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Monitoring of the Pesticide Levels in Natural Waters of the Valencia Community (Spain)

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Pesticide determination at the required EC level of 0.1 μg/L in tap water, and at the 1-3 μg/L level in surface water (E.C. Council Directive 1980) is recognized as difficult and prone of errors due to the very low concentration of the compounds (Kwakman et al. 1992; Bagheri et al. 1992). On the other hand, several hundred pesticides with different physical and chemical properties may be applied for agricultural purposes. All of them, can eventually contaminate the water (Fingler et al. 1992; Miliadis 1993). Because of this, there is a need for a system providing both selectivity (identification) and sensitivity (detectability).

Sample preparation of water samples involves a change of solvent and an enrichment step to obtain the required sensibility. The change of solvent is carried out either by liquid-liquid extraction (Rodier 1984, American Public Health Association 1985) or by solid phase extraction (Font 1993). Selectivity can be obtained by using a selective GC detector, e.g., a nitrogen-phosphorus detector (NPD) (Mañes et al. 1989; Moltó et al. 1991), flame photometric detector (FPD) (Miliadis 1993) or an electron capture detector (ECD) (Mañes et al. 1990; Moltó et al. 1990; Moltó et al. 1992). However, only a particular structural group of pesticides shows adequated sensibility for each particular detector. To extend the range of chemical structures used as pesticides that could be determined in the same sample, the conection in parallel of more than one specific detector is a suitable solution (Bernal et al. 1992).

In the present study, capillary gas chromatography with simultaneous electron capture and nitrogen-phosphorus detection was used to monitor natural waters for 72 pesticides. Surface river, irrigation channel and lake water originated from various points of Valencia Community were analyzed.

MATERIALS AND METHODS

Water samples (40) were collected between February 1992 and July 1992,

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from the rivers Canyoles, Albaida, Clarià, Serpis, Polop, Belcaire, Turia and Xuquer, the lake Albufera and from the irrigation channels located in the site. These rivers, lake and irrigation channels provide the South coast franje, which is the most important agricultural zone in Valencia Community, with both, industrial and agricultural water. All the samples were collected in 2.5 L topaz glass bottles and stored at 4 °C before the analysis, which was normally carried out within 24 hr of sampling.

Ethyl acetate and n-hexane were "pesticide grade", methanol and water were HPLC grade. Preparative octadecylsilica with a size of (55-105 μm) was used. Reference standards of the 72 pesticides were purchased from commercial sources.

Pesticides were extracted from the water according to a method previously described (Mañes et al. 1989; Mañes et al. 1990; Moltó et al. 1990; Moltó et al. 1991, Moltó et al. 1992). A 0.5 g amount of octadecylsilica was inserted in a glass column (100 mm x 9 mm I.D.) with a sintered-glass coarse frit (No. 3) and covered with a plug of 0.1 g of silanized glass-wool. The column was conditioned with 5 mL of methanol and 10 mL of distilled water. After this, it was connected to a separating funnel with glass joints. A volume of 1 L of water samples was passed through the column. Vacuum by water aspiration was applied to obtain a flow rate about 40-45 mL/min. The C_{18}-bonded porous silica was then dried by drawing room air (previously filtered) through the cartridge using a vacuum. Pesticide residues were eluted with 5 mL of ethyl acetate and 5 mL of n-hexane. The organic layer was concentrated to 0.2 mL using a gentle stream of nitrogen. Samples of 2 μL were injected into the gas chromatograph.

A Konik model 2000-C gas chromatograph equipped with a splitless injector, equipped with nitrogen-phosphorus and an electron capture detectors, and a Spectra Physics SP 4290 double channel integrator was used. The injector was connected to 25 m x 0.22 mm I.D silica capillary column containing BP-5 with a 0.25 μm film thickness. The end of the column was connected by means of a Y piece of two 12 cm x 0.22 mm i.d. uncoated silica capillary pieces. Each piece is connected to one detector of the chromatograph. In this way, the injected sample after the chromatographic separation is split to two different detectors. The signals of the two detectors were simultaneously collected in the integrator. Helium was used as a carrier gas, at flow rate of 2 mL/min. The injector temperature was 260 ° C and the detector temperatures 300 °C. Splitless injection was performed at oven temperature of 50 °C. This temperature was programmed (50 ° C to 140 ° C at a rate of 30 $^{\circ}\mathrm{C}\cdot\mathrm{min}^{-1}$, held 2 min, then at 5 $^{\circ}\mathrm{C}\cdot\mathrm{min}^{-1}$ to 280 °C).

