Chlorinated Hydrocarbons in Open-Ocean Atlantic Organisms

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Introduction

Within the past year we have collected a considerable series of open ocean organisms specifically to be analyzed for chlorinated hydrocarbons, for petroleum residues, and for a variety of toxic elements; some sediment cores were also collected. This is part of a multi-institution program, being supported by the U. S. National Science Foundation under its program for the International Decade of Ocean Exploration, to measure the concentrations of a variety of chemical pollutants in organisms of the open ocean, and to assess the significance of these concentrations in terms of possible effects on open ocean ecosystems.

It is our purpose here to present the data so far accumulated showing concentrations of p, p'-DDT (1, 1, 1-trichloro-2, 2-bis (p-chlorophenyl) ethane) and its degradation product p,p'-DDE (1, 1-dichloro-2, 2-bis (p-chlorophenyl) ethylene), and of the class of polychlorinated biphenyls (PCBs); this small body of data appears surprisingly self-consistent and suggests some reasonably straightforward hypotheses of the biological pathways of the two groups of compounds. We realize that the number of analyses is very small but we are also acutely conscious that there is much thought about the control of open-ocean concentrations of chlorinated hydrocarbons without the support of any data. In view of this, and of the facts both that our data indicate some hypotheses as more immediately preferable than others, and that some open-ocean organisms are shown to have already accumulated pesticide concentrations in the physiologically active range, we decided to present the data now, and to work as hard as could be done at explaining them. It is, of course, our hope that this will stimulate others to examine facets of the problems exposed.

Methods of Collection and Analysis

Figure 1 shows the various sampling transects we have so far made, and indicates the sorts of samples obtained. It was our intention to look for gradients of pollutant concentrations in reference to a few major features, such as the river-borne supplies to the Hudson and Savannah estuaries, the southward transport, in the Canaries Current, of European petroleum (Horn et al, 1970), trade-wind transport to the North Equatorial Current, the gyral circulation of the Sargasso Sea, and the large currents of the South Atlantic.

Organisms have been collected by dip-netting (Sargassum, flying-fish, trigger-fish, squid, etc.), by hook and line (dolphins, sharks) or by nets (standard plankton nets, or Isaacs-Kidd mid-water trawls). A full description of the precautions we have taken against contamination has been prepared for publication elsewhere (Grice et al, 1972); in essence it has depended on the use of residue-free ethanol (from ethylene hydration) for washing of implements and containers, avoidance of plastics, and preservation by freezing in glass or in washed aluminum foil. We believe the data presented here confirm that on general research cruises such samples can be obtained, substantially free from contamination by chlorinated hydrocarbons; a smaller amount of data appears to show this also in respect to petroleum.

The extraction and cleanup procedure used was essentially as described in the "Pesticide Analytical Manual", Vol. 1, of the U. S. Federal Drug Administration. The sample was 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 from the column with 6% ethyl ether in hexane (v/v). The eluate was then concentrated to an appropriate volume (0.1 to 5 ml), chosen, by gas chromatography of intermediate stages in the concentration step, to give a measurable amount of DDT or DDE. Tests have shown that concentration to as little as 0.1 ml can be done in the Kuderna-Danish apparatus with no serious loss of total DDT-family compounds; in some cases, however, local over-heating of the concentrator converts DDTs to DDEs, as has occurred, we believe, to cause the low ratios observed in the second and eighth samples of Table 1. After concentration an aliquot, not more than 10 microliters, was injected into a gas chromatograph having a 2-mm by 2-m glass column packed with 8% QF-1 and 2% OV-17 on Gas Chrom Q, and with a nickel-63 electron capture detector. The presence of the DDT family was confirmed by dehydrochlorination with potassium hydroxide in methanol. PCBs were determined by matching the array of peaks on the chromatogram to the nearest-fitting Aroclor (usually 1254) and measuring the areas of four corresponding peaks.

Results

In Table 1 are shown the data now available; in every case the concentration is shown in reference to drained, fresh weight of organism; in some cases it is also shown in reference to lipid -- defined here as all that group of compounds extractable with n-hexane. The organisms are arranged, in Table 1, in two groups: the surface-living organisms and plankton in order of increasing trophic level, and the mesopelagic organisms in order of increasing depth of habitat.

