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Organochlorine Pollutants in Water, Soils, and Earthworms in the Guadalquivir River, Spain

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Organochlorine compounds (insecticides and polychlorinated biphenyls) are known to mantain their stability in the aquatic environment for long periods. DDT and cyclodiene insecticides were used widely in Spain until their use was banned in 1976; DDT and its degradation products are still found in environmental samples (Hernández et al. 1988). Since DDT has been legally restricted for use, lindane has become important as a substitute for DDT.

This study has been carried out along Guadalquivir River, Spain. This river runs across an agricultural area where pesticides are used extensively. The Guadalquivir basin is the most economically important area of the South of the Iberian Peninsula; its economic importance stems from its proximity to a major metropolitan areas (Cordova, Seville), which indicates the presence of numerous urban, commercial, and industrial locations in the vicinity of the sampling stations.

The purposes of this investigation are: 1) to determine the levels of organochlorine compounds in water, soils, and earthworms sampled in ten stations of the Guadalquivir River; 2) to evaluate biological accumulation of pollutants studied within the food webs; 3) to evaluate regional patterns and time trends of residues.

MATERIALS AND METHODS

Location of sampling stations is shown in Figure 1. All stations were located in the shore of Guadalquivir River. Ten stations were selected; collection sites were selected near suspected sources of agricultural or industrial pollution. All samples were collected 29, 30, and 31 May 1990. Station 1 was situated near of source of the Guadalquivir River; station 10 was situated in the delta of the Guadalquivir River (36° 47' Noth latitude and 6° 21' West longitude).

Water samples (3 L at a depth of 25 cm) were collected in glass bottles. Soil samples were collected by manual coring (0–5 cm) from the moist shore and stored in glass jars. Earthworms (Lumbricus terrestris L.) removed from these soils, were placed in petri dishes

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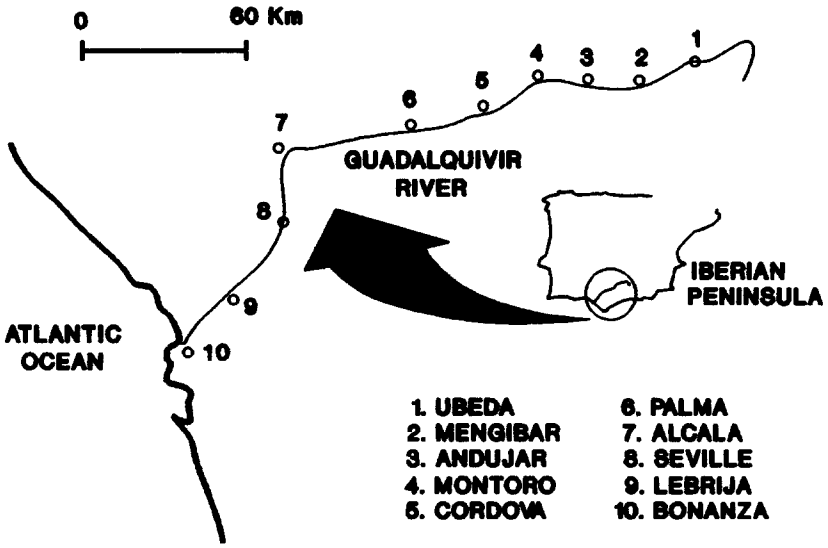

Figure 1. Study area and sampling locations

on moist filter paper 3 d to void their gut. It was impossible to obtain earthworms in sampling station 10. Soil samples were dried at 65°C for 5 d and ground using a stainless steel grinder.

