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Monitoring of Organophosphorus Insecticides in the Guadalete River (Southern Spain)

C. Gómez-Gómez, M. I. Arufe-Martínez, J. L. Romero-Palanco,
J. J. Gamero-Lucas, M. A. Vizcaya-Rojas

Department of Legal Medicine and Toxicology, Faculty of Medicine, University of Cádiz, Cádiz 11003, Spain

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During the last thirty years, organophosphorus insecticides have been commonly used as an alternative to organochlorine compounds for pest control. These chemicals are included in several priority lists of pollutants in Europe due to their worldwide consumption, their high toxicity for biotic systems and the probability of their being discharged into the aquatic environment (Barceló 1993). In fact, previous studies have reported their presence in surface and ground water (Monteoliva and Augustin 1985; Richards et al. 1987; Pionke et al. 1988). It results from different migration pathways: erosion of contaminated lands by rainfall or wind, leaching from soil into ground water, spray drifting onto water surface, or accidental spillage (Miles and Harris 1978).

The Cádiz Countryside is an agricultural area located in the watershed of the Guadalete River situated in the South of Spain. Continuous pesticide application, aquifer abundance and drainage of irrigated lands into the river increase the agricultural water pollution risk in the zone. In order to survey the presence of certain organophosphorus pesticides in surface water, the Guadalete River was monitored, in this study, during the agricultural annual period from the middle of September 1990 to the middle of August 1991.

MATERIALS AND METHODS

The Countryside of Cádiz spreads over 240,872 ha. It consists mainly of croplands, but also contains important industries and urban areas. An extensive irrigation system of about 117 km that depends on the Guadalcacín Reservoir drains into the Guadalete River (Figure 1).The seasonal irrigation begins in April and finishes in October. The largest rainfalls in 1990-1991 occurred in autumn and winter with a maximum in February (160.9 mm). Some of the most frequently applied insecticides in this period were the organophosphorus compounds: Trichlorfon, Phorate, Dimethoate, Chlorpyrifos, Parathion-Methyl and Parathion.

