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Observations on the Distribution of Chlorinated Hydrocarbons in Atlantic Ocean Organisms[1]

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ABSTRACT

Industrial polychlorobiphenyls (PCBs) and the DDT family (t-DDT) were measured in several species of organisms collected from the open Atlantic Ocean between 66°N and 35°S latitude. All the organisms had higher concentrations of PCBs than t-DDT. Many trophic levels were represented in the collections, but the analytical data offer no support for food chain magnification among gilled organisms. Mixed plankton contained a higher average concentration of PCB (100 μg/kg) than any other class of gilled organism in the Atlantic. Analyses of mesopelagic organisms revealed the presence of PCBs and t-DDT well below the mixed layer, although in concentrations ten times lower than pelagic species.

No horizontal concentration gradients were discernible within the plankton or mesopelagic fish, although North America is the presumed major source of the chlorinated hydrocarbons in the Atlantic.

The PCB/t-DDT ratio is about thirty in the marine atmosphere, surface water and plankton. The ratio decreases to about three in high predators and in the mid-water organisms, indicating that although similar in molecular structure, t-DDT and PCBs move differently through the marine environment.

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1. Introduction. During the past three decades the surface of the earth has been dosed with megaton quantities of synthetic halogenated hydrocarbons such as pesticides, Freons, polychlorobiphenyls (PCBs) and ethylene dichloride. In recent years great concern has been expressed about the possible harmful effects of these chemicals in the environment to man and wild-life (Hammond, 1972). The oceans are of particular concern in this regard because their dominance of *the earth's surface makes them the logical final repository for stable pollutants.* In spite of these considerations only coastal zones and continental seas have been assessed for prevailing concentrations of these pollutants.

We have been engaged in the first open-ocean study to determine the concentrations of PCBs and members of the DDT family (t-DDT) in organisms of the Atlantic Ocean. In this paper we present the results of our analyses, and observations on the distribution of PCBs and t-DDT in Atlantic biota. The collecting was accomplished between *December 1970* and *August 1972*. The frozen specimens were analyzed within six months after capture. The cruise tracks are set out in Figure 1.

Some of our previously published data is included in the tables to facilitate discussion (Harvey et al., 1972). The data recorded here should also serve as a 1970–1972 baseline reference for future efforts to determine the effect of the self-imposed worldwide restrictions on PCB usage commencing about 1971.

2. Methods. a. *Collection* — Our published procedures for collecting and preserving marine organisms for hydrocarbon analyses were followed rigorously (Criss et al., 1973). Plankton was collected in a # 6 mesh nylon net (1 meter). Samples which contained any visible tar or plastic were discarded (Harvey and Tsui, 1973). Pelagic fish were caught by hook and line or dipnet. The commercial groundfish were taken from the trawler nets as soon as they arrived on deck. The mesopelagic *organisms* were caught in standard Isaacs—Kidd midwater trawls. We were fortunate that none of the six ships used for collecting had PCBs in their paints or lubricants, or hydraulic fluids.

b. *Analysis* — The samples were extracted (10–25 g of tissue or of whole organism) with three 100 ml portions of hexane which had been distilled from sodium in an all glass still. The hexane extract was concentrated to 10 ml in a Kuderna—Danish apparatus on a steam bath. One ml was withdrawn and allowed to evaporate in a tared dish to determine the per cent lipid. An aliquot of the remaining 9 ml., containing 1 g or less of lipid, was applied to the top of a 12×2 cm column of Florisil packed in hexane. The chlorinated hydrocarbons were eluted with 200 ml of 6% ethyl ether in hexane (v/v). (The lipids of the Myctophidae (Table V) contain mainly wax esters (Nevenzel, 1970) which behave as hydrocarbons on Florisil and elute with the PCBs. These must be removed before gas liquid chromatography (GLC) or serious contamination of the detector will occur. This was accomplished by storing the extract for 3–5 days with concentrated sulfuric acid). The cleaned-up extract was concentrated in a calibrated tube fitted with a micro-Snyder column to a volume suitable for GLC (0.2–2 ml).

