PCB Residues in Atlantic Zooplankton

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Studies of the polychlorinated biphenyls in marine ecosystems that have been accomplished to date have shown that these compounds are more abundant than the chlorinated hydrocarbons of agricultural origin in the majority of ecosystems examined. Thus, PCB was present in higher concentrations than the DDT compounds in marine birds of the south Atlantic (1), in fish from the north Atlantic (2), in the Brown Pelican (Pelecanus occidentalis) populations of Florida (3), in fish and fish-eating birds from Long Island Sound (4), in marine birds of Amchitka Island in the northern Pacific (5), in some of the marine birds from Peru (6), and in sea birds breeding in Antarctica but spending the remainder of the year in Australian waters (1). Apparently only in the waters of coastal California and northwestern Mexico (7, 8) and in the Baltic (9) are DDT compounds more abundant than PCB. In California the exceptionally high concentrations of DDT compounds in marine organisms are associated with the large amounts of DDT residues in the effluent of a DDT manufacturing company (10, 11).

Most of the accumulated data refer to fish and fish-eating or tube-nosed marine birds. In this paper we present the results of measurements of PCB and other chlorinated hydrocarbons in zooplankton samples from the Atlantic Ocean. A traditional dogma of pollution ecology has asserted that residues of non-polar chlorinated hydrocarbon pollutants such as PCB are trophically accumulated in food chains. Ample documentation is available to support this thesis in terrestrial food chains or in food webs that pass from fish or other aquatic organism to mammals or birds, but the data that might support the food chain concentration theory in marine and fresh-water food webs consisting only of fish and invertebrates are surprisingly few.

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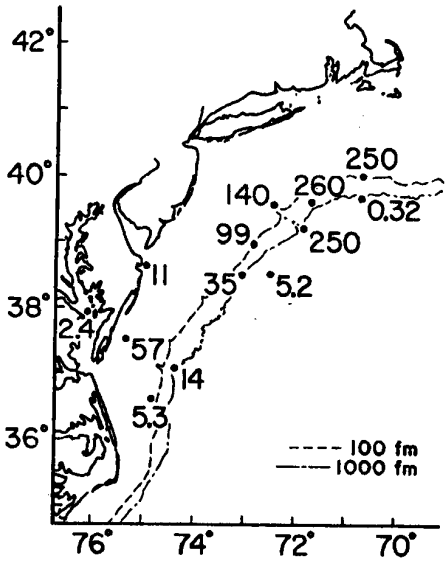

Figure 1: PCB concentrations in zooplankton of the north-west Atlantic Shelf, parts per million of the lipid weight

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MATERIALS AND METHODS

Samples were obtained during three cruises of R/V ATLANTIS II of the Woods Hole Oceanographic Institution with a #6 mesh plankton net. Station sites and other relevant data are presented in Table I. The plankton were immediately transferred to polycarbonate or glass jars and frozen. Collection of marine organisms from oceanographic vessels for pollutant analysis requires that precautions be taken to prevent accidental contamination during collection and storage (12). Hexane rinses of the collection jars, followed by concentration and gas chromatographic analysis, showed that they contained no PCB. Chips of the marine paint used on ATLANTIS II were also extracted with hexane and found to be free of PCB. Since PCB has in the past been added to hydraulic fluids to reduce flammability, contamination from leakage of hydraulic fluids on the vessel was another potential source of the PCB found. No halogenated biphenyls have been used, however, in the recent past as components of hydraulic fluids on WHOI vessels. Chlorinated paraffins were added in 1969 to reduce flammability, but this use was discontinued in 1970 (Mobil Service Dept., personal communication). Hexane extracts of the mesh of new plankton nets were free of PCB, but PCB with chlorine composition similar to that of Aroclor 1254 could be extracted from nets that had been in use. We conclude that the source of this PCB was the water, with associated organisms and petroleum droplets, through which the nets had been towed. A fraction of the PCB in the plankton may therefore be secondarily derived from the net. Relatively high PCB concentrations in fish livers from the same localities indicate the presence of PCB in the ecosystems examined (2).

