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# Chlorinated Hydrocarbons: Some Observations on Distribution in Atlantic Ocean Organisms

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ABSTRACT

Analysis of several open-Atlantic Ocean organisms for DDT and polychlorinated biphenyls (PCB) has revealed that these materials reach the ocean mainly through the atmosphere. Their incorporation into the biomass shows no dependence on food chain relationships. PCB and DDT appear to follow different pathways through open-ocean organisms.

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We are engaged in determining the concentrations of polychlorinated biphenyls (PCB) and of members of the DDT-family in several series of organisms recently collected from the open Atlantic Ocean both North and South; some preliminary descriptions of this work including collecting and avoiding contamination at sea have already been made (1). DDT in snow and organisms of Antarctica had indicated that atmospheric distribution is important for this pollutant, but knowledge of its distribution among marine organisms has been restricted to those of coastal waters and continental seas. This report presents data from organisms of the North Atlantic between 14° and 66°N, and from the South Atlantic between 13° and 36°S.

We have observed (1) DDT (p, p'-DDT and p, p'-DDE) and PCB in all organisms we have examined from both the North and South Atlantic. In a few cases, clearly shown in the Tables, DDT has not been quantifiable because of interference by very high concentrations of PCB. In other cases, to be discussed below, PCB were not quantifiable because the pattern of elution peaks had been so far degraded as not to match that of any commercial PCB mixture (Aroclors). In all cases confirmation of DDT and DDE was achieved by alkaline dehydrochlorination. In a significant number of selected samples, mass spectrometry has been used to confirm the chlorinated hydrocarbons of the classes reported (2).

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We have never observed dieldrin, nor aldrin even though a careful search for these pesticides was made in our early samples. It seems unlikely, because of the much lower tonnages produced and their shorter persistence in nature, that these other compounds would be observable in open-ocean samples. We believe that report of high dieldrin levels (3) in oceanic organisms of the South Atlantic are misidentifications. We believe also that reports of very high DDT levels, unless accompanied by additional confirmation and the PCB

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analysis, must always be suspect.

The Tables show analyses of organisms for DDT-family (p,p'DDT plus p,p'DDE) and for PCB. In Table 1 are data from mid-latitudes of the North Atlantic, in Table 2 data from the South Atlantic, and in Table 3 data from high latitudes of the North Atlantic about Iceland. The data are arranged, for surface-living organisms, in order of increasing trophic level, and, for meso-pelagic and benthic organisms, in order of increasing depth of collection.

Three main points will be discussed: the bearing of the data on the question of atmospheric transport of chlorinated hydrocarbons; their bearing on the question of food chain magnification of concentration ; and the special problems presented by the PCB data.

In three ways our data support the view that the atmosphere provides the major path for delivery of both DDT and PCB to the ocean.

Firstly, there is no systematic East to West gradient of concentrations of these pollutants in North Atlantic open-ocean organisms. In fact our data for DDT in zooplankton of the open North Atlantic overlap those of Risebrough (personal communication) for mixed zooplankton collected at about the 1000 meter contour off the New York Bight. Considering the high concentrations of DDT that are observed in organisms from the North Sea and the Baltic (4), and the relatively slow circulation of the North Atlantic gyre, this open-ocean uniformity of concentrations appears to require a direct, atmospheric supply of DDT to the ocean surface, and in sufficient amount to obliterate the concentrations gradients due to run-off.

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Secondly, comparing Tables 1 and 2, there is very little difference in concentrations of these pollutants between the North and South Atlantic. 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

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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 (5) but details of the pathways are not yet well worked out.

Thirdly, the very high concentration of PCB in one plankton sample, collected off Iceland in the East Greenland Current, is explicable only in terms of atmospheric transport. The East Greenland Current flows southwest from the Arctic Ocean. Two weeks before this plankton sample was collected, a high-pressure mass of European air (of certainly high PCB concentration) occupied the Denmark Strait for four days. Apparently PCB, delivered from this air mass, were rapidly absorbed by the plankton, although little effect was shown on the concentrations in ground-fish sampled at the same time.

