Chlorinated Hydrocarbon Residues in Marine Animals of Southern California

by T. O. Munson
Westinghouse Ocean Research Laboratory
Annapolis, Md.

Many reports document widespread environmental contamination by chlorinated hydrocarbons (polychlorobiphenyls (PCB's) and chlorinated pesticides). In particular, several reports indicate that the marine environment of southern California receives high levels of chlorinated hydrocarbons. Fish-eating birds of southern California have relatively high levels of DDT (1.), and fish from the nearshore area off Los Angeles have extremely high (100-1000ppm) levels of DDT in their tissues (2.). Sewer outfalls appear to add many tons of PCB's each year to the southern California nearshore waters (3.).

As part of our research on nearshore ecology, we started a study to characterize the entry routes of chlorinated hydrocarbons into the nearshore area. The initial task of this study was to find a good "indicator" organism for determining the regional distribution of chlorinated hydrocarbons in the southern California marine environment. Because the Westinghouse Ocean Research Laboratory recently moved to Annapolis, Maryland, this research program probably will not be continued, but our preliminary findings may be helpful to other investigators.

METHODS

The sample organisms were wrapped in aluminum foil a few hours after collection and stored frozen until analysis. Sample preparation is described below (4.) (solvents were pesticide quality and chemicals were reagent grade).

1) Extraction. Grind the tissue with 4 to 6 times its weight sodium sulfate (anhydrous) in a blender or mortar and extract for 8 hours with hexane-acetone (2:1) in a Soxhlet extractor. Concentrate to about 75 ml with a Kuderna-Danish evaporative concentrator and add the concentrate to a separatory funnel containing 25 ml distilled water. Allow the mixed layers to separate for about 4 hours and discard the aqueous layer. Concentrate the organic layer to

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about 30 ml and transfer to a small beaker to air dry at room temperature (1 or 2 days). After weighing, dissolve the lipid in hexane and store the solution for cleanup.

2) Cleanup. Mix 9 ml fuming sulfuric acid (20-30%) with 9 ml concentrated sulfuric acid. Add slowly with stirring to 30 gm celite. Immediately add about 200 ml petroleum ether. Transfer the slurry to a 90 mm sintered-glass filter funnel and pack by pressing with a small beaker. After drawing the petroleum ether down to the surface of the column and discarding the filtrate add the lipid solution to the column and stir into the upper layers. Wash the column with 500 ml petroleum ether and concentrate the filtrate to an appropriate volume for the gas chromatographic analysis.

The samples were analyzed with a Barber-Coleman 5360 electron-capture gas chromatograph modified to hold two columns. Two glass columns 4mm (I.D.) by 1.8m were used (10% DC200 and 5% QFI on chromabsorb WHP, 100/120 mesh) at 190°C with filtered high purity nitrogen carrier gas flowing at 60 and 100 ml/min respectively. Quantitative data were obtained by comparing relative peak heights to standard compounds. Because the PCB peaks found nearly duplicated the retention times and peak height ratios of Aroclor 1254, the height of the peak at 1.55 relative to aldrin on the QFI column was used for quantitation of the PCB. The peak heights corresponding to p,p' DDE and p,p' DDD were corrected for PCB interference by subtracting amounts calculated from the height of the 1.55 peak. Needless to say, such a method leads to approximate values. Although none of these samples have been analyzed with a gas-liquid chromatograph-mass spectrometer, the expected PCB isomers were identified by this method in extracts of fish (from Pennsylvania) which gave identical elution patterns when analyzed in this laboratory (5.).

RESULTS AND DISCUSSION

Table 1 presents the data from a series of samples gathered at New Hope Rock, a reef about 1 mile from the San Diego sewer outfall on October 1, 1970. Table 2 presents the data from a series of samples gathered on October 7, 1970 about 60 miles northward off Orange County (samples 1 and 2 were taken from Crystal Cove and samples 4-6 were taken about 2 miles southward near the Laguna Beach sewer outfall). Because rather large individual variations in the body burdens of chlorinated

