by sonification only did not give disturbing blank peaks in the region of interest when NPD was used for detection (Fig. 2A). Several workers have found resin artefacts, such as alkylbenzenes, biphenyl, hydrocarbons and phthalate esters. Higher concentrations of artefacts have been associated with XAD-4 than with XAD-2 resin [5,16]. Specific detection methods such as NPD are insensitive to most of the artefacts reported. This advantage becomes obvious when the chromatographic trace in Fig. 1A is examined.

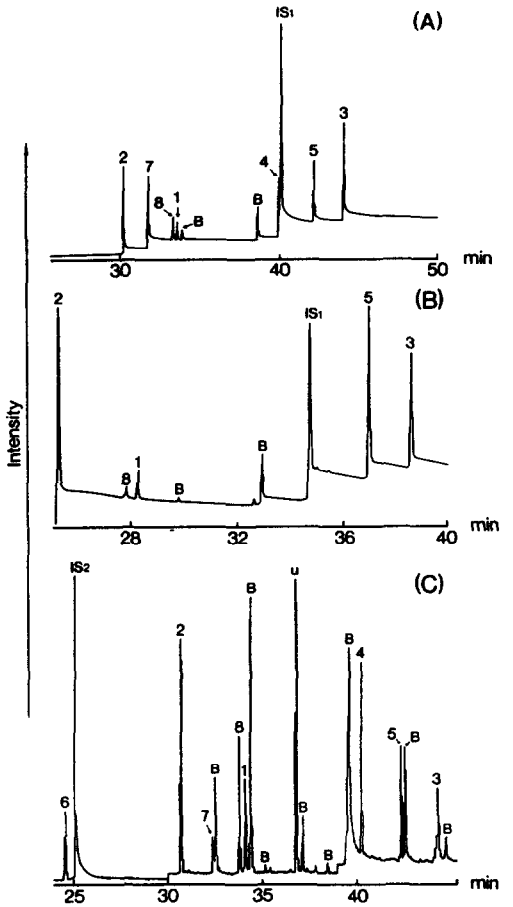

Fig. 1. (A) GC–NPD trace obtained for a groundwater sample spiked with 5 μg/l of each pesticide and extracted on XAD-2 resin. (B) GC–NPD trace for a groundwater sample spiked with the same concentration of pesticides and extracted on a Sep-Pak C_{18} cartridge. (C) GC–MS-SIM trace for a groundwater sample spiked with 0.25–0.3 μg/l of each compound and extracted with a Sep-Pak C_{18} cartridge. B = peaks corresponding to blanks; u = unidentified compounds; IS_1 = parathion ethyl; IS_2 = hexamethylbenzene. For compound numbers, see Table 1.

With respect to the blank peaks corresponding to the C_{18} cartridges (Fig. 2B), we did not observe a significant difference in favour of the Sep-Pak cartridges when NPD was used. Blanks occurring when Sep-Pak cartridges are used could be more disturbing when the MS detection is applied. Nevertheless, even with MS-SIM the cartridges also produced relatively clean chromatograms in the region of interest (Fig. 1C).

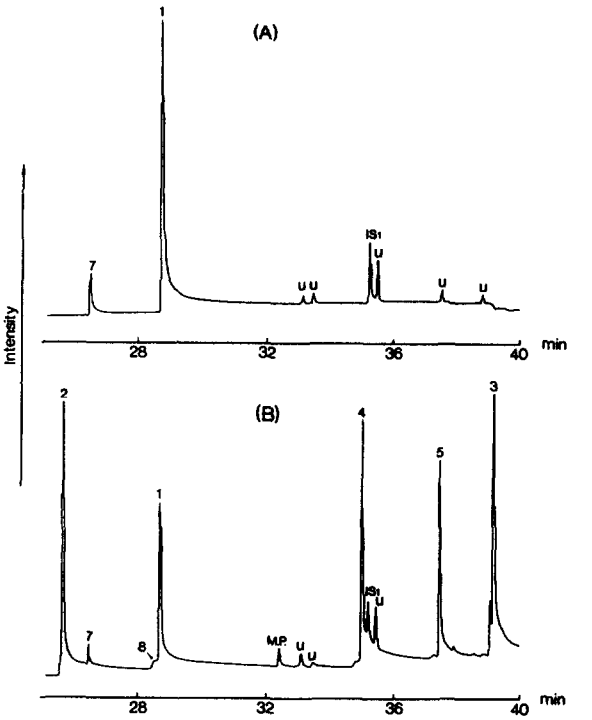

Fig. 2. (A) NPD trace for a groundwater sample. (B) Coinjection of the same sample with a solution containing standard compounds. IS_1 = Parathion ethyl; M.P. = Parathion methyl; u = unidentified compounds. For compound numbers, see Table 1.