Discussion

The data do not speak strongly to an east-west gradient of concentrations of chlorinated hydrocarbons in the North Atlantic; there is not even any consistent indication of a systematic pattern of PCB to DDT ratios. It is well known (Richardson et al, 1971) that ratios of PCB to DDT are very much higher in pollution from mean European sources than in that from North America. We have seen only two samples (zooplankton K-19-4-28 and flying fish K-19-4-17) that could possibly represent North American pollution unmodified. There are, however, indications that DDT and PCB are transported by the atmosphere in different physical states. Risebrough (1968) found up to 164 μg/kg of DDT in the trade-wind dust at Barbados but has never found PCB in dust samples either from Atlantic or Pacific collections (Risebrough, personal communication). If a large fraction of atmospheric DDT is carried on dust, and delivered (as in nuclear-test fallout) in formed precipitation, whereas most PCBs are moved as gases in the atmosphere, then it would not be surprising to find that the European ratio PCB:DDT preponderates in the region of largely easterly winds. We are arranging to extend our collections into the North Atlantic region of westerlies, to examine this question further. Clearly this ratio difference will be illuminating in considering the South Atlantic samples (see Figure 1).

The strikingly high DDT (and low PCB) in plankton sample K-19-4-28 we attribute specifically to Bermuda as a source. This sample was collected only about 40 km from the island, and near the area where Chow and Patterson (1966) observed high (and we believe island-influenced) concentrations of lead in surface water.

On two other points we believe the data support tentative conclusions:

1) While both DDT and PCBs increase in concentration along oceanic food chains, there are significant differences in their pathways.

2) There is a significant downward pathway out of the euphotic zone in the bodies of mesopelagic organisms undertaking daily vertical migrations.

1. Food-Chain Relationships

The Sargassum samples are the only representatives of the primary producer level; open-ocean samples collected with number-6 nets (0.23-mm operture) rarely contain significant amounts of phytoplankton. Both Sargassum samples show appreciable concentrations of DDT-family and of PCB hydrocarbons. At this stage, a reasonable simplifying assumption is that these have been accumulated by surface absorption, but it is not yet possible to confirm whether this has been a direct process of the plant surface or whether uptake has been mediated by the petroleum residues also associated with the Sargassum surface (Youngblood and Blumer, Teal and Burns, personal communications). Considering the usual variability of chlorinated hydrocarbon content found among individuals of the same species and habitat (Holden, personal communication), one cannot be sure that the differences shown by these Sargassum samples are significant. The DDT-family concentration was higher in the sample collected closer to areas rich in observable petroleum waste, whereas the PCB level trended oppositely. Clearly, in any case, both classes of chlorinated hydrocarbons are entering the Sargassum food web at the producer level.

Considering the concentrations observed in Sargassum, the three zooplankton samples not influenced by Bermuda are surprising; these collections consisted roughly, less than half of grazers, and half or more of stage-1 predators and detritus feeders, if comparable to Sargasso Sea collections described by Grice and Hart (1962). The extremely low concentrations of DDT-family in two of the samples and the extremely high concentrations of PCBs, in all three, are equally unexpected. The latter are possibly attributable to ship contamination: PCBs are usual constituents of hydraulic fluids, which tend to be widely dispersed on research vessels because of leaks from hydraulically governed winches or other gear. We are assured, however, that on the vessels used in collecting our samples neither hydraulic fluids nor heat exchangers were potential sources of any chlorinated compounds similar to those we measured. The three open-ocean plankton samples agree closely, and the two fish liver samples (which we believe could not have been contaminated by hydraulic fluid) showed PCB concentrations of the same range as those of the plankton. All

