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HCH and DDT Residues in Drinking Water from the South of Spain, 1991-1994

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South of Spain is an agricultural area where pesticides are used extensively (Hernández et a1.,1976). The combination of relatively large rural population density with intensive agriculture means that the large usage of pesticides and agricultural chemicals has a potential environmental impact (Ang et al., 1989).

Efforts have been made to check the quality of local drinking water supplies and the risk of contamination by pesticides, particularly the organochlorine group. It is known that organochlorine pesticides may pass through food chain and drinking water and lead to an accumulation of residues in environmental samples (WHO, 1992).

Present study is the result of a survey of residues of lindane and its isomers and also DDT and its metabolites in drinking water supplies from the South of Spain. Samples were collected trimonthly from water treatment plants (1991-1994). There is to say that during those years, South of Spain experienced a severe period of drought, so water from Guadalquivir river, main river of the area, was used for human consumption.

MATERIALS AND METHODS

Water samples came from different water treatment plants which provide drinking water to Seville (main town of the area) and the little towns which surround it. Samples were protected from light by storage in 2 5-L amber glass bottles and on arrival in the laboratory were stored in a 4°C cold room. Each sample was analysed for the presence of HCH and DDT residues.

All glassware were rinsed before use with acetone and dried before use. Rinsings were checked in order to see if they were adequate to clean-up glassware. Reagents used were analytical grade and standards were purchased from Supelco.

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Stock solutions (1000 and 100 µg/mL) and working solutions (1,0,1 and 0.01 µg/mL) of lindane (γ-HCH), α-HCH, β-HCH, 4,4-DDE, 4,4'DDE, 2,4'-DDT and 2,4'DDD were prepared in acetone according to the standard practices (Chau and Lee, 1982).

500 mL of water were extracted using solid phase extraction (SPE) with pre-packed reverse phase C_{18} (octadecylsiloxane) bonded silica cartridges (Baker, 1982). Columns were previously conditioned with 6 mL of n-hexane:diethylether (l:l), 6 mL of HPLC grade methanol and 10 mL of deionized water. Pesticides were eluted with 1.5 mL of n-hexane:diethylether (1:1).

Organochlorine pesticides were analysed using a ^{63}Ni ECD (electron capture detector) fitted on a Hewlett-Packard model 5890 chromatograph. The 25m x 530µ internal diameter column had phenylmethylcyanopropil silicone as stationary phase. The operating conditions were: injector and detector temperatures 250 and 300°C respectively, carrier gas (H_2) flows 20 mL/min and make-up gas flow (N_2) 30 mL/min, oven temperature 80°C for 1,2 minutes, increasing by 25°C/min to 175 °C increasing after by 2.5°C/min to 225°C and finally by 10 °C/min to 300°C, remaining at this temperature for 10 minutes. A CPSil-8CB column (25m x 530 µ i.d.) with 5% phenyl, 45% methylpolysiloxane was used for confirmation, being the chromatographic conditions the following: 100 °C for 2 minutes, increasing by 12 °C/min to 270 °C, remaining at this temperature for 5 minutes.

The external standard technique was chosen for the purpose of indentifying the unknown peaks found in samples by comparison of their retention times (RT) with known RT of pesticide standards. The identity of each peak was confirmed using a second column and comparing again their RTs in the samples with those obtained with the standards. The concentration of pesticide residues in the water was calculated using the formula:

$$C\ (\text{ppm}) = \frac{W \times A_1 \times V_1}{A_2 \times V_2 \times V_3}$$

having:

W = ng pesticide standard
A_1 = peak area of standard
A_2 = peak area of sample
V_1 = extract volume (mL)
V_2 = volume injected (µL)
V_3 = volume of sample extracted (mL)

Method was linear for any of the organochlorine pesticides analysed between 0.002µg/L- 2 µg/L. Method average recovery ranged from 73-104% at 0.01 µg/L fortification level. The detection limit for the organochlorine pesticides studied along with their retention times (minutes) in both columns used are shown in table 1.

RESULTS AND DISCUSSION

84 drinking water samples were analysed between 1991 and 1994. Trace levels residues of the organochlorine pesticides studied (those above detection limits) were found in 70 samples (83.3%)(Tables 2 and 3).

Tables 2 and 4 show HCH isomers' residues found, the percentage in which α-HCH and γ-HCH appeared on analysed samples respectively. Table 3 show DDT related residues found.

Samples from public water supplies were relatively free from significant pesticide residues. Levels above public health guidelines were detected in only two samples, one in 1991 (0.199 µg/L α-HCH and 0.228 µg/L γ-HCH) and the other in 1993 (0.111 µg/L α-HCH). EC Council (1980) regards 0.l µg/L as the maximun level permitted for only one substance and 0.5 µg/L for more than one pesticide.

No compound that interfered with the detection any of the organochlorine pesticides studied was observed, or the samples' concentration values (Table 2) were not corrected for procedural blanks.

Application of SPE (solid phase extraction) technique to the determination of pesticide residues in water is generally accepted after being validated by different official institutions (Junk and Richard, 1988).

Lindane (γ-HCH) and its isomer α-HCH were the pesticides most frequently found (Table 3). Lindane (γ-HCH) levels have been decreasing from 1991 until 1994. Except in 1993, α-HCH levels were lower than lindane levels. In 1993 an important increase in α-HCH levels was detected. However β-HCH was only detected in 1991.

HCH total levels (sum of isomers' average) have been decreasing from 1991 to 1994 in the samples analysed (Table 2). When comparing our results with those previously reported in our area (Hernández et al.,1976) we observed an important decrease of the concentration levels found.

