TRANSFER OF HIGHER-MOLECULAR WEIGHT CHLORINATED HYDROCARBONS TO THE MARINE ENVIRONMENT

Robert W. Risebrough

Brock W. de Lappe

Wayman Walker II

Bodega Marine Laboratory
University of California
Bodega Bay, California 94923

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ABSTRACT

A variety of synthetic organochlorine compounds has been detected in marine environments; those of the PCB and DDT groups are the most abundant and the most ubiquitous. Contamination levels in the marine environments of Amchitka Island in the North Pacific are equivalent to those in the vicinity of Iceland. The sum of PCB compounds, principally penta- and hexachlorobiphenyls, is several times higher in marine birds of these areas than the concentration of p,p'-DDE, the principal DDT metabolite. In the Auckland Islands, at an equivalent latitude in the South Pacific, DDE levels in seabirds are comparable to those in birds of the Aleutians, but penta- and hexachlorobiphenyls are an order of magnitude lower.

In the Antarctic, DDE concentrations in birds are also higher than the sum of penta- and hexachlorobiphenyls. The ratio of DDE:PCB in a series of penguin eggs from the Antarctic Peninsula between 1970 and 1975 was approximately 3. Comparable ratios and absolute levels of contamination north and south of the Antarctic Convergence support the hypothesis of atmospheric transfer of these pollutants. In more contaminated areas, p,p'-DDE and possibly also one or more groups of PCBs has had deleterious effects on populations of marine birds.

Global mass balance equations of polychlorinated biphenyls of the pentachlorobiphenyl class indicate that many PCB determinations in seawater may have been too high. Development of an in situ sampling system has reduced sources of contamination, providing the determination of maximum levels of PCB and DDT compounds in seawater off western Mexico in 1975 in the picogram per liter range. Only in the vicinity

of the wastewater outfalls in Southern California were levels in the low nanogram per liter range recorded.

The majority of environmental samples contain complex mixtures of chemicals, some of which are of natural origin; others are most likely pollutants as yet unrecorded in the marine environment. Further work on their identification is necessary.

In antarctic snow and in snow precipitated from marine air in the Olympic Peninsula, p,p'-DDT was the dominant organochlorine compound. Measurements of organochlorines in strata of permanent snowfields provide a way of determining past changes in the atmospheric flux of these compounds. Differences in vapor pressure of p,p'-DDT, p,p'-DDE and pentachlorobiphenyls may explain their observed distribution in marine water, air and precipitation.

Marine sediments constitute an ultimate sink for PCB and DDT compounds; some of the p,p'-DDT and o,p'-DDT that enters the sea is transported undegraded to the sediments through the water column.

Global mass balance considerations suggest an unsuspected major pathway of breakdown of p,p'-DDE; in most, if not all, marine systems, however, the distribution of p,p'DDE parallels that of the pentachlorobiphenyls. Formulations of global mass balance equations for PCB and DDT compounds would provide models useful for the prediction of behavior of other pollutants with similar physical and chemical properties.

INTRODUCTION

At the beginning of the International Decade of Ocean Exploration Program in the early 1970's, there were insufficient data to assess the significance of contamination of the global marine environment by synthetic organic chemicals. Excessively high concentrations of DDT and PCB compounds were being reported from several oceanic areas; species of marine birds that are entirely dependent on marine food webs were unable to reproduce successfully in the marine environments of Southern California, New England and the Baltic. Moreover, organochlorine compounds were being detected in organisms from the remotest of marine environments, including those of Antarctica and the Arctic. It was not known whether the levels at that time would progressively increase as the DDT and PCB compounds entered the marine environment from the atmosphere, rivers, wastewater outfalls and other input sources. Such increases in contamination levels might result in the appearance of new kinds of deleterious effects, as well as a higher incidence of those already documented. Moreover, it was impossible at that time to reject the hypothesis that heavy metals of anthropogenic origin in the marine environment were contributing to the reproductive failures of marine fish-eating birds. Largely as a result of research carried out under the auspices of the International Decade of Ocean Exploration Program, it is now possible to begin to formulate a global perspective of the significance of chlorinated hydrocarbon pollution of the marine environment.

The present paper describes results of research on the higher-molecular weight organochlorine pollutants carried out at the University of California's Bodega Marine Laboratory with support from

the IDOE program. The lower-molecular weight halogentated hydrocarbons and other synthetic organic compounds, which require analytical procedures different from those currently used to determine the higher-molecular weight chlorinated hydrocarbons, are not discussed in this report. Research with heavy metals in the marine environment carried out during the IDOE program is briefly reviewed only to document the failure to find evidence for elevated levels of these elements at higher levels of marine food webs.

Use of the terms "DDT" and "PCB" as names of diverse and frequently very different compounds is no longer acceptable. DDT compounds in the environment are usually present in ratios quite different from the ratio in the original insecticide; PCB entering the sea in waste waters may consist predominantly of the tri- and tetra-chlorobiphenyls, but the PCB in marine mammals and birds frequently consists of penta- and hexachlorobiphenyls. Use of the term "PCB" to describe both groups of compounds may therefore be misleading. Reference can readily be made to individual DDT compounds such as p,p'-DDE and o,p'-DDT, however at present there is no satisfactory alternative to identifying individual PCB compounds. Laboratories without a mass spectrometer are not sufficiently well equipped to do this. Usually the PCB in an environmental sample approximates one of the North American Aroclor preparations 1242, 1248, 1254 or 1260. Tri-, tetra-, penta-, and hexachlorobiphenyls predominate respectively in these mixtures, yet each contains both lower and higher chlorinated compounds. In the present report PCB mixtures most closely resembling Aroclor 1242, 1248, 1254 or 1260 are referred to respectively as trichloro-biphenyls, tetrachlorobiphenyls, pentachlorobiphenyls and

hexachlorobiphenyls. This is clearly not an entirely satisfactory description, since commercial PCB mixtures contain a broader range of chlorobiphenyls.

Considerably more data on the distribution of the DDT and PCB compounds [illegible] other synthetic [illegible] of the [illegible] of the DDT and [illegible] [illegible] [illegible] and the physical [illegible] properties of the DDT and PCB compounds should therefore be related to their present distribution in the global marine environment. [illegible] data should [illegible] a determination of how changes [illegible] and usage patterns will affect future environmental [illegible] levels to those which would harm the [illegible] ecosystem by affecting the viability [illegible] group of species.

IDENTIFICATION OF [illegible] MOLECULAR [illegible] CHLORINATED HYDROCARBONS IN THE MARINE ENVIRONMENT

A wide variety of synthetic chlorinated hydrocarbons have been used as insecticides in agriculture, [illegible] public health; polychlorinated biphenyls are only one group of chlorinated compounds which have had widespread application in industry. Electron capture gas chromatography facilitates the detection of chlorinated hydrocarbons in environmental samples; accurate molecular identification is, however, considerably more difficult. In Figure 1 are shown

chromatograms of extracts of seawater obtained off western Mexico at 15° 19.0'N, 115° 26.0'W on March 21, 1975; passage of the extract through an alkaline side column (Miller and Wells, 1969) changes the gas chromatographic profile by converting some of the compounds to derivatives. Collection and analytical techniques are described below. The expected position of p,p'-DDE on these chromatograms is given as a point of reference. None of the peaks on these chromatograms can be presently dientified by the gas chromatographic techniques used for DDT and PCB analysis. Perhaps they are halogenated compounds of natural origin (Fenical, 1975). Their presence interferes with both the detection and measurement of polychlorinated biphenyl and DDT compounds, particularly when concentrations of the latter compounds are below 100 pg/l. In this sample concentrations of p,p'-DDT, p,p'-DDE and PCB were less than 5, 2, and 100 pg/l, respectively.

Figure 2 shows chromatograms of extracts of wastewater from a Southern California treatment plant. Wastewaters are major sources of pollutants to the Southern California marine environment (Schmidt et al., 1971; D. R. Young, R. W. Risebrough, B. W. de Lappe, T. C. Heesen, and D. J. McDermott, unpublished data). None of the peaks on this chromatogram can be identified by the gas chromatographic techniques which are currently used routinely to determine chlorinated hydrocarbons in environmental samples. More sophisticated techniques, such as gas chromatography/mass spectrometry would be required to determine unknown compounds. For example, analysis of these extracts by high resolution mass spectrometry showed the presence of trichloro-, tetrachloro-, and pentachloroanisoles (Burlingame et al., in press, 1976). Perhaps these compounds derived from the methylation of the respective chlorinated

Figure 1. Gas chromatograms of an extract of seawater obtained off western Mexico at 15° 19.0'N, 115° 26.0'W on March 21, 1975. Depth 3 meters, volume 137 liters. Chromatogram on the right is of the same extract after passage through a saponification side column. 3% OV-1, 100/120 Gas Chrom Q.

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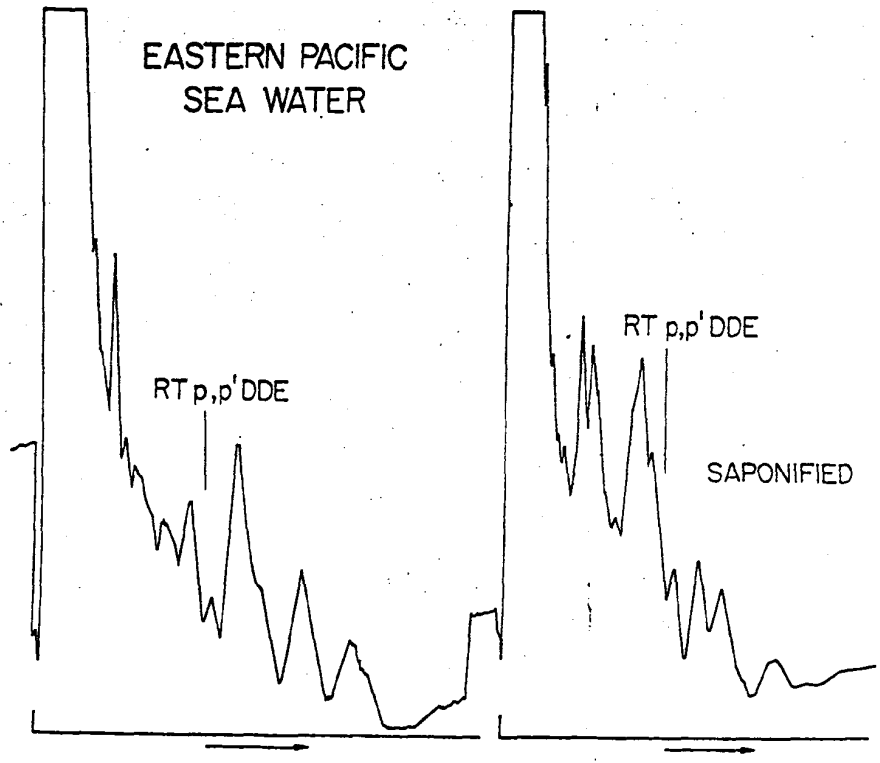

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Figure 2. Gas chromatograms of replicate extracts of wastewater of Los Angeles County Sanitation Districts. Extraction procedures are described in the text. 6% florisil fraction. 2 m, 2 mm ID glass column packed with OV-1, 100/120 mesh Gas Chrom Q. Somo of these peaks have been identified as chlorinated anisoles (Burlingame et al., 1976).

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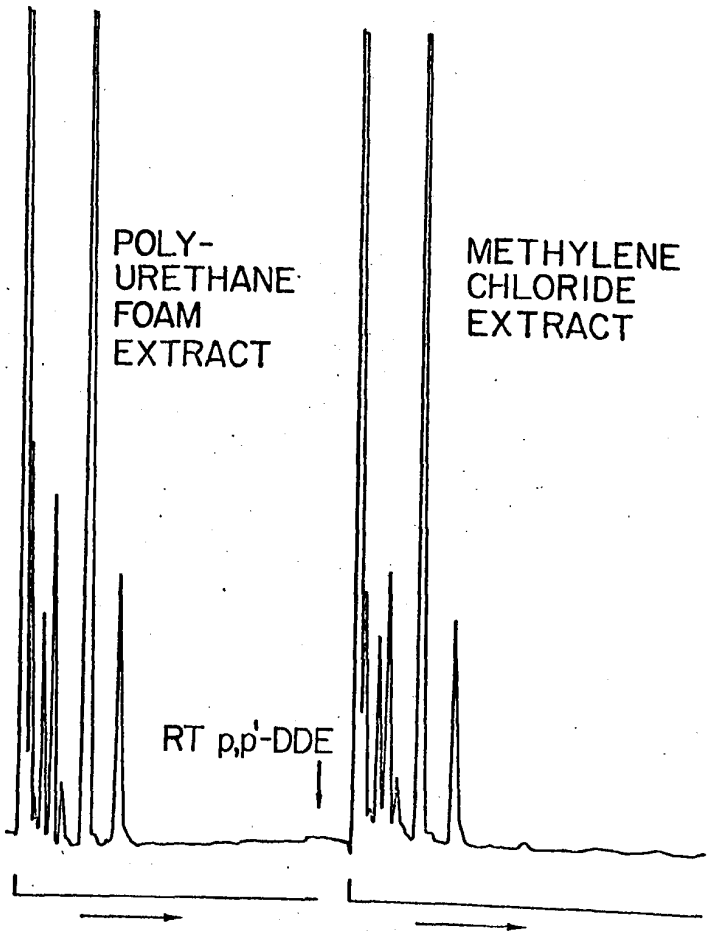
LOS ANGELES SEWAGE WATER



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phenols by bacteria. It is possible that they constitute some of the unidentified "early" peaks frequently seen in extracts of marine samples. In addition, dichloro-, trichloro-, tetrachloro-, and pentachlorobenzene were present in these extracts (Burlingame et al., in press, 1976).

Polychlorinated biphenyl preparations have been found to contain chlorinated dibenzofurans as impurities. These compounds are highly toxic and lethal to embryos in submicrogram quantities (Vos and Koeman, 1970; Vos et al., 1970; Bowes et al., 1973). Their structural similarity to the chlorinated dibenzodioxins which are teratogenic at low concentrations (Sparschu et al., 1971) suggested that they were possible causes of birth defects and other abnormalities observed in coastal marine birds (Hays and Risebrough, 1972). If present in the marine environment, these compounds would pose a hazard to both marine species and to human consumers. Zitko et al. (1972) examined marine samples from the Bay of Fundy for chlorinated dibenzofurans, but were unable to detect them. Detection limits were, however, substantially higher than the levels which would be expected in such tissues. The chlorinated dibenzofurans may be assumed to have entered the environment as a component of PCB, and might be present but as yet undetected in areas heavily contaminated with PCB compounds.

As a preliminary step in the search for chlorinated dibenzofurans in environmental samples, we measured the concentrations of these contaminants in various preparations of North American and European PCBs. Tetrachloro-, pentachloro-, and hexachlorodibenzofurans were detected in American PCB mixtures, with the exception of Aroclor 1016, in total concentrations from 0.8 to 2.0 μg/g. Higher concentrations were found in the French and German PCBs, Phenoclor DP-6 and Chlophen

A-60 (Bowes et al., 1975). Substantial quantities of these very toxic materials must then have been released to the environment over the past several decades with PCB. Little is known, however, of their environmental persistence or transport.

One of the Aroclor 1254 preparations, in which we measured the chlorinated dibenzofuran content, was incidentally used in a feeding experiment with Mallards (Anas platyrynchos). Subsequently, tissues of these ducks were pooled and the fat extracted. An aliquot of the lipid of known PCB content was analyzed for chlorinated dibenzofurans; a sample of corn oil with the same PCB content and with a known amount and composition of chlorinated dibenzofurans was simultaneously carried through the analytical procedures. Dibenzofurans could not be detected in the duck lipids, although they were recovered from the corn oil. It was concluded that the persistence of chlorinated dibenzofurans is low in ducks and probably also in other vertebrates (Norstrom et al., in press). It therefore seemed unlikely that these compounds would persist in the marine environment and we have not continued our searches for them. The causes of the observed birth defects remain unknown, and the possibility that dibenzofurans may be formed in vivo from PCB compounds with structures favorable for their formation cannot be excluded.

Because levels of chlorinated hydrocarbons are frequently much higher in terminal members of marine food webs such as the birds and seals, compounds new to the marine environment have frequently been first detected in marine bird or mammal tissues. The majority of synthetic organic compounds so far identified in the marine environment have contained chlorine. Hexachlorobenzene (HCB), which has been

detected in tissues of Great Cormorants (Phalacrocorax carbo), Sandwich Terns (Thalasseus sandvicensis) and Common Eiders (Somateria mollissima) from coastal areas of the Netherlands (Koeman and van Genderen, 1972; Koeman et al., 1972) has been considered a potentially hazardous marine pollutant (National Academy of Sciences, 1975); HCB is used as a fungicide but may enter the marine environment in significant quantities as a component of the tarry waste products from the manufacture of such chlorinated hydrocarbons as ethylene dichloride (U.S. Environmental Protection Agency, 1973).

Chlorinated styrenes have been identified by gas chromatography/mass spectrometry in tissues of Common Eiders, Sandwich Terns and Great Cormorants from the Netherlands (Ten Noever de Brauw and Koeman, 1972); their source apparently remains unknown. Chlorinated naphthalenes have also been identified in tissues of the Great Cormorant (Koeman et al., 1973a).

Mirex has been reported in eggs of herons and of the White Ibis (Eudocimus albus) from estuaries of the U.S. Atlantic and Gulf coasts (Ohlendorf et al., 1974) and has also been found in the blubber of a seal (Phoca vitulina) from the Netherlands (Ten Noever de Brauw et al., 1973). In addition to its use as an insecticide, Mirex, under various trade names is also used as a flame retardant.