Our data appear to offer no support for the widely held view that concentrations of chlorinated hydrocarbons are magnified along food chains. Earlier (1) we noted that flying fish, largely predators on zooplankton, exhibit lower concentrations of PCB and only slightly higher concentrations of DDT than their prey. A trigger fish (Table 1) showed a very low level of each pollutant in spite of its occupying a rather high trophic level, and there is no clear-cut difference in pollutant concentrations between the Chauliodus species and Systellaspis in spite of the probably lower trophic level of the latter. Data confirming these points are set out in Tables 1 and 2. In Table 3 it is shown that the small Arctic cod (Boreagadus esmarcki) was richer in PCB, and probably in DDT also, than was the Atlantic cod (Gadus callarias); every examined specimen of the latter caught on this cruise, had recently eaten Arctic cod. Perch and halibut, which have similar diets, show a three-fold difference in both PCB and DDT-levels in their fat (Table 3).

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There are several possible explanations for these observations. The simplest is that more extensive sampling may show food-chain magnification. Another could be that certain oceanic animals possess mechanisms for excluding or selectively degrading particular chemicals. The most likely explanation, however, is that the lipid fractions of aquatic organisms are in equilibrium with the water, by a partitioning of hydrocarbons between blood lipids (and, by circulation, with other body lipids) and the sea water directly through permeable body surfaces. This has been reported to occur in lentic environments (6) and has been suggested for some Baltic organisms (4). Lipids vary among species, in species at different seasons, and in different parts of the body (7). It is likely that some of these lipid mixtures are better hydrocarbon solvents than others. 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 ratio. Differences in hydrocarbon content that result from such variables have no relation to position in food chains. Similar conclusions were reached recently based on the analysis of a mathematical model (8). Because of this many individuals from the same region must be collected at different times accompanied by samples of the water, if these processes are to be better understood. DSW 029481

Plankton appear to be functioning as the major trap for chlorinated hydrocarbons in the Atlantic Ocean, with concentrations ranging from 100 to 900 ppm in their lipids, although it is possible the data are biased by the nets used. Generally, we have not observed such high concentrations in higher trophic levels. If the oceanic standing crop of plankton is $3 \times 10^{12}$ kg and the average PCB concentration is $3 \times 10^{-4}$ g/kg, there is now $9 \times 10^{8}$ g of PCB in marine plankton. This is 0.3% of the amount produced by the U.S. in the last decade (9). Even if these figures are in error, the persistence of PCB is emphasized by the comparison with DDT which has been produced in the same

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quantities, used only in open systems, but is found in much lower concentrations in organisms of the Atlantic Ocean.

While DDT is found abundantly associated with over-ocean atmospheric dust, PCB have thus far been undetectable on dust samples (1). This is surprising in view of the large amounts of PCB we find in oceanic organisms and of the generally lower vapor pressures of PCB than of DDT and its derivatives. In organisms from the upper layers of the oceans the PCB pattern of elution peaks matches very precisely one of the commercial Aroclor formulatio (Fig. ). The Aroclor most commonly matched is 1254, the product most used in open systems. Instances of matching to other Aroclors (1242 or 1260) are seen. What is surprising is that the match should always be so exact for as many as twelve elution peaks. It appears that near surface organisms retain PCB after uptake only for brief periods. Aroclor 1254 could represent statistical average of all PCB mixtures from Europe and North America; observations of Aroclor 1242 or 1260, however, occur at concentrations too low to have arisen by superposition of an overwhelming amount of the observed Aroclor. Our data on bottom feeding organisms show degradation of PCB in nature, and at rates that affect the elution-peak spectrum severely. Unless this degradation takes place only at depth in the oceans, it is difficult to understand how the PCB mixture in organisms of the upper layers of the oceans is maintained free of these degraded mixtures. Holden (4) has noted that PCB in blubber of North Sea seals often departs from the Aroclor 1254 pattern, and Jernelov (personal communication) reports that bottom feeding organisms of the North Sea normally show PCB patterns so degraded as not to match any Aroclor, although perfect match is the rule among North Sea surface organisms. Both Jernelov and Ui (10) believe that PCB must be introduced to the atmosphere as aerosol so that the individual droplets (of a single commercial formulation) never mix. These data suggest that clouds