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TABLE I
CHLORINATED HYDROCARBONS IN SAMPLES FROM SAN DIEGO

SAMPLE *	Weight Gms. (% Lipid)		DDT(ppm)** w.wt.	(lip.wt.)	PCB(ppm) w.wt.	(lip.wt)	DDT/PCB
1. Rockfish							
liver	8.5	(31)	.46	(1.5)	1.0	(3.3)	.43
pyloric caeca	2.5	(21)	.83	(3.9)	1.0	(4.5)	.87
2. Sand Bass							
liver	12.0	(9.0)	.21	(2.3)	.31	(3.5)	.66
pyloric caeca	4.5	(12)	.52	(4.5)	.24	(2.1)	2.1
flesh	27.0	(1.5)	.078	(5.0)	.04	(2.7)	1.9
3. Sargo							
liver	7.0	(2.9)	.40	(14)	.51	(18)	.76
flesh	6.5	(.68)	.14	(2.1)	.16	(2.4)	.87
4. Sheepshead							
liver	9.0	(3.3)	.21	(6.5)	.29	(8.8)	.74
gonad	12.0	(2.1)	.073	(3.6)	.066	(3.2)	1.1
flesh	8.0	(1.3)	.065	(5.1)	.045	(3.6)	1.4
5. Red Abalone							
gonad	5.5	(1.8)	ND	(<.10)	ND	(<2.0)	-
flesh	4.3	(.49)	ND	(<.48)	ND	(<9.5)	-
6. Red Sea Urchin							
gonad	8.1	(8.1)	.072	(.89)	.21	(2.6)	.34

*_Sebastodes_ sp., _Paralabrax nebulifer_, _Anisotremis davidsoni_, _Pimelometapon pulchrum_, _Haliotis rufescens_, _Strongylocentrotus franciscanus_.

**DDT represents the sum of p,p'DDT, p,p'DDE and p,p'DDD expressed in parts per million (ppm) wet weight (w.wt.) and lipid weight (lip.wt.).

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Table 2

Chlorinated Hydrocarbons in Samples from Orange County

Sample*	Weight-Gms (%Lipid)	DDT(ppm)** w.wt.(lp.wt.)	PCB(ppm) w.wt.(lp.wt.)	DDT/PCB
1. Red Sea Urchin gonad	9.5 (19)	.057 (.30)	.12 (.66)	.45
2. Rock Scallop gonad	16 (1.2)	.032 (1.7)	.50 (9.0)	.19
3. White Abalone				
gonad	16 (1.2)	.006 (.48)	.008 (.62)	.77
digestive gland	6.0 (8.1)	.042 (.42)	.20 (2.4)	.18
4. Kellet's Whelk	24 (1.4)	.077 (5.7)	.23 (17)	.34
5. Red Sea Urchin gonad	12 (4.8)	.073 (.77)	.16 (3.3)	.23
6. Spiny Lobster				
digestive gland	6.0 (3.7)	.051 (1.4)	1.4 (38)	.37
muscle	12 (4.8)	.037 (.77)	.16 (3.3)	.23

*_Strongylocentrotus franciscanus, Hinnites multirugosus, Haliotis corrugata, Kelletia kelletii, Strongylocentrotus franciscanus, Panulirua interruptus._

** DDT represents the sum of p,p'DDT, p,p'DDE and p,p'DDD expressed in parts per million (ppm) wet weight (w.wt.) and lipid weight (lp.wt.).

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hydrocarbons have been observed between individual samples from the same populations, only the most tentative observations should be made from data such as those presented here. Bearing this point in mind, some interesting ovservations can be made.

The four samples from Laguna Beach support the idea that higher body burdens are accumulated by organisms at higher trophic levels. The lowest levels were in the abalone, a strict herbivore, the second lowest levels were in the red sea urchin, a herbivore-scavenger, and the whelk and the spiny lobster, both scavengers, had the highest levels. The data from San Diego show the urchin higher than the abalone but the fish much higher than either.

The samples from San Diego have an average DDT/PCB ratio of 1.02±.44 while the group of samples from Orange County have a ratio of 0.35±.14. While these somewhat low ratios agree with earlier observations (1.), one might be tempted to suppose that the lower ratio from the Orange County samples reflects the recent report that large amounts of PCB's are added to the marine environment by certain sewer outfalls in the Los Angeles-Orange County area and apparently none in the San Diego area. Upon examining the individual ratios, however, one finds that the urchin ratio from San Diego is nearly the same as the two from Orange County. One cannot rule out the possibility that the difference is due to a different type of uptake mechanism in the fish as compared to the invertebrates.

These preliminary data suggest the Kellet's Whelk would be a good "indicator" organism for studying the regional distribution of chlorinated hydrocarbons. In addition to being a scavenger-carnivore, a trophic level high enough to accumulate relatively high levels of chlorinated hydrocarbons, this animal appears to be a good possibility for the following reasons: 1) it is numerous enough to be easily collected over the entire southern California area; 2) it does not range far during its lifetime; 3) it is small enough to be easily composited thus avoiding the uncertainty inherent in analyzing one tissue or another; and 4) all mature individuals in the population mate and lay eggs during the same period of each year (6.) thus avoiding possible variations due to rapid lipid turnover before or after spawning.

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