Correspondence to: M. I. Arufe-Martínez

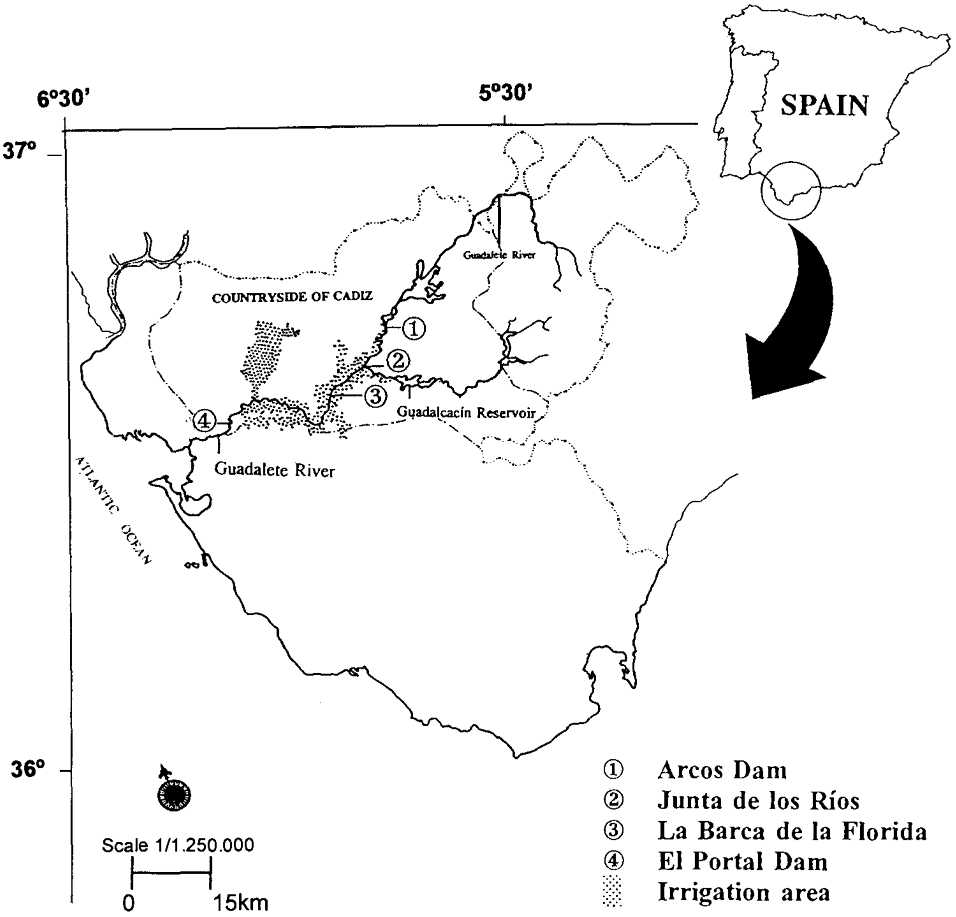

Figure 1. Location map showing water sampling stations in Cádiz Contryside (Southern Spain).

Samples were collected at monthly intervals from four stations (Figure 1) to cover a wide range of drained areas. Station 1 (Arcos Dam) served as a control because chemical pesticides have not been applied to that zone. On the contrary, station 4 (El Portal Dam) received strongly polluted water coming mainly from urban and industrial wastes. Sampling was conducted during the days of rainfall which correspond with those of maximun runoff. Three replicate water samples were collected, placed into 1 L amber glass bottles and refrigerated at 5 °C until extraction. For each monthly sampling a distilled water blank was run. Prior to analysis samples were filtered and pH was measured.

One-liter river (or distilled) water sample was pretreated following an established multirresidue method for LLE (Rodier et al. 1984), using petroleum ether:diethyl ether and methylene chloride. The final volume was adjusted to 0.5 mL so that a high concentration ratio (1:2000) was achieved. Pesticide recoveries were calculated as mean as five analysis of 1 L distilled water spiked with the target pesticides at levels between 0.5-5 µg/L.

The analysis was carried out in a Hewlett-Packard 5890 series II gas chromatograph equipped with a nitrogen-phosphorus detector. Data acquisition and processing were performed by means of HP 3365 ChemStation Software. Two fused-silica capillary columns were coupled for pesticide separation: a) a 25 mx0.32 mm id (0.52 µm) Ultra-2® (nonpolar phase); b) a 25 mx0.25 mm id (0.25 µm) SGE-1701® (intermediate polar phase). Helium was used as carrier gas at a flow of 1.3 mL/min and as make-up gas at 29 mL/min. The detector gases consisted of air at 95 mL/min and hydrogen at 3.2 mL/min. The injector and detector temperatures were 280 and 300 °C, respectively. A 1 µL volume of the extracts was injected in splitless mode with the split valve closed for 0.8 min. The oven programmed temperatures were: a) Ultra 2® column, from 50 °C for 0.8 min, at 30 °C/min to 140 °C for 2 min and a further heating at 10 °C/min to 280 °C for 2 min; b) SGE 1701® column, from 50 °C for 0.8 min, at 20 °C/min to 150 °C for 2 min and a further increase at 10°C/min to 240 °C for 9 min.

Two of the triplicates carried out for each sample were analyzed in the Ultra 2® for tentative identification, the third one in the SGE-1701® column for confirmation. A method blank (1 L of high purity water) was analyzed with each set of samples to avoid possible interferences. Peaks were identified by absolute retention times and quantification was achieved by the external standard method using peak areas.

Recovery was estimated by analysing fortified distilled water samples and comparing peak areas to those of the calibration standards. The six target pesticides of 94-99% purity were obtained from Chem Service.

Analytical procedure requirements as well as detection limits were conditioned by the maximum admissible concentration (MAC), 0.1 µg/L, established in the 80/778/EEC Directive on the Quality of Water Intended for Human Consumption.