Five microliters of the concentrated extract was injected into a Perkin Elmer

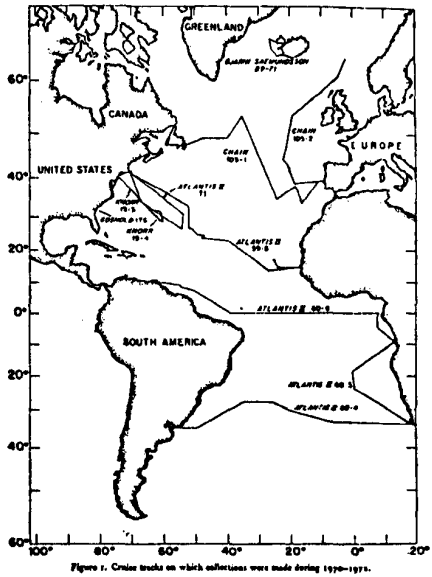

Figure 1. Cruise tracks on which collections were made during 1970–1972.

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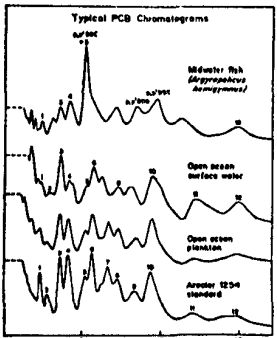

Figure 2. Typical gas chromatograms of chlorinated hydrocarbon extracts.

gas chromatograph (Model 900) equipped with a 2 m × 2 mm glass column and a Ni-63 electron capture detector. The column packing was 1:1 2% OV-17 and 8% QF-1 on Anakrom. The chromatogram was run isothermally at 190°. The chromatogram was assessed for its approximate PCB chlorine content and the closest matching PCB standard and a t-DDT mixture were injected immediately after the extract. In most cases the chromatographic pattern matched the commercial mixture Aroclor 1254 (Monsanto). For quantification, six peaks were chosen from the sample chromatogram that eluted after p, p'-DDE, and, clearly (on the basis of position and shape) matched peaks on the standard chromatogram. From the sum of the heights of these six peaks versus those of the corresponding standard peaks, and the quantity of PCB represented in the standard, the quantity of PCB's represented in the sample was calculated. Missing peaks in the sample chromatogram were included in the summation as zero, e.g., peak 7 in the fish chromatogram shown in Fig. 2. The DDT family was quantified by measuring the peak heights of p, p'-DDE, p, p'-DDD and p, p'-DDT and comparing them to the standards. In all cases the procedural blank gave values less than 0.5% of the measured values.

Table I. Interlaboratory intercalibrations.

1. Shark liver homogenate Laboratory:	WHOI	#2	#3	#4	#5	#6
t-DDT (ppm)	11	11	15	~	14	14
PCB'S (ppm)	15	14	6	16	15	13

2. O.E.C.D. Spiked Corn Oil	WHOI ppm	True ppm
DDT	4.5	4.5
DDD	5.8	7.5
DDE	10.0	15.0
Dieldrin	4.5	5.0

DDT presence was confirmed by alkaline dehydrochlorination to DDE and in a number of cases by selected mass range mass spectrometry. PCB presence was confirmed by the persistence of the peaks after alkaline treatment, and, in a number of cases by perchlorination to decachlorobiphenyl with antimony pentachloride followed by GLC (Armour, 1973).

The above described procedures have been verified in two intercalibrations which are tabulated in Table 1. The shark liver was homogenized by us, analyzed and distributed to five other laboratories in the U.S., Canada and the United Kingdom. The spiked corn oil has been prepared by the Organization of Economic Cooperation and Development (OECD).

Some typical chromatogram are shown in Figure 2. The match between the standard chromatogram and the plankton and surface water chromatograms were generally quite good. However, there was present some alteration of the relative peak heights, even in the mid-boiling range, i.e., peaks 5 through 9. The chromatogram of the midwater fish is typical and shows significant alteration of several of the PCB isomers while the DDT family becomes more prominent.

3. Results. The results of 53 analyses for PCB in plankton are graphically presented in Figure 3. The mean concentration of PCB's in both North and South Atlantic plankton was 200 μg/kg (wet weight). The four samples containing more than 1000 μg/kg were all very rich in phytoplankton. The rest were mainly mixed zooplankton. The PCB/t-DDT ratio was always greater than 30.

Chlorohydrocarbon analyses of commercial fish from the New England and Icelandic fishing grounds are presented in Tables II and III. The Icelandic fish contained about an order of magnitude less than those from Georges Bank.

