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Flux of Aroclor 1254 Between Estuarine Sediments and Water

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Aquatic sediments adsorb organic industrial contaminants such as polychorinated biphenyls (PCB). Concentrations of PCB in marine sediments, given in the review by PAVLOU and DEXTER (1979), range from trace levels in the open ocean to 8 ppm near industrial areas.

The flux of organic contaminants between sediment and water depends upon adsorption-desorption phenomena, which are influenced by the physical and chemical characteristics of the sediment, chemical characteristics of the water, pH, ionic concentration, temperature, and rate of water replacement (HUANG 1974).

Several authors have used the Freundlich adsorption isotherm to describe the adsorption of PCB by various substrates. HIRAIZUMI et al. (1979) review much of this work, including adsorption by standardized sediments (HAQUE et al. 1974) and resin adsorbents (LAWRENCE and TOSINE 1976), as well as their own work using plankton, fish, suspended particulates, sand, mud and activated carbon as adsorbents. For these materials, the Freundlich isotherm exponents were close to unity, and the equilibrium coefficients indicated by K values varied by several orders of magnitude. STEEN et al. (1978) reported equilibrium coefficients of 600 to 1400 for two PCB mixtures and two PCB isomers with four natural sediments as adsorbents. The K value is a reasonable approximation of the concentration factor provided the exponent is close to unity.

Adsorption of PCB's by sediments occurs rapidly (HIRAIZUMI et al. 1979, STEEN et al. 1979, MUTO et al. 1974), but little attention has been given to rates of desorption for PCB's. Reported rates of desorption range from rapid (STEEN et al. 1979) to very slow and negligible (HIRAIZUMI et al. 1979, HAQUE et al. 1974).

Frequently, sediments are dredged and transported for dumping to areas where characteristics of water are different. This study examines the adsorption and desorption of a representative PCB mixture, Aroclor 1254, by various size fractions of a marine sediment over a range of salinities. The information will be useful in relating toxicological and bioaccumulation data to estimated PCB concentrations in sea water at disposal sites.

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EXPERIMENTAL METHOD

Materials

Estuarine water (salinity = 28 o/oo) and deionized tap water (≈10 Megaohms/cm) were filtered through 0.45 μm Gelman glass fiber filters prior to spiking with Aroclor 1254 in acetone (PCB in .1mL acetone:300 mL water). An intertidal sediment sample from the St. Croix estuary was wet sieved into the four size fractions (Table 1). Each fraction was analyzed for percent dry weight by drying for 24 h at 100°C and for organic carbon content by a modified Walkley-Black oxidation of the dried sample (AKAGI and WILDISH 1975).

TABLE 1

Percent dry weight and percent organic carbon content of sediment fractions used in adsorption and desorption experiments

Sediment	Particle size range, μm	% dry weight	% organic carbon
A Coarse sand	500-1000	82.1	0.2
B Medium and fine sand	250-500	71.1	0.6
C Very fine sand	125-250	69.6	0.6
D Silt/clay	<63	36.7	3.0

The background levels of PCB in untreated water and sediment used in the experiments were below the detection limits of 0.2 μg/L and 0.1 μg/g respectively.

Protocol

A static, batch method was used to determine adsorption and desorption.

In adsorption experiments 35 mL of water spiked with Aroclor 1254 was added to a known wet weight of sediment in a 50-mL centrifuge tube. Experimental conditions were varied either by changing the Aroclor 1254 concentration or the sediment wet weight (1-7 g). The tubes were tightly capped with aluminum foil and then agitated on a rotary shaker-water bath (350 rev/min, 10°C) for up to 4 h. After centrifuging at 15,000 rpm for 10 min, 25 mL of supernatant was extracted by partitioning into 3 x 2 mL pesticide grade hexane. The sediment was discarded and the centrifuge walls washed with 3 x 2 mL hexane to extract Aroclor 1254 adsorbed on the walls.

