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Toxicities of Eight Organochlorine Compounds in Sediment and Seawater to *Crangon septemspinosa*

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The Ocean Dumping Control Act of Canada limits organohalogens in materials to be dumped in the marine environment to "quantities not exceeding 0.01 parts of a concentration shown to be toxic to marine animal and plant sensitive species... ." The toxicity of organochlorine contaminants in seawater to marine organisms has been studied in relative detail, but there is little information on the lethality of these compounds when they are associated with sediment.

A summary of available 24- and 96-h LC50 data for water-borne organochlorines (KLAPOW & LEWIS 1979) indicates that acute lethal thresholds for marine and freshwater organisms range from 0.1 µg/L to greater than 1.0 mg/L. Information on the lethality of organochlorines in sediment is limited to two studies with Aroclor 1254. NIMMO et al. (1971) found no mortality of crabs and shrimp exposed to sediment containing 60 mg/kg of Aroclor 1254. Aroclor 1254 concentrations in sediment of 500 mg/kg were not lethal to the minnow Pimephales promelas (HALTER & JOHNSON 1977).

In this study, data are presented on the lethalities of endosulfan, endrin, DDT, dieldrin, technical chlordane, hexachlorobenzene, Aroclor 1242 and Aroclor 1254 in seawater and in sandy sediment to the shrimp Crangon septemspinosa. The lethality of these compounds is discussed in relation to their distribution between sediment and water.

METHODS AND MATERIALS

Lethality of the organochlorine compounds in water was determined in static tests using three Crangon (2.0 g each) in 2 L of seawater. The compounds, dissolved in hexane, were added to the bottom of dry glass beakers and after evaporation of the solvent, 2 L of seawater and animals were added. After 48 h, the animals were transferred to new beakers with freshly prepared solutions and tests were terminated at 96 h. Air was bubbled into the solutions through glass pipets. All compounds were tested at 20°C and in addition, chlordane, endrin, Aroclor 1242 and DDT were tested at 10°C.

From selected lethality tests, 100-mL water samples were taken at 2, 8, 24 and 48 h to determine the patterns and rates of dissolution of toxicants from the bottom surfaces of the beakers. Solutions from the the remaining tests were sampled at 2, 24, or 48 h to measure the concentration of the toxicant.

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Lethality of organochlorines in sediment was determined in static tests using three Crangon (2.0 g each) in a 2-L beaker. The compounds dissolved in hexane were added to the bottom of the beaker, the solvent was allowed to evaporate and sediment and seawater were added. After settling of sediment, the animals were added. Each beaker contained 500 g wet weight of sandy sediment (3 cm) and 250 mL of seawater (1.5 cm). Sediment was prepared by wet sieving between 1- and 2-mm metal sieves. Air was bubbled through glass pipets, and temperature was maintained at 10°C. Sediment and water were not renewed during the 96-h duration of the test.

Sediment samples of approximately 15 g wet weight were taken from selected tests at 24, 48 and 96 h to determine the pattern and rate of toxicant uptake by the sediment. Sediments were sampled from the other tests at 24, 48 or 96 h to measure the concentration of the test compound. In addition, in other lethality tests with endrin, chlordane or dieldrin, four identical tests were run at each concentration, and the overlying surficial water was sampled from successive tests (100 mL) at 2, 24, 48 and 96 h. In these cases, sediment samples were not taken.

Times to 50% mortality (LT50) were estimated from plots of percentage mortality against time on logarithmic probability paper. The 96-h LC50 was estimated from the geometric mean of the highest concentration without and the lowest concentration with 50% mortality. The lethal thresholds were calculated from the lethality curve by the method of ZITKO (1979).

Organochlorines were extracted from water with 15 mL of pesticide-grade hexane. Extraction of organochlorines from sediment and removal of elemental sulfur from the extracts were done by methods presented in McLEESE et al. (in press). The efficiences of extraction were determined by extracting water and sediment samples fortified at concentrations representative of those in lethality tests. Analysis results were adjusted to account for unextracted material.

A gas chromatography equipped with a ^{63}Ni detector was used. The 2 m x 2 mm I.D. glass column was packed with 3% OV-101 on 80/100 Chromosorb W-HP and injector, column and detector temperatures were 210, 190, and 300°C, respectively.