Open ocean pelagic fish contained DDT and PCB levels slightly lower than the Icelandic groundfish (Table IV).

Table V lists the analyses of 56 mesopelagic organisms in six families and

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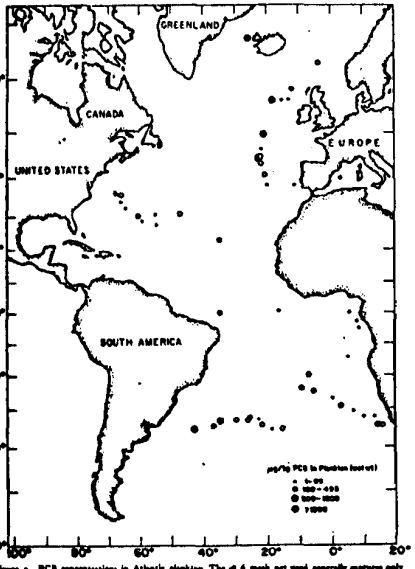

Figure 3. PCB concentrations in Atlantic plankton. The ø 6 mesh net used generally captures only zooplankton.

eleven genera. Within each family the organisms are arbitrarily arranged in order of increasing latitude of capture.

Table II. Chlorinated hydrocarbons in Georges Bank[1] fish.

Sample	Identification	Date	PCB (µg/kg)	t-DDR µg/kg
1	Cod (Gadus morhua) muscle	6/71	58 (94,000)[2]	11 (9,700)
	liver		22,000 (41,000)	2700 (5,100)
2	Pollock (Polachius virens) muscle	6/71	57 (30,000)	9 (2,100)
	liver		2800 (4,000)	1,100 (1,800)
3	Pollock (" ") liver	2/72	65,000 (70,000)	5900 (4,790)
4	Pollock (" ") liver	2/72	1335 (4,200)	950 (2,600)
5	Haddock (Melanogrammus aeglefinus) muscle	6/71	30 (30,000)	2 (2,500)
	liver		8,800 (35,000)	390 (1,500)
6	Haddock (" ") liver	2/72	3,900 (11,000)	1600 (4,300)
7	Haddock (" ") liver	2/72	2200 (8,600)	1100 (4,600)
8	Redfish (Sebastes marinus) muscle	6/71	190 (17,000)	73 (6,600)
	liver		1,900 (10,000)	670 (3,700)
9	Redfish (" ") liver	2/72	1,500 (7,700)	1,300 (6,700)
10	Shrimp (Pandalus borealis)	6/71	360 (28,000)	7 (500)

[1] The New England commercial fishing grounds, located about 42°N, 66°W.
[2] Concentrations in parentheses are on a lipid weight basis.

Table III. Chlorinated hydrocarbons in Denmark Strait[1] organisms.

Sample	Identification	Position North	Position West	Depth (m)	PCB (µg/kg)[2]	t-DDT µg/kg
1	Cod (Gadus morhus) muscle	65°45′	25°33′	90	2 (830)[3]	3 (1300)
	liver				730 (1900)	170 (440)
2	Shrimp (Pandalus borealis)	63°55′	22°38′	0–200	18 (850)	1 (27)
3	Haddock (Gadus aeglefinus) muscle	65°48′	26°10′	220	–	3 (2900)
	liver				480 (1100)	260 (590)
4	Arctic Cod (Boreogadus saxarcki) whole	65°23′	21°15′	240	2100 (31,000)	9 (130)
5	Argentine (Argentina silus) muscle	65°25′	26°15′	240	19 (2,500)	6 (750)
	liver				1100 (10,000)	51 (470)
6	Wolf-fish (Anarhichas lupus) muscle	65°23′	26°18′	240	22 (4,500)	3 (330)
7	Halibut (Reinhardtius Hippoglossoides) muscle	66°15′	26°10′	370	88 (740)	21 (730)
	liver				96 (280)	330 (930)
8	Redfish (Sebastes marinus) muscle	66°15′	26°10′	370	360 (5600)	22 (300)
	liver				900 (3080)	190 (620)

[1] Collected in September 1971 from the Icelandic research trawler, Bjarni Saemundsson.
[2] All the samples contained mixtures of the three Aroclors, 1262, 1254 and 1260. The closest match was used for quantification.
[3] Concentrations in parentheses are on a lipid weight basis.