RESULTS AND DISCUSSION

The extraction method that was used is well established and validated procedure (Mañes et al. 1989; Mañes et al. 1990; Moltó et al. 1990; Moltó et

Table 1. Detection limits of the proposed method in μg/L for both detectors

Compound	ECD	NPD
HALOGENATED PESTICIDES		
Aldrin	0.004	---
Captafol	0.007	---
Captan	0.007	---
Chloranil	0.070	---
Dacthal	0.003	---
o,p'-DDD	0.009	---
p,p'-DDD	0.005	---
o,p'-DDE	0.007	---
p,p'-DDE	0.005	---
p,p'-DDT	0.007	---
Dichlobenil	0.010	---
Dicofol	0.026	---
Dieldrin	0.004	---
α-Endosulfan	0.006	---
ß-Endosulfan	0.005	---
Endrin	0.007	---
Folpet	0.088	---
Heptachlor	0.025	---
Heptachlor epoxide	0.025	---
HCB	0.015	---
Lindane	0.018	---
Metoxychlor	0.087	---
Mirex	0.055	---
Propanil	0.398	---
Trifluoraline	0.035	---
POLYCHLORINATED BIPHENYLS (BPC)		
2-PCB	1.238	---
2,2'-PCB	0.990	---
2,4-PCB	0.089	---
4,4'-PCB	0.992	---
2,4,5-PCB	0.079	---
3,3',4,4'-PCB	0.062	---
2,2',4,5,5'-PCB	0.041	---
2,2',4,4',5,5'-PCB	0.015	---
Decachlorobiphenyl	0.010	---
CARBAMATES		
Carbaryl	1.049	0.482
Carbofurane	0.711	0.100
Molinate	0.325	0.095
Pirimicarb	0.143	0.065
Vegadex	0.006	---
TRIAZINES		
Atrazine	0.143	0.100
Prometryne	0.075	0.075
Propazine	0.157	0.075
Simazine	0.317	0.100
ORGANO-PHOSPOROUS		
Chlorpyriphos	0.010	0.005
Cumaphos	0.162	0.098
Dialifor	0.027	0.048
Diazinon	0.006	0.006
Dichlorvos	0.142	0.106
Dimethoate	---	0.298
Disulfoton	0.012	0.003
Parathion	0.014	0.006
Ethion	0.007	0.002
Fentoate	0.043	0.005
Fonophos	0.005	0.002
Formothion	0.076	0.053
Fosmet	0.042	0.026
Heptenophos	0.270	0.006
Malathion	0.008	0.008
m-Chlorpyriphos	0.009	0.004
Methylparathion	0.008	0.008
Mevinphos	0.208	0.217
Piridafenthion	0.033	0.028
Profenofos	0.017	0.018
Pyrazophos	0.085	0.024
Quinalphos	0.059	0.007
Sumithion	0.020	0.002
Tetrachlorvinphos	0.034	0.034
Tiometon	0.060	0.019
Triazophos	0.010	0.049
Trichlorfon	0.901	2.431
Trithion	0.009	0.006