Extraction, purification, and analysis of organochlorine insecticides and PCBs present in water samples were carried out according to a method previously described (Rico et al. 1989). The rest of the samples were homogenized, extracted, cleaned and analyzed following methods already described (Hernández et al. 1988; Hernández et al. 1989). The eluates were analyzed with a Hewlett-Packard 5890 gas chromatograph equipped with Ni 63 Electron Capture Detector. A 30 m long capillary column covered with RSL-200 was used. Chromatographic conditions as follow: detector 280°C; injector 300°C; temperature programme, isothermal phases at 180°C (1 min) and 250°C (30 min), with intermediate increase rate of 2°C/min. Peaks were identified on the integrator by retention times; tolerance allowed was ± 0.05 min. The peaks were measured by area counts given by the integrator (minimum count 500).

Identification and quantitation of chlorinated compounds was accomplished using reference solutions of: α-benzenehexachloride (α-BHC) 0.011 ng/µL, ß-benzenehexachloride (ß-BHC) 0.012 ng/µL, lindane 0.017 ng/µL, δ-benzenehexachloride (δ-BHC) 0.013 ng/µL, heptachlor 0.025 ng/µL, heptachlor epoxide 0.017 ng/µL, aldrin 0.023 ng/µL, dieldrin 0.045 ng/µL, p,p'-DDE 0.050 ng/µL, p,p'-TDE 0.094 ng/µL, p,p'-DDT 0.148 ng/µL, dichlorobenzophenone 0.114 ng/µL, and PCBs (as Aroclor 1260) 0.896 ng/µL. Duplicates were carried out for all samples. Minimum detection limit was 0.01 µg/kg. Recoveries of organochlorine compounds ranged from 81-94%, but the residue data in the Table 1 were not adjusted on the basis of these recoveries. All

the residues, including water, are expressed as µg/kg.

RESULTS AND DISCUSSION

Results given in Table 1 present the concentration levels of organochlorine insecticides and PCBs found in water samples from ten collection sites in the Guadalquivir River during May 1990. Presence of ß and δ-BHC was found in all the samples analyzed, lindane was detected in 40% samples. The mean concentration of total BHC (lindane + ß-BHC + δ-BHC) was 0.054 µg/kg (range 0.009-0.137). Presence of dichlorobenzophenone and p,p'-DDE was found in 90 and 80% samples analyzed, respectively. The mean concentration of total DDT (dichlorobenzophenone + p,p'-DDE) was 0.007 µg/kg (range 0.001-0.033). No residues of other chlorinated insecticides included in the analytical survey were detected (α-BHC, aldrin, dieldrin, heptachlor, heptachlor epoxide, p,p'-TDE, and p,p'-DDT). PCBs occurred in all water samples; the mean concentration was 0.141 µg/kg.

The residue levels of the total DDT are still low compared with the permissible levels in the ground water established by Ministry of Works of Spain (25 µg/L), however, in 40% collection sites the residue levels of the total BHC are higher than those established by Ministry of Works of Spain (0.05 µg/L). W.H.O. (1976) estimated that nonpolluted fresh waters for PCBs should contain not more than 0.5 ng/L up to 5 ng/L, 50 ng/L for moderately polluted rivers and 500 ng/L for highly polluted rivers. Accordingly, Guadalquivir River is moderately polluted for PCBs.

Our results show that the average total BHC (54 ng/kg), total DDT (7 ng/kg), and PCBs (141 ng/kg) of the water samples studied are higher than those reported by Murray et al. (1981) (0.38 ng/kg for total DDT and 3.1 ng/kg for PCBs) in water from Galveston Bay, Texas, than those assumed by El-Dib and Badawy (1985) (0.1-16.5 ng/kg for total BHC, 8.0-54.1 ng/kg for total DDT, and 6.8-48.2 ng/kg for PCBs) in water for Nile River and those shown by Rihan et al. (1978) (0.08 ng/kg for total BHC and 10 ng/kg for total DDT) in streams and lakes of Northern Mississippi. However, our results are lower than those reported by Caceres et al. (1985) (440-1,416 ng/kg for total BHC and 207-760 ng/kg for total DDT) in Sao Paulo, Southern Brazil. The values reported in this study fall within the range reported by Achari et al. (1975) (1.2 ng/kg for total BHC and 37.7 ng/kg for total DDT) in Georgetown County, South Carolina.