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of individual Aroclors pass their whole atmospheric history without mixing. Kuroda (11) suggests this for the debris-clouds from closely-spaced atmospheric nuclear explosions.

The dilemma from these data is that PCB in marine plankton represents a respectable fraction of world production over the past decade, yet the mixtures analyzed appear to preclude their representing averaged accumulation even over periods of weeks. PCB degradation occurs in the oceans, and, (less certainly)these degraded mixtures alone occur on the sea floor. Restriction of PCB degradation to the ocean floor is inconsistent with our knowledge of their properties and the existence of major removal of PCB from the upper layers of the ocean makes it even more difficult to strike the material balance.

Previously (1) we noted that DDT and PCB appear to have different pathways both in the atmosphere and in the oceans. In the South Atlantic a West to East gradient of concentration in plankton was observed for both chlorinated hydrocarbons, but the gradient was more than thirty-fold for PCB compared to just over 10 for DDT. The gradient itself appears explicable only in terms of exhaustion of the pollutants from the air mass during the over-ocean trajectory of the South Atlantic westerlies; it will take more data to suggest whether the DDT:PCB gradient ratio is indicative of more rapid purging of PCB from over-ocean air, or of more rapid removal of DDT from the ocean photic zone. As discussed before (1), it seems not unlikely that DDT moves vertically in the bodies of organisms rather more rapidly than does PCB.

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2. We have participated in the Organization of Economic Cooperation and Development Intercalibration Program for Pesticides. In these analyses the recovery of DDT family averaged 78% and the precision at the 1 ppb level was ±0.5. We are indebted to Dr. David Shaw of Harvard University for several mass spectrographic confirmations of the PCB and DDT components.
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Tables 1 and 2. Discussions with Backus and Teal have aided data interpretation. Mr. I. Hallgrimsson, Reykjavik, and the scientists on board the Icelandic vessel, made ship time and accomodations available on very short notice, and identified the organisms in Table 3. This work was supported by the U.S. National Science Foundation, International Decade of Ocean Exploration, under Grant GX 28334, and by the U.S. Atomic Energy Commission under contract AT(30-1)-3563. Contribution Number 2794 from the Woods Hole Oceanographic Institution.

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## Figure Legend

Chromatographic elution peaks of an authentic commercial PCB (Aroclor 1254), and of an identically-treated extract from an open-ocean zooplankton sample. Note the differences in relative height and shape of the first two peaks, but the extraordinarily good match of the rest of the elution curve.

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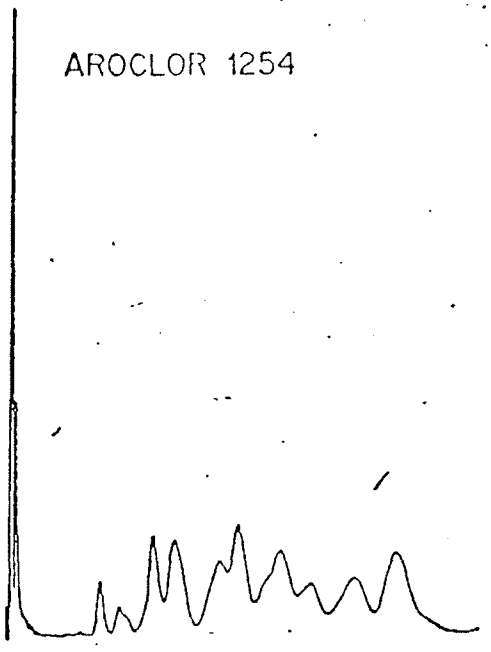