Desorption experiments were carried out as above except that sediment from adsorption tests was placed in the centrifuge tube and 35 mL of clean water added. In later experiments glass centrifuge tubes were replaced by stainless steel ones because less PCB is adsorbed on stainless steel than on glass.

Chemical analysis

Hexane extracts were evaporated to dryness and redissolved in pesticide grade iso-octane. PCB's were determined by gas chromatography with a Varian model 3700 gas chromatograph equipped with a ^{63}Ni electron capture detector and column packed with 3% OV-101 on Chromosorb W. Column temperature was 190°C and injector and detector temperatures were 210°C and 300°C, respectively. Five peaks of Aroclor 1254 with retention times relative to DDE (=100) of 70, 84, 125, 146 and 174 (WEBB and McCALL 1973) were quantified by reference to standards. The sum of the concentrations was multiplied by 1.555 to account for unquantified Aroclor 1254 isomers.

PCB in deionized water was completely extracted. All results from half and full-strength sea water were adjusted to account for average extraction efficiencies for Aroclor 1254 of 78% and 61%, respectively. The extraction efficiencies were relatively constant over the range of PCB concentrations found in the tests.

Adsorption by sediments was calculated from the difference between Aroclor 1254 concentrations in the spiked water, before and after agitation, minus the Aroclor 1254 adsorbed to the centrifuge tube walls. Desorption was calculated from the concentration in the water and on the centrifuge tube walls after agitation.

RESULTS AND DISCUSSION

The concentration of Aroclor 1254 in water, sediment and centrifuge tube walls in adsorption and desorption tests reached equilibrium within 2 h. Agitation in all subsequent tests was continued for 2 h to ensure equilibrium conditions on all surfaces.

The solubility of Aroclor 1254 in sea water has been reported to be as low as 4 μg/L (DEXTER AND PAVLOU 1978) and as high as 56 μg/L (HAQUE 1974). Equilibrium concentrations in water after adsorption ranged from about 0.1 μg/L to 50 μg/L for sediments B, C and D, and from 1 μg/L to 1000 μg/L for sediment A (Fig. 1). It was assumed that the Freundlich isotherms determined over these ranges apply to the natural situation where equilibrium concentrations are much lower.

Adsorption of Aroclor 1254 from sea water by sediments is influenced by the sediment type (Fig. 1). Table 2 lists the exponent n, and equilibrium coefficient K for each Freundlich isotherm:

$$S = KC^n$$

Where: S = Equilibrium concentration of Aroclor 1254 in sediment (μg/kg wet weight).

C = Equilibrium concentration of Arcolor 1254 in water (μg/L).

In tests with 7 g of coarse sand, all adsorption sites are saturated at equilibrium concentrations in sea water above 5 μg/L (Fig. 1A). Silt-clay sediment may also have been saturated at water concentrations above approximately 40 μg/L.

Data for the adsorption of organochlorine contaminants on various sediments conform to single Freundlich isotherm when equilibrium concentrations in sediment are expressed on an organic carbon basis (CHOI and CHAN 1976, STEEN et al. 1978). In these data, adsorption equilibria for all sediments expressed as μg PCB/kg organic carbon yield the single Freundlich isotherm $S = 140{,}000C^{0.8}$ ($r = 0.93$).

Desorption of Aroclor 1254 from sediment to sea water varies with sediment type, as indicated by Freundlich isotherms for desorption (Fig. 1, Table 2). The differences between adsorption and desorption isotherms indicate that adsorption of PCB's is relatively irreversible. HUANG (1974) speculated that similar results with other organochlorine contaminants were due to ionic interactions and hydrogen bonding with the sediment particles. Aroclor 1254 concentrations in the aqueous phase did not exceed about 5 μg/L, indicating that this concentration may be close to the solubility limit.

When concentrations of Aroclor 1254 in sediment are expressed in terms of μg PCB/kg organic carbon, the data from all desorption tests fit a single Freundlich isotherm $S = 430{,}000C^{1.1}$ $r = 0.92$). The analytical method for organic carbon used in our work involves partial oxidation of carbon, and therefore, coefficients presented here will not be strictly applicable to studies in which other organic carbon analyses are used.