Concentrations of total BHC, total DDT, and PCBs detected in soil samples from ten collection sites in the Guadalquivir River are given in Table 1. Total BHC (α-BHC + ß-BHC + lindane + δ-BHC) ranged from 0.66 to 2.49 µg/kg with a mean concentration of 1.44 µg/kg; α-BHC was detected in 50% samples, ß-BHC in 80%, lindane in 70%, and δ-BHC in 90% samples. Total DDT (p,p'-DDE + p,p'-TDE + p,p'-DDT + dichlorobenzophenone) ranged from 3.49 to 46.30 µg/kg with a mean concentration of 18.18 µg/kg ; p,p'-DDE and p,p'-TDE were present in all soil samples, dichlorobenzophenone was detected in 90% samples, and p,p'-DDT in 70% samples. No residues of aldrin,

Table 1. Levels of organochlorine compounds, expressed in µg/kg, in samples collected in the shore of Guadalquivir River.

WATERS			
Site	total BHC	total DDT	PCBs
1	0.106	0.006	0.152
2	0.066	0.001	0.085
3	0.045	0.033	0.178
4	0.048	0.010	0.180
5	0.137	0.005	0.222
6	0.015	0.002	0.119
7	0.087	0.002	0.124
8	0.017	0.002	0.098
9	0.010	0.002	0.109
10	0.009	0.005	0.145
Mean ± S.D., all sites	0.054±0.044	0.007±0.010	0.141±0.043
SOILS*			
Site	total BHC	total DDT	PCBs
1	1.121	15.230	7.418
2	0.776	12.600	19.334
3	2.495	35.170	7.162
4	2.079	46.037	14.872
5	2.181	13.873	5.646
6	0.666	3.490	3.398
7	1.489	15.075	4.458
8	0.759	8.830	15.889
9	1.406	17.241	38.066
10	N.A.	14.294	5.757
Mean ± S.D., all sites	1.441±0.678	18.184±12.70	12.200±10.60
EARTHWORMS			
Site	total BHC	total DDT	PCBs
1	27	771	94
2	164	1,060	355
3	30	799	138
4	42	3,552	317
5	69	840	1,315
6	69	813	1,355
7	108	907	1,093
8	19	384	3,759
9	74	202	1,233
10	N.A.	N.A.	N.A.
Mean ± S.D., all sites	67±46.15	1,036±979.9	1,073±1,134

S.D. = Standard Deviation; * = Dry weight; N.A. = Not Analyzed.

Table 2. Trends in organochlorine residues in water and soil of the Guadalquivir River.

	WATER			
	*1975 (11)	**1990 (10)	F	α
Total BHC	0.089±0.094	0.054±0.044	1.141	0.299
Total DDT	5.131±4.114	0.007±0.010	15.519	0.001
PCBs	0.806±0.436	0.141±0.043	23.110	0.000
	SOIL			
	*1975 (11)	**1990 (10)	F	α
Total BHC	22±9.21	1.441±0.678	50.632	0.000
Total DDT	138±74.26	18.18±12.70	25.472	0.000
PCBs	336±170.7	12.20±10.60	35.666	0.000

Concentrations in µg/kg. * = Survey conducted by Hernández et al. (1976); ** = This study. ( ) = Number of samples.

dieldrin, heptachlor, and heptachlor epoxide were detected in any of the soil samples. PCBs occurred in all samples; PCBs concentration ranged from 3.39 to 46.03 µg/kg with a mean concentration of 12.20 µg/kg.

Our results show that the average total BHC (1.44 µg/kg) total DDT (18.18 µg/kg), and PCBs (12.20 µg/kg) of the soil samples studied are higher than those reported by Murray et al. (1981) (0.21 µg/kg for total DDT and 1.1 µg/kg for PCBs) in sediment from Galveston Bay, Texas; however, our results are lower than those reported by Wan et al. (1989) (240-870 µg/kg for total DDT) in soils used for vegetable and tropical fruit production in New South Wales (Australia) and those shown by Saxena et al. (1987) (1,430-1,670 µg/kg for total DDT) in soils of 50 sites surrounding a DDT manufacturing factory in Delhi (India).