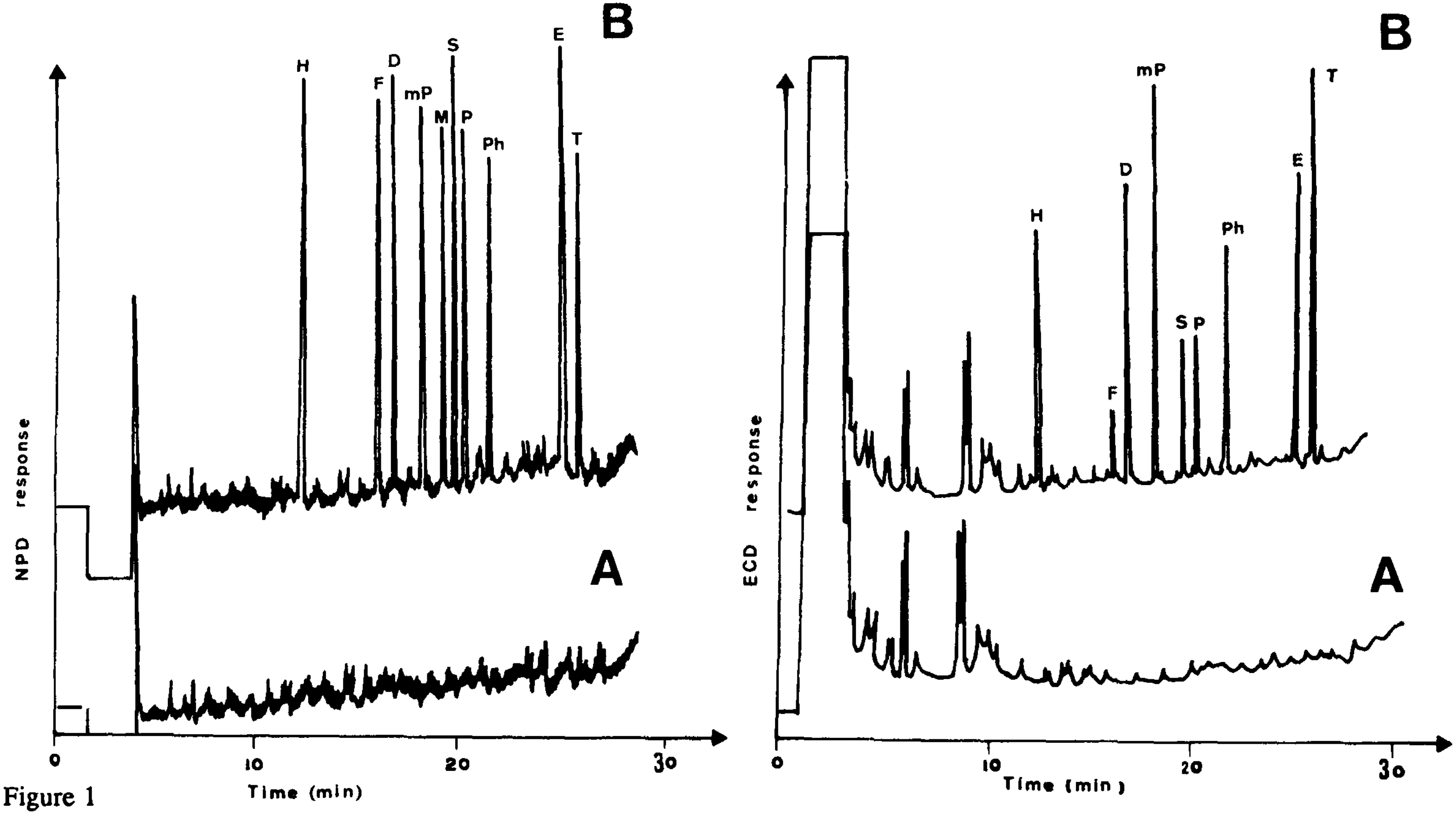

Figure 1
GC-NPD-ECD Chromatograms of (A) 1 L of Albufera Lake water (B) 1 L of Albufera Lake water spiked with 10 OPP's (concentration in ng/L): heptenophos (H; 150), fonofos (F; 30), disulfoton (D; 600), methyl parathion (mP; 30), malathion (M; 30), sumithion (S; 140), parathion (P; 16), phentoate (Ph; 12), ethion (E;30) and trithion (T; 277).

al. 1991). A large enrichment factor can be obtained by concentrating the analytes from 1000 mL sample, into, 0.2 mL of ethyl acetate. Analyte losses by poor extraction or due to the breakthrough on the octadecylsilice column is the major problem. The recoveries for 62 of the 72 compounds were larger than 89 %. For Dichlobenil, Propanil and Disulfoton recoveries were 67, 78 and 70 % respectively. For Chloranil, Vegadex, Carbaryl and Mevinphos recoveries were between 40 and 45 %. Dimethoate and Trichlorfon were recovered in a 10 %. These low recoveries were due to breakthrough during preconcentration (Mañes et al. 1989; Kwakman et al. 1992). Diminishing the sample volume (to approximately 100 μL) improved the recoveries of these compounds (Mañes et al. 1989), but not their detection limits which obviously, will be much higher than for the rest of the pesticides.

The linearity of the total procedure was tested over the concentration range of 0.1 μg/L (when was possible) to 100 μg/L (5 points). Regression coefficients obtained were between 0.9999 and 0.9965. The repeatability found using the proposed method at the 1-2 μg/L was better than 12 % for all the compounds (except Dimethoate, Dichlorvos and Vegadex).

The detection limits in Table 1 show that the required sensitivity of 3 μg/L for natural waters can easily be obtained. Moreover, sensitivity 0.1 μg/L for water intended for human consumption is attained for most of the pesticide residues. Only Carbaryl, Dimethoate, Propanil, Mevinphos, Trichlorfon and three polychlorinated biphenyls of low chloro contain can not be detected at 0.1 μg/L. These detection limits were calculated using HPLC-grade water and tap water.

Other factors that can affect the efficacy of the extraction are the pH of the water, the presence of surfactants, the amount and composition of the organic matter (Moltó et al. 1990; Moltó et al. 1991). These factors are more variable in natural water than in HPLC-grade water or tap water.

To demonstrate the suitability of the method for its application to natural waters, different surface waters spiked and without spiking were analyzed. The number and height of inteferring peaks are much larger than in HPLC or tap water. However, detection and identification of the analytes are possible at this low level and no adverse effects over the recoveries are observed. The chromatograms obtained from Albufera lake water samples, which is one of the dirtier samples, without spiked and spiked with 10 organophosphorus pesticides (OPP's) with the two detectors are shown in figure 1. These 10 OPP'S. give response in the two detectors used, but the intensity is different. This fact, is used for the correct identification.