Dieldrin has been found in eggs and tissues of several species of marine birds inhabiting coastal waters of Great Britain (Robinson et al., 1967) and of New Zealand, and in addition has been found in pelagic species such as the Sooty Shearwater (Puffinus griseus) breeding in New Zealand subantarctic islands (Bennington et al., 1975). It is accumulated by Ospreys (Pandion haliaetus) feeding on coastal marine

fish of the eastern United States (Wiemeyer et al., 1975; Spitzer et al., in press). Brown Pelicans (Pelecanus occidentalis), also feeding on coastal marine fish, have been found to contain endrin in Florida (Schreiber and Risebrough, 1972) and in the Gulf of California (Risebrough et al., 1968b). In addition, heptachlor epoxide, toxaphene, and the several isomers of hexachlorocyclohexane (benzene hexachloride or BHC) are occasionally reported in local estuarine environments. Heptachlor epoxide and BHC isomers have been reported in antarctic birds breeding in the South Orkneys (Tatton and Ruzicka, 1967) but their identification has not been confirmed (Risebrough, in press, 1976).

Bidleman and Olney (1974a) reported the presence of both cis- and trans-chlordane in samples of marine air obtained on Bermuda and aboard ship during passage between Bermuda and Rhode Island. Concentrations occasionally exceeded those of p,p'-DDT. Chlordane has also been reported in rainwater of Hawaii (Bevenue et al., 1972). The accumulation of chlordane compounds in food webs had, however, not been documented in these or other areas of the marine environment prior to 1974.

Eggs of the Common Tern (Sterna hirundo) from a marine population that breeds on Great Gull Island in Long Island Sound and winters in the Caribbean, and fish of several species from the vicinity of Great Gull Island were analyzed for chlordane compounds. Residues of alpha-(cis-)chlordane, gamma-(trans-)chlordane (both of which may also include other chlordane compounds), and oxychlordane were detected. On a lipid basis the pooled sample of fish contained 0.22 ppm, 0.10 ppm and 0.05 ppm of alpha-(cis-)chlordane, gamma-(trans-) chlordane, and oxychlordane, respectively. Analysis of 27 individual

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eggs of the Common Terns yielded values of 0.86, 0.03 and 0.52 ppm, lipid weight, of cis-chlordane, trans-chlordane, and oxychlordane, respectively. Two pooled samples of eggs, consisting of 10 unhatched eggs found intact and 109 eggs found broken, contained respectively 0.73 and 0.75 ppm of cis-chlordane, 0.03 and 0.02 ppm of trans-chlordane and 0.22 and 0.31 ppm of oxychlordane (P. Robinson and R. W. Risebrough, unpublished ms.). Chlordane compounds may therefore be more widespread in the marine environment than previously suspected. Several of the methodologies employed in routine analyses of chlorinated hydrocarbons do not detect the chlordane compounds; thus their presence has most likely been overlooked.

A dilemma is posed: a thorough examination of the fluxes of synthetic organic compounds in the marine environment requires detailed analytical studies of the very complex mixtures found in both seawater and in wastewaters which enter the sea. Yet such detailed chemical studies, which are both time-consuming and costly, may cause diversions from the overall assignment of understanding pollutant fluxes through the sea. This is particularly true if the compounds identified are of relatively minor importance in the marine environment. At the present time it is frequently difficult to assign priorities (Blumer, 1975).

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INTERCALIBRATION

Intercalibration of different methods used to analyze marine samples and intercalibration among laboratories has become an integral and essential part of collaborative programs such as those undertaken under the auspices of the International Decade of Ocean Exploration program. Different laboratories frequently report widely differing results of analysis of the same sample (Holden, 1970; 1973). An initial intercalibration carried out among members of the IDOE program utilized a homogenate of shark liver. It contained approximately equivalent amounts of DDT and PCB compounds; substantially good agreement was obtained (Harvey et al., 1974b). A subsequent intercalibration program coordinated by S. Pavlou and W. Hom of the University of Washington included IDOE investigators. A sample of marine sediment from Puget Sound was thoroughly mixed and then distributed among the participating laboratories.

The results indicated that surprisingly good agreement was obtained for the PCB determinations (coefficient of variation: 22); but agreement on the total DDT determinations was less satisfactory (coefficient of variation: 88). Pentachlorobiphenyls predominated in this sample, and analysis was less difficult than of samples containing not only PCB but a number of other organochlorines in equivalent concentrations. In addition, one laboratory reported the presence of chlordane compounds; these were not reported by other laboratories (Pavlou and Hom, in press).

Previous programs (Holden, 1973; Harvey et al., 1974b) as well as the recent program undertaken by Pavlou and Hom (in press) designated participating laboratories by number or letter. However, identification

of the laboratories seems desirable. As reported below, considerable discrepancy apparently exists among laboratories which utilize different methods in the determinations of chlorinated hydrocarbons in seawater. These differences should be identified and resolved through an intercalibration program as soon as possible.

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PHYSICAL CHEMISTRY OF PCB AND DDT COMPOUNDS

The behavior of PCB and DDT compounds in marine systems is dependent ultimately upon their physical and chemical characteristics; the available data are briefly reviewed here. The chemistry of PCB has been recently reviewed by Hutzinger et al. (1974). Selected solubility and vapor pressure data assembled by Mackay and Wolkoff (1973) and by Spencer and Cliath (1972) are presented in Table 1. Solubilities of such compounds are very difficult to determine accurately as a result of the formation of aqueous emulsions, adsorption from emulsion by surfaces and loss into the atmosphere. Schoor (1975) has discussed in detail the problems associated with determining solubilities of Aroclor 1254. Using a technique in which organochlorine compounds were applied to florisil in acetone, evaporation of the acetone, and elution with distilled water, Weil et al. (1974) estimated the solubility of p,p'-DDE and p,p'-DDT to be 14 µg/l and 5.5 µg/l, respectively. The solubility of PCB isomers was determined to range from 0.016 µg/l to 4130 µg/l. The estimated solubility of p,p'-DDT by Weil et al. (1974) is therefore several times higher than the value presented in Table 7. Schoor (1975) estimated the solubility of Aroclor 1254 in water containing 30 g/l NaCl to be approximately 40% of that in distilled water. Other data for solubility of these compounds in seawater are apparently not available. The mixture of pentachlorobiphenyls (Aroclor 1254) is approximately ten times as soluble in water as is p,p'-DDT (Table 1). On an individual compound basis, therefore, solubilities would appear to be approximately equivalent. Lower chlorinated PCBs are considerably more soluble than the penta- and hexachlorobiphenyls.

The order of magnitude difference in the vapor pressures of p,p'-DDT and p,p'-DDE would suggest significant differences in the

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Table 1. Solubility and Vapor Pressure data for PCB and DDT compounds, from Mackay and Wolkoff (1973) and Spencer and Cliath (1972).

	Temp.	Solubility mg/L	Vapor pressure mm Hg
p,p'-DDT	25°C	1.2×10^{-3}	1×10^{-7}
	30°C	-	7×10^{-7}
p,p'-DDE	30°C	-	65×10^{-7}
o,p'-DDT	30°C	-	55×10^{-7}
Trichloro-biphenyls*	25°C	0.24	4×10^{-4}
Tetrachloro-biphenyls*	25°C	5.4×10^{-2}	4.9×10^{-4}
Pentachloro-biphenyls*	25°C	1.2×10^{-2}	7.7×10^{-5}
Hexachloro-biphenyls*	25°C	2.7×10^{-3}	4.1×10^{-5}

* Aroclors 1242, 1248, 1254 and 1260, respectively. The solubility and vapor pressure data apply therefore to complex mixtures of compounds.

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atmospheric behavior of these two compounds. For example, 66% of the total DDT in the atmosphere over a field containing residual DDT consisted of p,p'-DDE (Cliath and Spencer, 1972). These authors concluded that most of the p,p'-DDT now present in well-aerated soils probably will be volatilized as p,p'-DDE. The vapor pressure of p,p'-DDE has been determined to be 6.5×10^{-6} mm Hg at 30°. The vapor pressure of Aroclor 1254 at 25°C has been estimated to be an order of magnitude higher. Yet this vapor pressure was determined for a mixture of compounds and therefore represents the sum of vapor pressures of a number of individual compounds. The vapor pressure of individual pentachlorobiphenyl isomers might therefore be equivalent to or only slightly higher than that of p,p'-DDE.

Mackay and Leinonen (1975) have estimated rates of the total evaporation process of low-solubility compounds from a water body to the atmosphere. The time required for concentrations to drop to half of the original value from a water depth of one meter was several hours for low molecular weight aromatic compounds, 74 hours for p,p'-DDT and 10.3 hours for Aroclor 1254. Several research groups (Bidleman and Olney, 1974a; Williams and Robertson, 1975) have reported that the concentrations in sea surface films were substantially higher than those in subsurface waters; the existence of the sea surface film may therefore impede the rate of evaporation. Nevertheless, the calculations of Mackay and Leinonen (1975) indicate that PCB and DDT compounds readily enter the atmosphere from water. In both marine and freshwater systems, however, DDT and PCB compounds also partition into the biota and inanimate particulates. The rate of loss into the atmosphere might therefore be significantly retarded.

Some of the difficulties in determination of solubilities and vapor pressure of individual compounds might be circumvented by measuring their concentrations in separate components of the marine environment including the atmosphere, subsurface water with particulates above a given size fraction removed, particulates, and selected members of the biota. Differences in partition coefficients pertaining to components would indicate differences in solubility and/or vapor pressure.

PATTERNS OF GLOBAL CONTAMINATION OF THE MARINE ENVIRONMENT BY PCB AND DDT COMPOUNDS

Although the data are few and sample sizes are frequently small, a reasonably complete picture of global marine contamination by DDT and PCB compounds can be presented using various species of marine birds as indicator organisms. Table 2 summarizes some of the available data on species of cormorants of the genus Phalacrocorax. All feed on fish and occupy similar ecological niches in marine food webs. With the exception of the residue values reported for the Double-crested Cormorants in Southern California, which have been exposed to industrial contamination from the Los Angeles area (Gress et al., 1973), the samples were obtained from areas reasonably remote from point sources of contamination. Samples obtained in estuaries and from inland waters are not therefore included. DDE residues in the Auckland Island Shags were somewhat lower than the majority of the DDE residues in cormorant eggs from Amchitka and Agattu in the Aleutians at the same equivalent latitude in the northern hemisphere. PCB values in the southern hemisphere birds were, however, 1-2 orders of magnitudes lower. Other data from biocoenetic equivalents in the two areas support the conclusion

Table 2. PCB and DDE residues in cormorants, Phalacrocorax sop., in ppm lipid weight

Locality, date	Species	N	Tissue	% lipid	DDE	PCB	PCB/DDE
Amchitka, 1971 (1)	Red-faced cormorant	1	Yolk	20	3.8	19	5
Amchitka, 1974 (1)	Red-faced cormorant	1	Pectoral muscle	3.9	3.5	21	6
Agattu, 1974 (1)	Red-faced cormorant	1	Pectoral muscle	3.8	2.4	14	6
Amchitka, 1974 (1)	Pelagic cormorant	1	Pectoral muscle	4.0	0.8	8	10
Auckland Islands, 1972 (2)	Auckland Is. shag	4	Egg lipid	100	0.9	0.3	0.3
Iceland, 1973 (3)	Shag	10	Egg	5.0	3.8	23	6
	Great cormorant	13	Egg	4.8	3	10	3
Peru, 1969 (4)	Guanay	4	Egg lipid	100	12.2	15	1.2
Southern California, 1969 (5)	Double-crested cormorant	7	Egg lipid	100	754	87	0.1
Greenland, 1972 (6)	Great cormorant	3	Body fat	-	9.8	23	2.3

1) White and Risebrough, in press; 2) Bennington et al., 1975; 3) Sproul et al., in press; 4) R. W. Risebrough, D. W. Anderson and J. McGahan, unpublished data; 5) Gress et al., 1973; 6) Braestrup et al., 1974.

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that at the fiftieth degree of latitude, DDE residues are equivalent or slightly lower in the southern hemisphere but PCB residues are 1-2 orders of magnitude lower. For example, DDE levels in an egg of a New Zealand Falcon (Falco novaeseelandiae) were equivalent to those in peregrines (Falco peregrinus) from Amchitka but PCB levels were an order of magnitude lower. Comparable differences were found between auklets (Aethia pusilla and Cyclorrhynchus psittacula) and the Tufted Puffin (Lunda cirrhata) of the Aleutians and the Diving Petrel (Pelecanoides urinatrix) from the Snares Islands of southern New Zealand as well as between seals and sea lions of the two island groups (White and Risebrough, in press; Bennington et al., 1975).

Somewhat higher DDE levels in eggs of the Guanay (Phalacrocorax bougainvillei) suggest local sources of DDT contamination in Peru (R. W. Risebrough, D. W. Anderson and J. McGahan, unpublished data).

A comparison between the cormorant samples from the Aleutians and the eggs of two species, the Great Cormorant (Phalacrocorax carbo) and the Shag (Phalacrocorax aristotelis) from Iceland suggests that levels of DDE and PCB contamination in the two oceanic areas are similar. This conclusion is furthermore supported by comparison of available residue data from fish. In five species of fish obtained from Amchitka in 1974, DDE residues on a wet weight basis ranged from 1 to 5 µg/kg; PCB residues ranged from 8 to 20 µg/kg, wet weight (White and Risebrough, in press). DDE residues in seven species of fish obtained from the coastal waters of Iceland in 1973 ranged from 1 to 9 µg/kg, wet weight (Sproul et al., in press). On a lipid basis, PCB residues expressed as trichloro-, tetrachloro- or pentachlorobiphenyls ranged from 0.3 to 2 µg/g in the Amchitka fish and from 0.2 to 3 µg/g

in the Icelandic fish.

Although sample sizes, particularly for the Amchitka samples, are small, a comparison of DDE and PCB residue levels in Black-legged Kittiwakes (Rissa tridactyla), the Fulmar (Fulmarus glacialis), and the Thick-billed Murre (Uria lomvia) suggest somewhat higher levels in the Icelandic birds although of the same order of magnitude and with comparable ratios (White and Risebrough, in press; Sproul et al., in press). The differences probably reflect a higher level of contamination in those areas of the ocean where the Atlantic birds spent the winter months.

Earlier data (Risebrough et al., 1968b) suggested that DDT compounds were more abundant than PCB in Pacific waters; the samples, however, were heavily biased towards coastal California waters where DDT contamination had been particularly severe.

Sproul et al. (in press) have presented a detailed comparison between residue levels in the breast muscles of Icelandic birds obtained in 1975 with those in birds obtained earlier by Bourne and Bogan (1972), principally in 1971 from areas north of Britain. Residue levels and PCB DDE ratios were comparable.

In the northern Atlantic and Pacific, therefore, in areas comparatively remote from sources of contamination, PCB residues predominate over the DDT compounds. In the New Zealand area, however, including the subantarctic islands, DDT residues were found frequently to be present at higher concentrations than the sum of PCB (Bennington et al., 1975). In the Antarctic, PCB compounds are also less abundant than those of the DDT group in resident species. Initially, PCB could

not be detected in penguin eggs. Thus, maximum amounts of PCB in eggs of the Adelie Penguin (Pygoscelis adeliae) obtained from Cape Crozier near the big American base at McMurdo, in October 1967 were less than one-eighteenth of the concentration of DDT compounds (Risebrough et al., 1968b). Fourteen unhatched eggs of the Adelie Penguin obtained in January 1970 near Palmer Station, the American base on Anvers Island in the Antarctic Peninsula, were analyzed in 1972; PCB residues were not detected at that time because of the presence of interfering substances. It was subsequently found that these could be removed by rigorous saponification, permitting detection and measurement of PCB. PCB was also detected in eggs of the Adelie Penguin obtained on Anvers Island in December 1973 and in January 1975, as well as in eggs of P. antarctica and P. papua obtained elsewhere in the Antarctic Peninsula in 1975. The median DDE:PCB ratio was 3.0 (R. W. Risebrough, W. Walker II, T. T. Schmidt, B. W. de Lappe, C. W. Connors, unpublished data). Since it is likely that DDT use in the southern hemisphere has been greater than total PCB use, these ratios may be assumed to reflect these differences.

DDE residues in eggs of the Rockhopper Penguin (Eudyptes crestatus) from the Auckland Islands north of the Antarctic Convergence were only slightly but not significantly higher, 0.10-0.18 µg/g lipid weight, than those in penguin eggs from the antarctic continent (Risebrough, in press 1976) and were equivalent to residues in eggs of the three species cited above obtained in the Antarctic Peninsula in 1975. Similarly, DDE concentrations in eggs of the Wandering Albatross (Diomedea exulans) from the Auckland Islands ranged from 0.1 to 0.8 µg/g, lipid weight ($N = 4$), only slightly higher than the mean values

(N = 10) in eggs and whole body homogenates of the Snow Petrel (Pagodroma nivea) from Hallett Station on the Antarctic Continent. DDE residues in four eggs of the Antarctic Tern (Sterna vittata) from the Auckland Islands ranged from 0.6 to 1.1 µg/g comparable to those in nine eggs from the Antarctic Peninsula with an average of 0.7 µg/g (Bennington et al., 1975; Risebrough and Carmignani, 1972). From these limited data, it would appear that DDE levels are comparable over the Antarctic and Subantarctic regions and that no pronounced difference occurs in the area of the Antarctic Convergence.

Sproul et al. (in press) have examined available data for seabirds in the North Atlantic. PCB levels increased from west to east, between Iceland and Europe, with high levels reported in Gannets (Morus bassanus), murres (Uria aalge) (Parslow and Jefferies, 1973; Parslow et al., 1973), and Great Cormorants (Koeman et al., 1973a). DDT residues were highest in the immediate vicinity of the Atlantic coast of the North American continent (Gilbertson and Reynolds, 1974; Zitko et al., 1972) and dropped more rapidly than did PCB moving eastward into the Atlantic.