this seems to indicate that the high PCB levels in zooplankton are real. Accepting this, it is reasonable to argue that the levels of PCBs in zooplankton and in Sargassum are interpretable simply in terms of the surface:volume ratios of the two kinds of samples. This suggests either that some zooplankton surfaces exclude DDT-family hydrocarbons or that these compounds are rapidly absorbed and excreted by some zooplankters. Neither of these hypotheses is very attractive; a third, less obvious, alternative is that the zooplankton samples, each collected at night because of the much greater nighttime density of plankton in the upper 100 meters, may have been heavily weighted with deep-living organisms that had not had time to raise their DDT levels by feeding, but had quickly come into equilibrium, by surface uptake, with the PCB content of the upper layer of the ocean. This last hypothesis has the advantage of being readily testable, by comparing concentrations in daytime versus nighttime plankton tows; we are proceeding to make this comparison. It does appear, to the extent that these plankton are representative, that predators on zooplankton ingest much greater amounts of PCBs than of DDT.

Flying fish are typically predators on zooplankton (Parin, 1970), although with considerable variations in prey-selectivity among the various species. Off Barbados (Hall, 1955; Lewis, Brundnitt and Fish, 1962), larval fish, crustacea and thaliacea are preferred, in that order; more important, perhaps, is that feeding is confined to nighttime; consequently the diet is strongly biased toward zooplankters that are vertical migrators. The levels of PCB in flying fish muscle indicate that these compounds are relatively unavailable to these predators, compared to the DDTs. This, of course, depends now on the assumption that the ratio PCB in muscle to PCB in liver (surely the major depository) in flying fish is like that in dolphin; by analyses of whole flying fish we are now examining this question; the one whole flying fish in Table 1 gave results in the right direction. The increases in DDT concentration from prey to predator (1 to 3 orders of magnitude) are not unreasonable by comparison with better unravelled food webs.

The trigger fish, as a probable scavenger, was expected to show much higher DDT levels than we observed. A careful examination of stomach contents of this and related species may be illuminating in respect to patterns of DDT avoidance. The pattern shown could, however, reflect simply a very different disposition of fat deposits between trigger fish and flying fish.

Dolphin and white-tip shark represent two more trophic levels: dolphin generally are described (Parin, 1970) as predators chiefly on flying fish, although one of us (RHB) has observed a great variety of surface fishes in dolphin stomach contents; the white-tip shark feeds on squid (which are predators on flying fish, migratory mesopelagic fish, and anything else that moves) and on fish, including predators such as scombrids (Backus, Springer and Arnold, 1956). The increase in DDTs content in dolphin muscle over that of flying fish is less than expected but this is shown, by the values of DDT in lipid, to be largely a reflection of different fat-storage patterns in the dolphin. The shark would have been expected to show higher DDT levels than the dolphin, as occupying a higher trophic level; the considerable difference in DDE:DDT ratio may show that the shark actually metabolizes and excretes DDT more efficiently than do the bony fish. It is also likely, considering the very much greater proportion of liver to body in sharks than in bony fish, that the total DDT concentration per gram body weight was higher, as expected. Calculations supporting this are discussed below.

We cannot explain the very much higher PCB level in dolphin versus shark liver, just as we cannot explain the very low PCB levels in the lower-stage predators. It appears that the DDT data are consistent with a progressively increasing concentration at each higher trophic level, once the step plants-to-grazers has been passed, whereas the PCB data do not show this. The high PCB levels in shark and dolphin are perfectly consistent with the hypothesis that these compounds are not transferred along food chains, but are absorbed directly from the water and show high concentrations either in relation to rapid equilibration (because of high surface-to-volume ratio) or in relation to the long

equilibration times available for large (and long-lived) predators. Clearly, examination of age-series of several predator species will illuminate this question; we have begun such an examination.

2. Vertical Movement by Biota

To assess both the importance of organisms in transferring chlorinated hydrocarbons down from the euphotic zone, and the degree to which mesopelagic and benthic organisms may be protected, by their positions, from exposure to such pollutants, we have begun analyzing a considerable variety of relatively abundant deep-water organisms collected in Isaacs-Kidd midwater trawls. Data are presented in Table 1 for five collections, of three such species.

a) The mesopelagic fishes, Chauliodus danae and C. sloani, spend the daytime hours deeper than 400 m, and migrate at night into the upper 100 m (Badcock, 1970); C. sloani spends the day slightly deeper than does C. danae.

b) The caridean decapod, Systellaspis debilis, spends the daytime hours about 700 m (± 100 m), and at night migrates upward but rarely to shallower than 150 m (Foxton, 1970); some of our catches (see Table 1) show S. debilis may migrate to a somewhat shallower depth in the open Atlantic than that observed by Foxton near the Canaries.