The combination of the solid phase extraction and the GC with simultaneous NP and EC detection offers excellent sensitivity and selectivity in the identification and ng/L level determination of all the pesticides tested in surface waters performing only one injection of the extract in the GC. Identity

Table 2. Concentrations range of the pesticides in different natural water from the Comunitat Valenciana (Spain).

PESTICIDE	CONCENTRATIONS RANGE (μg/mL)	SAMPLE NUMBER
HALOGENATED		
Captan	0.008-0.036	No. 13, 17, 25
Captafol	0.008	No.23
o,p'-DDD	0.010-0.027	No.8, 11
o,p'-DDE	0.007	No. 13
α-Endosulfan	0.024-0.353	No. 12, 14
ß-Endosulfan	0.012-0.112	No. 12,14
Folpet	0.153-6.525	No.7, 11, 15, 33
Lindane	0.015-0.537	No. 14, 17
POLYCHLORINATED BIPHENYLS (BPC)		
Aroclors (as 1248)	0.010-0.313	No. 18, 19, 20, 21, 34
CARBAMATES		
Carbaryl	1.231-6.484	No.7, 8, 10, 13, 15, 16
Carbofuran	0.543-1.632	No. 10, 25
Molinate	1.073	No. 10
Pirimicarb	0.067-0.094	No. 5, 6
Vegadex	2.247	No. 14
TRIAZINES		
Atrazine	0.183-1.113	No.15, 24, 25
Prometryne	0.176	No. 12, 14
Propazine	0.444	No. 15
Simazine	0.308-0.629	No. 7, 14
ORGANO-PHOSPHORUS		
Chlorpyriphos	0.010	No. 25
Cumaphos	0.152	No. 4
Diazinon	0.007-0.032	No. 1, 10
Disulfoton	0.057-0.103	No. 14, 16
Ethion	0.002-0.010	No. 5, 10, 16, 17, 35
Fonofos	0.004	No. 6
Fosmet	0.045-0.264	No. 24, 25
Formothion	0.072	No. 24
Malathion	0.008-0.16	No. 1, 17
Methylchlorpiriphos	0.009	No. 13
Methylparathion	0.081-0.084	No. 17, 19
Parathion	0.012-0.176	No. 9, 10, 11, 12, 14, 15, 16, 17
Piridafenthion	0.036-0.065	No. 9, 11, 12, 13, 15
Profenophos	0.024-0.069	No. 8, 9, 11, 12
Quinalphos	0.012-0.063	No. 10, 25
Sumithion	0.005-0.030	No. 5, 12, 38
Tetradifon	0.025	No. 10
Tetrachlorvinphos	0.036-0.074	No. 12, 15
Triazofos	0.069-1.134	No. 7, 14, 24
Trition	0.021-0.585	No. 8, 15, 16, 25, 33

confirmation requires use of a second column of different polarities or the fortification of a subsample with the suspect pesticide residue. The second method was used for confirmed the identity of the pesticides when the method was applied to real samples.

Forty surface water samples collected from the rivers, lakes and irrigation channels were analyzed according to the method. Table 2 summarizes the pesticides found, the concentration range and the number of samples where that pesticide residue appears.

No pesticide residues were found in 15 of the 40 water samples analyzed. The samples usually contain more than one pesticide residue. The mean number of pesticide residues detected per sample is about 4 and the major number is 9. The samples with major number of pesticide residues are from the territory of Sueca which is the most important agricultural area.

In 5 samples arochlors were detected, compounds analogous to some pesticides but used in industry. All these samples were collected near of industrial complexes.

The most usual compound is Parathion that appears in 8 of the 40 samples analyzed. Follow by Carbaryl that appears in 6 samples. It could be observed that the most abundant pesticide residues in water are organophosphorus pesticides, carbamates and triazines. These pesticide have an agricultural used as insecticides and herbicides predominantly. The crops in the studied area are orange and rice.

The presence of organohalogenated pesticide residues is lower. The most common are fungicide residues like captan or folpet. Folpet shows the highest concentration 6.525 μg/L. This value is higher than the EC limit of 3 μg/L established for natural water.

The EC limit is reached only in 3 samples analyzed, in 2 of them the pesticide is Folpet and in the other Carbaryl. All the other samples are within the EC limit.

There are no persistent organochlorine pesticide residues, whose use has been forbidden, only small amounts of o,p'-DDE and p,p'-DDD that are products from the DDT metabolism have been detected.

These results indicate that the pollution in natural waters from the Comunitat Valenciana are caused by the agricultural and industrial activities. Satisfactorily, the levels of pesticides found are in the most cases lower than the established tolerance of the EC. Needless, pesticide residue monitoring program should be implanted to improve the quality of the surface waters.

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