The adsorption of Aroclor 1254 by silt-clay sediments increases with salinity, which is consistent with results for other organochlorine contaminants (HUANG 1974, PICER et al. 1977). The mean concentration factors [S (μg/kg)/C (μg/L)] for 1 g of silt-clay exposed to 0.2 μg/L Aroclor 1254 were 810 for deionized water, 2710 for half-strength sea water and 4240 for sea water (Table 3).

The sediments from each of the replicates of the adsorption series were tested for desorption at salinities of either 0, 14 or, 28 o/oo. In all cases, the concentration factors for desorption were greater than for adsorption, indicating that PCB is firmly bound to the sediment. In the case of replicates from the 0 o/oo salinity adsorption tests which were subsequently desorbed at 3

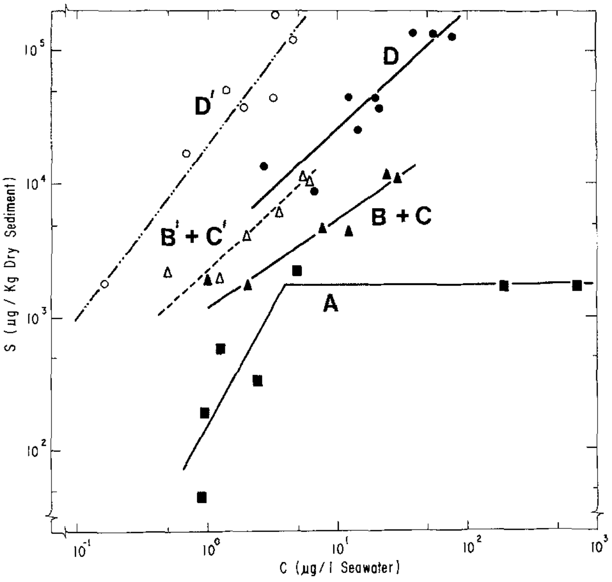

Fig. 1. Adsorption isotherms for Aroclor 1254 and coarse sand (A), fine and medium sand (B+C), and silt-clay (D) and desorption isotherms for fine and medium sand (B'+C') and silt clay (D').

TABLE 2

Exponent and equilibrium coefficient of Freundlich isotherm $S = KC^n$, for each adsorption and desorption series.

Sediment	Adsorption		Desorption	
	n	K	n	K
A Coarse sand	1.8	160	-	-
B+C Fine and medium sand	0.7	1,100	0.9	2,260
D Silt-clay	0.9	3,260	1.1	16,590

ionic concentrations, there was progressively less desorption with increasing salinity. However, since there was no discernible effect of salinity in the other two groups of desorpton tests, no conclusions can be derived from the data. HUANG (1974) showed that salinity has little effect upon the desorption of several organochlorine contaminants from sediment. The coefficients presented here should give an estimate of desorption equilibria in estuarine and marine sediments.

TABLE 3

Concentration factors (C.F.) for adsorption and desorption of Aroclor 1254.

Adsorption		Desorption	
Salinity (o/oo)	C.F.	Salinity (o/oo)	C.F.
0	570	0	1470
0	460	14	3360
0	1410	28	6530
	$\bar{x}$ = 810		
14	2190	0	3870
14	3070	14	4050
14	2880	28	3170
	$\bar{x}$ = 2710		
28	4640	0	5270
28	3830	28	4680
	$\bar{x}$ = 4240		

CONCLUSIONS

Comparison of the Freundlich isotherms for adsorption and desorption of Aroclor 1254 indicate that adsorbed PCB does not desorb readily. The Freundlich exponent and K value for desorption, based on the organic carbon content of the sediment, may be of practical use in predicting PCB concentrations in the pore water of settled dredge spoil, provided that the replacement rate of pore water is slow enough to allow establishment of equilibrium conditions. It is assumed that these coefficients may apply to other sediments with different combinations of organic and inorganic components. However, further study to check this and whether the Freundlich isotherms apply at lower concentrations of PCB is required.

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