Five peaks of Aroclor 1254 with retention times relative to DDE (=100) of 70, 84, 125, 146 and 174 (WEBB & McCALL 1973) were quantified and the sum of these concentrations multiplied by the factor 1.55. Similarly, five peaks of Aroclor 1242 with relative retention times of 21, 28, 37, 40 and 70 were quantified and the sum of their concentrations multiplied by 1.78. The concentration of chlordane was calculated by quantifying a single peak (relative retention time = 117) of technical chlordane. This peak corresponds to α-chlordane (chlordane) identified by SAHA & LEE (1969). A single peak with a relative retention time of 81, corresponding to α-endosulfan, was used to quantify endosulfan concentrations. Sediments were analyzed by the methods of AKAGI & WILDISH (1975).

RESULTS AND DISCUSSION

Sandy sediment used in the lethality tests contained 97% sand with particle sizes between 0.5 and 2.0 mm and had a low content of organic carbon (0.28%). When placed in test beakers, Crangon burrowed into the sediment immediately and only their eyestalks remained visible. As the tests progressed, the shrimp moved out of the sediment into the surficial water. Because the water was shallow (1.5 cm), the animals remained in contact with the sediment.

Extraction efficiencies of the organochlorine compounds from seawater and sediment (Table 1) appear to be inversely related to their water solubilities.

TABLE 1. Extraction efficiencies of organochlorine compounds from seawater and sediment and published aqueous solubilities.

Compound	% extraction efficiency		Aqueous solubility (µg/L)
	Sea water	Sediment	
Endrin	80	74	260[b]
Endosulfan	72	61	530(α), 280(β)[b]
DDT	100	85	17[a]
Dieldrin	63	78	200[b]
Chlordane	53	59	1900[b]
Aroclor 1242	61	62	72-350[c]
Aroclor 1254	72	60	6-47[c]
HCB	100	52	5[c]

[a]From BIGGAR & RIGGS (1974) - filtered water at 15°C
[b]From WEIL et al. (1974) - distilled water at 25°C
[c]From DEXTER & PAVLOU (1978) - distilled water at 11°C

The concentration of organochlorines in seawater followed three patterns (Fig. 1) as a result of dissolution from the bottom of the beakers and losses from seawater by volatilization, adsorption on beaker walls and accumulation by animals (GILLESPIE et al. 1975). Concentrations from selected lethality tests were fitted to the second degree polynomial: $C = a_0 + a_1t + a_2t^2$ where C = concentration (µg/L); t = time (h); a_0, a_1, a_2 = empirical coefficients. The average exposure concentration (C) for each lethality test was calculated by the equation:

$$C = \frac{C_M}{SC_M} \cdot \frac{1}{t} \int_0^t (a_0+a_1t+a_2t^2)dt = \frac{C_M}{SC_M} (a_0+a_1t/2+a_2t^2/3)$$

Where: C = average exposure concentration (µg/L) for each lethality test; C_M = maximum concentration (µg/L) measured in each lethality test; SC_M = maximum conentration (µg/L) measured in the selected lethality tests from which coefficients a_0, a_1 and a_2 were determined.

The concentration of compounds in sediment conformed to two patterns (Fig. 2). Average concentrations of organochlorine compounds in the sediment were estimated as described above, except that maximum concentrations over a 96-h test period were used and concentrations were expressed as µg/kg sediment.

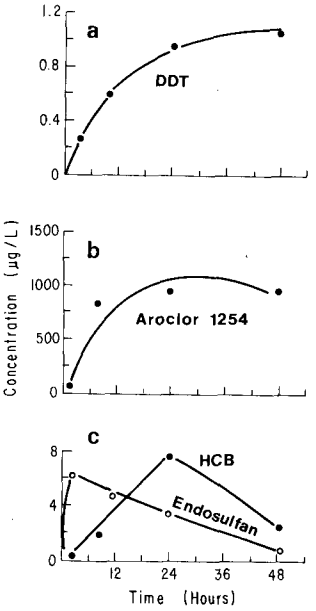

Fig. 1

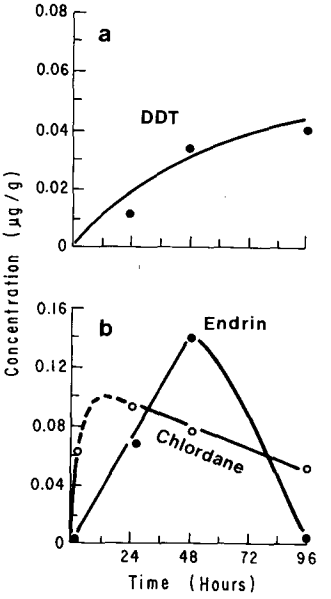

Fig. 2

Fig. 1. General patterns of movement of organochlorines into water in lethality lethality tests with Crangon. Pattern A: DDT; Pattern B: Aroclor 1242, Aroclor 1254; Pattern C: Dieldrin, endrin, chlordane, endosulfan, HCB.