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Table IV. Chlorinated hydrocarbons in open North Atlantic pelagic fish[1].

Sample	Identification		Position North	Position West	PCB (μg/kg)	t-DDT μg/kg
1	Flying fish	whole....	31°	79°	50	7
2	Flying fish (Cypselurus cyanleus)	muscle...	14°50′	10°18′	1.4 (410)[2]	0.6 (180)
3	Flying fish (Prognichthys pondeletii)	muscle...	30°	60°	4 (1500)	4 (1500)
4	Trigger fish (Canthidermis maculatus)	muscle...	19°30′	29°57′	1.9 (1900)	0.1 (120)
5	Dolphin (Coryphaena equiselis)	liver.....	17°47′	28°35′	1100 (21,000)	95 (2000)
6	Dolphin (Coryphaena hippurus)	muscle...	25°06′	36°03′	10 (10,000)	3 (3300)
7	Shark (Carcharhinus longimanus)	liver.....	14°30′	22°17′	1200 (2500)	400 (820)
8	Silky shark	liver.....	31°	78°	5800 (13,000)	4800 (11,000)

[1] Collected during the winter of 1970–1971 with nets and by jigging.
[2] Concentrations in parentheses are on a lipid weight basis.

In Tables II–V the concentrations are presented in μg/kg (ppb) wet weight, and, in parentheses, μg/kg per lipid weight. Table V is graphically summarized in Figure 4 which shows average concentrations of PCBs and t-DDT in each genera.

4. Discussion. Our observations contradict some generally accepted notions on DDT and PCB behavior in the environment. We will discuss three of these observations in particular. 1) There are no discernable horizontal concentration gradients from near shore to the open sea. 2) There is no consistent evidence for food chain magnification. 3) PCBs and DDT move through the marine ecosystem differently.

a. *Concentration gradients.* The concentrations of PCBs in Atlantic plankton, illustrated in Figure 3, reveal no consistent horizontal gradient. The lower levels seen in the Sargasso Sea plankton correlate well with the lower concentrations of dissolved PCB's found there (Harvey et al., 1973) and may be due to the small amount of precipitation.

On the other hand, levels of soluble radionuclides from atmospherically delivered fallout are not noticeably low in the Sargasso Sea (Bowen et al., 1968) at OWS ECHO. It is likely that the delivery mechanism that seems to operate for Sr 90 at OWS ECHO is different for PCB. It is also likely that PCB, once delivered to the Sargasso Sea surface is re-evaporated (this is a high evaporation area) which is not possible for Sr 90, or that it is efficiently scavenged from the water surface by the large numbers of tarballs found in this ocean region. We also observed low PCB concentrations in plankton samples taken off the coast of Southwest Africa. In this region, also the Sr 90 data indicate

Table V. Atlantic mesopelagic organisms.