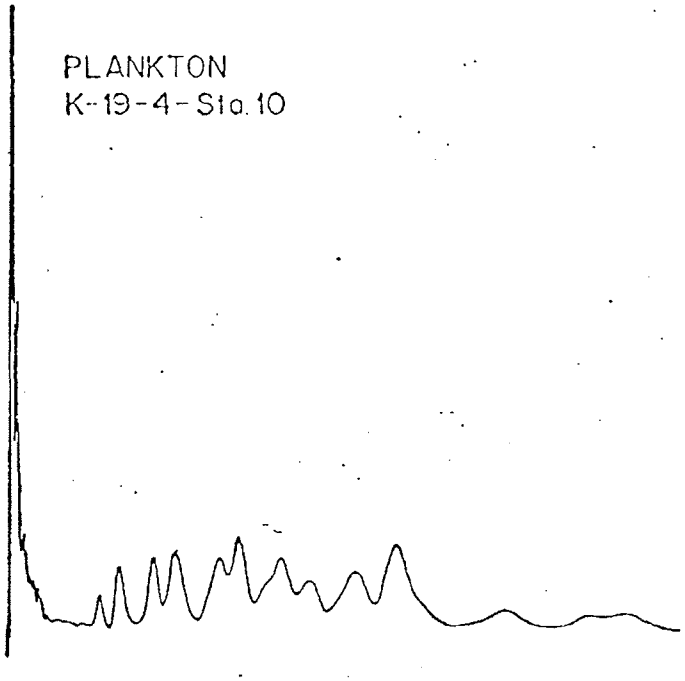


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TABLE 1

Chlorinated Hydrocarbons in North Atlantic Organisms

(µg Per kg. Fresh Wt. - Values in Brackets are Per kg. Lipid)