In neither case is there good information on the trophic level occupied; both are predators, Systellaspis certainly on prey of smaller size than that of Chauliodus.

The concentrations of DDTs and PCBs in these organisms are surprising both for their high values and for their similarity. Systellaspis, living deeper in the water column and (probably) at a lower trophic level, exhibits a range of DDT or PCB concentrations overlapping those of Chauliodus. In comparing these data with those of the "surface" organisms one must bear in mind that the deep organisms were analyzed whole. For better comparison we may calculate that the white-tip shark (estimating liver at one-seventh body weight and muscle concentrations like those of dolphins) would have shown a whole-organism level of not less than 17 ppb DDT-family and 47 ppb PCB. A similar

computation can be made for the dolphins (assuming that the dolphin liver, as does that of blue-fin tuna, white or blue marlin -- Krumholz, 1959 -- represents only 0.5 to 1 per cent of the body weight); in this case one calculates that the "mean" dolphin would have shown a whole-organism level of not less than 4 ppb DDT-family and 21 ppb PCB. Considering the relatively small percentage of body weight probably represented by viscera other than liver (total viscera ranged from 2.5 to 5.5% body weight of large marine fish, and from 3 to 7.5% of fresh water fish -- Krumholz, 1959), very much higher than the expected concentrations of chlorinated hydrocarbons would be required in viscera other than liver to raise the "whole organism" concentrations significantly above those estimated.

It is evident that organisms spending most or all of their time below the euphotic zone of the open ocean have been able to accumulate both DDTs and PCBs to concentration levels directly comparable to those in near-surface high-trophic level organisms. It appears to us also that the existence of these high concentrations in the bodies of organisms undertaking regular extensive vertical migrations in the open ocean confirms a biological mechanism that may be quite active in controlling surface-ocean concentrations of chlorinated hydrocarbons. Analysis of sediment cores, of large diameter and undisturbed surfaces (Burke, 1968), already collected for this purpose will allow us to estimate how effective the biological process is in removing these toxic materials from the whole water column.

The concentrations of chlorinated hydrocarbons reported here are in the ranges known or believed to be of physiological significance for some organisms. For example, eggs of peregrine falcons containing as little as 23 μg DDT per kg, have been reported to have failed to hatch for that reason (Ratcliffe, 1967). At sublethal concentrations of DDT, parr of Atlantic salmon have shown severe disruption both of their learning responses and of their thermal acclimation (Anderson, 1971); application to the sublethal concentrations used in this study, of reasonable (5×10^4 or 10^5) concentration factors

for DDT by aquatic organisms leads to the range of whole organism concentrations we have found. Very little is yet known about the metabolism of PCBs or about their sublethal concentration ranges; their persistence in nature is expected (Risebrough, personal communications) to be much longer than that of DDT, and we believe some of the high concentrations we have found in open ocean organisms to be real causes for concern.

Summary

PCB has been readily demonstrable in all, and DDT in most of a series of organisms collected from the open North Atlantic Ocean. No strong evidence was obtained of an east-west gradient in concentration between the Cape Verde Islands and Bermuda.

The data are compatible with a systematic increase in concentration along food chains, although details of the patterns suggest that the mechanisms of uptake may be different for PCB than for DDT.

A group of fish and crustacea which feed near the sea surface at night but migrate to considerable depths during the day show DDT and PCB concentrations not greatly different from those of predaceous organisms whose lives are spent mostly in the upper layers. We believe this shows that biological removal processes may help to control chlorinated hydrocarbon concentrations in the open ocean.

