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Persistence of Some Pesticides in the Aquatic Environment

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The widespread ocurrence of pesticides has stimulated research into the nature, behavior, and fate of these compounds and their metabolites in the environment. Insecticides applied to agricultural crops, forests, or recreational areas may be transported by wind and water into drainage canals, rivers, lakes, and oceans. Pesticides may also be applicated directly to water to control aquatic pests. The degradation of pesticides in aqueous systems is attributed to both chemical and biological action (Sharom *et al.* 1980; Andreu *et al.* 1986; Miles *et al.* 1988; Singh and Seth 1989; Wang *et al.* 1989).

Most organophosphorus (OP) and carbamate insecticides are regarded as being non-persistent, but some reports have indicated that residues of OP insecticides are persisting for extended periods in organic soils and in surrounding drainage systems (Harris and Miles 1975; Miles *et al.* 1978).

The object of this study was to measure the persistence of some pesticides, representing the organochlorine (OC), organophosphate and carbamate groups in natural water, from Albufera Lake (Spain), and in experimental water, from our laboratory, and to asses the differences in the degradation process of these pesticides in the aqueous environment.

MATERIAL AND METHODS

The natural water unfiltered used in this study was colleted from the Albufera Lake, that is located in an important vegetable growing area of Valencia, Spain (39°20' N; 0°20' W). We used tap water, from our laboratory, as experimental water. Some properties of both media are given in Table 1.

Experiments were conducted in 20 L glass aquaria (UV transmittance) containing a fixed amount of each insecticide in 15 L of each medium. The pesticides used were: organochlorine insecticides (lindane,endosulfan), organophosphate insecticides (methylparathion, diazinon) and one carbamate (thiobencarb). Commercial, alternative and chemical names of the pesticides tested, along with purity and the chemical companies which provided these compounds, are listed in Table 2.

Concentrations of insecticides used were: 0.5 mg/L for lindane and endosulfan; 0.2 mg/L for methylparathion and thiobencarb and 1.0 mg/L for diazinon. The insecticides were dissolved in acetone and added into the aquaria. Triplicate samples

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Table 2. Commercial, alternative and chemical names of the pesticides tested; purity, and the Chemical Companies which provided these compounds for testing.

Commercial names	Alternative names	Chemical names	Percent active ingredient	Chemical Company
Lindane	ENT 7796, Gamaphex gamma BHC, Gammex Lindafor	Gamma isomer of 1,2, 3,4,5,6-hexachlorocyclohexane	99%	AGRONEXA (Spain)
Endosulfan	Bio-5462, Cyclodan, Thiodan, Thionex	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide	96%	HOECHT Ibérica S.A. (Spain)
Methylparathion	Bayer E-601, Metaphos Metron, Wotafox	Phosphorothioic acid, O, O-dimethyl O-(4 nitrophenyl) ester	80%	BAYER HISPANIA S.A. (Spain)
Diazinon	AG-500, Basudin, Diazine, Diazol	0,0-Diethyl 0-(2-isopropyl-6-methyl-4-prymidinyl) phosphorothioate.	92%	CEQUISA (Spain)
Thiobencarb	Thiobencarb	S-4-chlorobenzyl diethylthiocarbamate	93%	ARGOS S.A. (Spain)

were used for each treatment. The aquaria were well-aerated with compressors (the dissolved oxygen concentration was between 60% and 100% saturation during the first 48 hr of the test and was between 40% and 100% saturation after 48 hr) and exposed to a photoperiod of 12 hr (8.0 to 20.0 hr); the temperature of the tests was 22.0±0.5ºC. Samples of 100 mL of each treatment were taken at the beginning of the experiment and after 24, 48, 72 and 96 hr exposure to the different pesticides.

The amounts of remaining insecticide were determined (some previous experiments were carried out to find out the amount of compound dissolved in water and the recovery rate in the extraction process, in order to check pesticide loses, caused by adsorption to sides of container). In all cases the percentage of recovery was 95-100%.