The high frequency (Table 4) of low levels of lindane and its isomers is consistent with the prior and current use of the chemical in the area for agricultural purposes. In Spain, since 1976 when DDT was legally restricted for agricultural use, lindane had become an important substitute (García-Repetto et al., 1995).

The main cause of DDT total level(Table 3) decrease in these years is probably the ban on its agricultural use. Those levels were lower than those reported for Sao Paulo state waters, drinking water of India and Malaysian rivers (Cáceres et al., 1987; Jani et al., 1991; Tan et al., 1994), but higher than those previously published by Achari et a1.(1975) and Rihan et a1.(1978) in waters from different rivers of the United States.

Our results are within the range of those published by Hernández et a1.(1992) for HCH total and DDT total residues in Guadalquivir river waters (main river of the south of Spain). They are also similar to the results obtained in a study of rainfall waters levels of HCH in India (Dua et al., 1994).

In conclusion, although low level residues of organochlorine pesticides were detected in a 83.3% of samples, public water supplies were generally found to be free from significant pesticide contamination as only two of the samples analysed during this period were above public health guidelines.

Table 1. Detection limits for the organochlorine pesticides studied (μg/L) and their retention times in columns used.

Pesticide	Detection limit (μg/L)	RT (min) CPSil-19CB	RT(min) CPSil-8CB
Lindane (γ-HCH)	0.002	14.75	17.82
α-HCH	0.003	13.14	15.91
β-HCH	0.005	15.95	17.36
4,4'-DDE	0.005	25.17	30.18
4,4'-DDD	0.003	27.24	30.52
2,4'DDT	0.004	29.65	31.63
2,4'DDD	0.004	26.86	31.22

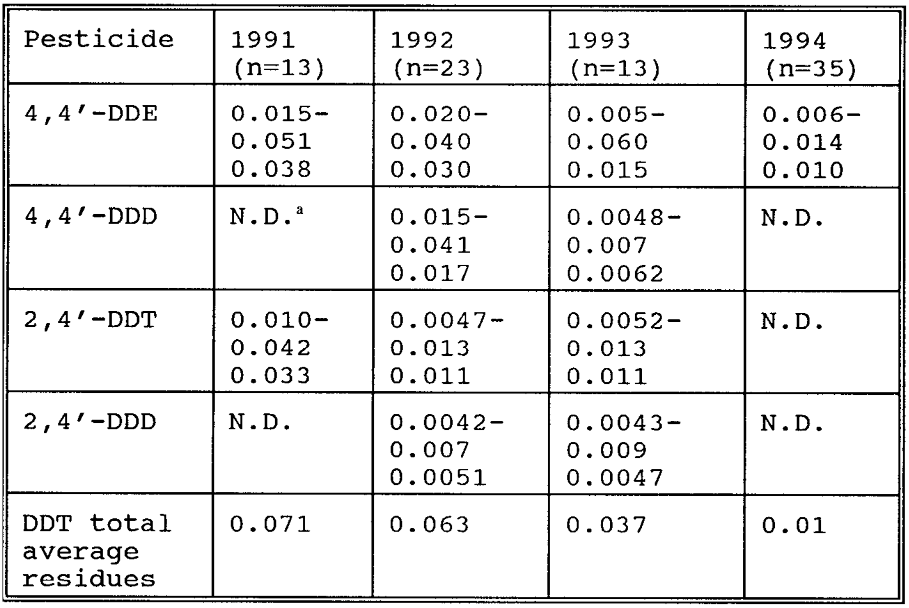
Table 2. HCH isomers' residues found in drinking water between 1991-1994 (ppm).

Pesticide	1991 (n=13)	1992 (n=23)	1993 (n=13)	1994 (n=35)
α-HCH	0.0046- 0.199 0.0035	0.008- 0.050 0.027	0.0045- 0.111 0.026	0.009- 0.01 0.0095
β-HCH	0.005- 0.021 0.012	N.D.[a]	N.D.	N.D.
Lindane (γ-HCH)	0.014- 0.228 0.0655	0.006- 0.092 0.035	0.0085- 0.04 0.022	0.002- 0.037 0.021
HCH total residues average	0.081	0.062	0.048	0.031

[a] N.D. means not detected.

Note : ranges of concentrations found are expressed along with their averages.

Table 3. DDT and its related compounds found in drinking water between 1991-1994 (ppm).



Pesticide	1991 (n=13)	1992 (n=23)	1993 (n=13)	1994 (n=35)
4,4′-DDE	0.015- 0.051 0.038	0.020- 0.040 0.030	0.005- 0.060 0.015	0.006- 0.014 0.010
4,4′-DDD	N.D.[a]	0.015- 0.041 0.017	0.0048- 0.007 0.0062	N.D.
2,4′-DDT	0.010- 0.042 0.033	0.0047- 0.013 0.011	0.0052- 0.013 0.011	N.D.
2,4′-DDD	N.D.	0.0042- 0.007 0.0051	0.0043- 0.009 0.0047	N.D.
DDT total average residues	0.071	0.063	0.037	0.01

[a] N.D. means not detected.

Note: ranges of concentrations found are expressed along with their averages.

Table 4. Presence of α-HCH and γ-HCH (lindane) in samples analysed (n=84).

Pesticide	1991	1992	1993	1994
α-HCH	76.92%	37.39%	92.3%	45.71%
γ-HCH	76.92%	47.83%	53.80%	85.71%

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