A population of the Sooty Tern (Sterna fuscata), a pelagic species, breeds on the Dry Tortugas in Florida and ranges widely over the tropical Atlantic. DDE and PCB levels in the breast muscle of 20 adults of known age were 2.5 and 7.8 ppm lipid weight, respectively (mean percent of lipid was 2.6%) (P. G. Connors, W. Robertson, S. A. Jacobs and R. W. Risebrough, unpublished data). These levels were equivalent to those in breast muscles of Arctic Terns (Sterna paradisea) that breed in the Shetlands but that migrate widely over the Atlantic and winter in the Antarctic. They are also equivalent to those

reported in Great Shearwaters (Puffinus gravis), another species which ranges widely over the North and South Atlantic, and in Manx Shearwaters (Puffinus puffinus) breeding in Scotland (Bourne and Bogan, 1972). These levels and ratios appear therefore to be typical of those in the mid-Atlantic at this level of the food web. Substantially higher values have been reported in Fulmars (Fulmarus glacialis) and Black-legged Kittiwakes that breed in the North Atlantic region (Bourne and Bogan, 1972) and in Wilson's Petrels (Oceanites oceanicus) which breed in Antarctica but which spend the northern summer in the North Atlantic. The PCB:DDE ratio of arithmetic mean concentrations in the Wilson's Petrels was 4.0; the average of individual ratios was, however, closer to 2.0 (N = 9) (Risebrough and Carmignani, 1972). Thus PCB:DDE ratios between 2 and 4 appear to be characteristic of many seabirds of the Atlantic.

DEGRADATION OF DDT AND PCB COMPOUNDS

The global contamination pattern by DDT and PCB compounds presented above suggests a previously unsuspected degradative pathway of the DDT compounds. Nisbet and Sarofim (1972) estimated that the total rate of loss to the environment of all PCBs in North America in 1970 was in the order of 1.5 to 2 x 10^3 tons/year into the atmosphere, 4 to 5 x 10^3 tons/year into fresh and coastal waters and 1.8 x 10^4 tons/year into dumps and landfills. The major portion of this PCB consisted of tri-, tetra- and pentachlorobiphenyls. In contrast to PCB, the DDT compounds have been released directly into the environment. U.S. production of DDT in the 1960's varied between 4.8 x 10^4 and 8.3 x 10^4 tons per year. Global DDT production was estimated to be in the order of 1 x 10^5 tons per year at that time (National Academy of Sciences, 1971; Goldberg, 1975a). Approximately half of the DDT manufactured in the United States in the 1960's was exported, principally to tropical countries. If the proportion of pentachlorobiphenyls in the estimated total PCB input into the atmosphere and into fresh and coastal waters of North America in the late 1960's is estimated to be 2 x 10^3 tons/year, the environmental input of pentachlorobiphenyls was substantially lower than that of p,p'-DDT.

Metabolism of p,p'-DDT to water soluble derivatives via p,p'-DDD has been documented in a number of species, but the principal metabolite is usually p,p'-DDE; moreover, this is the most abundant of the DDT compounds in the great majority of environmental samples. Both DDE and PCB compounds are metabolized to hydroxylated derivatives by marine mammals and birds (Jansson et al., 1975). Nevertheless, the available data do not suggest a higher rate of metabolic breakdown of

p,p'-DDE than of pentachlorobiphenyls. In species such as the Brown Pelican (Pelecanus occidentalis) ratios of DDE to pentachlorobiphenyls are equivalent in all individuals of a locality, are independent of concentrations and are characteristic of a locality (Schreiber and Risebrough, 1972). Moreover, the same ratio is usually found in other vertebrates of the local ecosystem (Risebrough et al., 1968b).

Under experimental conditions in the laboratory, DDE is degraded by ultraviolet light to a variety of derivatives (Kerner et al., 1972). PCB compounds are also degraded, under experimental conditions, by ultraviolet light (Ruzo et al., 1972; Safe and Hutzinger, 1971; Herring et al., 1972; Hutzinger et al., 1972). The relative sensitivity of p,p'-DDE and the various chlorobiphenyls to ultraviolet light under environmental conditions, however, has apparently not yet been determined. A higher sensitivity of p,p'-DDE to degradation by ultraviolet light might explain why pentachlorobiphenyls are present in higher amounts than p,p'-DDE in the majority of marine ecosystems of the northern hemisphere.

The majority of polychlorinated biphenyls which have been produced have been tri- and tetrachlorobiphenyls. Frequently these can not be detected in environmental samples which contain penta- and hexachlorobiphenyls. Wong and Kaiser (1975) have reported that bacteria present in lake water readily utilize Aroclor 1221 and Aroclor 1242 but not Aroclor 1254 as a sole carbon and energy source for growth. Metabolism of the lower chlorinated forms to polar derivatives in mammals and birds would also partially explain the lower persistence of these compounds in the environment.

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FLUX OF ORGANOCHLORINES INTO THE SEA FROM RIVERS AND WASTEWATER OUTFALLS

A committee of the National Academy of Sciences (1971) estimated that about 0.1% of the annual production of DDT reaches the oceans by surface runoff. Surface runoff of DDT into the sea from rivers in the United States during the 1960's was estimated to be in the order of 100 tons per year based on determinations of DDT compounds in principal rivers such as the Sacramento, the San Joaquin and the Mississippi. Input of PCB into the oceans from North American rivers has been estimated by Nisbet and Sarofim (1972) and the Panel on Hazardous Trace Substances (1972) to be in the order of 200 tons per year. For these calculations, one-tenth of the total runoff from the continent (3×10^{15} liters/year) was assumed to contain a mean level of 500 ng/l, one-third of the runoff was assumed to have a mean level of 50 ng/l, and the remainder was assumed to contain much lower amounts of PCB. Therefore, the total input of PCB into the oceans from North American sources other than the atmosphere, including losses from ships at sea was estimated to be less than 10^3 tons/year. In the peak years of PCB use, 4 to 5 x 10^3 tons/year were estimated to have been discharged into all fresh and coastal waters. Unfortunately, relatively few measurements which include data on the kinds of DDT and PCB compounds are available for the peak years of use of both groups of compounds.

In coastal areas, wastewaters are frequently discharged directly into the sea rather than into a river; thus, in 1970 we began to measure chlorinated hydrocarbons in California wastewater effluents (Schmidt et al., 1971). Four billion liters are currently discharged into the ocean from treatment plants in Southern California. In

contrast, the total annual surface runoff from river, drainage channels, and urban storm sewers have averaged 400 billion liters per year between 1941 and 1970. On a daily basis, therefore, the amount of water discharged into the sea from the wastewater treatment plants is about three times greater than the total contributed by storm runoff (D. R. Young, R. W. Risebrough, B. W. de Lappe, T. C. Heesen and D. J. McDermott, unpublished ms.). Since the Southern California Bight had become highly contaminated with both DDT and PCB compounds (Risebrough et al., 1968b), we expanded these studies in 1971 in collaboration with the Southern California Coastal Water Research Project to include determinations of chlorinated hydrocarbons in all major wastewater outfalls in Southern California and in surface runoff from rivers and storm channels (Young et al., unpublished ms.).

Measurements of DDT compounds and other chlorinated hydrocarbons in the waters entering the treatment plant of the Los Angeles County Sanitation Districts were begun in 1969 by personnel of the Sanitation Districts. One hundred forty-three separate analyses were carried out previous to April 1970. The mean value of these determinations, applied to a daily volume of 1.4 billion liters, indicated that approximately 290 kg of DDT compounds per day were entering the treatment plant from sources discharging into the sewage network of Los Angeles County. These sources included the world's largest manufacturer of DDT, the Montrose Chemical Corporation of California (rry and Redner, 1970). Until April 1970, this factory passed its liquid wastes through a settling pond which was flushed with a minimum quantity of 1,900,000 liters of water per day. In April 1970, the company began to

haul its DDT-containing liquors to a sanitary landfill (Sobelman, 1971), and amounts of DDT compounds entering the waste treatment plant from the sewage system dropped sharply thereafter (Carry and Redner, 1970). Between May and December of 1970, the DDT input into the water pollution control plant ranged between 50 and 100 kg per day (Carry and Redner, 1970). The organic deposits lining the sewer pipes below the DDT factory have proven to be a major storage site of DDT compounds, and thus they have been a continuing source of the DDT compounds entering the treatment plant since April 1970 (Redner and Payne, 1971).

Our program has included an extensive series of intercalibrations with the laboratory of the Los Angeles County Sanitation Districts, laboratories of the other sanitation districts of Southern California, and the laboratory of the Southern California Coastal Water Research Project (Young et al., op. cit., unpublished ms.).

Input of DDT compounds into the Southern California Bight from the outfall of the County Sanitation Districts of Los Angeles County has continued to decline: in 1970 the total input was 21,600 kg; input was reduced to 1,440 kg in 1974 (Young et al., op. cit., unpublished ms.) During this period DDT residues in Northern Anchovies (Engraulis mordax) and Brown Pelicans inhabiting the Southern California Bight have declined significantly (Anderson et al., 1975). Some of the principal results of the program are summarized in Table 3. Most of the DDT, dieldrin and PCB in surface runoff enters the sea during the periods of storms; close correlations were observed between the chlorinated hydrocarbon concentrations and the particulate content of these waters. Dry weather flow during the remainder of the year contained substantially lower amounts of chlorinated hydrocarbons.

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TABLE 3. Comparison of chlorinated hydrocarbon inputs (kg/yr) to the Southern California Bight v surface runoff, municipal wastewater, and other routes.***

Route/Year	Total DDT	Dieldrin	Trichloro-biphenyls	Pentachloro-biphenyls	Tota
Surface Runoff 1971-72	106-108	25	96-201	96-119	192
Surface Runoff 1972-73	320-325	66	0-552	248-282	248
Municipal Wastewater 1972	6490*	100	≥ 19,200	≥ 260	≥ 19,
Municipal Wastewater 1973	3920	≤ 275	≥ 1,930	1,510	≥ 3,
Municipal Wastewater 1974	1560	84	5,480	1,020	6,
Industrial Discharges** 1973 (1)	20	5	-	50	
Antifouling Paints 1973 (2)	< 1	-	< 1	< 1	
Aerial Fallout 1973-74 (3)	1300	-	-	1,500	1,

* 1971 for total DDT: 21,600 kg.

** San Pedro Harbor only.

*** From D. R. Young, R. W. Risebrough, B. W. de Lappe, T. C. Heesen and D. J. McDermott, unpublis
1) Young and Heesen, 1974; 2) Young et al., 1974; 3) SCCWRP, 1975.

Input of chlorinated hydrocarbons from all surface runoff was found to be substantially lower than input from municipal wastewaters. In some cases estimates of PCB are minimum values since all wastewaters were not sampled. The estimate for total PCB input in 1972, 20,000 kg or 20 tons, may be compared to the estimate by Nisbet and Sarofim (1972) of an input into fresh and coastal waters of North America of 5000 tons per year around 1970. As anticipated, trichlorobiphenyls predominated over the pentachlorobiphenyls in wastewaters entering the sea.

A chromatogram of an extract of seawater obtained from the Whites Point outfall area in May, 1973 is shown in Figure 3. The sample was obtained with the in situ system described below, at a depth of 25 meters. The DDT compounds p,p'-DDE and p,p'-DDD predominate; trichlorobiphenyls are also present. As discussed below, the wastewater outfalls of southern California have had a dominant effect on contamination levels in the Southern California Bight.

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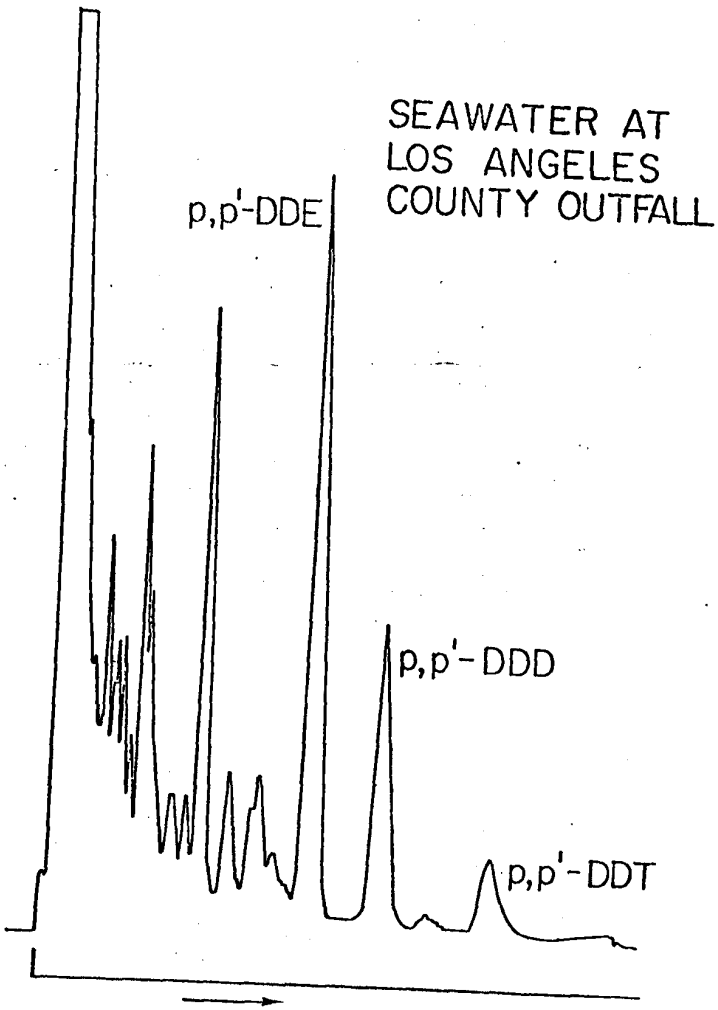
Figure 3. Chromatogram of seawater receiving input from the outfall of the Los Angeles County Sanitation Districts, obtained at a depth of 25 meters in the vicinity of the diffusers. Volume: 15 liters. 3% OV-1 column. OUTFALL II cruise of R.V. THOMAS THOMPSON, May 1973.

MONS 067258



MGNS 067259

AERIAL TRANSPORT OF CHLORINATED HYDROCARBONS

The reported detection of DDT compounds in resident antarctic wildlife (Sladen et al., 1966; George and Frear, 1966; Risebrough et al., 1968b; Brewerton, 1969) indicated global contamination by synthetic organic compounds; the atmosphere appeared to be the most plausible medium of transport. The possibility that these DDT residues may have derived from human activities in Antarctica have been examined by Risebrough (in press) and were considered unlikely. Initially, PCB compounds could not be detected in a number of samples, including the eggs of the Adelie Penguin obtained near McMurdo and Hallett stations on the Antarctic Continent; DDT compounds were, however, present (Risebrough et al., 1968b; Risebrough and Carmignani, 1972). A considerable amount of refuse has been burned at the bases of all nations participating in the antarctic program; discarded waste was likely to consist of material containing PCBs. (Contamination by PCB would be of higher probability than contamination by the DDT compounds.)

Brewerton (1969), on the contrary, concluded that DDT contamination in the Antarctic most likely derived from scientific bases from a comparison of residues in eggs of the Adelie Penguin from the vicinity of the large American base at McMurdo with those from the vicinity of a relatively small base at Cape Hallett. Inclusion of other data, however, showed that no significant differences in DDT contamination existed between the two areas (Risebrough, in press). Moreover, as discussed above, DDE residues do not appear to differ across the Antarctic Convergence. Since waters south of the Convergence derive from the melting of the antarctic icecap or the upwelling of deep waters, a barrier to transport by ocean currents exist. The DDT

residues in resident antarctic wildlife therefore most likely derive from the atmosphere.

Peel (1975) was unable to detect PCB compounds in samples of antarctic snow obtained in December 1969 inland from the British Antarctic Station at Halley Bay (75° 31'S, 26° 42'W). The samples represented the previous 5-10 years snow accumulation. Total concentrations of p,p'-DDT and p,p'-DDE ranged from 0.1 to 2.0 ng/l. On this basis, the argument was advanced that on a global scale the atmosphere is not the predominant mode of transport for PCBs. This conclusion appears inconsistent with that of Bidleman and Olney (1974a; 1974b) and Harvey and Steinhauer (1974) who were able to detect PCB in samples of marine air in the North Atlantic at concentrations considerably in excess of those of the DDT compounds.

Earlier studies in this laboratory (Risebrough et al., 1968a) failed to detect PCB in samples of marine atmospheric particulates, collected on nylon mesh screens on Barbados which sampled the Northeast trades, and in La Jolla, California. Studies on Barbados were continued by Seba and Prospero (1971) and by Prospero and Seba (1972). No correlations were found between the air concentrations of the pesticides and that of airborne dust; pesticides were believed to have originated from the higher latitudes, either Europe or North America.

The failure to find polychlorinated biphenyls on the particulates trapped on nylon mesh screens may be explained from the results of Bidleman and Olney (1974a; 1974b). The majority of the organochlorine residues, particularly of PCB, were not trapped by a glass fiber filter placed before the polyurethane foam column through which air was passed; however, residues were recovered in the foam. Although some evaporation from particulates entrapped on such a filter

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might be anticipated, it would appear that the majority of PCB in the atmosphere is present in the vapor phase. The greater affinity for particulate matter of p,p'-DDT might be predicted from its low vapor pressure (Table 1).

Marine air trapped by Bidleman and Olney (1974a; 1974b) contained principally tri- and tetrachlorobiphenyls; PCB in seawater at these sites consisted predominantly of penta- and hexachlorobiphenyls. Such a partitioning between water and air might be expected from the vapor pressure data (Table 1), but the calculations of Mackay and Leinonen (1975) indicate equivalent residence times in water of mixtures of tri-, tetra-, penta-, and hexachlorobiphenyls. More data are clearly needed on the partitioning of organochlorines between water and the atmosphere.