Plankton samples obtained on ATLANTIS II cruise 52 by J. H. Ryther were analyzed in Berkeley. They were placed in a 65° oven overnight for determination of dry weight, ground with anhydrous sodium sulfate, and Soxhlet-extracted with 2:1 hexane:acetone. All materials extracted by this procedure were defined to be lipids, although various amounts of carotenoid pigments were also present. Because the latter compounds are comparatively non-polar, it is likely that PCB dissolves readily in them. The comparative efficiencies of extraction with hexane alone and with 2:1 hexane:acetone were not determined. Lipid samples were dried overnight at 65° for lipid weight determinations.

rth-west
pid weight

Cleanup was accomplished by passage through a celite: sulfuric acid:fuming sulfuric acid column (13) or by shaking lipid extracts in petroleum ether in a 500 ml erlenmeyer flask with 2 volumes of fuming sulfuric acid. The flask was placed on dry ice, causing the acid mixture to freeze, permitting the removal of the liquid petroleum ether fraction (14). Aliquots

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TABLE I

PCB and DDT residues in zooplankton. Parts per million wet weight (W), dry weight (D), or lipid weight (L).

Station, Sample Number, Date	Position	Depth (meters) Time Out	p,p'-DDT	p,p'-DDE	PCB	PCB/Total DDT
North-west Atlantic Shelf						
Asterias 12-71 12/10/71	41°30'N 70°40'W	0-12 30 min	N.D.	N.D.	23 (L)	----
A-II-52-1498 9/7/69	39°43'N 70°40'W	0-30 15 min	0.007 (L) 0.0015 (D)	0.035 (L) 0.010 (D)	0.32 (L) 0.071 (D)	7.7
A-II-52-1499 9/7/69	40°04'N 70°40'W	0-25 7 min	N.D.	7.0 (L)	250 (L)	36
A-II-52-1512 9/11/69	39°37'N 71°40'W	0-10 10 min	N.D.	N.D.	260 (L)	>50
A-II-52-1513 9/12/69	39°13'N 71°50'W	0-10 15 min	N.D.	N.D.	250 (L)	>50
A-II-52-1514 9/12/69	39°37'N 72°25'W	0-10 13 min	N.D.	N.D.	144 (L) 1.9 (D)	>50
A-II-52-1520 9/14/69	38°59'N 72°50'W	0-85 13 min	N.D.	N.D.	99 (L) 3.0 (D)	>50

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TABLE I
(Continued)

Station, Sample Number, Date	Position	Depth (meters) Time Out	p,p'-DDT	p,p'-DDE	PCB	PCB/Total DDT
North-west Atlantic Shelf (continued)						
A-II-52-1521 9/14/69	38°32'N 72°25'W	1800 1 hr 36 min	0.08 (L)	0.21 (L)	5.2 (L)	18
A-II-52-1522 9/16/69	38°33'N 73°00'W	0-20 15 min	N.D.	0.54 (L) 0.016 (D)	30 (L) 0.87 (D)	55
A-II-52-1525 9/17/69	38°39'N 74°59'W	0-20 11 min	N.D.	2.4 (L) 0.11 (D)	11 (L) 0.53 (D)	4.8
A-II-52-1527 9/17/69	37°30'N 75°21'W	0-20 15 min	N.D.	N.D.	57 (L)	>50
A-II-52-1532 9/20/69	37°56'N 76°10'W	Surface 10 min	N.D.	N.D.	2.4 (L) 0.10 (D)	----
A-II-52-1539 9/23/69	36°35'N 74°51'W	0-20 13 min	N.D.	0.090 (L) 0.003 (D)	5.3 (L) 0.18 (D)	60
A-II-52-1541 9/23/69	37°04'N 74°25'W	0-20 20 min	N.D.	0.34 (L) 0.015 (D)	13.6 (L) 0.65 (D)	40
Open North Atlantic						
A-II-59-22 11/70	23°41'N 54°29'W	0-100	<0.00001 (W)	<0.00001 (W)	0.30 (W)	>30,000

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TABLE I
(Continued)