In Table 2 overall average of total BHC, total DDT, and PCBs in water and soil samples of Guadalquivir River were compared with those obtained in a similar investigation of the same sites in 1975 (Hernández et al. 1976). It is evident from the present data that water and soil samples residues have shown a downward trend from 1975; thus, the residue levels of the studied compounds in water declined 1.6 fold fot total BHC, 733 fold for total DDT, and 5.7 fold for PCBs. In soils the residue levels declined 15.3 fold for total BHC, 7.6 fold for total DDT, and 27.6 fold for PCBs. In order to verify these assertions an analysis of variance (ANOVA) was used: (a) No significant differences could be observed in total BHC in water ($\alpha > 0.05$); (b) significant differences could be observed in total DDT and PCBs in water and in total BHC, total DDT, and PCBs in soil ($\alpha < 0.05$). The ban on agriculture use of organochlorine insecticides in Spain may be the reason for decrease in the

concentration of total BHC and total DDT recorded in the present study.

Concentrations of total BHC, total DDT, and PCBs detected in earthworms from nine collection sites in the Guadalquivir River are given in Table 1. Total BHC (α-BHC + lindane + δ-BHC) ranged from 19 to 164 μg/kg with a mean concentration of 67 μg/kg; α-BHC and ß-BHC were present in all samples; lindane was present in 78% samples. Total DDT (p,p'-DDE + p,p'-TDE + dichlorobenzophenone) ranged from 202-3,552 μg/kg with a mean concentration of 1,036 μg/kg; p,p'-DDE was detected in all samples, p,p'-TDE in 78% samples and dichlorobenzophenone in 44% samples. No residues of ß-BHC, aldrin, dieldrin, heptachlor, heptachlor epoxide, and p,p'-DDT were detected. PCBs occurred in all samples; PCBs concentration ranged from 94 to 3,759 μg/kg with a mean concentration of 1,073 μg/kg.

Our results revealed considerable variations in residue levels of the organochlorine insecticides and PCBs according to the sampling sites. Thus, maximum residue levels of total BHC and total DDT in waters, soils, and earthworms were found in the sampling stations 2, 3, and 4; this area represents one of the most productive agricultural location in the Guadalquivir River: highest concentrations of residue levels in sampling stations 2, 3, and 4 reflect the extensive use of organochlorine insecticides before the ban of these compounds. By contrast, highest concentrations of PCBs were found in sampling stations 5 (water), 9 (soils), and 9 (earthworms). These stations are located in the area round Cordova and Seville, metropolitan areas with presence of numerous urban, commercial, and industrial activities; therefore, the effect of anthropogenic inputs on these sampling stations is expected to be high.

The data obtained in this study indicate an accumulation of organochlorine compounds in soils and earthworms relative to water concentrations. In effect, the average concentration factor, defined as the ratio of the concentration in soils or earthworms to concentration in water is 30.4 and 1,267 for total BHC, respectively; 4,161 and 219,700 for total DDT, and 68.1 and 4,310 for PCBs. Likewise, there is bioaccumulation of organochlorine compounds in earthworms relative to soils (41.7 for total BHC, 52.8 for total DDT, and 63.3 for PCBs). Some regulatory authorities such as the Japanese Ministry of International Trade and Industry, consider that chemicals with bioconcentration factor greater 1,000 may represent an environmental hazard (Connell 1990). Using these criteria, a potential environmental hazard may exist with total BHC, total DDT, and PCBs in earthworms. So then residue levels of the studied organochlorines in the river may affect aquatic life and lead to their accumulation into the food chain (Menzie 1972, Moore and Ramamoorthy 1984).

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