In order to obtain additional data on the distribution of chlorinated hydrocarbons, particularly of PCB, in Antarctica, samples of antarctic snow were extracted in situ on Doumer Island on the Antarctic Peninsula (64° 51.3'S, 63° 35.5'W) in January-February 1975; eggs of three species of antarctic penguins (Pygoscelis adeliae, P. papua, P. antarctica) were obtained to look for PCB in the food webs and to compare residues with those in eggs obtained five years previously. Eleven 99-liter samples of snow were extracted by techniques described elsewhere (R. W. Risebrough, W. Walker II, T. T. Schmidt, B. W. de Lappe, and C. W. Connors, unpublished ms.). PCB concentrations expressed as as pentachlorobiphenyls ranged from 30 to 1200 picograms per liter; median concentration was 300 pg/l. The median total DDT:PCB ratio in these samples was 6. Samples were obtained

between the surface and a depth of 6 meters; lowest concentrations were recorded in 4 samples obtained between the surface and a depth of 1 meter; melting and evaporation of snow may account for the higher concentrations at greater depths. A gas chromatogram of an extract of the antarctic snow is shown in Figure 4a. The dominant component is p,p'-DDT; o,p'-DDT and p,p'-DDE were also present. In contrast, Peel (1975) recorded higher concentrations of p,p'-DDE than of p,p'-DDT but was unable to detect polychlorinated biphenyls. The chromatogram of Figure 4a shows no polychlorinated biphenyl compounds, but concentration and injection through the saponification side column permits both detection and quantification of pentachlorobiphenyls (Figure 4b).

The median DDE:PCB ratio in penguin eggs obtained between 1970 and 1975 in the Antarctic Peninsula was 3.0 (R. W. Risebrough, W. Walker II, T. T. Schmidt, B. W. de Lappe, and C. W. Connors, unpublished data). Total DDT:PCB ratios recorded in several of the subantarctic samples from the Auckland Islands ranged between 2 and 4 (Bennington et al., 1975), comparable to those recorded in the antarctic penguin eggs. These findings further support the conclusion previously advanced that fallout patterns appear to be similar in areas north and south of the convergence, indicating the importance of atmospheric rather than oceanic transport of the pollutants.

The relative contributions of precipitation and dry fallout in the flux of chlorinated hydrocarbons into the sea from the atmosphere remains unknown; moreover, the interchange at the air-sea interface is poorly understood. Below we present results that indicate that "dry" fallout to the sea surface may be important and that precipitation

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Figure 4. Chromatograms of antarctic snow, extracted in situ on Doumer Island, Antarctic Peninsula, in January, 1975. Figure 4a (above) shows no discernible PCB peaks, surface snow, volume 99 liters. Figure 4b (below) shows the chromatogram of an extract that has been concentrated and passed through a saponification side column. 3% OV-1 column, 100/120 Gas Chrom Q. Depth 4-5 meters, volume 99 liters.

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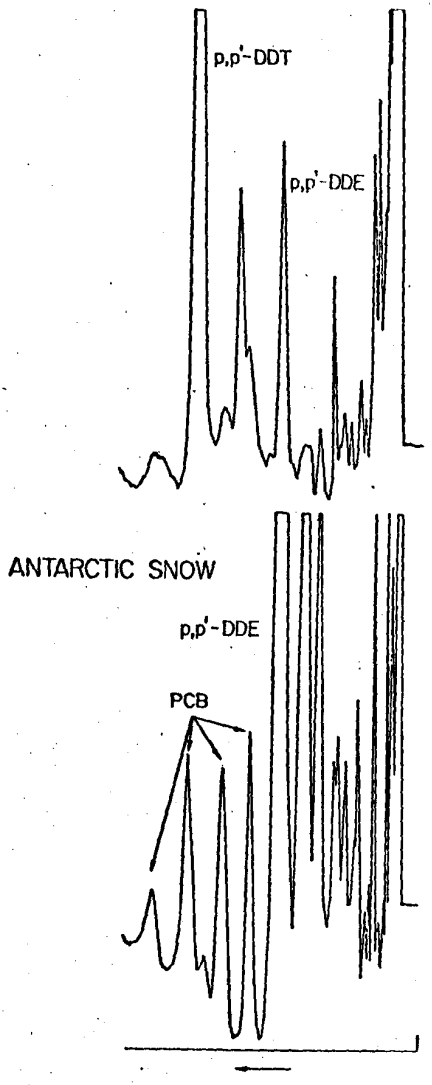

p,p'-DDT
p,p'-DDE
ANTARCTIC SNOW
p,p'-DDE
PCB

is not the only route of entry of organochlorine compounds to the sea. This conclusion was advanced previously (Risebrough et al., 1968a) with reference to fallout of organochlorine pesticides on atmospheric particulates into the tropical Atlantic.

Bidleman and Olney (1974a; 1974b) have shown that the majority of organochlorine compounds in the atmosphere are present in the vapor phase. As equilibrium conditions between the atmosphere and the sea surface would prevail, the lower chlorinated PCB compounds, which predominate in wastewaters entering the Southern California Bight (Table 3), would be expected to dissipate into the atmosphere. Ultraviolet degradation may therefore be a more significant degradative pathway than microbial breakdown.

Experimental studies of the volatility and flux into the atmosphere are more extensive for the DDT compounds than for the PCBs. Lloyd-Jones (1971) has estimated that about half of the DDT applied to field crops may enter the atmosphere. Spencer and Cliath (1972) and Cliath and Spencer (1972) have shown that the vapor pressure of p,p'-DDE is about 9 times that of p,p'-DDT; much of the DDT present in the soil may therefore volatilize as p,p'-DDE. p,p'-DDT has been shown to volatilize readily from surfaces (Quraishi, 1970). Aroclor 1260, p,p'-DDT, and other organochlorine insecticides were found to escape readily into the atmosphere from waters obtained from two rivers and from a subtidal zone (Oloffs et al., 1972).

In 1970, a committee of the National Academy of Sciences (1971) speculated that up to 25% of the DDT applied to the land would eventually enter the sea. Determinations of fluxes across the air-sea interface, of fluxes through the water column, and fluxes between the

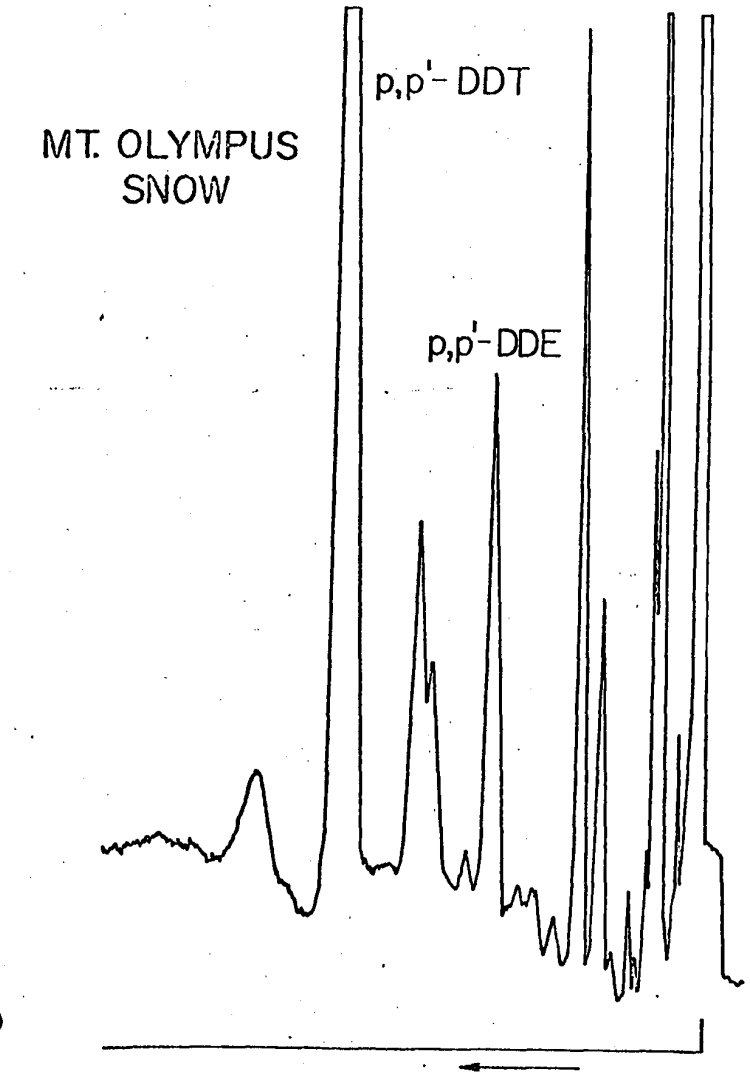
water column and the sediments are needed to complete the global mass balance equation of the DDT compounds, as well as of the various kinds of polychlorinated biphenyls. Such models will be useful in predicting behavior of other synthetic organic pollutants. Needed, however, are estimates of past fluxes from the atmosphere to the sea.

ESTIMATES OF INTEGRATED FLUXES FROM THE ATMOSPHERE TO THE SEA

Analysis of dated anaerobic sediments in the Santa Barbara Basin has permitted determinations of changes in the fluxes from the water column to the sediments (Hom et al., 1974). Analysis of varved anaerobic sediments in freshwater lakes and reservoirs will also be useful in determining changes in past fluxes. Permanent snowfields constitute other records which will permit determination of changes in the fluxes of organochlorines from the atmosphere over the time periods these compounds have been in use. Because local meteorological conditions may significantly affect results, areas remote from input sources with a relatively uniform climate would be more suitable for total flux determinations.

The snowfield on Snow Dome on Mount Olympus, Washington, was sampled in September 1975 to a depth of 22.5 meters. Volumes analyzed ranged from 90 liters to 177 liters. A chromatogram of an extract is shown in Figure 5. As in the antarctic samples, p,p'-DDT was the predominant residue. The median concentration of p,p'-DDT was 10 ng/liter: concentrations of PCB were lower by two orders of magnitude (R. W. Risebrough and W. Walker II, unpublished results). In view of the general predominance of PCB compounds over DDT in the North Pacific (White and Risebrough, in press), it would appear that

Figure 5. Chromatogram of snow from Mount Olympus, Washington, extracted *in situ*, September 1975. 3% OV-1 column, Gas Chrom Q.



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precipitation contains only a small fraction of the PCB. Alternatively, high rates of evaporation on Mount Olympus, coupled with the higher vapor pressure of the PCB compounds, might result in a greater release of PCB into the atmosphere than the DDT compounds. Dating of these samples by lead-210 indicates that all samples were deposited within the last decade, in agreement with stratigraphy data (R. W. Risebrough, W. Walker and V. C. Anderlini, unpublished results). Snowfields with lower rates of precipitation, which would facilitate obtaining older samples, with more uniform deposition, and in colder climates, such that evaporation rates might be lower, would be more suitable for estimates of past changes in fluxes.

DETERMINATION OF CHLORINATED HYDROCARBONS IN SEAWATER: DEVELOPMENT OF AN *in situ* SAMPLING SYSTEM

Accurate determinations of the chlorinated hydrocarbon content in seawater is preliminary to determinations of the fluxes between water and other components of the marine environment, particularly air, sediments, particulates and the biota. Concentrations are expectedly low and large volumes may be necessary to obtain sufficient quantities for accurate measurement.

Cox (1971) measured DDT residues in seawater obtained from a shipboard seawater system, using a continuous-flow, liquid-liquid extraction, along transects off Oregon and Washington and off the California coast. Concentrations of individual DDT compounds were not presented but total residues reported ranged from 2.8 ng/l off Oregon and Washington to 5.6 ng/l off Southern California. In 1970, when the samples were obtained, DDT contamination in the Southern California Bight, particularly in the area near Los Angeles, was exceptionally severe and a greater difference between Southern California and Oregon-Washington might be expected. Moreover, no differences were found between the outer regions of the Bight and the area immediately off Los Angeles. The volumes extracted ranged from 1.6 liters to 4.3 liters.

Williams and Robertson (1975) have reported PCB, p,p'-DDT and p,p'-DDE values in subsurface water from the outer California current and at two stations in the North Central Pacific Gyre, both in the vicinity of 31°N, 155°W. Water was collected in 2.5-liter glass bottles, 10-15 cm below the surface. Reported PCB values in the

subsurface water were 2.5 ng/l in the California current and 4.5 ng/l at one of the North Central Pacific Gyre stations.

Scura and McClure (1975) utilized a column containing 5% activated carbon powder, 10% MgO and 85% refined diatomaceous earth for the determination of chlorinated hydrocarbons in 1-liter samples of seawater collected off the Southern California coast. Reported PCB concentrations in surface seawater at 5 stations in the Southern California Bight ranged from 3 ng/l to 9.6 ng/l. Concentrations reported in 5 samples obtained at depths from 500 to 1500 meters ranged from 2.3 to 10.3 ng/l. In the majority of samples, both p,p'-DDE and p,p'-DDT were detected; DDE concentrations ranged from <0.1 ng/l to 1.0 ng/l at the surface and from 0.3 to 1.2 ng/l at depths from 500 to 1500 meters. Concentrations of p,p'-DDT were somewhat lower.

Bidleman and Olney (1974a) have reported PCB and DDT concentrations at 8 stations in the Sargasso Sea in 1973. PCB concentrations in subsurface water were lower than detectability (<0.9 ng/l) at four of the stations and ranged from 1.0 to 3.6 ng/l at the others. Concentrations of p,p'-DDT were 0.5 ng/l at one station but were below detectability (<0.15 ng/l) at the others. Samples were collected in 3.8-liter glass jugs at depths approximately 30 cm below the surface. Substantially higher concentrations were measured in the surface microlayer. These concentrations were calculated by reference to Aroclor 1260. Concentrations calculated by reference to Aroclor 1254 may have been up to 2 times higher (Risebrough and de Lappe, 1972).

Because of the difficulties in extracting large volumes of seawater with organic solvents, Harvey et al. (1973) developed an

extraction system using Amberlite XAD-2 resin. Seawater, in volumes ranging from 19 and 80 liters, was obtained in a large volume sampler, passed through the resin, and analyzed on board ship. Reported PCB concentrations, calculated relative to Aroclor 1254, averaged 35 ng/l at the surface and 10 ng/l at 200 meters. At depths of 100, 1500 and 3000 meters reported concentrations were greater than one ng/l. Samples were obtained in the summer of 1972 (Harvey et al., 1973).

In 1973 and 1974, substantially lower values were recorded and it was concluded that PCB concentrations in North Atlantic surface waters had declined 40-fold over the two-year period as a result of restrictions on PCB use (Harvey et al., 1974a). At two stations in 1973 (09°N, 40°W and 32°N, 70°W) samples were obtained at various depths of the water column. PCB concentrations ranged from 4.3 ng/l at 10 meters to 1 ng/l at 3000 meters at the former site and from 0.4 to 1.9 ng/l at depths between 10 meters and 5100 meters at the latter.

Harvey et al. (1974a) estimated that the decline of PCB concentrations would require removal of 2×10^4 tons of PCB from the upper 200 meters over the 2-year period, assuming a mean concentration in 1972 of 20 ng/l in the upper 200 meters of the North Atlantic between 26°N and 63°N; the volume was assumed to be 10^{18} liters. The estimate of the volume over this area at a depth of 200 meters appears, however, to be low, perhaps by an order of magnitude since the corresponding area would be 5×10^6 km^2. The area of the Atlantic, including the North and South Atlantic, is 82×10^6 km^2 (Sverdrup, Johnson and Fleming, 1942). Thus, since the PCB reported consisted predominantly of pentachlorobiphenyls, in the order of 10^5 metric tons

of pentachlorobiphenyls would have to be removed from the upper 200 meters. From 1957 through 1974, a total of only 123,723 thousand pounds, equivalent to 5.6×10^4 metric tons of pentachlorobiphenyls (Aroclor 1254), was sold in the United States (Monsanto Chemical Company, 1975). Sales in 1970, the peak year of U.S. production, amounted to 5.6×10^3 tons. The mean depth of the Atlantic is 3926 meters (Sverdrup et al., 1942) and since PCB was recorded by Harvey et al. (1973) at depths to 3000 meters, the estimated pentachlorobiphenyl content of the North Atlantic would be correspondingly higher. With the assumptions of 1 ng/l concentration throughout the water column, 3900 meter average depth and the area of the North Atlantic between the equator and 65°N in the order of 47×10^6 km^2, the pentachlorobiphenyl content would be in the order of 180,000 metric tons, higher than the total U.S. domestic use from 1957 through 1974.

Similarly, a mean PCB concentration of 1 ng/l in the North Pacific would appear to be too high. If a mean value of 1 ng/l of pentachlorobiphenyls were assumed for the upper 200 meters of the North Pacific and the area from the equator to 65°N is 82×10^6 km^2, 16,000 tons of pentachlorobiphenyls would be present in this volume. This represents almost one-third of total U.S. use from 1957 through 1974. Nisbet and Sarofim (1972) and the Panel on Hazardous Trace Substances (1972) estimated that $1.5\text{-}2.5 \times 10^3$ tons per year of PCB, including tri- and tetrachlorobiphenyls, had been discharged into the atmosphere from North America. If this estimate is correct, the atmospheric input of pentachlorobiphenyls into the North Atlantic must have been substantially less, perhaps by an order of magnitude.