RESULTS AND DISCUSSION

Attempts to separate the six organophosphorus compounds failed in the primary column where Chlorpyrifos and Parathion overlapped (Figure 2). However, between-day retention time reproducibility for Ultra 2® (C.V.≤0.73%, n=51) and SGE-1701® (C.V.≤0.31%, n=15) columns showed that absolute retention times served for identification purposes. In the second column, both differences in elution order and very good resolution

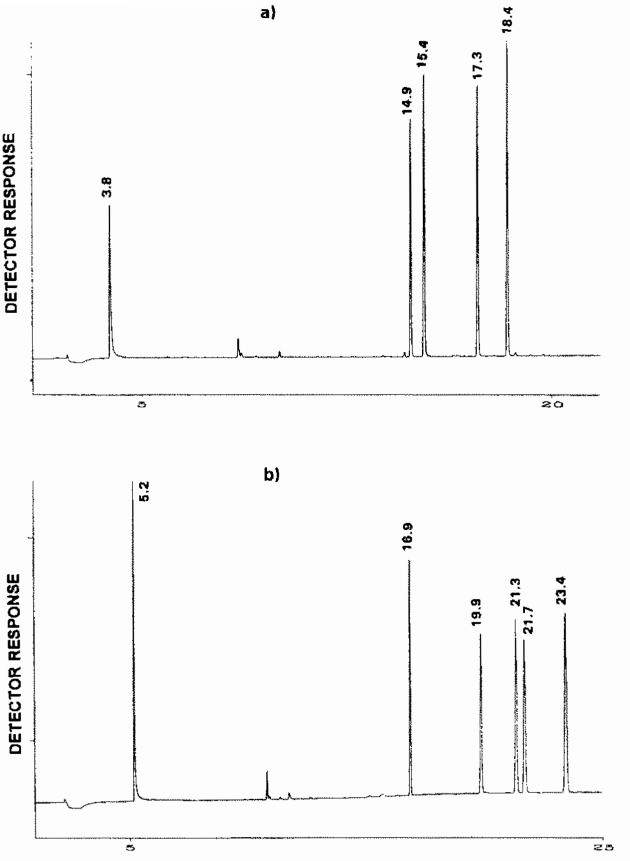

Figure 2. Chromatograms for the separation of six OPs. a) in Ultra 2® column, in order of elution: Trichlorfon, 10 ng; Phorate, 10 ng; Dimethoate, 10 ng; Parathion-methyl, 10 ng; Parathion, 10 ng (Chlorpyrifos elutes at the same retention time). b) in SGE-1701® column, in order of elution: Trichlorfon, 50 ng; Phorate, 5 ng; Dimethoate, 10 ng; Chlorpyrifos 10 ng; Parathion-Methyl, 20 ng; Parathion, 10 ng.

for all compounds were achieved, which allowed the use of this stationary phase for confirmation.

Reproducibility of detector response and linearity were found to be satisfactory with both chromatographic systems. The NPD performance showed reasonable within-day and between-day precision with relative standard deviations ≤9% and ≤18%, respectively (Ripley and Braun 1983). The detection limits were set at levels ranging between 18-107 pg depending on the compound and on the column. Trichlorfon offered the worst chromatographic performance: a wider response variation (18%

relative standard deviation with both columns) and a higher detection limit (180 pg in Ultra 2® and 997 pg in SGE-1701®) because it exhibits peak tailing and elutes early, near to the solvent front. However, these results agreed with others established in the literature (Ambrus et al. 1981; Holland and Greenhalgh 1981; Moltó et al. 1991).

Mean recoveries were between 91.8% and 103.4% (C.V. ranged from 8-17%), except for Trichlorfon with a recovery of 41.3% and C.V. of 51%. Comparing the LLE method (Rodier et al. 1984) with a SPE procedure (Mañes et al. 1989; Moltó et al. 1991) used in a preliminary study, it was found that SPE required less solvent consumption, was faster and easier to perform than LLE, but it only allowed to recover quantitatively four of the six target organophosphorus insecticides. Trichlorfon and Dimethoate possess a polar group (-OH and -CONH-) which could form hydrogen bonding to active sites on C_{18} silica surface or to water, preventing quantitative yield (Loconto and Gain 1989; Mallet and Mallet 1989).

Table 1 summarizes the pesticide residues either tentatively identified or confirmed in the 48 water samples collected (in triplicate) from the Guadalete river in the period of study. The pH of these samples was neutral or slightly alkaline with values oscillating between 7.16 and 7.90. After extraction, the first screening of duplicate eluates in the Ultra 2® column suggested the presence of residues of Dimethoate, Parathion-methyl and Parathion and/or Clorpyrifos only in 10 of the 48 (x2) samples analyzed. Analysis of the corresponding triplicates in the SGE-1701® column only confirmed the presence of Parathion in the samples of November 1990 (0.204 µg/L) and January 1991 (0.201 µg/L) from station 2, and Dimethoate in samples taken in June from stations 2 (0.082 µg/L) and 3 (0.211 µg/L). Residue data represent the average concentration of the triplicates, and have been adjusted to 100% recovery using the mean percentage recovery for each compound. Figure 3 shows the chromatograms corresponding to environmental water sampled in November 1990 from station 2. No interfering peaks were found in distilled water blank runs.