3.2. SPE capacity

Table 2 shows the different pesticide recoveries obtained at different spiking levels for 1 l of ground water. Preliminary recovery experiments performed with Nanopure and tap water, with the same spiking levels, did not show significant differences (<2–5%) compared with the recoveries obtained when groundwater samples were used.

Reuse of XAD-2 resin (three times) showed the same recovery efficiency, and at the same time the amount of artefacts released decreased. Groundwaters with different conductivities (*e.g.*, 325 and 435 μS/cm) did not affect the recovery of the compounds studied, probably because they are not ionizable. Also in the range of pH values (7.50–8.09) measured in the ground waters used, no difference was noticed concerning

Table 1
Main ions, relative abundances and relative response factors (RRF, selected ion for internal standard m/z 162) of organophosphorus and triazine pesticides used for the GC–MS-SIM

Molecular mass	No.	Compound and ions (m/z and tentative identification)	Relative abundance (%)	RRF
215	1	Atrazine		1.9
		215 $[M]^+$	58	
242	2	Ethoprophos		0.7
		158 $[CH_3CH_2OPO(SH)_2]^+$	100	
303	3	Fenamiphos		1.4
		303 $[M]^+$	69	
		154 [m-CH_3, p-$CH_3SC_6H_3OH]^+$	100	
278	4	Fenthion		0.4
		278 $[M]^+$	100	
		125 $[SP(OCH_3)_2]^+$	78	
345	5	Isophenphos		1.2
		213 $[M-(CH_3)_2COCH_3CH_2O]^+$	88	
224	6	Mevinphos		1.3
		224 $[M]^+$	4	
		192 $[M-CH_3OH]^+$	23	
223	7	Monocrotophos		0.4
		223 $[M]^+$	3	
		127 $[(CH_3O)_2P(OH)_2]^+$	100	
201	8	Simazine		1.4
		201 $[M]^+$	100	

Table 2
Mean recoveries (%) and standard deviation (%) (in parentheses) of the pesticides used ($n = 3$–5 for each compound) in spiked groundwater samples using XAD-2 resin and Sep-Pak C_{18} cartridges

Pesticide	XAD-2			Sep-Pak C_{18}		
	5 μg/l	0.5 μg/l	0.1 μg/l	5 μg/l	0.5 μg/l	0.1 μg/l
Atrazine	83 (11)	82 (12)	85 (9)	81 (10)	80 (9)	78 (3)
Ethoprophos	79 (8)	76 (8)	68 (9)	95 (12)	104 (18)	103 (5)
Fenamiphos	82 (3)	78 (6)	71 (50)	90 (8)	89 (9)	92 (8)
Fenthion	81 (4)	70 (8)	63 (9)	91 (14)	88 (9)	89 (10)
Isophenphos	78 (5)	80 (5)	69 (8)	101 (10)	103 (15)	98 (13)
Mevinphos	88 (6)	89 (7)	72 (5)	96 (8)	101 (8)	95 (11)
Monocrotophos	85 (8)	82 (5)	68 (7)	89 (16)	93 (8)	90 (7)
Simazine	79 (10)	83 (15)	80 (9)	78 (7)	75 (6)	74 (5)

Water volume, 1 l. Determinations of analytes were performed by GC–NPD.

Table 3
Limits of detection (LOD) for pesticides following extraction with C_{18} cartridges and determination by GC–NPD or GC–MS-SIM

Pesticide	LOD (μg/l)	
	NPD	MS-SIM
Atrazine	0.30	0.05
Ethoprophos	0.20	0.03
Fenamiphos	0.10	0.13
Fenthion	0.08	0.04
Isophenphos	0.20	0.05
Mevinphos	0.30	0.04
Monocrotophos	0.10	0.08
Simazine	0.60	0.06

Spiking levels, 1–0.1 μg/l; water volume, 2.5 l; peak measured when signal-to-noise ratio was 5.

the recoveries. Lower recoveries were observed when we passed from a high spiking level (5 ppb) to a lower spiking level (0.1 ppb), and especially for the most lipophilic compounds such as fenamiphos, fenthion and isophenphos. The concentration of the analytes in the water did not affect the extraction recoveries of atrazine and simazine. The recovery of the adsorbed organophosphorus pesticides from the XAD-2 resin was affected by the presence of water on the resin during the elution procedure. Flushing with nitrogen, after the sample had passed through the XAD-2 column, for less than 10 min resulted in lower recoveries for ethoprophos, fenamiphos and isophenphos. The recoveries obtained in this study are comparable to those obtained in other studies with other organophosphorus pesticides [17].