In an effort to reduce the very significant problems of contamination during the collection and extraction of trace organics from seawater, we have worked towards the development of an *in situ* sampling system. Such a system eliminates the need for intermediary sampling and storage containers by providing extraction at depth through the use of filter-columns which have been pre-cleaned in the laboratory to known background levels. Columns may be transported to and from the field in clean containers, with controlled exposure only at the time of sampling. The essential component of such a system is a filter medium with a high chemical affinity for chlorinated hydrocarbons in seawater. It is also necessary that such a substance retain particulates without clogging, provide suitable blanks for sampling at pg/l concentrations and function efficiently at flow rates which would permit samples of 100 liters or more to be extracted within a reasonable period of time.

The use of polyurethane foam as an absorptive medium for the extraction of a wide variety of metal derivatives and organic compounds from aqueous solutions was first reported by Bowen (1970). Following this initial report, Gesser *et al.* (1971) demonstrated the ability of polyurethane foam to recover PCB from distilled water spiked at 2 µg/l. Two foam plugs (22 mm diameter, 38 mm long, density 0.027 gm/cm^3) with a total volume of 29 cm^3 produced recoveries of 91-98% at flow rates of 250 ml/min. Subsequent studies by Uthe *et al.* (1972) indicated that coating foam plugs with DC-200 enhanced the recovery of ten chlorinated hydrocarbon insecticides from spiked distilled water solutions. Recoveries averaged between 86-100% for DC-200 coated plugs and 45-84% with untreated foam. An application of DC-200 coated foam plugs for monitoring a fresh water stream was described by Uthe *et al.* (1974).

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Musty and Nickless (1974) have presented recovery data for PCB and thirteen chlorinated insecticides using four untreated foam plugs (22 mm diameter, 40 mm long, total volume 60.8 cm^3) at flow rates of 100 ml/min. Under these conditions, the extraction efficiency of all thirteen insecticides tested was greater than 90%. Recoveries of Aroclor 1242, 1248 and 1254 ranged from 87-99%; recovery of Aroclor 1260 was only 40%. Using two foam plugs (34 mm diameter, 44 mm long, total volume 80 cm^3) Bedford (1974) reported recoveries of Aroclor 1254 varying between 91% from distilled water to 69% from unfiltered lake water at flow rates of 250-275 ml/min. Bedford hypothesized that PCB was adsorbed to the surface of fine particles in the lake water which were not effectively retained by the foam. Experiments with Montmorillonite clay suspensions failed, however, to produce a comparable condition. Recoveries of 91% of Aroclor 1254 were obtained from distilled water solutions with clay concentrations ranging from 0-30 mg/l.

Initial studies in our laboratory evaluated the extraction of chlorinated hydrocarbons from seawater by a high density, high ether content polyurethane foam (81% polyether glycol, 19% toluene di-isocynate, density 0.036 gm/cm^3, United Foam Company, Los Angeles) which had previously been shown effective in the removal of phthalate esters from solution (Carmignani and Bennett, in press). After determining that satisfactory blanks and recoveries could be obtained, equipment was prepared for a seawater sampling program off Southern California aboard the R.V. THOMAS THOMPSON in May 1973. Polyurethane foam plugs (66 mm diameter, 57 mm thick) were cut from sheets, using a heated tube with a sharpened end. Plugs were Soxhlet-extracted with

acetone prior to being packed in stainless steel columns (60 mm I.D., 280 mm long). Five plugs were used in each column, providing a total volume of 975 cm^3. Columns were rinsed with 300 ml portions of acetone and hexane which were collected and reduced on a rotary evaporator until appropriate blanks were obtained (at 300:1 concentration, no peaks greater than 1 pg p,p'-DDE). Columns were wrapped in aluminum foil for transport to and from the field.

Water was collected in a 60 liter Bodman sampler (Benthos, Inc., North Falmouth, Mass.) which was drained by gravity through stainless steel tubing, through a tee, splitting the sample between two columns. In this manner, replicate samples were taken which established analytical reproducibility. Columns were fitted to the stainless steel transfer lines by means of a stainless steel female adaptor fitted with a viton O ring. A second adaptor, fitted at the exit end of the column, provided the attachment of a stainless steel needle valve which was used to regulate the flow rate at 500 ml/min. Column effluent was collected and volumes measured for each column.

Columns were extracted with successive 500 ml volumes of glass distilled acetone and hexane (Burdick and Jackson, Muskeegon, Mich.). Elutants were transferred to a two liter separatory funnel and shaken vigorously with 700 ml distilled water which had previously been cleaned by passage through a foam column. A considerable amount of salt is normally present in the column elutant, thus adding additional NaCl was unnecessary. After standing a minimum of two hours to provide for complete separation, the hexane fraction was collected. Cleanup

was accomplished by passage through a column containing celite, sulfuric acid and fuming sulfuric acid (Stanley and LeFavoure, 1965). Samples were analyzed on a Tracor MT-220 gas chromatograph equipped with Ni_{63} electron capture detectors. Inlet, column and detector temperatures were 225°, 190° and 300°C respectively. Glass columns, 2 meters long, with 4 mm I.D., were fitted with saponification side columns as described by Miller and Wells (1969). Two types of column packings were employed; 3% OV-1 and 1.5% OV-1, both on 100/120 Gas Chrom Q. The results of the 1973 Outfall II Cruise are presented in Table 4.

In the immediate vicinity of the outfall, concentrations of p,p'-DDE in May 1973 were 26 ng/l. DDE concentrations of 8-12 ng/l were recorded elsewhere in the Los Angeles area and dropped to 1 ng/l or less in waters further offshore (Table 4). Trichlorobiphenyls were present in concentrations of 27 ng/l in the immediate vicinity of the outfall and dropped to 2 to 3 ng/l in offshore waters in the coastal current. Because of the predominance of trichlorobiphenyls, pentachlorobiphenyls were not determined in the immediate vicinity of the Whites Point outfall; elsewhere concentrations were in the order of 1 to 3 ng/l. During the week of May 4-10, 1973, immediately prior to the offshore sampling, a composite of wastewaters entering the sea through the Whites Point outfall of the Los Angeles County Sanitation Districts treatment plant was analyzed for chlorinated hydrocarbons. Replicate analyses showed mean values of 4.1 µg/l of p,p'-DDE, 2.4 µg/l of p,p'-DDD, 0.29 µg/l of p,p'-DDT and 3.4 µg/l of trichlorobiphenyls (Aroclor 1242). Analytical procedures were identical to those described

LE 4. Chlorinated hydrocarbons in California coastal waters, May 1973. Concentrations in nanograms per liter. Outfall II Cruise, R.V. Thomas Thompson.

Locality	Date	Depth (meters)	Volume (liters)	p,p'-DDE	p,p'-DDD	p,p'-DDT	Tri-chloro-biphenyls	Penta-chloro-biphenyls
Whites Point Outfall	May 10, 1973	25	32.7	23.1	12.6	NM	24.9	NM
			19.2	29.3	14.0	7.7	28.3	NM
118° 16.7'W, 33° 40.8'N So. of Pt. Ferrin off San Pedro Bay	May 9, 1973	30	30.1	8.0	5.7	0.4	5.7	2.1
			19.0	9.0	6.8	0.6	NM	5.9
118 23.2'W, 33° 41.6'N So. of Palos Verdes Peninsula	May 10, 1973	40	33.3	10.0	7.5	0.9	14.0	2.7
			22.8	12.0	8.4	0.8	14.0	3.1
118° 27.4'W, 33° 34.3'N San Pedro Channel	May 8, 1973	3	29.0	0.21	0.24	0.17	2.4	1.4
			24.3	0.23	0.23	0.24	3.2	1.2
	May 11, 1973	3	14.3	1.5	1.6	0.35	2.1	1.8
			30.0	1.1	1.0	0.13	3.2	1.9
122° 1.0'W, 35° 35.9'N	May 13, 1973	3	30.8	<0.1	<0.2	<0.1	2.7	1.4
121° 55.0'W, 36° 40.5'N	May 13, 1973	3	24.3	0.13	0.17	0.30	NM	1.9
			34.3	0.15	0.20	0.25	NM	1.4
121° 49.2'W, 36° 47.9'N	May 14, 1973	3	33.6	0.09	0.13	0.09	2.8	1.4
			23.0	0.05	0.05	0.08	1.7	1.1
San Francisco Bay, 1 mile east of Golden Gate	May 15, 1973	3	24.0	0.11	0.30	<0.1	NM	2.7

NM: Not measured

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elsewhere (Young et al., unpublished ms.). Thus, the organochlorine composition of the seawater in the vicinity of the outfall closely resembled that of the local effluent.

The concentrations of DDE and of PCB compounds recorded in San Francisco Bay in May 1973 were equivalent to those in offshore waters of the California Current (Table 4). The water sampled, however, may have been predominantly oceanic rather than estuarine.

In September, 1973, a transect was run directly south of Point Conception, California, passing west of San Miguel Island. Replicate samples were taken at 7 stations (Table 5). Seawater was collected in a stainless steel bucket from the bow of the ship, which was steaming slowly forward. The collected water was passed into two 15-liter aluminum pots. Water was then pumped from the pots through stainless steel columns prepared as previously described, using an impeller pump in-line behind the column. The volumes of all samples was 39 liters. "Santa Ana" conditions prevailed during the collections: Winds were from the land and temperatures were warmer than usual in the Southern California Bight. The predominant compound in these extracts was p,p'-DDT and the profiles were significantly different from those observed on other cruises when winds were onshore. We suggest that these results indicate that "dry" fallout to the sea surface may be important and that precipitation is not the only route of entry of organochlorine compounds to the sea. This conclusion was advanced previously (Risebrough et al., 1968a) with reference to fallout of organochlorine pesticides into the tropical Atlantic.

Subsequent developments, utilizing a shipboard vacuum system capable of producing a 680 mm Hg vacuum under continuous operation,

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TABLE 5. Chlorinated hydrocarbons in surface seawater along the western boundary of the Southern California Bight, September 1973, obtained from the vessel PAISANO.

Concentrations in ng/l.

Station	Locality	Column no.	p,p'-DDE	p,p'-DDT	Penta-chloro-biphenyls*
1					
9-26-73, 0545	120° 35'W, 34° 26'N	1	.12	.37	
		2	.10	.32	.27
2					
9-26-73, 0900	" 34° 18'N	3	.09	.35	
		4	.07	.27	.36
3					
9-26-73, 1145	" 34° 10'N	5	.12	.79	
		6	.13	.82	.49
4					
9-26-73, 1500	" 34° 02'N	7	.10	.51	
		8	.13	.75	.46
5					
9-26-73, 1745	" 33° 54'N	9	.08	.46	
		10	.09	.53	.44
6					
9-26-73, 2300	" 33° 34'N	11	.13	1.3	
		12	.08	.79	.49
7					
9-27-73, 0200	" 33° 14'N	13	.06	.47	
		14	.06	.53	.38

*Quantified from Aroclor 1254

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enabled columns to be lowered and pumped directly at depth (Figure 6). A stainless steel one-way flap valve with a viton O ring and 1/3 lb spring was fitted inline between the column adaptor and the vacuum tubing to reduce the possibility of contamination from back-flow.

The results of an intercalibration study carried out in Los Angeles Harbor in 1974 are presented in Table 6. Solvent extractions were three stage in two liter separatory funnels, using 400 ml of solvent at each stage. Water was sampled with foam columns in two manners. One set of columns was pumped in situ at a depth of 1 meter using a vacuum pump system. The second set received water from stainless steel bucket collections taken with efforts to avoid surface concentrations. This water was passed directly to a six liter stainless steel reservoir fitted at the top end of a column held vertically in a ring stand assembly, with flow rates controlled by a valve connected by an adaptor to the exit end of the column. Reasonably consistent results were obtained from the four extraction procedures.

An additional intercalibration study was carried out during a wastewater sampling program at an experimental plant of the Los Angeles County Sanitation District in December 1974. Twenty-four liters of secondary effluent were passed by gravity flow through a polyurethane foam packed stainless steel column fitted with a six liter stainless steel reservoir. A replicate sample was obtained by methylene chloride batchwise extraction, as described elsewhere (Burlingame et al., 1976). Final extracts were reduced to a volume of 10 ml in hexane and fractionated on a florisil column eluting sequentially with 6% and 15% solutions of diethyl ether in hexane (Mills, P.A., 1961). Figure 2 presents the chromatograms of the 6% fractions of both extraction

Figure 6. The "Slocum"* selective organic *in situ* sampler for determining trace levels of organochlorine compounds in seawater. Seawater is pumped at depth through a stainless steel column packed with polyurethane foam plugs utilizing a shipboard vacuum system.

*Captain Joshua Slocum 1844 - ?

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SELECTIVE ORGANIC *IN SITU* SAMPLER

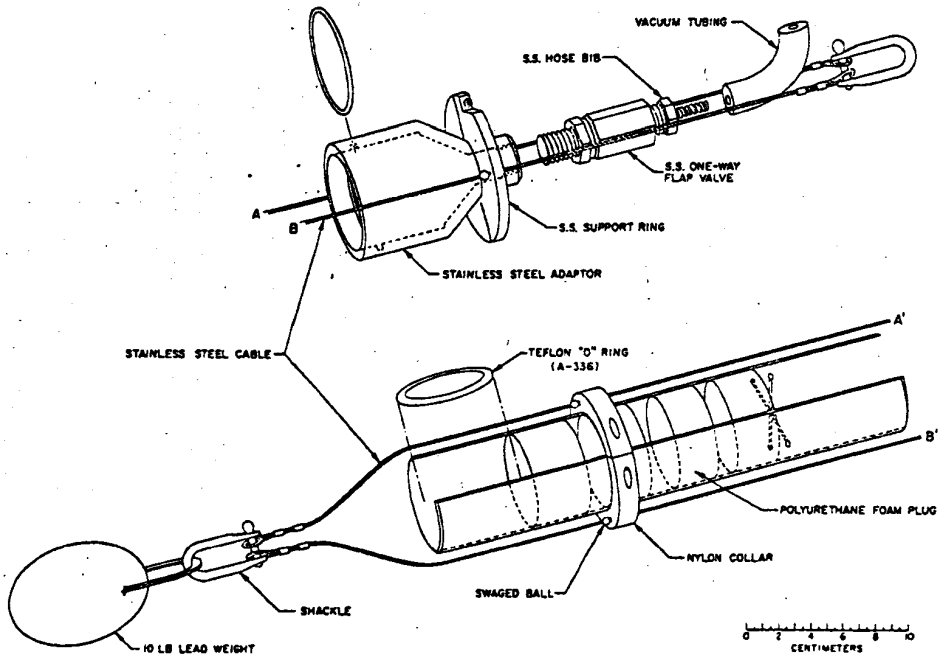

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Table 6. Intercalibration of methodologies

Extraction of organochlorines from sea water

Los Angeles Harbor, May 1974

Mean concentrations with the range (ng/l).

Method	N	Volume extracted liters	p,p'-DDE	p,p'-DDD	PCB
Blank (column)	1	Assume 40	< .02	< .017	< .14
Solvent extraction hexane	2	16.1	1.9 (1.8-1.9)	1.0 (0.9-1.0)	1.5 (1.4-1.6)
Solvent extraction methylene chloride	1	25.3	1.6	0.9	2.8
Foam column gravity	8	23 - 45	1.8 (1.1-2.3)	1.1 (0.7-1.3)	3.6 (1.7-7.4)
Foam column vacuum	3	26 - 79	1.8 (1.5-2.3)	1.1 (0.9-1.3)	3.0 (1.0-6.4)

procedures. Under these conditions, both extracts were virtually identical in the composition of compounds producing a response with the electron capture detector.

The "Slocum" in situ sampler (Figure 6) was used to extract PCB and DDT compounds at depth from seawater during a cruise of R.V. CAYUSE in the Southern California Bight and from Mazatlan to San Diego in February-March 1975. Results of analysis of the samples obtained in Pacific offshore waters of Mexico are presented in Table 7. None of the samples obtained in the waters off western Mexico had detectable levels of any of the compounds looked for. Detection limits were imposed not only by background contamination of the system but by the presence of unknown compounds in the seawater (Figure 1).

In Table 8 are presented the results of analysis of seawater extracts obtained in the Southern California Bight in February 1975. Levels of p,p'-DDE were in the order of tens or hundreds of parts per quadrillion (pg/l) in the outer stations but approached 5-6 ng/l in the vicinity of the Whites Point outfall. Levels of pentachlorobiphenyls were below the limits of detectability, in the range of hundreds picograms per liter at the outer stations and approached 1-2 ng/l in waters in the vicinity of the wastewater outfalls. The high levels of DDT compounds in the vicinity of the Whites Point outfall are assumed to have leached from the sewer pipes below the DDT manufacturing plant, which in the past was the principal source of DDT residues entering the Southern California Bight.

Table 7. Maximum DDT and PCB concentrations in Pacific offshore waters of Mexico. pg/l. March 16-28, 1975. Depth of 3 m.