No.	Identification	Date	Lat.	Long.	Depth	PCB (μg/kg)	t-DDT (μg/kg)
			A. Chauliodontidae				
1	Chauliodus danae	6/71	36°10′S	07°23′W	600	2.5 (210)[1]	2 (170)
2	" "	5/71	25°59′S	03°28′W	450	4 (580)	1 (170)
3	Chauliodus sloani	6/71	12°52′S	08°15′E	500	5 (800)	2 (270)
4	" "	11/70	14°50′N	25°51′W	660	14 (1,900)	5 (660)
5	Chauliodus danae	11/70	24°55′N	35°53′W	900	10 (1300)	5 (700)
6	" "	12/70	28°00′N	45°00′W	800	60 (7300)	12 (1,500)
7	Chauliodus sloani	7/8/72	34°54′N	15°03′W	700	10 (5,500)	2 (900)
8	" "	7/8/72	44°41′N	30°44′W	660	30 (760)	12 (300)
9	" "	8/1/72	51°25′N	20°21′W	725	42 (9,200)	12 (2,700)
10	" "	6/30 72	52°31′N	35°02′W	510	78 (2,200)	9 (250)
			B. Stomiatidae				
11	Stomias boa	7/12/72	39°55′N	18°11′W	110	54 (1,700)	7 (230)
12	" "	7/4/72	43°58′N	30°36′W	95	1 (4,500)	14 (7,000)
13	" "	8/25/72	48°29′N	48°44′W	90	87 (2,000)	16 (450)
14	" "	6/26/72	48°58′N	45°00′W	510	33 (2,200)	9 (300)
15	" "	8/1/72	51°25′N	20°21′W	725	28 (1,600)	11 (640)
16	" "	8/4/72	55°41′N	15°02′W	30	20 (340)	47 (1,200)
			C. Myctophidae				
17	Benthosema glaciale	7/23/72	38°19′N	19°28′W	50	45 (780)	–
18	" "	7/22/72	38°23′N	11°11′W	70	86 (700)	3 (25)
19	" "	7/8/72	44°41′N	30°44′W	660	73 (470)	4 (30)
20	" "	8/25/72	48°29′N	48°44′W	90	82 (470)	7 (40)
21	" "	8/26/72	49°00′N	41°54′W	650	72 (430)	6 (34)
22	" "	8/26/72	42°00′N	44°54′W	650	6 (40)	–
23	" "	6/30/72	52°31′N	35°02′W	510	170 (890)	17 (90)
24	" "	6/30/72	52°31′N	35°02′W	510	120 (700)	14 (82)
25	" "	8/4/72	55°41′N	15°02′W	30	70 (950)	0.5 (7)
26	" "	8/1/72	60°05′N	05°53′W	65	160 (1100)	10 (70)
27	" "	8/9/72	63°14′N	02°52′W	50	170 (1100)	29 (190)
28	Myctophum punctatum	6/25/72	48°30′N	48°37′W	55	110 (810)	10 (52)
29	Myctophum punctatum	6/30/72	52°31′N	35°02′W	510	54 (350)	5 (30)
30	Protomyctophum arcticum	6/28/72	49°49′N	39°22′W	520	33 (540)	10 (170)
31	Protomyctophum arcticum	6/30/72	52°23′N	34°31′W	590	74 (1,800)	11 (230)
32	Protomyctophum arcticum	6/30/72	"	"	"	45 (1,800)	17 (600)
33	Ceratoscopelus warmingi	7/12/72	39°39′N	16°16′W	60	10 (140)	5 (70)
34	Ceratoscopelus warmingi	7/7/72	35°08′N	24°25′W	40	11 (280)	3 (85)

[1] Concentrations in parentheses are on a lipid weight basis.

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Table V (continued).

No.	Identification	Date	Lat.	Long.	Depth	PCB (µg/kg)	t-DDT (µg/kg)
35	Ceratoscopelus maderensis	7/6/72	37°28'N	26°38'W	75	16 (320)	8 (120)
36	Hygophum hygomi	7/8/72	34°44'N	21°33'W	40	–	2 (120)
37	" "	7/23/72	38°19'N	19°28'W	50	18 (380)	5 (70)
			D. Oplophoridae				
38	Acanthephyra hoeckelii	5/71	34°28'S	18°13'E	750	6 (240)	3 (120)
39	Acanthephyra purpurea	7/72	34°54'N	15°03'W	700	50 (890)	17 (890)
40	Acanthephyra hoeckelii	6/72	48°58'N	45°06'W	510	26 (230)	4 (37)
41	Systellaspis sp	4/71	34°09'S	42°52'W	200	14 (370)	8 (220)
42	Systellaspis debilis	11/70	15°30'N	26°20'W	90	9 (490)	3 (170)
43	" "	12/70	28°00'N	45°00'W	800	35 (1000)	6 (170)
44	" "	7/72	33°37'N	16°12'W	125	30 (1000)	5 (1700)
45	" "	7/72	36°15'N	25°33'W	760	36 (610)	12 (200)
46	" "	7/72	44°41'N	30°44'W	660	40 (710)	6 (300)
			E. Sternoptychidae				
47	Argyropelicus hemigymnus	7/72	35°10'N	18°56'W	660	22 (3,500)	4 (600)
48	Argyropelicus hemigymnus	7/72	36°12'N	13°43'W	600	28 (2,300)	6 (470)
49	Argyropelicus hemigymnus	7/72	42°17'N	29°39'W	130	66 (4,000)	11 (660)
50	Argyropelicus hemigymnus	7/72	44°01'N	22°06'W	370	28 (2,400)	7 (360)
51	Argyropelicus hemigymnus	7/72	44°54'N	22°07'W	510	37 (2100)	11 (650)
52	Argyropelicus Oulpherni	7/72	"	"	510	19 (440)	6 (180)
53	Argyropelicus hemigymnus	8/72	57°18'N	12°02'W	280	24 (1000)	11 (320)
			F. Gonostanomidae				
54	Cyclothone microdone	7/3/72	44°41'N	30°44'W	660	37 (5000)	8 (720)
55	Cyclothone microdone	6/30/72	32°31'N	35°17'W	510	41 (38,000)	14 (12,000)
56	Cyclothone microdone	8/5/72	38°10'N	11°29'W	850	140 (2,200)	20 (320)