Fig. 2. General patterns of movement of organochlorines into sediment in lethality tests with Crangon. Pattern A: Aroclor 1242, Aroclor 1254, HCB, dieldrin, DDT; Pattern C: Chlordane, endrin, endosulfan

The 96-h LC50's and lethal thresholds to Crangon are listed in Table 2. Seven of the eight compounds in water are extremely toxic with 96-h LC50's ranging from about 0.2 to 13 µg/L. The order of lethality in water closely follows the order of LC50 values reported by KLAPOW & LEWIS (1979), with the exception that they found endrin to be more toxic than endosulfan. The LC50's of DDT, endosulfan, dieldrin, Aroclor 1242 and Aroclor 1254 for C. septemspinosa were approximately one order of magnitude lower than the nominal LC50's reported for C. crangon by PORTMANN & WILSON (1971). Nevertheless, the order of lethality of these compounds did not differ. Lethal thresholds were approximately equal or

lower than the 96-h LC50's, except in the case of dieldrin where a large difference between concentrations used to calculate the geometric mean may have resulted in the underestimation of the LC50. The low lethal threshold for Aroclor 1254 may be attributed to the poor resolution of the lethality line used to calculate this value.

In the tests with sediment (Table 2), there were no mortalities with HCB, Aroclor 1242 and Aroclor 1254 at the maximum concentrations tested. The order of toxicity of the remaining compounds in sediment differs from the order of toxicity in sea water tests. The 96-h LC50's for the remaining five of the eight compounds range from 4 to 120 µg/kg sediment. In general, the organochlorines are about 10-80 times less toxic in sediment than in water.

LT50's for four organochlorines in water at 10 and 20°C are similar (Table 3). Therefore, it is permissible to compare results from lethality tests in water at 20°C with those from lethality tests in sediment at 10°C.

TABLE 2. LC50's (96-h) and lethal thresholds for eight organochlorines in sea water (20°C) or sediment (10°C) and Crangon.

	Seawater tests		Sediment tests	
Compound	96-h LC50 (µg/L)	Threshold (µg/L)	97-h LC50 (µg/L)	Threshold (µg/L)
Endosulfan	0.2	0.2	6.9	9.0
Endrin	0.6	0.5	47	41
DDT	0.4	0.2	31	20
Dieldrin	0.4	0.5	4.1	2.6
Chlordane	2.0	1.0	120	110
Aroclor 1242	13.0	6.5	>780[a]	-
Aroclor 1254	12.0	0.5	>3400[a]	-
HCB	>7.2[a]	-	>300[a]	-

[a]No mortalities at highest concentration tested.

In some of the tests with sediment, the concentration of endrin, chlordane and dieldrin in the surficial water was measured with time. There is close agreement between LT50's for Crangon at the average concentrations measured in the surficial water and the LT50's from tests without sediment but with similar concentrations in the water (Fig. 3). These results indicate that the compounds adsorbed to sediment contribute little towards the toxicity.

The equilibrium relationships for organochlorines between water and sediment depend largely upon the chemical and physical properties of the sediment and the compounds (WILDISH et al. 1980, KARICKHOFF et al. 1979, HUANG 1974). Changes in the order of lethality of the compounds between water and sediment tests suggest that the sediment-water partitioning properties of the compounds influence their apparent toxicity. The 96-h LC50 for

Aroclor 1254 in sediment is greater than 3.4 mg/kg (Table 2). Calculations using the adsorption coefficient (K_{OC}) for Aroclor 1254 distributed between seawater and a sediment with 0.28% organic carbon content (WILDISH et al. 1980) indicate that 3.4 mg/kg of Aroclor 1254 in sediment would be at equilibrium with .0086 mg/L in seawater. The latter concentration is lower than the 96-h LC50 of 0.012 mg/L for Aroclor 1254 in water (Table 2). Therefore, mortalities would not be expected at the Aroclor 1254 concentration measured in the sediment.