Acknowledgements

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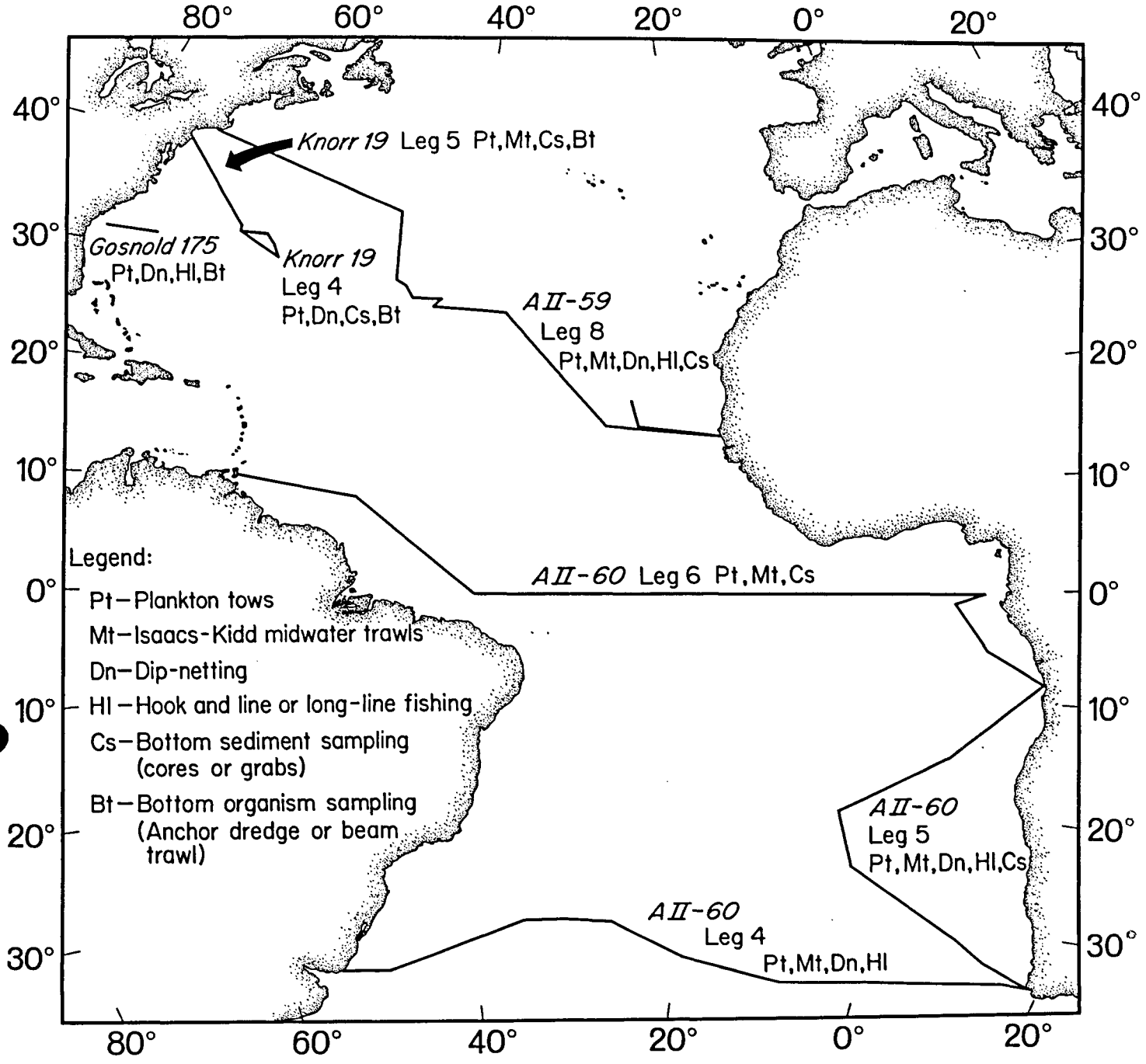
Legend for Figure:

Figure 1 Cruise Tracks, and kinds of sampling employed in collecting samples to be analyzed for pollutants in the open Atlantic Ocean.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Knorr 19 Leg 5 Pt,Mt,Cs,Bt
Gosnold 175
Pt,Dn,Hl,Bt
Knorr 19
Leg 4
Pt,Dn,Cs,Bt
AII-59
Leg 8
Pt,Mt,Dn,Hl,Cs
AII-60 Leg 6 Pt,Mt,Cs
AII-60
Leg 5
Pt,Mt,Dn,Hl,Cs
AII-60
Leg 4
Pt,Mt,Dn,Hl
Legend:
Pt—Plankton tows
Mt—Isaacs-Kidd midwater trawls
Dn—Dip-netting
Hl—Hook and line or long-line fishing
Cs—Bottom sediment sampling (cores or grabs)
Bt—Bottom organism sampling (Anchor dredge or beam trawl)

Running Title

DDT and PCBs in Atlantic Ocean organisms

Chlorinated Hydrocarbons in North Atlantic Organisms

(μg per kg fresh weight - values in brackets are per kg lipid)

Sample #	IDENTIFICATION	Date Collected	Position	Depth Caught(m)	p,p'-DDT	p,p'-DDE	Total DDT	PCB(as Aroclor 1254)
AII-59-29	Sargassum	Nov.70	26°N;36°W	Surface	0.4	0.1	0.5	10
AII-59-39	Sargassum	Dec.70	35°N;48°W	Surface	<0.01	0.2	0.2	20
AII-59-22	Zooplankton (#6 mesh)	Nov.70	23°41'N;34°29'W	0-100	<0.01	<0.01	<0.01	300
AII-59-36	Zooplankton (#6 mesh)	Dec.70	30°52'N;47°30'W	0-100	<0.01	<0.01	<0.01	450
K-19-4-10	Zooplankton (#6 mesh)	Mar.71	30°N;60°W	0-200	0.7 (120)	<.01	0.7	110 (19200)
K-19-4-28	Zooplankton (#6 mesh)	April 71	32°N;64°W	0-200	9 (1180)	0.6 (70)	9.5	7 (925)
AII-59-1	Flying Fish (Cypselurus exsiliens) (muscle)	Nov.70	14°N; 19°W	Surface	0.4 (115)	0.2 (64)	0.6 (179)	1.4 (410)
AII-59-16	Flying Fish (whole)	Nov.70	22°N;33°W	Surface	2 (150)	0.5 (32)	2.5 (185)	6.8 (490)
K-19-4-17	Flying Fish (Prognichthys rondeletii) (muscle)	March 71	30°N;60°W	Surface	<0.01	4 (1480)	4 (1480)	<4
AII-59-14	Trigger Fish (Canthidermis maculatus) (muscle)	Nov.70	19°N;30°W	Surface	0.05 (50)	0.07 (70)	0.1 (120)	1.9 (1900)
AII-59-11	Dolphin (Coryphaena equiselis) (liver)	Nov.70	17°N;28°W	Surface	60 (1190)	35 (800)	95 (1990)	1056 (21,100)
AII-59-27	Dolphin (Coryphaena hippurus) (muscle)	Nov.70	25°N;36°W	Surface	2 (1940)	1 (1350)	3 (3300)	10 (10,000)
AII-59-2	Shark (Carcharhinus longimanus) (liver)	Nov.70	14°N;22°W	Surface	38 (79)	62 (127)	100 (206)	300 (620)
AII-59-8	Mesopelagic Crustacean (Systellaspis debilis) (37, whole)	Nov.70	15°30'N;26°20'W	90	1.8 (96)	1.3 (72)	3.1 (168)	8.9 (490)
AII-59-4	Mesopelagic Fish (Chauliodus sloani) (1, large, whole)	Nov.70	14°50'N;25°34'W	660±60	3.3 (432)	1.8 (232)	5.1 (664)	14.5* (1900)
AII-59-33	Mesopelagic Fish (Chauliodus danae) (5, whole)	Dec.70	28°N;45°W	800±50	5 (630)	7 (880)	12 (1510)	59 (7300)
AII-59-34	" Crustacean (Systellaspis debilis) (17, whole)	Dec.70	28°N;45°W	800±50	3.4 (100)	2.3 (69)	5.7 (169)	35 (1040)
AII-59-26	Mesopelagic Fish (Chauliodus danae) (5, whole)	Nov.70	24°55'N;35°53'W	900±10	3.2 (372)	2.2 (318)	5.4 (700)	10* (1460)

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