that delivery processes of atmospheric pollutants are normal for those latitudes (Bowen et al., unpublished). It is possible to explain the low PCB value as produced by dilution with recently upwelled deep water and by rapid removal to the sediments because of the very high productivity of the area.

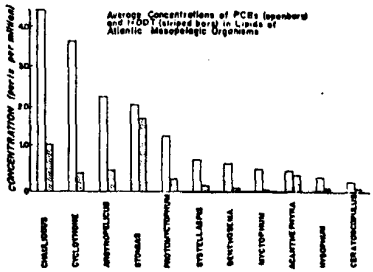

Figure 4. Average concentrations of PCBs (open bars) and t-DDT (striped bars) in lipids of Atlantic mesopelagic organisms.

Williams and Holden (1973) have reported a discernable PCB concentration gradient in Atlantic plankton collected between the Firth of Clyde (Scotland) and OWS India (59°00'N 19°00'W). Furthermore, the PCB concentrations reported in the plankton collected near OWS India are lower (10–70 µg/kg) than our average concentrations found in that region (Fig. 3). These apparent discrepancies may be due to the radically different sampling methods used. Williams and Holden towed a silk plankton net (0.3 mm mesh) at a depth of 10 m at 8 knots. The plankton used in our work were collected in a nylon net (0.24 mm mesh) towed obliquely from 150 m to the surface at 1 knot or less. We believe these sampling differences do not allow a direct comparison of the data at this time since the plankton collected by the two methods would be not comparable (Tranter, 1968).

Atmospheric measurements of PCB's over the Atlantic do reveal that more is being delivered to the coastal areas than the open sea. In fact, the decrease is exponential (Harvey and Steinhauer, 1973). It seems likely that particulate matter in the water is mediating the quantity of PCB's available for uptake. The higher particulate load in coastal waters (Manheim, et al., 1970) allows for greater adsorption scavenging and sedimentation of chlorinated hydrocarbons out of the water. There is a decrease in suspended matter seaward to about 100 times less than inshore concentrations. Thus, most of the PCB's and t-DDT delivered to the open ocean is available in the dissolved phase (Harvey et al., 1973). The open ocean is made even more vulnerable to chemical con-

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tamination by the slow sedimentation rate. Thus, if there is a concentration gradient in the ocean, as seems likely, it should be seen in the sediments and bottom feeders. This is substantiated by the ten-fold higher concentrations of chlorinated hydrocarbons seen in the groundfish of George's Bank (Table II), and the Baltic (Otterlind et al., 1971) over those from the Denmark Strait (Table III) which is over 2,000 km downwind of the nearest American sources.

The lack of difference in the PCB concentrations in the North and South Atlantic plankton cannot be explained at this time. The much smaller land surface of the southern hemisphere, the relatively low level of industrialization of the countries bordering the South Atlantic, and the lack of north to south circulation of Atlantic Ocean surface waters, all appear to require that the high concentrations of pollutants we observe in the South Atlantic represent materials contributed to the environment in the northern hemisphere, largely in Europe and North America, and transported in the atmosphere to the southern hemisphere. Such transport is shown by the atmospheric movements of various tracers, including fallout radioactivity (Newell et al., 1969) but details of the pathways are not yet well worked out. North to south gradients have been observed for true gaseous hydrocarbons such as Freon (Lovelock et al., 1973). However, high boiling chlorinated hydrocarbons do not behave as inorganic radionuclides or true gases. They can be transported in the vapor, aerosol, adsorbed and dissolved states depending on various equilibria and routes into the open environment and the details of the interhemispheric transport of these compounds must await further research.

b. *Food Chain Relationships.* Marine food webs are very complicated and there is much disagreement among marine biologists on prey-predator relationships. Many marine organisms are very opportunistic and flexible in their diets. Any attempt to use a chemical tracer for food web information will be confounded by these facts, as well as by the differences between individuals of a species. Thus, we must accept "order of magnitude" comparisons.