TABLE 3. Lethality of chlordane, endrin, DDT and Aroclor 1242 to Crangon in seawater tests at 10° and 20°C.

	10°C		20°C	
Compound	Calculated avg. conc. (µg/L)	LT50 (h)	Calculated avg. conc. (µg/L)	LT50 (h)
Chlordane	12	30	12	35
	2.4	0/3 dead at 96 h	2.8	50
Endrin	2.3	23	2.4	20
	0.7	52	0.9	45
DDT	1.9	15	1.8	20
	1.1	15	0.9	16,21
Aroclor 1254	20	75,50	21	65
	14	30	15	40

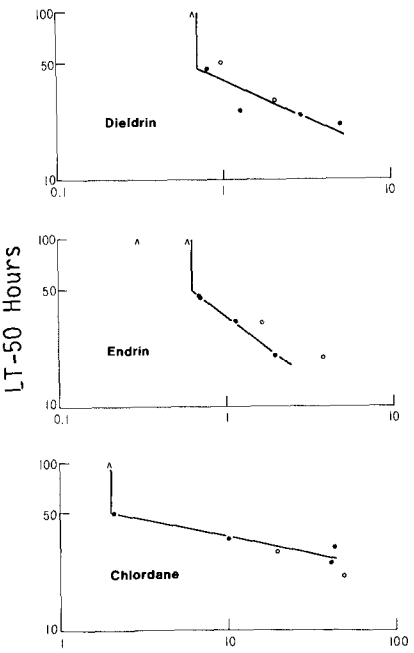

Fig. 3. Lethality lines for Crangon exposed to dieldrin, endrin and chlordane in seawater at 20°C (closed circles). LT-50's from sediment tests plotted against the avreage concentration in surficial water (open circles). ^ refers to concentration at which there was less than 50% mortality.

The adsorption coefficients (K_{OC}) and equilibrium concentrations in sediment at lethal concentrations in water were calculated for six of the compounds (Table 4) from aqueous solubilities (Table 1) by the equation of KENAGA and GORING (1979). The calculated equilibrium concentrations in sediment are not directly comparable to the LC50 concentrations in our sediment tests (Table 2) since the aqueous solubilities and adsorption coefficients were calculated for freshwater systems and salinity is known to affect both of these parameters (DEXTER & PAVLOU 1978, WILDISH et al. 1980, PICER et al. 1977). However, with the exception of DDT and to a lesser extent dieldrin, the order of equilibrium concentrations (Table 4) and order of LC50'S for organochlorines in sediment (Table 2) are the same. Again, this indicates that the concentration in surficial water is the primary factor controlling the lethality of the compounds to epibenthic species such as Crangon.

Table 4. Adsorption coefficients (K_{OC}) and concentrations in sediment at equilibrium with measured lethal threshold concentrations in water, calculated by the method of KENAGA & GORING (1979) for freshwater systems.

Compound	Lethal threshold for Crangon in seawater (µg/L)	Calculated K for fresh water ($x10^{-3}$)	Calculated equilib. conc. in sediment at lethal threshold-fresh water (µg/kg)
Endosulfan	0.2	6.2(α), 8.8(β)	3.5(α), 4.9(β)
Endrin	0.6	9.2	15.4
DDT	0.4	41.0	45.9
Dieldrin	0.4	10.6	11.9
Chlordane	2.0	3.1	17.4
HCB	>7.2	80.5	>1,622.0

The data from this study can be applied directly to the calculation of concentrations of organochlorines in sediment to be considered lethal to aquatic species. Since coarse sediments with a low organic content do not bind organochlorines as firmly as fine sediment (WILDISH et al. 1980, KARICKHOFF et al. 1979), the data for sediments reported here would represent conservative estimates of lethality. It is reasonable to consider Aroclor 1254, Aroclor 1242, HCB and perhaps chlordane in sediments to be relatively non-toxic and to consider dieldrin, endosulfan, endrin and DDT in sediments to be potentially hazardous to benthic and epibenthic invertebrates. The type of sediment and rate of flushing of surficial water are parameters which will modify the apparent lethality of the organochlorine compounds in the natural situation.

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