Station, Sample Number, Date	Position	Depth (meters) Time Out	p,p'-DDT	p,p'-DDE	PCB	PCB/Total DDT
Open North Atlantic (continued)						
A-II59-36 12/70	30°52'N 47°30'W	0-100 60 min	<0.00001 (W)	N.D.	0.45 (W)	>45,000
Open South Atlantic						
A-II-60-4-13 4/71	34°05'S 42°40'W	0-200 20 min	0.50 (L) 0.003 (W)	N.D.	120 (L) 0.64 (W)	200
A-II-60-4-33 4/71	32°50'S 26°24'W	0-200 20 min	0.61 (L) 0.001 (W)	N.D.	53 (L) 0.12 (W)	100
A-II-60-S-PT-106 6/71	14°03'S 05°55'E	0-200 20 min	0.068 (L) 0.0002 (W)	0.023 (L) 0.00007 (W)	7.3 (L) 0.021 (W)	80
A-II-60-S-PT-89 5/71	32°49'S 13°09'E	0-200 20 min	0.132 (L) 0.0002 (W)	N.D.	10 (L) 0.018 (W)	80

N.D.: Not Detected

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of the extracts were injected into a Microtek 220 gas chromatograph equipped with a nickel-63 electron capture detector. The column used was 3% QF-1 on Chromosorb W, 80-100 mesh, acid washed and DMCS treated. Nitrogen was the carrier and purge gas. Flow through the column was 95 ml/min., and flow through the purge was 45 ml/min. Column temperature was 190°, injection port temperature 230°, and the detector temperature 250°.

The remaining samples were analyzed in Woods Hole. They were extracted three times with redistilled hexane in a Virtis homogenizer. The dried extract was concentrated in a Kuderna-Danish apparatus and was partitioned three times with acetonitrile to separate the chlorinated hydrocarbons from the fat. The acetonitrile solution was diluted with brine and extracted twice with hexane. The dried and concentrated extract was applied to the top of a 10 x 2.5 cm column of activated florisil. The chlorinated hydrocarbons were eluted with 6% ethyl ether in hexane (v/v). An 8% QF-1:2% OV-17 column on Gas Chrom Q was used.

The presence of p,p'-DDT was confirmed by saponification (15). The profile of PCB peaks matched closely that of Aroclor 1254, which was therefore used as a standard.

RESULTS AND DISCUSSION

The results of the analyses are presented in Table I. The station locations of ATLANTIS II cruise 52 from which plankton samples were obtained are shown in Figure 1, together with the PCB concentrations found in the lipids of the zooplankton of each station.

Expressed on a lipid basis the concentrations are relatively high and are comparable to the PCB levels in fish from Long Island Sound. PCB in the lipids of 8 fish species obtained in the vicinity of Great Gull Island, Long Island Sound, ranged from 10 to 180 ppm, with a median value of 60 ppm (4). PCB in the zooplankton from the stations on the continental shelf and slope ranged from 2.4 to 260 ppm, with a median value of approximately 40 ppm. Median percent lipid weight of dry weight was 3.8%. On a dry and wet weight basis, with the assumption that dry weight constitutes 10% of wet weight, representative concentrations in zooplankton from the shelf and slope areas would be in the order of 1.5 ppm and 0.15 ppm respectively. Median PCB concentration on a wet weight basis of the fish from Long Island Sound was in the order of 1 ppm (4).

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In all samples the ratio of the total PCB to the total DDT concentrations was comparatively high, considerably higher than that found in marine birds of the north and south Atlantic (1) or in marine fish (2). The reasons for the discrepancy are not clear. DDE concentrations have been shown to be linearly related to PCB concentrations among the Brown Pelicans of Florida (3), among several species of aquatic birds in the Gulf of California (8), and in aquatic birds of several California ecosystems (8). PCB-DDE ratios, however, were not determined in fish or invertebrates of these ecosystems, but the data suggest that the mechanisms of accumulation and excretion for both groups of compounds are comparable. Clarification of this apparent inconsistency would require determination of the relative solubilities of DDT and PCB compounds in sea water and of the partition coefficients between concentrations in sea water and the various lipid fractions of marine organisms.