Careful scrutiny of the data in the Tables and Figure 3 reveals no evidence for biomagnification of chlorinated hydrocarbons on a wet or lipid weight basis. In fact, plankton exhibit the highest average concentrations. Flying fish (Table IV and Giam et al., 1972) which feed largely on plankton carry order of magnitude less PCB and DDT. The low concentrations seen in the trigger fish have been confirmed by others in the Gulf of Mexico (Giam et al., 1973). Of high trophic level predators, sharks consistently carry high loads of PCB's and DDT while barracuda have concentrations two orders of magnitude less (Giam et al., 1972).

The midwater fish offer a better opportunity for comparison because they are relatively isolated from the wind-mixed surface waters. The genera are arranged in Figure 4 in order of decreasing average PCB concentration in their lipid. *Chauliodus* and *Stomias* are the highest predators, which eat fish as well as plankton. *Cyclothone*, the smallest and deepest living is probably the lowest

predator. *Acanthephyra* and *Systellaspis* are decapods. The rest are myctophidae. We have been unable to find any correlations between the PCB or DDT concentrations in these species and their depth of habitat, lipid content, migratory habit, age or trophic level. The most likely explanation is that the lipid fractions of gilled organisms are in physical-chemical equilibrium with the water, by a partitioning of hydrocarbons between blood lipids (and, by circulation, with other body lipids) and the seawater directly through permeable body surfaces. Partitioning directly from the water has been postulated by others as the major intake pathway for fresh water fish (Reinert, 1967; Hamelink, et al., 1971; Sodergren, et al., 1972). However, in those cases in which well-defined food webs were studied (Hamelink, et al., 1971) the chlorinated hydrocarbon concentrations happened to show food chain magnification. Our data represent members of several complex food chains and show no consistent trend between PCB or DDT concentrations and prey-predator relationships. A similar conclusion was reached from a fresh water fish monitoring program (Henderson et al., 1971).

The lack of food chain magnification is readily understood. The lipid stores of organisms are the major repository for chlorinated hydrocarbons. Lipid composition varies among species, within species at different seasons and ages, and, in different parts of the body (Love, 1970). Some of these different lipids will be better hydrocarbon solvents than others regardless of trophic level. Furthermore, some organisms will have equilibration times with the water that are significantly different from others as a result of metabolic activity, blood supply and surface to volume ratios. The result of such variables is the diverse interspecies relationships shown in Tables II–V. Thus, the vertically migrating mesopelagic organisms can ingest great quantities of chlorinated hydrocarbons associated with the plankton at night. During the day spent at depth, part of the ingested contaminants will be lost to the water by diffusion, excretion, etc. in as to satisfy equilibrium conditions. The result is that these organisms contain 100 times less chlorinated hydrocarbon (wet or lipid weight basis) than their prey.

c. *PCB/t-DDT Relationships.* We have pointed out that based on production and release estimates there should be much more t-DDT than PCB in the ocean (Harvey, et al., 1973). This is clearly not the case, but the PCB/t-DDT ratio shows some consistent trends and may be a useful probe into dietary behaviour, migration habits and environmental stability. The ratio tends to be greater than 30 in the atmosphere, surface seawater and plankton. It decreases to 10 or less in the high trophic level predators, and to 5 or less in the mesopelagic organisms which live at depths below the thermocline. However, there are intriguing exceptions. Eleven species of North Atlantic sea birds were observed to have an average PCB/t-DDT ratio of 5, but the Kittiwake, which has a diet similar to many of the others, had a ratio of 30 (Bourne and Bogen, 1972). A similar relationship exists between the shrimp,

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Pandalus borealis and all the groundfish living in the same water. It is interesting to note that the seabirds which carry prey up and out of the mixed layer, and the midwater animals which take prey down below that region should have the same PCB/t-DDT ratio (5) although they differ in absolute concentrations by 10x. Plausible explanations elude us at this time. We can only state the observation that PCB's and t-DDT, although similar in molecular structure and physical properties, appear to behave differently in the marine environment.