| Sample # | Identification | Date Collected | Position | Depth Caught (m) | Total DDT | PCB (as Aroclor 1254) |
|---|---|---|---|---|---|---|
| A11-59-29 | Sargassum | Nov. '70 | 26°N;36°W | Surface | 0.5 | 10 |
| A11-59-39 | Sargassum | Dec. '70 | 35°N;43°W | Surface | 0.2 | 20 |
| A11-59-22 | Zooplankton (#6 mesh) | Nov. '70 | 23°41'N;34°29'W | 0-100 | N C | 300 |
| A11-59-35 | Zooplankton (#6 mesh) | Dec. '70 | 39°52'N;47°30'W | 0-100 | N C | 450 |
| K-19-4-10 | Zooplankton (6 mesh) | Mar. '71 | 30°N;60°W | 0-200 | 0.7 (120) | 110 (19200) |
| K-19-4-28 | Zooplankton (#6 mesh) | April '71 | 32°N;64°W | 0-200 | 9.5 (1250) | 7 (925) |
| G-175-7 | Flying Fish | Feb. '71 | 31°N;79°W | Surface | 6.6 | 50 |
| A11-59-1 | Flying Fish (Cypselurus exsiliens) (muscle) | Nov. '70 | 14°N;19°W | Surface | 0.6 (179) | 1.4 (410) |
| A11-59-16 | Flying Fish (whole) | Nov. '70 | 22°N;33°W | Surface | 2.5 (185) | 6.8 (490) |
| K-19-4-17 | Flying Fish (Prognichthys rondeletii) (muscle) | Mar. '71 | 30°N;60°W | Surface | 4 (1480) | 4 (1480) |
| A11-59-14 | Trigger Fish (Canthidermis maculatus) (muscle) | Nov. '70 | 19°N;30°W | Surface | 0.1 (120) | 1.9 (1900) |
| A11-59-11 | Dolphin (Coryphaena equiselis) (liver) | Nov. '70 | 17°N;26°W | Surface | 95 (1990) | 1056 (21,100) |
| A11-59-27 | Dolphin (Coryphaena hippurus) (muscle) | Nov. '70 | 25°N;36°W | Surface | 3 (3300) | 10 (10,000) |
| A11-59-2 | Shark (Carcharhinus longimanus) (liver) | Nov. '70 | 14°N;22°W | Surface | 4 00+ (824) | 1200+ (2480) |
| G-175-7 | Silky Shark (liver) | Feb. '71 | 31°N,78°W | Surface | 4800 (11,000) | 5800 (13,000) |
| A11-59-8 | Mesopelagic Crustacean (Systellaspis debilis) (37, whole) | Nov. '70 | 15°30'N;26°20'W | 90 | 3.1 (168) | 8.9 (490) |
| A11-59-4 | Mesopelagic Fish (Chauliodus sloani) (1, large, whole) | Nov. '70 | 14°50'N;25°34'W | 650±50 | 5.1 (664) | 14.5** (1900) |
| A11-59-33 | Mesopelagic Fish (Chauliodus danae) (5, whole) | Dec. '70 | 28°N;45°W | 800±50 | 12 (1510) | 59 (7300) |
| A11-59-34 | Crustacean (Systellaspis debilis) (17, whole) | Dec. '70 | 28°N;45°W | 800±50 | 5.7 (109) | 35 (1040) |
| A11-59-26 | Mesopelagic Fish (Chauliodus danae) (5, whole) | Nov. '70 | 24°55'N;35°53'W | 900±10 | 5.4 (700) | 10* (1450) |
| K-19-5-7 | Anemone (Solocera tuediae)(1 whole) | April '71 | 38°10'N;71°25'W | 3100 | 1.6 (700) | 1.2 (500) |
| K-19-5-7 | Sea Cucumber (Molpadia sp.) (4 whole) | April '71 | 38°10'N;71°25'W | 3100 | 3.3 (2660) | N. A. |

* Corrected value after an intercalibration analysis revealed low recoveries when shark liver is partitioned between hexane-acetonitrile.

**As Aroclor 1260, because of better matching of the chromatographic pattern.

N. C. - Not calculated due to serious interference.

N. A. - Not analyzed because insufficient peaks remain to permit matching to commercial Aroclor.

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TABLE 2

Chlorinated Hydrocarbons in South Atlantic Organisms

(µg.kg Fresh wt. - Values in Brackets are Per kg. lipid)

| Sample | Identification | Date Collected | Position | Depth Caught | Total DDT | PCB (as Aroclor 125 |
|---|---|---|---|---|---|---|
| A-II-60-4-13 | Zooplankton #6 mesh | April 1971 | 34°05'S 42°40'W | 0-200 | 2.6 (500) | 638 (124,000) |
| A-II-60-4-33 | Zooplankton #6 mesh | April 1971 | 32°50'S 26°24'W | 0-200 | 1.4 (625) | 118 (52,700) |
| A-II-60-5-PT-106 | Zooplankton #6 mesh | June 1971 | 14°03'S 05°55'E | 0-200 | 0.3 (90) | 21 (7,300) |
| A-II-60-5-PT-89 | Zooplankton #6 mesh | May 1971 | 32°49'S 13°09'E | 0-200 | 0.2 (130) | 18.5 (10,300) |
| A-II-60-4-5 | Systellaspis sp. (7 whole) | April 1971 | 34°09'S 42°50'W | 200 | 8.4 (220) | 14.1* (375) |
| A-II-60-5-102 | Chauliodus sloani (1 whole) | June 1971 | 12°52'S 08°15'E | 300 | 1.58 (270) | 4.7 (816) |
| A-II-60-5-73 | Chauliodus danae (1 whole) | May 1971 | 25°59'S 03°28'W | 450 | 1.2 (175) | 4.1 (582) |
| A-II-60-4-41 | Chauliodus danae (2 whole) | April 1971 | 36°10'S 07°23'W | 600 | 2.1 (174) | 2.5 (210) |
| A-II-60-4-56 | Acanthephyra haeckelii (12) | May 1971 | 34°28'S 16°13'E | 750 | 2.6 (116) | 5.8 (245) |