The recoveries obtained when Sep-Pak solid-phase extraction was used are given in Table 2. The recoveries, especially for the organophosphorus compounds, are higher than those obtained with the XAD-2 columns. The environmental factors measured (pH, conductivity, etc.) do not vary extensively (see Experimental) so as to affect the extraction recoveries of both the triazine and organophosphorus pesticides. A study [7] concerning the effect of pH on the recovery showed that pH values between 5 and 8 gave the best recoveries (77–98%) for other organophosphorus pesticides. As the natural groundwater pH was within this range, we also obtained the optimum recoveries without adjustment of the working pH. The higher affinity of the different organophosphorus pesticides, ethoprophos, fenamiphos, fenthion and isophenphos, compared with those of atrazine and simazine can be seen in Table 2. This was also confirmed by the retention times observed when these compounds were determined using reversed-phase HPLC [18]. Triazines showed shorter retention times than the organophosphorus compounds. The use of dichloromethane as the eluent was satisfactory especially for the more lipophilic organophosphorus compounds.

Comparable extraction recoveries have been reported for other organophosphorus pesticides when the analytes were eluted from C_{18} cartridges with a mixture of ethyl acetate, *n*-hexane and light petroleum [7]. In contrast to XAD-2 extraction, with the C_{18} material cartridges we did not find significant differences in recoveries between high (5 μg/l) and low (0.1 μg/l) spiking levels (Table 3).

Comparing the two SPE materials, the use of C_{18} cartridges for preconcentration of pesticides has an important advantage concerning collection efficiency for the simultaneous determination of triazine and organophosphorus compounds in ground- and drinking water samples.

3.3. Detection systems

GC–NPD gave satisfactory results for the determination of both triazine and organophosphorus compounds. The greater sensitivity of NPD for organophosphorus compounds than for triazines makes it suitable for the determination of low concentration levels of organophosphorus pesticides in a mixture. This is evident when we compare the limits of detection (LOD) for the organophosphorus compounds with those of triazines (Table 3). The relative response factors obtained for both compound classes also indicate that NPD is inherently more sensitive to organophosphorus than to triazine compounds. This fact has been stressed by other workers [3,9].

In the SIM technique, ions for determination

were chosen on the basis of the structural characteristics of each compound and also with respect to high abundance, maximum selectivity and low susceptibility to interference from other compounds. Monocrotophos and mevinphos both have as the most abundant ion that at m/z 127. Therefore, for mevinphos another characteristic ion, with respect to its structure, was chosen (Table 1). A comparison of the results obtained by the combination of Sep-Pak C_{18} cartridges with GC–MS-SIM for atrazine, simazine and fenamiphos with those obtained with Empore C_{18} extraction discs and liquid chromatography–thermospray mass spectrometry in the positive- and negative-ion modes [12] revealed lower limits of detection when the former technique was used (Table 3 and Fig. 1C). For compounds amenable to GC conditions, the use of MS-SIM with differentially programmed mass scanning has important advantages over NPD, especially if specific ions (for each compound structure, Table 1) are selected, *i.e.*, high sensitivity and specific compound identification. GC–MS-SIM can be used for the reliable determination of pesticides, and not only for the purpose of confirmation [19].

Although liquid chromatographic systems have some advantages over GC for the determination of polar and thermally labile pesticides, these are limitations (UV adsorbability) when UV detection is used. The use of NPD (or MS) does not necessitate the inclusion of UV absorbability as a criterion, as is the case when HPLC is used [8,10]. We could determine, with sufficient sensitivity, ethoprophos using GC–NPD (Fig. 1A and Table 3) or GC–MSD-SIM (Fig. 1C and Table 3). This compound was not detectable using HPLC–UV detection [18].

We applied the combination of C_{18} cartridge extraction with both GC–NPD and GC–MS-SIM techniques to the determination of pesticides in ground- and well water samples collected in Crete. The GC–NPD analysis of a groundwater samples and also the coinjection of these sample extracts with standard compounds indicated the presence of atrazine, isophenphos and monocrotophos (Fig. 2B). GC–MS-SIM confirmed only the presence of atrazine in some of the samples, at concentrations of 0.07–0.42 μg/l. This means that any GC–NPD method which makes use of only one GC column for the identification of a large number of pesticides has a high probability of producing false-positive results. Therefore, NPD, in combination with other detection systems, is a usefull screening technique for organophosphorus and triazine pesticides. If a thermionic detector is the only available detector, confirmation through a second analysis on a capillary column of different polarity is certainly needed.

4. Conclusions

The results presented here show that capillary GC–NPD and GC–MS-SIM combined with solid-phase extraction using XAD-2 resin or Sep-Pak C_{18} cartridges have some important advantages over HPLC–UV detection for the determination of semi-polar or non-polar organophosphorus and triazine pesticides. The use of NPD and MS-SIM techniques allows the sensitive determination of the above compound classes without specific blank problems and without the inclusion of UV compound absorbability as an analysis criterion, when lability is not a limiting factor. The use of a second capillary GC column for identification purposes is considered necessary if NPD is the only available detection method.

The GC–MS-SIM technique was more suitable for the identification and determination of all the compounds examined, with very low detection limits.

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6. References

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