5. Environmental Effects: A discussion of observations of chlorohydrocarbons in organisms would clearly be incomplete without some comment on its relevance to marine environmental quality. During the course of our work we have observed no evidence of effects of these pollutants on marine life, nor have we seen any evidence that there is a decline in the abundance of the various populations sampled—at least none that is measurable by reference to comparable collections made in the last 20 years by the staff of this Institution (personal communications). This is not surprising, since both PCB and DDT are known to operate in subtle ways, producing susceptibility to disease, impairment of instinct, and reduction of reproductive potential (Lichtenstein, 1972). Such effects might easily require several generations to become evident in population reduction. However, the concentrations of PCB that we have found to prevail in Atlantic Ocean organisms during 1970–1972, are within the range that could produce effects. We are most concerned about the plankton, and especially about the high PCB levels we have observed in samples rich in phytoplankton, since these represent the basic energy source for marine life. Plankton samples show the highest of marine concentrations, with PCB levels in their body lipids ranging up to hundreds of parts per million (thousands, in samples rich in phytoplankton). We believe that such levels must be affecting the marine biota. Our belief is supported by recent laboratory studies that showed that some PCB concentrations we have measured in Atlantic water (100 ng/l) caused changes in the species composition of mixed algal populations (Mosser et al., 1972), and possible interference with algal uptake of various nutrients (Fisher, 1973). It has also been shown that, as predicted, phytoplankton isolated from the open ocean are more sensitive to PCB stress than are populations of the same species from near-shore or estuarine environments (Fisher et al., 1973). Although it is reasonably well known that laboratory studies of chemical toxicity usually underestimate the resistance of natural populations, we are convinced that the measured present-day levels of PCB's in oceanic organisms do present cause for concern.

We hope that the recently instituted controls on uses of DDT and PCB will lead to reduction in worldwide body-burdens before large-scale effects are observed on populations. Data from the worldwide radioactive fallout experiments (Bowen et al., 1969, 1969) have shown a lag of almost two years between the maximum rate of fallout delivery to the land surface and the maximum

mean concentrations of Sr 90 in surface water of the North Atlantic Ocean. A considerably greater time lag would be expected after reduction of PCB production, where the avenues of introduction to the atmosphere are both more various and more complex than were those for worldwide fallout.

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Inorganic Speciation of Boron in Seawater[1]

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ABSTRACT

Boric acid-borate apparent dissociation constants were determined in synthetic media and in seawater using a glass pH electrode. In seawater of 34.97‰ salinity at 25°C, $pK'_B = -\log (a'_H m_{B(OH)_3}/m_{B(OH)_4}) = 8.731$ this value is in good agreement with previous measurements of this constant. Formation constants, $K^*_{MB} = [MB]/([M][B])$, for the species $NaB(OH)_4^0$, $MgB(OH)_4^+$ and $CaB(OH)_4^+$ were calculated from the variation in pK'_B with composition of the synthetic media. At 25°C and ionic strength $\mu = 0.68$, $K^*_{NaB} = 0.07$, $K^*_{MgB} = 8.0$ and $K^*_{CaB} = 15.0$. These results indicate that 64% of the borate ions in seawater are complexed with sodium, magnesium, and calcium.

INTRODUCTION. Boron is one of the major constituents of seawater, having a concentration of 4.4×10^{-4} moles per kg H_2O at a salinity of 34.8‰. Its ionic interactions are probably the least understood of the major elements. In the past, the major inorganic species of boron explicitly considered in the marine environment were $B(OH)_3^0$, $B(OH)_4^-$, and HBO_3^{2-} (Lyman 1956, Buch 1933). Borate, however, is known to form a variety of complexes. Boron is second only to hydroxide in forming complexes with ferric ions in seawater (Kester and Byrne 1972). There are strong aluminum borate complexes and there is evidence of boron complexes with sodium, calcium, cobalt and nickel (Nies and Campbell 1964, Sillen and Martell 1964).

Since boron is a major constituent of seawater, its principal species will be found among the possible ion pairs between boric acid or borate ions and the other major constituents of seawater. Polynuclear complexes of boron are only significant at concentrations greater than 0.025 M (Ingri *et al.*, 1957) and therefore need not be considered in seawater. The existence of the HBO_3^{2-} ion which has been postulated at high pH seems doubtful. Investigations subsequent to Lyman's have not supported the existence of such a species. Ingri (1963) and Edmond and Gieskes (1970) state that the supposition of this

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