Longitude	Latitude	Volume (liters)	p,p'-DDE	p,p'-DDD	p,p'-DDT	Pentachloro-biphenyls
106° 34.0' W	22° 59.0' N	96	< 2	< 3	< 5	< 30
107° 05.5'	22° 18.6'	96	< 10	< 10	< 10	< 70
108° 27.2'	20° 29.0'	114.5	< 1	< 10	< 2	< 70
109° 00.0'	19° 47.9'	96	< 3	< 5	< 10	< 50
110° 16.1'	18° 05'	114	< 1	< 1	< 1	< 100
110° 43.0'	17° 27.0'	116	< 1	< 1	< 2	< 100
112° 27.5'	15° 59.5'	115	< 10	< 10	< 20	< 100
113° 06.0'	15° 24.1'	96	< 1	< 80	< 2	< 10
114° 44.5'	13° 42.0'	117	< 3	< 5	< 9	< 300
115° 25.0'	13° 06.0'	95	< 2	< 3	< 6	< 100
115° 26.0'	15° 19.0'	137	< 2	< 2	< 5	< 100
115° 32.0'	16° 03.0'	114	< 2	< 3	< 6	< 100
114° 48.0'	18° 09.5'	60	< 2	< 2	< 5	< 100
114° 41.0'	18° 44.5'	91	< 2	< 3	< 5	< 30

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Table 7, continued

Longitude	Latitude	Volume (liters)	p,p'-DDE	p,p'-DDD	p,p'-DDT	Pentachloro-biphenyls
114° 50.0'	20° 37.5'	104	< 1	< 1	< 3	< 100
114° 39.0'	21° 28.5'	80.8	< 1	< 2	< 4	< 40
114° 54.0'	23° 33.5'	116	< 10	< 4	< 7	< 80
115° 02.0'	24° 22.8'	105	< 1	< 2	< 3	< 20
115° 10.2'	26° 12.8'	81.8	< 2	< 2	< 5	< 20
114° 47.5'	28° 19.8'	91.2	< 10	< 3	< 5	< 30
115° 28.2'	28° 47.3'	79.8	< 2	< 4	< 8	< 40
116° 46.7'	30° 25.3'	70.4	< 2	< 3	< 7	< 30
117° 02.0'	31° 04.3'	89.3	< 4	< 5	< 10	< 50
117° 20.5'[a]	32° 34.7'[a]	79.8	200[a]	80	< 2	500[a]

[a] In U.S. waters off San Diego

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Table 8. DDT and PCB residues in waters of the Southern California Bight. ng/l. February 21-27, 1975.

Longitude	Latitude	Depth (meters)	Volume (liters)	p,p'-DDE	p,p'-DDD	p,p'-DDT	Pentachloro-biphenyls
119° 13.1' W	34° 04.6' N	3	38	0.3	< 0.04	< 0.08	< 0.4
119° 21.9'	33° 57.5'	3	38	0.2	< 0.08	< 0.09	< 0.5
119° 54.5'	33° 46.8'	3	38	0.09	< 0.03	< 0.05	0.4
120° 23.6'	33° 35.2'	3	38	0.07	< 0.03	< 0.06	< 0.3
119° 31.0'	33° 44.8'	3	38	< 0.05	< 0.07	< 0.1	< 0.7
118° 48.0'	33° 54.1'	3	38	0.1	< 0.03	< 0.06	< 0.3
118° 31.1'	33° 54.8'	3	38	0.3	0.2	< 0.1	< 0.6
118° 31.4'	33° 48.7'	3	38	0.07	0.04	< 0.06	< 0.03
118° 27.6'	33° 36.2'	3	38	0.05	0.04	0.05	< 0.1
118° 20.3'	33° 23.5'	3	38	0.06	< 0.03	< 0.06	0.1
118° 19.5' 4.5 mi SW Pt. Fermin	33° 37.6'	3	38	2.1	0.7	0.3	0.7
118° 17.9' 0.9 mi S Pt. Fermin	33° 41.4'	3	38	4.5	1.5	< 0.4	1.5
118° 19.4' Over Wt Point outfall	33° 41.8'	3	39	3.5	1.0	< 0.2	1.0
118° 22.2' 7 mi SW Wt Point outfall	33° 35.4'	3	40	0.7	0.3	0.3	0.04

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Table 8, continued

Longitude	Latitude	Depth (meters)	Volume (liters)	p,p'-DDE	p,p'-DDD	p,p'-DDT	Pentachloro-biphenyls
118° 20.9'	33° 42.3'	3	38	5.9	2.2	0.5	2.0
1.3 mi NW Wt Point outfall							
118° 19.9'	33° 40.6'	3	38	3.5	1.7	0.8	0.3
1.3 mi SW Wt Point outfall							
118° 24.6'	33° 43.5'	3	38	4.0	1.2	0.4	0.7
S of Pt. Vicente							
118° 19.4'	33° 41.8'	16	23	5.0	3.0	< 0.4	1.5
Over Wt. Pt. outfall							
118° 19.0'	33° 41.7'	36	23	4.0	2.0	< 0.07	1.5
0.4 mi S Wt. Pt. outfall							
118° 21.7'	33° 42.2'		19	2.0	2.0	0.7	1.5
NW of Wt. Pt. outfall							
118° 20.0'	33° 40.0'	3	38	0.06	0.09	< 0.09	0.3
Entrance Los Angeles Harbor							
118° 20.0'	33° 30.0'	3	38	< 0.06	< 0.09	< 0.2	0.2
14 mi SW Pt. Fermin							
		65	57	0.2	0.08	< 0.1	0.2
117° 17.2'	32° 40.8'	3	38	0.1	0.1	< 0.1	0.3
0.5 mi NE Pt. Loma							

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To date, we have no evidence of the channeling of water in the column systems used, which might result from the entrapment of air and compression of foam/at greater depths. Another version of an *in situ* sampler with which we are currently experimenting prevents this possibility by requiring water to pass through concentric layers of polyurethane foam, Zitex (a pure Teflon filter material, Chemplast, Inc., Wayne, N.J.) and other absorbents. We are also experimenting with coating polyurethane foam with various silicone liquid phases which other investigators have shown to enhance the recovery of trace organics from solution (Uthe *et al.*, 1972; Aue *et al.*, 1972). Modifications have also been made to the "Slocum" *in situ* sampler which provide for a glass fiber filter to be fitted in-line prior to the polyurethane foam column. Such a unit offers accurate determinations of residue concentrations in both the particulate and dissolved fractions of seawater. Teflon columns have been found to provide a smoother connection with the stainless steel adaptors. These columns may also be adapted to form the body of a Soxhlet apparatus, simplifying extraction procedures and further reducing the possibilities of contamination.

The *in situ* sampling systems so far employed require that water be pumped to the ship and collected for volume determinations. Use of a submersible pump with a flow meter would eliminate this requirement. Such a system could also be coupled with standard physical oceanographic *in situ* probes (temperature, depth, conductivity, turbidity, etc.), providing a more detailed characterization of the water body sampled. The depth capabilities of such a fully submersible system would greatly exceed the limitations imposed by the shipboard vacuum pumping system.

CHLORINATED HYDROCARBONS IN PLANKTON AND OTHER PARTICULATES

Because of the low water solubilities of the higher molecular weight chlorinated hydrocarbons, a substantial fraction of the chlorinated hydrocarbons in the water system can be expected to be associated with particulates, including plankton, and with other members of the biota. Satisfactory determinations have not yet been made, however, of the portion of DDT and PCB residues in a seawater system that are present in the "dissolved" state. The seawater analytical system employed by Harvey et al. (1973) included a glass fiber filter or a glass wool plug which removed much of the particulate matter before the water passed through the Amberlite resin column. Residues in the filter or glass wool plug were estimated to constitute a maximum of 10% of the PCB present in the filtered seawater samples. Thus, the residues reported would be in the "dissolved" phase. The analytical methods employed by other investigators have provided chlorinated hydrocarbon determinations of the total seawater sample, including plankton and other particulates.

Plankton samples obtained on R.V. ATLANTIS II cruise 52 in 1969 with a #6 mesh plankton net were analyzed for chlorinated hydrocarbons. The data were compared with those subsequently obtained by G. R. Harvey and co-workers on R.V. ATLANTIS cruises 59 and 60 (Risebrough et al., 1972). The chlorobiphenyls detected closely resembled the composition of Aroclor 1254, and PCB compounds were present in substantially higher concentrations than those of the DDT group. PCB in the zooplankton from the stations on the Continental Shelf and Slope ranged from 2.4 to 260 ppm, lipid weight, 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 the dry weight constitutes 10% of wet weight, representative concentrations in zooplankton in the Shelf and Slope areas were estimated to be in the order of 1.5 ppm and 0.15 ppm respectively.

Since these data were published we have examined the possibility that some if not all of the samples were contaminated by shipbottom anti-fouling paint. Such contamination would explain the close resemblance of the gas chromatographic profiles of the plankton extracts to that of Aroclor 1254 and would account for the exceptionally high PCB:DDT ratios; fish and other organisms higher in the food web were consistently found to have substantially lower ratios.

Shipbottom paint until recently has contained PCB (Young et al., 1974) and is therefore a possible source of such contamination. Thus, Jensen et al. (1972) found that the plankton samples obtained in the wake of a boat had significantly higher concentrations of PCB than did those obtained before the bow. Moreover, the gas chromatograph profile of plankton samples obtained in the wake closely resembled that of the commercial pentachlorobiphenyl preparation Clophen A-50, which closely resembles the American preparation Aroclor 1254. DDT compounds observable in chromatograms of extracts of plankton obtained before the bow were not visible in chromatograms of extracts of plankton obtained in the wake. Because of the close similarity in gas chromatographic profiles of plankton extracts obtained in both our laboratory (Risebrough et al., 1972) and at the Woods Hole Oceanographic Institution (Harvey et al., 1974b) with those of the pentachlorobiphenyl preparation Aroclor 1254 it is possible that these samples were contaminated with antifouling shipbottom paint.

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Ware and Addison (1973) have determined PCB residues in plankton from the Gulf of St. Lawrence. Extensive precautions were taken to ensure that the samples were not contaminated. Estimations of the PCB content of #6 mesh plankton net samples were comparable to those we had earlier reported from the Atlantic (Risebrough et al., 1972). PCB concentrations were inversely related to particle size. Total PCB residues associated with #20 mesh plankton net samples ranged from 20 to 930 pg/l at 8 stations in the Gulf of St. Lawrence in the summer of 1972. Concentrations therefore approached 1 ng/l of the water mass. Concentrations in particulate material smaller than 73 µm, which would pass through the #20 mesh plankton net, were not determined. Particles in the size range 73 µm to 202 µm, however, ranged up to 31 ppm wet weight, apparently the highest PCB concentrations so far reported in natural plankton. It is therefore possible that particles smaller than 73 µm might contain still higher PCB concentrations.

Simultaneous determinations of organochlorine concentrations of the total water system and of one or more particulate size classes would appear to be needed to understand the partitioning among and fluxes between components of these systems.

SEDIMENTS: FLUXES THROUGH THE WATER COLUMN

Organochlorines may be expected to be associated with fecal pellets and other organic detrital matter, as well as inorganic particulates, that pass through the water column and are deposited in the sediments. Although a substantial portion of these residues might then be incorporated by benthic fauna, deposition in the sediments

provides a pathway for the ultimate removal of these chlorinated hydrocarbons from marine food webs.

Varved anaerobic sediments of the Santa Barbara Basin off Southern California, dated by counting of the varves and by ^{210}Pb and $^{228}Th/^{232}Th$ radiometric age measurements, were analyzed for chlorinated hydrocarbons. Deposition of DDE in the sediments began about 1952; deposition of PCB began about 1945. Estimated deposition rates (in grams per square meter per year) in 1967 of DDE and PCB were 1.9×10^{-4} and 1.2×10^{-4}, respectively (Hom et al., 1974). The anaerobic nature of these sediments ~~precludes~~ MINIMIZES uptake by benthic organisms and recirculation in the marine biosphere. Although a high rate of local input of both DDT and PCB compounds into the waters of the Southern California Bight precluded extrapolation to other oceanic areas, the data suggest that a substantial portion of chlorinated hydrocarbons entering the sea from diverse sources was being deposited in the sediments.

Clues to the relative flux of DDT and PCB compounds through the water column may be obtained from the analysis of benthic organisms. The bathyl-demersal fish, Antimora rostrata, is a permanent resident of the Lower Continental Slope; bottom photographs indicate that these fish swim slowly over the bottom, crop benthic epifauna and root in the ooze for infauna (Marshall, 1971; Meith-Avcin et al., in press). Specimens collected on the upper continental rise southeast of Cape Hatteras in 1972 at a depth of 2500 meters were found to contain 3 to 7 ppm of total DDT compounds in the livers (Meith-Avcin et al., in press). Two of the livers were subsequently analyzed for PCB compounds. Lipid content was high, 84 and 87% of total dry weight respectively.

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Concentrations recorded on a lipid weight basis were as follows: p,p'-DDE, 5.9 and 19 µg/g; p,p'-DDT, 2.4 and 12 µg/g; o,p'-DDT, 0.6 and 3.1 µg/g; p,p'-DDD, 2.4 and 5.2 µg/g; pentachlorobiphenyls, 3.8 and 12.5 µg/g (R. T. Barber, S. M. Warlen, R. W. Risebrough and P. J. Whaling, unpublished data).

The substantial concentrations of undegraded p,p'-DDT and o,p'-DDT in these deep-sea fish indicate that these compounds may be transported unchanged through the water column. The predominance of DDT compounds over PCB in these fish is at variance with the PCB:DDT ratios recorded in various species of mesopelagic and surface fish from the North Atlantic, which almost invariably have had more PCB than DDT (Harvey et al., 1974b). In fish obtained below 200 meters and down through 900 meters, the median concentration of DDT in the lipid was 1 ppm (N = 36; Harvey et al., 1974b). If the two PCB values recorded in Antimora are typical, the benthic environment would appear to be enriched with PCB in relation to the water column. Concentrations of DDT compounds are higher, suggesting that transport of DDT compounds through the water column may be more rapid than transport of PCB.

Estimates of the transport of chlorinated hydrocarbons through the water column and of rates of deposition in the sediments are hampered by the same deficiencies present in all other studies of chlorinated hydrocarbon fluxes through the marine environment. Data are too few, too scattered and too widely separated in both time and space to permit little more than speculation on what might be occurring.

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whether the differences in bioconcentration factors are real, especially in view of the considerable discrepancy between those of p,p'-DDT and p,p'-DDE (Sanborn et al., 1975). Biological magnification factors for accumulation of ^{36}Cl-labeled Aroclor 1254 have been determined for several species of aquatic invertebrates (Sanders and Chandler, 1972). The lower chlorinated isomers were accumulated to a greater degree than the higher chlorinated isomers suggesting that availability to the organisms was limited by water solubilities and that the higher chlorinated isomers were not truly dissolved in the water medium (Schoor, 1975). Thus, it is extremely difficult to approximate natural conditions while undertaking uptake studies in the laboratory.

To begin investigations of the partitioning between seawater and the biota, we measured chlorinated hydrocarbon concentrations in seawater, including the particulate fraction, obtained at sites where mussels (Mytilus edulis or M. californianus) were also obtained. In Table 9 are presented the bioaccumulation factors of chlorinated hydrocarbons between Mytilus sp. and seawater from four sites on the Mediterranean coast of France and two in California. Equivalent factors were obtained in the samples from Marseille for PCB, predominantly pentachlorobiphenyls, and p,p'-DDT; for both the bioaccumulation factor was 690,000. Lower bioaccumulation factors, particularly for p,p'-DDT, were obtained at Valras-Plage and Stes.-Maries. The dominant DDT compound in the water was p,p'-DDT; o,p'-DDT was also present, suggesting a recent input source from aerial fallout. Possibly equilibrium between the mussels and the water of p,p'-DDT had not yet been reached. Bioaccumulation factors in San Francisco Bay were an order of magnitude lower than in Marseille. Factors which are different in the

Table 9. Bioaccumulation factors of chlorinated hydrocarbons between *Mytilus sp.* and seawater[1]

Location		Chlorinated hydrocarbon concentrations: Mussels ng/g wet weight	Seawater ng/l	Bioaccumulation factors
France				
Valras-Plage 9 July 1974	PCB	250	0.94	270,000
	P,P'-DDT	51	0.54	90,000
Stes-Maries 10 July 1974	PCB	450	0.95	470,000
	P,P'-DDT	13	0.35	40,000
Carro 11 July 1974	PCB	200	0.68	300,000
	P,P'-DDT	52	0.25	210,000
Marseille 12 July 1974	PCB	1,100	1.6	690,000
	P,P'-DDT	900	1.3	690,000
California				
Royal Palms, Los Angeles 19 September 1972	PCB	230 (N=2)	1.2 (N=4)	190,000
	P,P'-DDE	1,600 (N=2)	5.1 (N=4)	310,000
San Francisco Bay Means±SD January-March 1975	PCB	68±24 (N=47)	0.98±.47 (N=26)	69,000
	P,P'-DDE	5±2 (N=47)	0.11±.06 (N=26)	45,000

[1] From R. W. Risebrough, B. W. de Lappe and T. T. Schmidt, unpublished

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eggs of other seabirds in the Arctic has been attributed to PCB poisoning (Koeman et al., 1973a; Bourne and Bogan, 1972). Moreover, high body burdens of organochlorines possibly weaken birds at a time of external stress such as bad weather and the low availability of food (Holdgate, 1971; Parslow and Jefferies, 1973; Parslow et al., 1973; Lloyd et al., 1974).

Other aspects of effects of organochlorine compounds and petroleum on marine birds have recently been reviewed by Ohlendorf, Risebrough and Vermeer (in press).

Potential effects of organochlorine compounds on marine phytoplankton were observed by Wurster (1968), who reported that DDT inhibited the photosynthesis of several species of marine phytoplankton. Subsequently, PCB compounds were found to have comparable effects (Mosser et al., 1972; Fisher et al., 1973). Organochlorines were subsequently shown to affect growth rather than photosynthesis per se (Fisher, 1975). The concentrations required to produce these effects have, however, been much higher than those which occur in marine environments. Ecological effects resulting from differential effects on phytoplankton growth appear therefore unlikely.

RESEARCH NEEDS

Research carried out over the past five years has generated results which in turn have opened up a bewildering variety of potential research projects. Some of these are strictly "scientific" in the more classical sense of the term; others have more immediate aims to determine whether levels of a given pollutant are increasing in a particular area and whether or not a given level is exerting

harmful effects on the local marine environment. Among the many possibilities, we suggest the following priority. Since per capita production of synthetic organic compounds has continued to increase, it has become essential to determine which ones might be potentially significant marine pollutants (National Academy of Sciences, 1975). From the existing data on the global distribution of the DDT and PCB compounds, it is possible to present a preliminary model of the global mass balances. Many data, however, are required to complete the picture. Such a model would not only permit a definitive assessment of the effects of these pollutants on the marine environment but the model might be used to predict the global movements and effects of other relatively persistent organic pollutants which may appear in the future.