OC and OP insecticides were extracted with hexane. Chloroform was used to extract the carbamate insecticide. Each sample was extracted three times. After drying with sodium sulfate, the solvent was evaporated to dryness on a rotatory vacuum evaporator with the water bath at 45ºC. The residue was dissolved in 5 mL of hexane and injected directly into the gas chromatograph (Zweigh and Sherma 1972).The gas chromatograph used was a Perkin Elmer F-17 with an electron-capture detector for the organochlorine pesticides; and a Varian-6000 chromatograph with a flame fotometric detector for the organophosphate and carbamate pesticides (Table 3). Recoveries were in the range 85-99%.

Results were compared using Student's t-test. The significance level was fixed at $p < 0.05$.

RESULTS AND DISCUSSION

The persistence of lindane was similar in natural and experimental water (Fig. 1). Lindane in natural water was reduced from its initial value of 0.5 mg/L to 0.13 mg/L at 96 hr, showing a dissipation of 15% the first day (24 hr) and a 70% the last day (96 hr) (Fig. 1). On the other hand, in the experimental medium, after 96 hr the residue value was 0.17 mg/L and the dissipation rate a 15% at 24 hr and a 66% at 96 hr (Fig. 1). Thus, the degradation of this organochlorine pesticide followed the first order of reaction in both median, so the concentration was proportional to time elapsed. The half lives in natural and experimental water were 64.98 and 69.41 hours respectively (Table 4).

Similar results were found in the case of endosulfan (Fig. 1).The pesticide degradation ran almost parallel in both media until 48 hr whereas the amount of toxicant in the natural water was 38.9% and in the experimental water 55%. We found clearly differences at 96 hr, with an endosulfan percentage of 11% in natural water and a 31% in the experimental medium. The half life of this pesticide in the experimental water (67.8 hr) was similar to lindane half life in the same medium, however there were differences between both insecticides in natural water (Table 4).

Degradation of the organophosphorus insecticide methyl-parathion in both media was rapid, the calculated half lives were 11.1 and 13.4 hr (Table 4). As we expected, more degradation occurred in the natural medium suggesting some biological degradation. We did not find a linear regression between insecticide concentration and time of exposure, because at 24 hr the remaining compound was 8.2% in natural water and a 9.5% in the experimental medium, so the first day the

Table 1. Analysis of the natural and experimental water used in this study.

	Natural water	Experimental water
pH	9.0±0.5	7.5±0.5
Alkalinity (mmol/L)	3.7	3.8-4.4
Hardness as $CaCO_3$ (mg/L)	>600	180-300
Temperature (°C)	22.0±0.5	22.0±0.5
Conductivity (μmhos)	1900	1200
Suspended solids (mg/L) (bacterial and plankton)	84.4	<10

pesticide degradation was very fast in both media (Fig. 2). However, after 24 hr the degradation ran slowly until the end of the experiment.

Diazinon was more stable in natural and experimental water than lindane, endosulfan, and methylparathion were. As we found before with the other pesticides, the degradation was faster in the natural medium with respect to the experimental medium used (70.54 and 79.19 hr) (Table 4). Figure 2 shows the degradation process in both media. It was parallel until 96 hr . We found a 43.5% and a 49.4% of this insecticide at 96 hr, in natural and experimental water respectively.

Table 3. Chromatographic conditions.

	Varian	Perkin Elmer
Glass column	1 m x 2.4 mm 5% OV-101 Chromosob WHP 100/120	1 m x 2.4 mm 4% SE-30+6% QF-1 Chromosob W 100/120 mesh
Inyector temperature	240°C	300°C
Detector temperature	250°C	300°C
Column temperature	200°C	190°C
Nitrogen flow	30 ml/min	30 ml/min

Thiobencarb was the most stable compound tested. In this case, we found more differences between the degradation process in natural and experimental water. As we can see in Table 4, half lives for this insecticide were 74.27 and 247.66 in natural and experimental medium respectively. The differences between both degradation process started at 24 hr, the percentage of pesticide was 67.8% and 96%, in natural and experimental water, respectively. Figure 3 showns that these differences between both media continued until 96 hr exposure.