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*As Aroclor 1242

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TABLE 3

Chlorinated Hydrocarbons in Icelandic Organisms[1]

| Sample # | Identification | Date Collected | Position | Depth Caught (m) | Total DDT | PCB (as Aroclor 1260) |
|---|---|---|---|---|---|---|
| B-9-71-65-#15 | Phytoplankton (#3 mesh) | 9/71 | 66°15'N 26°10'W | 0-200 | | 1500 (915,000) |
| LH - 1 | Trout (1 whole) (Salvelinus alpinus) | 9/71 | Lake Myvatn | Surface | 0.8 (27.2) | 8.45 (276) |
| LH - 2 | Trout (1 whole) (Salvelinus alpinus) | 9/71 | Lake Myvatn | Surface | 1.0 (119) | 6.7 (760) |
| B-9-71-64-#2 | Cod muscle (Gadus callerias) | 9/71 | 65°45'N 23°33'W | 96 | 2.8 (1335) | 2.09 * (830) |
| B-9-71-64-#1 | (Gadus callerias) liver | 9/71 | 65°45'N 23°33'W | 96 | 172 (438) | 729 (1850) |
| B-9-71-64-#54 | Shrimp (Pandalus borealis) (6 whole) | 9/71 | 63°53'N 22°58'W | 0-200 | 0.8 (27.4) | 17.8 (633) * |
| B-9-71-68-#3 | Haddock muscle (Gadus aeglefinus) | 9/71 | 65°48'N 26°10'W | 230 | 2.7 (2507) | N C |
| B-9-71-68-#30 | Haddock liver (Gadus aeglefinus) | 9/71 | 65°48'N 26°10'W | 230 | 261.5 (509) | 490 ** (1020) |
| B-9-71-67-#18 | Arctic Cod (Boreogadus esmarcki) (1 whole) | 9/71 | 65°23'N 26°15'W | 240 | 8.6 (128) | 2070 (31,000)** |
| B-9-71-67-#21 | Argentine liver (Argentina silus) | 9/71 | 65°23'N 26°15'W | 240 | 50.9 (473) | 1070 (9930) ** |
| B-9-71-67-#19 | Wolfish muscle (Anarhichas lupes) | 9/71 | 65°23'N 26°15'W | 240 | 2.6 (535) | 22.1 (4530) |
| B-9-7-67-#21 | Argentine muscle (Argentina silus) | 9/71 | 65°23'N 26°15'W | 240 | 5.5 (754) | 18.5 (2530) ** |
| B-9-71-65-#5 | Greenland halibut liver (Reinhardtius hippoglossoides) | 9/71 | 66°15'N 26°10'W | 570 | 56.2 (275) | 226 (932) |
| B-9-71-65-#7 | Greenland halibut muscle (Reinhardtius hippoglossoides) | 9/71 | 66°15'N 25°10'W | 570 | 20.9 (231) | 67.7 (744) |
| B-9-71-65-#12 | Perch liver (Sebastes marinus) | 9/71 | 66°15'N 26°10'W | 570 | 188 (624) | 898 * (2970) |
| B-9-71-65-#13 | Perch muscle (Sebastes marinus) | 9/71 | 66°15'N 26°10'W | 570 | 32.3 (506) | 353 (5650) * |

1. All these samples contained mixtures of the three Aroclors. The quantities reported are for the closest fit.

* Calculated as Aroclor 1254

** Calculated as Aroclor 1242

N C Considerable material present but not calculated due to poor matching.

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