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REFERENCES

ANDERLINI, V.C., P.G. CONNORS, R.W. RISEBROUGH and J.H. MARTIN (1972) Concentrations of heavy metals in some Antarctic and North American sea birds. Pages 49-61 in B.C. Parker, ed., Proceedings of the Colloquium, Conservation Problems in Antarctica. Allen Press, Lawrence, Kansas.

ANDERSON, D.W., J.R. JEHL, JR., R.W. RISEBROUGH, L.A. WOODS, JR., L.R. DEWEESE and W.G. EDGECOMB (1975) Brown Pelicans: improved reproduction off the southern California coast. Science, 190, 806-808.

AUE, W.A., K. SHUBHENDER and C.R. HASTINGS (1972) The use of support-bonded silicones for the extraction of organochlorines of interest from water. J. Chromatogr., 73, 99-104.

BEDFORD, J.W. (1974) The use of polyurethane foam plugs for extraction of polychlorinated biphenyls (PCB's) from natural waters. Bull. Environ. Contam. Toxicol., 12, 622-625.

BENNINGTON, S., P.G. CONNORS, C. CONNORS and R.W. RISEBROUGH (1975) Patterns of chlorinated hydrocarbon contamination in New Zealand subantarctic and coastal marine birds. Environ. Pollut., 8, 135-147.

BEVENUE, A., J.N. OGATA and J.W. HYLIN (1972) Organochlorine pesticides in rainwater, Oahu, Hawaii 1971-72. Bull. Environ. Contam. Toxicol., 8, 238.

BIDLEMAN, T.F. and C.E. OLNEY (1974a) Chlorinated hydrocarbons in the Sargasso Sea atmosphere and surface water. Science, 183, 516-518.

BIDLEMAN, T.F. and C.E. OLNEY (1974b) High-volume collection of atmospheric polychlorinated biphenyls. Bull. Environ. Contam. Toxicol., 11, 442-450.

BLUMER, M. (1975) Organic compounds in nature: limits of our knowledge. Angewandte Chemie, 14, 507-514.

BOURNE, W.R.P. and J.A. BOGAN (1972) Polychlorinated biphenyls in North Atlantic seabirds. Marine Pollut. Bull., 3, 171-175.

BOWEN, H.J.M. (1970) Absorption by polyurethane foams; new method of separation. J. Chem. Soc. (A), 1082-1085.

BOWES, G.W., B.R. SIMONEIT, A.L. BURLINGAME, B.W. DE LAPPE and R.W. RISEBROUGH (1973) The search for chlorinated dibenzofurans and chlorinated dibenzodioxins in wildlife populations showing elevated levels of embryonic death. Environ. Health Perspectives: Experimental Issue No. 5, 191-198.

BOWES, G.W., M.J. MULVIHILL, B.R. SIMONEIT, A.L. BURLINGAME and R.W. RISEBROUGH (1975) Identification of chlorinated dibenzofurans in American polychlorinated biphenyls. Nature, 256, 305-307.

BRAESTRUP, L., J. CLAUSEN and O. BERG (1974) DDE, PCB and aldrin levels in arctic birds of Greenland. Bull. Environ. Contam. Toxicol., 11, 326-332.

BREWERTON, H.V. (1969) DDT in fats of antarctic animals. N.Z. Journal of Science, 12, 194-199.

BURLINGAME, A.L., B.J. KIMBLE, E.S. SCOTT, J.W. DE LEEUW, F.C. WALLS, B.W. DE LAPPE and R.W. RISEBROUGH. The molecular nature and extreme complexity of trace organic constituents in southern California municipal wastewater effluents. Proceedings of the Symposium on the Identification and Analysis of Organic Pollutants in Water, First Chemical Congress of the North American Continent, Mexico City, November-December 1975, Ann Arbor Science Publishers, L.H. Keith, editor, in press.

CARMIGNANI, G.M. and J.B. BENNETT. Filter media for the removal of phthalate ester in water of closed aquaculture systems. Aquaculture, in press.

CARRY, C.W. and J.A. REDNER (1970) Pesticides and heavy metals: progress report. December 1970. County Sanitation Districts of Los Angeles County, 2020 Beverly Boulevard, Los Angeles, California 90057. 51 pp.

CLIATH, M.M. and W.F. SPENCER (1972) Dissipation of pesticides from soil by volatilization of degradation products. I. Lindane and DDT. Environ. Sci. Technol., 6, 910-914.

CONNORS, P.G., V.C. ANDERLINI, R.W. RISEBROUGH, J.H. MARTIN, R.W. SCHREIBER and D.W. ANDERSON (1972) Heavy metal concentrations in brown pelicans from Florida and California. Cal-Neva Wildlife 1972, 56-64.

CONNORS, P.G., V.C. ANDERLINI, R.W. RISEBROUGH, M. GILBERTSON and H. HAYS (1975) Investigations of heavy metals in Common Tern populations. Canadian Field-Naturalist, 89, 157-162.

CONNORS, P.G., W. ROBERTSON, S.A. JACOBS and R.W. RISEBROUGH. Accumulation of metals and chlorinated hydrocarbons by Sooty Terns (Sterna fuscata) of known age. Unpublished ms.

COX, J.L. (1971) DDT residues in seawater and particulate matter in the California current system. Fisheries Bull., 69, 443-450.

DELONG, R.L., W.G. GILMARTIN and J.G. SIMPSON (1973) Premature births in California Sea Lions: association with high organochlorine pollutant residue levels. Science, 181, 1168-1169.

ENVIRONMENTAL PROTECTION AGENCY (1973) Environmental contamination from hexachlorobenzene, July 20, 1973. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. 27 pp.

FENICAL, W. (1975) Halogenation in the Rhodophyta - a review. J. Phycology, 11, 245-259.

FISHER, N.S. (1975) Chlorinated hydrocarbon pollutants and photosynthesis of marine phytoplankton: a reassessment. Science, 189, 463-464.

FISHER, N.S., L.B. GRAHAM, E.J. CARPENTER and C.F. WURSTER (1973) Geographic differences in phytoplankton sensitivity to PCBs. Nature, 241, 548-549.

GEORGE, J.L. and D.E.H. FREAR (1966) Pesticides in the Antarctic. J. Appl. Ecol. 3 (Suppl.), 155-167.

GESSER, H.D., A. CHOW, F.C. DAVIS, J.F. UTHE and J. REINKE (1971) The extraction and recovery of polychlorinated biphenyls (PCB) using porous polyurethane foam. Analytical Letters, 4, 883-886.

GILBERTSON, M. and L. REYNOLDS (1974) DDE and PCB in Canadian birds, 1969 to 1972. Canadian Wildlife Service, Occasional Paper No. 19. 18 pp.

GILMARTIN, W.G., R.L. DELONG, A.W. SMITH, J.C. SWEENEY, B.W. DE LAPPE, R.W. RISEBROUGH, L.A. GRINER, M.D. DAILEY and D.B. PEAKALL (1976) Premature parturition in the California sea lion. J. Wildl. Diseases, 12, 104-115.

GOLDBERG, E.D. (1975a) Synthetic organohalides in the sea. Proc. R. Soc. Lond. B., 189, 277-289.

GOLDBERG, E.D. (1975b) The Mussel Watch - a first step in global marine monitoring. Marine Pollut. Bull., 6, 111.

GRESS, F., R.W. RISEBROUGH, D.W. ANDERSON, L.F. KIFF and J.R. JEHL (1973) Reproductive failures of double-crested cormorants in southern California and Baja California. Wilson Bull., 85, 197-208.

HARVEY, G.R., W.G. STEINHAUER and J.M. TEAL (1973) Polychlorobiphenyls in North Atlantic Ocean water. Science, 180, 643-644.

HARVEY, G.R. and W.G. STEINHAUER (1974) Atmospheric transport of polychlorobiphenyls to the North Atlantic. Atmospheric Environment, 8, 888-782.

HARVEY, G.R., W.G. STEINHAUER and H.P. MIKLAS (1974a) Decline of PCB concentrations in North Atlantic surface water. Nature, 252, 387-388.

HARVEY, G.R., H.P. MIKLAS, V.T. BOWEN and W.G. STEINHAUER (1974b) Observations on the distribution of chlorinated hydrocarbons in Atlantic Ocean organisms. J. Mar. Research, 32, 103-118.

HAYS, H. and R.W. RISEBROUGH (1972) Pollutant concentrations in abnormal young terns from Long Island Sound. Auk, 89, 19-35.

HENRIKSSON, K., E. KARPPANEN and M. HEIMINEN (1966) High residue of mercury in Finnish White-tailed Eagles. Ornis Fennica, 43, 38-45.

HERRING, J.L., E.J. HANNAN and D.D. BILLS (1972) UV irradiation of Aroclor 1254. Bull. Environ. Contam. Toxicol., 8, 153-157.

HOLDGATE, M.W. (ed.) (1971) The sea bird wreck in the Irish Sea, Autumn 1969. Mimeographed, 76 pp., Natural Environmental Research Council, Alhambra House, 27-33 Charing Cross Road, London, W.C. 2.

HOLDEN, A.V. (1970) International cooperative study of organochlorine pesticide residues in terrestrial and aquatic wildlife, 1967/1968. Pesticides Monitoring Journal, 4, 117-135.

HOLDEN, A.V. (1973) International cooperative study of organochlorine and mercury residues in wildlife. Pesticides Monitoring Journal, 7, 37-52.

HOM, W., R.W. RISEBROUGH, D.R. YOUNG and A. SOUTAR (1974) Deposition of DDE and PCB in dated sediments of the Santa Barbara Basin. Science, 184, 1197-1199.

HUTZINGER, O., S. SAFE and V. ZITKO (1972) Photochemical degradation of chlorobiphenyls (PCBs). Environ. Health Perspectives, 1, 15-20.

HUTZINGER, O., S. SAFE and V. ZITKO (1974) The Chemistry of PCB's. CRC Press, Cleveland, Ohio.

JANSSON, B., S. JENSEN, M. OLSSON, L. RENBERG, G. SUNDSTROM and R. VAZ (1975) Identification by GC-MS of phenolic metabolites of PCB and p,p'-DDE isolated from Baltic Guillemot and Seal. Ambio, 4, 93-97.

JENSEN, S., A.G. JOHNELS, M. OLSSON and T. WESTERMARK (1972) The avifauna of Sweden as indicators of environmental contamination with mercury and chlorinated hydrocarbons. Fifteenth International Ornithological Congress, The Hague, 1970, 455-465.

JENSEN, S., L. RENBERG and M. OLSSON (1972) PCB contamination from boat bottom paint and levels of PCB in plankton outside a polluted area. Nature, 240, 358-360.

KERNER, I., W. KLEIN and F. KORTE (1972) Beiträge zur ökologischen chemie - XXXIII Photochemische reaktionen von 1,1-dichlor-2(p,p'-dichlorphenyl) äthylen (DDE). Tetrahedron., 28, 1575-1578.

KOEMAN, J.H. and H. VAN GENDEREN (1972) Tissue levels in animals and effects caused by chlorinated hydrocarbon insecticides, chlorinated biphenyls and mercury in the marine environment along the Netherlands coast. Marine Pollution and Sea Life, pp. 1-8. Published in Great Britain by The Whitefriars Press Ltd., London and Tonbridge.

KOEMAN, J.H., R.H. HADDERINGH and M.F.I.J. BIJLEVELD (1972a) Persistent pollutants in the white-tailed eagle in the Federal Republic of Germany. Biol. Conserv., 4, 373-377.

KOEMAN, J.H., T. BOTHOF, R. DE VRIES, H. VAN VELZEN-BLAD and J.G. VOS (1972b) The impact of persistent pollutants on piscivorous and molluscivorous birds. TNO-Nieuws, 27, 561-569.
KOEMAN, J.H., H.C.W. VAN VELZEN-BLAD, R. DE VRIES and J.G. VOS (1973a) Effects of PCB and DDE in cormorants and evaluation of PCB residues from an experimental study. J. Reprod. Fert., Suppl. 19, 353-364.
KOEMAN, J.H., W.H.M. PEETERS, C.H.M. KOUDSTAAL-HOL, P.S. TJIOE, J.J.M. DE GOEIJ (1973b) Mercury-selenium correlations in marine mammals. Nature, 245, 385-386.
DE LAPPE, B.W., R.W. RISEBROUGH, P. MILLIKIN and D.R. YOUNG. Use of Mytilus californianus to monitor changes in chlorinated hydrocarbon contamination of California coastal waters. In preparation.
LLOYD, C., J.A. BOGAN, W.R.P. BOURNE, P. DAWSON, J.L.S. PARSLOW and A.G. STEWART (1974) Seabird mortality in the North Irish Sea and Firth of Clyde early in 1974. Marine Pollut. Bull., 5, 136-140.
LLOYD-JONES, C.P. (1971) Evaporation of DDT. Nature, 229, 65-66.
MACKAY, D. and P.J. LEINONEN (1975) Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. and Tech., 9, 1178-1180.
MACKAY, D. and A.W. WOLKOFF (1973) Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. and Tech., 7, 611-614.
MARSHALL, N.B. (1971) Explorations in the life of fishes. Harvard Univ. Press, Cambridge, Massachusetts.
MARTIN, J.H., V.C. ANDERLINI, D. GIRVIN, S.A. JACOBS, R.W. RISEBROUGH, R.L. DELONG and W.G. GILMARTIN. Mercury-selenium-bromine imbalance in premature parturient California sea lions. Marine Biology, in press.
MEITH-AVCIN, N., S.M. WARLEN and R.T. BARBER (1976) Organochlorine insecticide residues in a bathyl-demersal fish from 2,500 meters. Environ. Letters, in press.
METCALF, R.L., J.R. SANBORN, P.Y. LU and D. NYE (1975) Laboratory model ecosystem studies of the degradation and fate of radio-labeled tri-, tetra-, and pentachlorobiphenyl compared with DDE. Arch. Environ. Contam. Toxicol., 3, 151-165.
MILLER, G.A. and C.E. WELLS (1969) Alkaline pre-column for use in gas chromatographic pesticide residue analysis. J.A.O.A.C., 52, 548-553.
MILLS, P.A. (1961) Collaborative study of certain chlorinated organic pesticides in dairy products. J.A.O.A.C., 44, 171.

MOSSER, J.L., N.S. FISHER, T.-C. TENG and C.F. WURSTER (1972) Polychlorinated biphenyls: toxicity to certain phytoplankters. Science, 175, 191-192.
MUSTY, P.R. and G. NICKLESS (1974) The extraction and recovery of chlorinated insecticides and polychlorinated biphenyls from water using porous polyurethane foams. J. Chromatography, 100, 83-93.
NATIONAL ACADEMY OF SCIENCES (1971) Chlorinated hydrocarbons in the marine environment. Washington, D.C.: National Academy of Sciences (U.S.).
NATIONAL ACADEMY OF SCIENCES (1975) Assessing Potential Ocean Pollutants: A Report of The Study Panel on Assessing Potential Ocean Pollutants to the Ocean Affairs Commission on Natural Resources, National Research Council. National Academy of Sciences, Washington, D.C. 438 pp.

MONS 067304

NISBET, I.C.T. and A.F. SAROFIM (1972) Rates and routes of transport of PCBs in the environment. Environ. Health Perspectives No. 1, 21-38.
NORSTROM, R.J., R.W. RISEBROUGH and D.J. CARTWRIGHT. Elimination of chlorinated dibenzofurans (CDFs) associated with PCBs fed to mallards (Anas platyrhynchos). Toxicology Applied Pharmacology, in press.
OHLENDORF, H.M., E.E. KLAAS and T.E. KAISER (1974) Environmental pollution in relation to estuarine birds. pp. 53-81. In: Survival in Toxic Environments, M.A.Q. Khan and J.P. Bederka, editors, Academic Press, New York. 555 pp.
OHLENDORF, H.M., R.W. RISEBROUGH and K. VERMEER. Exposure of marine birds to environmental pollutants. Proc. Pacific Seabird Congress, in press.
OLOFFS, P.C., L.J. ALBRIGHT and S.Y. SZETO (1972) Fate and behavior of five chlorinated hydrocarbons in three natural waters. Canadian J. Microbiol., 18, 1395-1498.
PANEL ON HAZARDOUS TRACE SUBSTANCES (1972) PCBs - Environmental Impact. Environ. Research, 5, 249-362.
PARSLOW, J.L.F. and D.J. JEFFERIES (1973) Relationship between organochlorine residues in livers and whole bodies of guillemots. Environ. Pollut., 5, 87-101.
PARSLOW, J.L.F., D.J. JEFFERIES and H.M. HANSON (1973) Gannet mortality incidents in 1972. Mar. Pollut. Bull., 4, 41-44.
PAVLOU, S.P. and W. HOM. Interlaboratory calibration results from chlorinated hydrocarbon analyses in marine sediments. Marine Chemistry, in press.
PEAKALL, D.B., T.J. CADE, C.M. WHITE and J.R. HAUGH (1975) Organochlorine residues in Alaskan Peregrines. Pesticides Monitoring J., 8, 255-260.
PEEL, D.A. (1975) Organochlorine residues in antarctic snow. Nature, 254, 324-325.
PROSPERO, J.M. and D.B. SEBA (1972) Some additional measurements of pesticides in the lower atmosphere of the northern equatorial Atlantic Ocean. Atmospheric Environment, 6, 363-364.
QURAISHI, M.S. (1970) Volatilization of DDT-^{14}C and Lindane-^{14}C from treated surfaces, and metabolism of DDT-^{14}C by house fly pupae. Canadian Entomologist, 102, 1189-1195.
RATCLIFFE, D.A. (1972) The peregrine population of Great Britain in 1971. Bird Study, 19, 117-157.
REDNER, J.A. and K. PAYNE (1971) Chlorinated hydrocarbons. Progress Report - December 1971. County Sanitation Districts of Los Angeles County, 2020 Beverly Boulevard, Los Angeles, California 90057.
RISEBROUGH, R.W. (1976) Transfer of organochlorine pollutants to Antarctica. Adaptations Within Antarctic Ecosystems. Scientific Committee for Antarctic Research, A. A. Llano, ed., in press.
RISEBROUGH, R.W., D.W. ANDERSON and J. MEGAHAN. Chlorinated hydrocarbons in a Peruvian coastal ecosystem. Unpublished ms.
RISEBROUGH, R.W., R.J. HUGGETT, J.J. GRIFFIN and E.D. GOLDBERG (1968a) Pesticides: transatlantic movements in the northeast trades. Science, 159, 1233-1236.
RISEBROUGH, R.W., P. REICHE, D.B. PEAKALL, S.G. HERMAN and M.N. KIRVEN (1968b) Polychlorinated biphenyls in the global ecosystem. Nature, 220, 1098-1102.