The appearance and nonappearance of the studied pesticides can be explained by examining geoclimatic characteristics of the Guadalete watershed, the physicochemical properties and the frequency of applications in conjunction with the efficiency of the analytical procedure. Actually, obtained data suggest several preliminary conclusions.

Organophosphorus insecticides were positively identified in stations no. 2 and 3 located in areas of intensive pesticide use. Parathion, which exhibits moderate persistence, slight water solubility (<24 mg/L) and it is strongly adsorbed onto soil particles, was detected in November and January samplings at concentrations exceeding the MAC. This compound

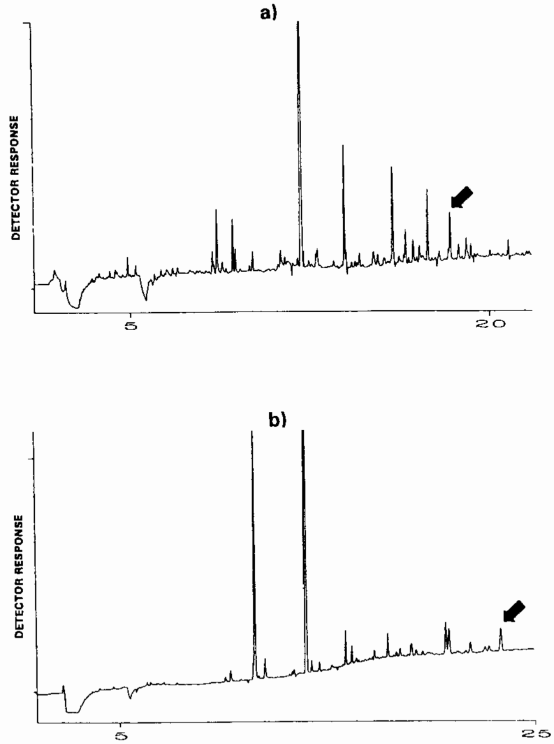

Figure 3. Chromatograms of an extract of environmental water taken in November 1990 from station 2, which contained 0.204 μg/L Parathion. a) in Ultra 2® column. b) in SGE-1701® column. Parathion is indicated with the arrows.

Table 1. Pesticide residues detected between September 1990 and August 1991 in the Guadalete River.

	Station 1	Station 2	Station 3	Station 4
Nov. 1990		P[a]/C (0.204 μg/L)		
Jan. 1991		P[a]/C (0.201 μg/L)		
Feb. 1991				D,P/C
Mar. 1991				D,P/C
Apr. 1991			D,P/C	D,M,C/P
Jun. 1991		D[a],P/C (0.082 μg/L)	D[a] (0.211μg/L)	
Aug. 1991				D,P/C

[a] Pesticide residue confirmed in the extract injected in the SGE-1701® column.
D: Dimethoate; P: Parathion; M: Parathion-methyl; C: Chlorpyrifos.

could have been transferred from contaminated soil to river water after rainfall and runoff events that occurred in these months (Miles and Harris 1978; Richards and Baker 1993).

Dimethoate was frequently sprayed on sugar beet in late spring 1991 for plant louse and sucking insect control. Although its characteristics are quite similar to those of Parathion, a rapid degradation is expected in presence of metal ions in soil (Valenzuela and Bernalte 1985). Therefore, its appearance in water samples collected in June, immediately after application, can be related to primary discharge into the Guadalete basin from drainage of irrigated lands. The residue levels exceeded the MAC only in station 3.

Remaining compounds (Trichlorfon, Phorate, Chlorpyrifos and Parathion-methyl) have not been detected or confirmed as can be explained by a low persistence or in the case of Trichlorfon due also to analytical limitations. Microbiological and physicochemical parameters suggest a high grade of water pollution in station 4 (Galán et al. 1988; Galán et al 1989). The presence of cationic detergents and abundance of organic matter could explain the absence of pesticide residues in that location.

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