The collections from the continental shelf and slope waters show a north-south gradient, with the highest concentrations at the latitude of New York City and northern New Jersey and lower concentrations east of Virginia (Figure 1). The sample obtained from surface waters at station 1498, where the depth exceeded 1,000 fathoms, contained very low concentrations of PCB, less than one part per million on a lipid basis. At station 1521, also a deep-water station, the samples were obtained below 200 meters and also had low amounts of PCB. High concentrations, however, were recorded in surface zooplankton over the mouth of the Hudson Canyon, where the depth exceeded 1,000 fathoms. The collections from the North Atlantic contained surprisingly high concentrations of PCB, ranging from 0.007 to 0.45 ppm on a wet weight basis. On the assumption that the dry weight constitutes 10% of the wet weight, these concentrations are equivalent to those recorded from shelf and slope waters. In the south Atlantic, a pronounced west-east gradient is evident (Table I). A possible source of the PCB is the highly industrialized area in the vicinity of Sao Paulo, Brazil.

We assume that the PCB levels in the zooplankton samples are in physical-chemical equilibria with those in the ambient aqueous environment and can be used to indicate levels of contamination in the water itself. Stalling and Mayer (16) have shown that levels of PCB accumulated by fish from ambient water are related to the PCB concentrations in the water. Other workers (17, 18) have shown that fish exposed to chlorinated hydrocarbon insecticides will lose them to the ambient water system when the contamination is removed. These experiments suggest that chlorinated hydrocarbon levels in fish are in equilibrium with the considerably lower concentrations in the surrounding water environment. Hamelink et al. (19)

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found that DDT residues in freshwater invertebrates under experimental conditions were a direct function of DDT concentrations in the water. The partition coefficients between lipids and water and between fresh weight and water were respectively in the order of 10^6 and 2×10^4. Stalling and Mayer (16) report partition coefficients for PCB between wet weight of fish and invertebrates with water to be in the order of 5×10^4 and 2×10^4 respectively. PCB residues acquired by trophic accumulation in food webs could therefore be released into the ambient media to satisfy equilibrium conditions.

The relative amounts of PCB present in solution in sea water, associated with organic particulate materials, and in the planktonic biomass are not yet known. If the amount in the water were substantially greater than in the plankton, the PCB concentrations in the plankton would not depend upon the total planktonic biomass. An increase in plankton density would not result in lower residue levels in the plankton. Under experimental conditions, however, DDT residues in algae were inversely proportional to the density of algae (19). In this system, the major fraction of the DDT residues was not in the water reservoir. Before concluding that equivalent PCB levels in zooplankton samples imply equivalent levels of local PCB contamination, it would be necessary to know, therefore, whether the sea water is a virtually infinite source of PCB for the planktonic biomass.

Aerial transport of DDT appears to be the major route of entry of these compounds to the marine environment (20). U.S. PCB production figures are lower than DDT production figures (21) and a large fraction of the PCB is not released to the environment. PCB was detected in all samples of rain water analyzed in an extensive study in Great Britain (22) and its presence in fish in remote Arctic lakes (23) also suggests that aerial transport is a significant dispersal pathway. The proportion of the PCB residues recorded in the zooplankton that derives from aerial fallout, and the chlorine percentage of this PCB, remain to be determined. Moreover, as discussed above, the exceptionally high PCB:DDT ratios in the zooplankton, as compared to those in the fish, require further investigation.

The chlorine composition of the PCB detected in the zooplankton was approximately 54%. U.S. production of Aroclor 1254 in 1970 amounted to 12 million pounds — only one quarter of the production of 49 million pounds of Aroclor 1242. It might be expected therefore that biphenyls with fewer chlorine atoms would predominate in planktonic samples unless these compounds were selectively degraded. Alternatively, since the

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solubilities and partition coefficients with organisms of the individual PCB compounds in a complex mixture present in an aqueous system can be expected to show considerable variation, the compounds detected in plankton would preferentially be those with lower solubilities in water and higher partition coefficients. The PCB compounds recorded in the plankton might not therefore reflect the overall PCB composition in the marine environment. Nevertheless, it is surprising and as yet unexplained that the relative amounts of PCB compounds should match the 54% mixture so closely.

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