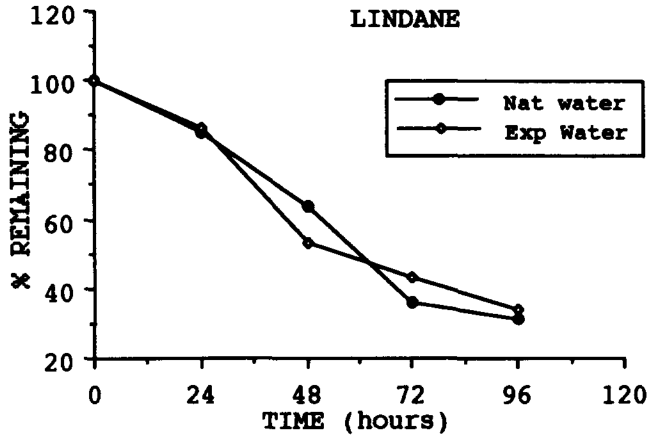

Figure 1. Persistence of the organochlorine insecticide lindane in natural and experimental water.

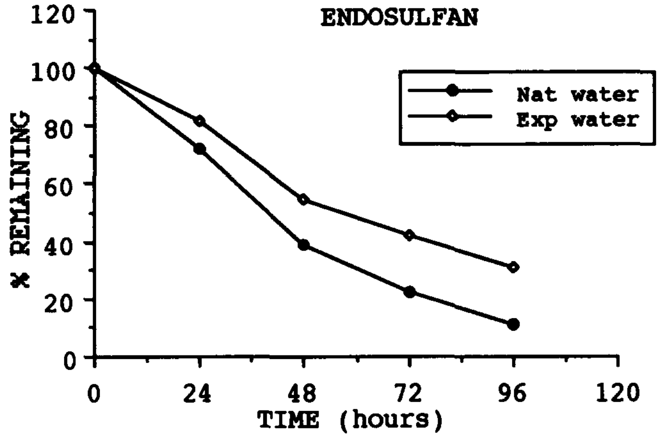

Figure 2. Persistence of the organochlorine insecticide endosulfan in natural and experimental water.

Table 4. Pesticide degradation in the two different aquatic medium tested.

	Half life (hours)	
Compound	Natural water	Experimental water
Lindane	64.98(63.99-65.97)	69.41(64.36-74.46)
Endosulfan	50.31(47.32-53.30)	67.83(57.82-77.84) *
Methylparathion	11.10(9.90-12.30)	13.40(8.20-18.60)
Diazinon	70.54(70.25-70.82)	79.19(78.46-79.92) *
Thiobencarb	74.27(73.22-75.32)	247.66(204.01-291.31) *

* $p< 0.05$

The persistence of lindane, endosulfan, and methylparathion was similar in natural and experimental water. Diazinon appeared slightly less persistent in the natural water. On the other hand, we found more differences between the degradation processes of thiobencarb in both media.

Our data agree with results obtained by Sharom *et al.* (1980). They found similar persistence for dieldrin, endrin, lindane and ethion in natural and distilled water, and they also reported that the carbamate pesticide carbaryl degraded more rapidly in natural water than in the other media.

Chemical degradation of these pesticides was significant during the 96 hr exposure, but more degradation occurred in the natural water suggesting some biological degradation. In those cases where the degradation process was similar in both media, we can say that chemical degradation is very important. Methylparathion degraded quickly in water, its degradation showed a two-step degradation process, with a rapid decrease in the first 24 hr. Half life of this insecticide was determined from the first portion of the curve. Sabharwal and Belsare (1986) reported a quick degradation process of methylparathion in water, it seems that for this insecticide the chemical degradation plays an important role.

Thiobencarb was the insecticide that showed more differences between both media. Miles *et al.*(1988) reported that carbamate pesticides are very influenced by changes in water pH. An increase in pH from 7 to 9 decreased the half-lives of these compounds more than ten times. These experiments indicate that degradation of insecticides in aqueous systems may be due to chemical and/or biological process. Insecticides such as thiobencarb were very persistent in experimental water, but degraded fairly quickly, through microbial action, in natural water.

Chemical degradation appeared to play a major part in the degradation in water of the organochlorine insecticides tested, with biological degradation having a secondary role in the degradation of insecticides such as diazinon, methylparathion, and thiobencarb. OP and carbamate insecticides are generally considered to be less persistent in the environment than OC insecticides. It is interesting to note that the most stable compounds tested, in both media, included one OP (diazinon) and one

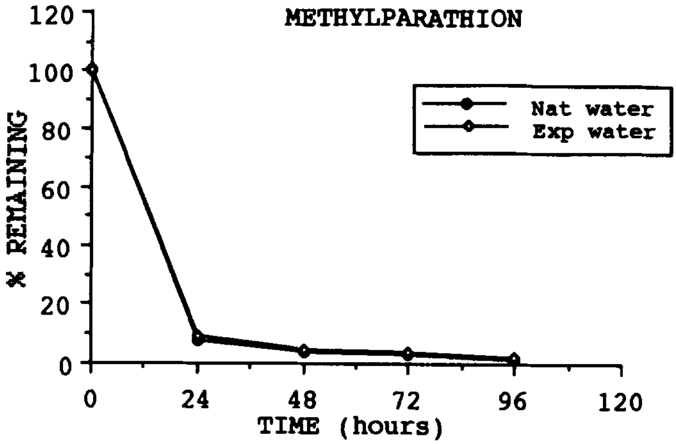

Figure 3. Persistence of the organophosphate insecticide methylparathion in natural and experimental water.

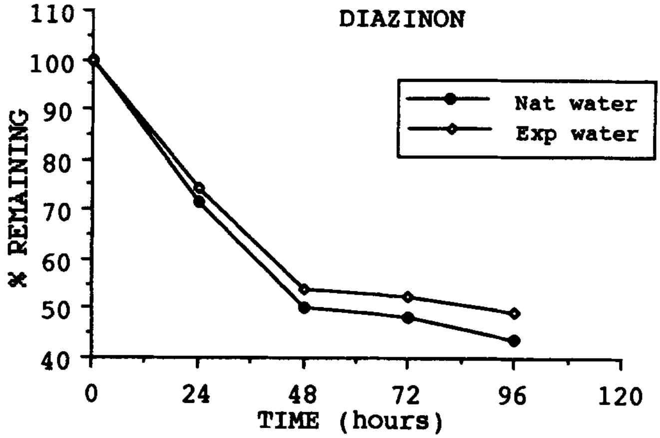

Figure 4. Persistence of the organophosphate insecticide diazinon in natural and experimental water.

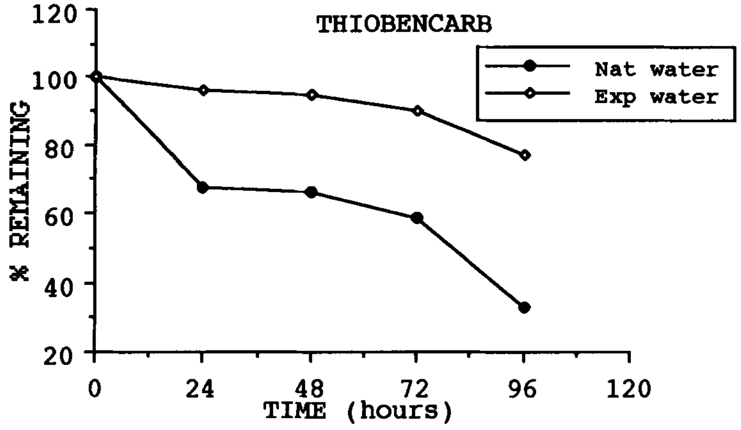

Figure 5. Persistence of the carbamate insecticide thiobencarb in natural and experimental water.

carbamate (thiobencarb). Sharom *et al.* (1980) found similar results with the organophosphorus insecticides ethion and leptophos. They also found that OC insecticides such as DDT were the least stable compounds tested, with a degradation process similar to some OP and carbamate compounds.

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