RISEBROUGH, R.W. and B.W. DE LAPPE (1972) Accumulation of polychlorinated biphenyls in ecosystems. Environ. Health Perspectives, 1, 39-45.
RISEBROUGH, R.W., F.C. SIBLEY and M.N. KIRVEN (1971) Reproductive failure of the Brown Pelican on Anacapa Island in 1969. American Birds, 25, 8-9.
RISEBROUGH, R.W. and G.M. CARMIGNANI (1972) Chlorinated hydrocarbons in Antarctic birds. pp. 63-78. In: Proceedings of the Colloquium, Conservation Problems in Antarctica, B.C. Parker, editor, Allen Press, Lawrence, Kansas.
RISEBROUGH, R.W., V. VREELAND, G.R. HARVEY, H.P. MIKLAS and G.M. CARMIGNANI (1972) PCB residues in Atlantic zooplankton. Bull. Environ. Contam. Toxicol., 8, 345-355.
RISEBROUGH, R.W., B.W. DE LAPPE, and T.T. SCHMIDT. Bioaccumulation factors of chlorinated hydrocarbons between Mytilus sp. and seawater. Unpublished ms.
ROBINSON, J., A. RICHARDSON, A.N. CRABTREE, J.C. COULSON and G.R. POTTS (1967) Organochlorine residues in marine organisms. Nature, 214, 1307-1311.
ROBINSON, P. and R.W. RISEBROUGH. Chlordane compounds in aquatic food webs. Unpublished ms.
RUZO, L.O., M.J. ZABIK and R.D. SCHUETZ (1972) Polychlorinated biphenyls: photolysis of 3,4,3',4'-tetrachlorobiphenyl and 4,4'-dichlorobiphenyl in solution. Bull. Environ. Contam. Toxicol., 8, 217-218.
SAFE, S. and O. HUTZINGER (1971) Polychlorinated biphenyls: photolysis of 2,4,6,2',4',6'-hexachlorobiphenyl. Nature, 232, 641-642.
SANBORN, J.R., W.F. CHILDERS and R.L. METCALF (1975) Uptake of three polychlorinated biphenyls, DDT, and DDE by the green sunfish, Lepomis cyanellus Raf. Bull. Environ. Contam. Toxicol., 13, 209-217.
SANDERS, H.O. and J.H. CHANDLER (1972) Biological magnification of a polychlorinated biphenyl (Aroclor(R) 1254) from water by aquatic invertebrates. Bull. Environ. Contam. Toxicol., 7, 257-263.
SCHMIDT, T.T., R.W. RISEBROUGH and F. GRESS (1971) Input of polychlorinated biphenyls into California coastal waters from urban sewage outfalls. Bull. Environ. Contam. Toxicol., 6, 235-243.
SCHOOR, W.P. (1975) Problems associated with low-solubility compounds in aquatic toxicity tests: theoretical model and solubility characteristics of Aroclor 1254 in water. Water Research, 9, 937-944.
SCHREIBER, R.W. and R.W. RISEBROUGH (1972) Studies of the Brown Pelican. Wilson Bull., 84, 119-135.
SCURA, E.D. and V.E. MCCLURE (1975) Chlorinated hydrocarbons in seawater: analytical method and levels in the Northeastern Pacific. Marine Chemistry, 3, 337-346.
SEBA, D.B. and J.M. PROSPERO (1971) Pesticides in the lower atmosphere of the northern equatorial Atlantic Ocean. Atmos. Environ., 5, 1043-1050.
SLADEN, W.J.L., C.M. MENZIE and W.L. REICHEL (1966) DDT residues in Adelie Penguins and a Crabeater Seal from Antarctica. Nature, 210, 670-673.
SOBLEMAN, M. Montrose Chemical Corporation, Torrance, California, in litt. (1971).

SOUTHERN CALIFORNIA COASTAL WATER RESEARCH PROJECT (1975) Coastal Water Research Project Annual Report. Southern California Coastal Water Research Project, El Segundo, California.

SPARSCHU, G.L., F.L. DUNN and V.K. ROWE (1971) Study of the teratogenicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin in the rat. Food Cosmet. Toxicol., 9, 405-412.

SPENCER, W.F. and M.M. CLIATH (1972) Volatility of DDT and related compounds. J. Agr. Food Chem., 20, 645-649.

SPITZER, P.R., R.W. RISEBROUGH, J.W. GRIER and C.R. SINDELAR. Eggshell-thickness-pollutant relationships among North American Ospreys. Proc. North American Osprey Symposium, J. Ogden, editor, in press.

SPROUL, J.A., JR., R.L. BRADLEY, JR. and J.J. HICKEY. Polychlorinated biphenyls, DDE, and dieldrin in Icelandic seabirds. Pesticides Monitoring J., in press.

STANLEY, R.L. and H.T. LEFAVOURE (1965) Rapid digestion and cleanup of animal tissues for pesticide residue analysis. J. Ass'n. off. Agric. Chem., 48, 666-667.

SVERDRUP, H.V., M.W. JOHNSON and R.H. FLEMING (1942) The Oceans: Their Physics, Chemistry and General Biology. Prentice Hall, New York. 1087 pp.

TATTON, J.O'G. and J.H.A. RUZICKA (1967) Organochlorine pesticides in Antarctica. Nature, 215, 346-348.

TEN NOEVER DE BRAUW, M.C. and J.H. KOEMAN (1972) Identification of chlorinated styrenes in cormorant tissues by a computerized gas chromatography mass spectrometry system. Sci. Total Environ., 1, 427-432.

TEN NOEVER DE BRAUW, M.C., C. VAN INGEN and J.H. KOEMAN (1973) Mirex in seals. Sci. Total Environ., 2, 196-198.

UTHE, J.F., J. REINKE and H. GESSER (1972) Extraction of organochlorine pesticides from water by porous polyurethane coated with selective absorbents. Environmental Letters, 3, 117-135.

UTHE, J.F., J. REINKE and H. O'BRODOVICH (1974) Field studies on the use of coated polyurethane plugs as indwelling monitors of organochlorine pesticides and polychlorinated biphenyl content of streams. Environmental Letters, 6, 103-115.

VOS, J.G. and J.H. KOEMAN (1970) Comparative toxicologic study with polychlorinated biphenyls in chickens with special reference to porphyria, edema formation, liver necrosis and tissue residues. Toxicol. Appl. Pharmacol., 17, 656-668.

VOS, J.G., J.H. KOEMAN, H.L. VAN DER MAAS, M.C. TEN NOEVER DE BRAUW and R.H. DE VOS (1970) Identification and toxicological evaluation of chlorinated dibenzofuran and chlorinated naphthalene in two commercial polychlorinated biphenyls. Food Cosmet. Toxicol., 8, 625-633.

WALKER, W. II, R.W. RISEBROUGH, J.T. MENDOLA and G.W. BOWES (1973a) South American studies of the peregrine, an indicator species for persistent pollutants. Antarctic Journal of the United States, 8 29-31.

WALKER, W. II, W.G. MATTOX and R.W. RISEBROUGH (1973b) Pollutant and shell thickness determinations of peregrine eggs from west Greenland. Arctic, 26, 256-258.

WARE, D.M. and R.F. ADDISON (1973) PCB residues in plankton from the Gulf of St. Lawrence. Nature (London), 246 (5431/Supp.), 519-521.

WELL, L., G. DURE and K.-E. QUENTIN (1974) Wasserloeslichkeit von insektiziden chlorierten Kohlenwasserstoffen und polychlorierten Biphenylen im Hinblick auf eine Gewaesserbelastung mit diesen Stoffen. Z. Wasser- Abwasser-Forsch., 7, 169-175.

WHITE, C.M. and R.W. RISEBROUGH (1976) Polychlorinated biphenyls in the ecosystems of Amchitka Island. In: The environment of Amchitka Island, Alaska, M.L. Merritt and R.G. Fullers, editors, Oak Ridge, Tennessee, Technical Information Center, Atomic Energy Commission.

WIEMEYER, S.N., P.R. SPITZER, W.C. KRANTZ, T.G. LAMONT and E. CROMARTIE (1975) Effects of environmental pollutants on Connecticut and Maryland ospreys. J. Wildl. Manage., 39, 124-139.

WILLIAMS, P.M. and K.J. ROBERTSON (1975) Chlorinated hydrocarbons in sea-surface films and subsurface waters at nearshore stations and in the North Central Pacific Gyre. Fishery Bull., 73, 445-447.

WONG, P.T.S. and K.L.E. KAISER (1975) Bacterial degradation of polychlorinated biphenyls. II. Rate studies. Bull. Environ. Contam. Toxicol., 13, 249-255.

WURSTER, C.F. (1968) DDT reduces photosynthesis by marine phytoplankton. Science, 159, 1474-1475.

WURSTER, C.F., JR. and D.B. WINGATE (1968) DDT residues and declining reproduction in the Bermuda Petrel. Science, 159, 979-981.

YOUNG, D.R. and T.C. HEESEN (1974) Inputs and distributions of chlorinated hydrocarbons in three southern California harbors. Rept. TM214. Southern California Coastal Water Research Project, El Segundo, California.

YOUNG, D.R., T.C. HEESEN, D.J. MCDERMOTT and P.E. SMOKLER (1974) Marine inputs of polychlorinated biphenyls and copper from vessel anti-fouling paints. Rept. TM212. Southern California Coastal Water Research Project, El Segundo, California.

YOUNG, D.R., R.W. RISEBROUGH, B.W. DE LAPPE, T.C. HEESEN and D.J. MCDERMOTT (1976) Input of chlorinated hydrocarbons into the Southern California Bight from surface runoff and municipal wastewaters. Unpublished ms.

ZITKO, V., O. HUTZINGER and P.M.K. CHOI (1972) Contamination of the Bay of Fundy - Gulf of Maine area with polychlorinated biphenyls, polychlorinated terphenyls, chlorinated dibenzodioxins, and dibenzofurans. Environ. Health Perspectives, 1, 47.

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two localities include the particulate content, the salinity, and the temperature. If the particulate content is high, a larger proportion of the residues in the seawater system might be associated with them, thereby diminishing the relative amount found in mussels.

Chromatograms of saponified extract of Mytilus from Carro, on the Mediterranean coast of France between Marseille and the mouth of the Rhone, and of seawater obtained at the same site are shown in Figures 7a and 7b. The seawater extract contained a large number of lower molecular weight compounds which were not significantly bio-accumulated by the mussels. The relative proportions of PCB compounds are somewhat different in the two extracts. Such differences presumably are a result of slightly different solubilities of individual PCB compounds (R. W. Risebrough, B. W. de Lappe and T. T. Schmidt, unpublished ms.).

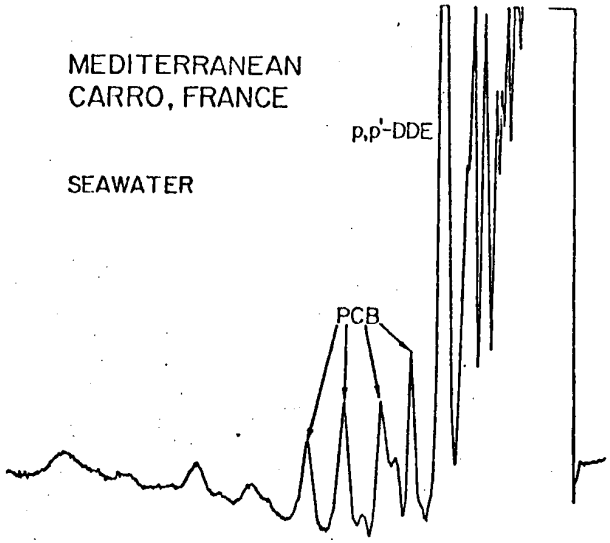
Total DDT residues in Mytilus californianus at southern California sites in 1971 are shown in Figure 8. Concentrations were highest in the vicinity of the Whites Point outfall of the Los Angeles County Sanitation Districts. The PCB concentrations in mussels from these sites indicated a number of input sources. Concentrations of both DDT and PCB declined at some of these areas between 1971 and 1974. Thus, the mussels appear to be good indicators of local point sources of pollution (B. W. de Lappe, R. W. Risebrough, P. Millikin, and D. R. Young, unpublished ms.).

Other factors which may affect partitioning of chlorinated hydrocarbons between the seawater system and mussels or other invertebrates include size, sex, gonadal condition, time of year and

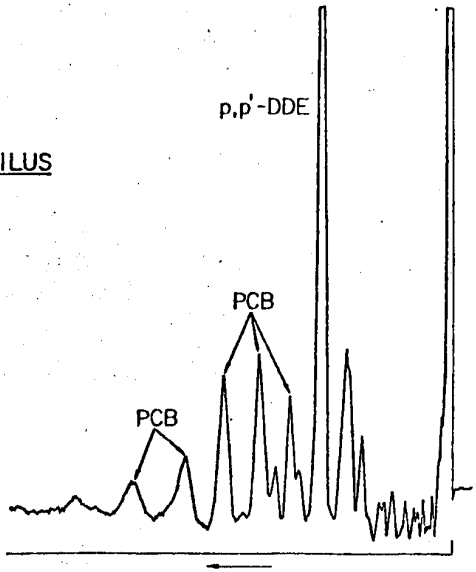
Figure 7. Chromatograms of extracts of seawater and Mytilus from Carro, on the Mediterranean coast of France, June, 1974. Aliquots used for GC analysis were passed through a saponification side column, 3% OV-1 column, Gas Chrom Q (from R. W. Risebrough, B. W. de Lappe, and T. T. Schmidt, unpublished ms.).

MEDITERRANEAN
CARRO, FRANCE

SEAWATER



MYTILUS



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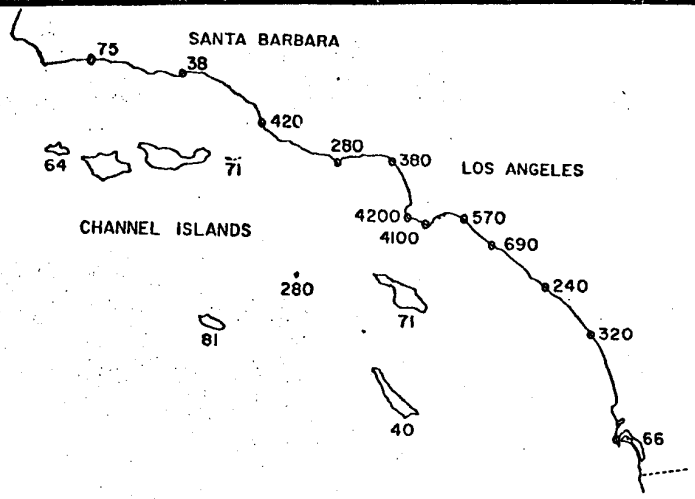

Figure 8. Total DDT residues in Mytilus californianus from Southern California, 1971. Concentrations in nanograms/gram of the wet weight. (Analytical procedures described in B. W. de Lappe, R. W. Risebrough, P. Millikin, and D. R. Young, unpublished ms.).

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the proportion of time which the organisms spend exposed to the air at low tide. The effects of these factors on the chlorinated hydrocarbon concentrations in Mytilus californianus from the California coast were examined. No relationships with size were found; concentrations appeared to fluctuate randomly throughout the year and the samples examined showed no significant differences in the chlorinated hydrocarbon content between sexes. Mussels living in the mid-tidal range appeared to have higher concentrations than those living at the low or high tide levels, respectively (B. W. de Lappe, R. W. Risebrough, P. Millikin and D. R. Young, unpublished ms.).

The "Mussel Watch" program (Goldberg, 1975b) will be initiated in the United States in 1976 to examine the use of mussels as indicator organisms for a variety of marine pollutants. Determination of partition coefficients between concentrations in the mussels and in the ambient seawater system would significantly enhance the value of such studies. Moreover, all factors which affect the variance of the numbers obtained, including the precision of the analytical determinations, size, sex, particulate content of the water, salinity in the case of estuaries, lipid content, time of year, microhabitat, etc. should be investigated if the mussels are to be used to detect differences in residue concentrations in time or space.

Unlike the chlorinated hydrocarbons which have a background level of zero in the marine environment, heavy metals and trace elements are natural components of marine food webs. Frequently it is difficult or impossible to estimate anthropogenic input of a given element into a marine food web, since knowledge of background "natural" levels are

lacking. The discovery of several abnormalities in some marine bird and mammal populations, discussed below, prompted investigations of levels of heavy metals and trace elements in those populations.

To determine whether a significant anthropogenic component might be present, levels of various heavy metals and trace elements were compared between two populations of the same species widely separated in breeding range and by comparing levels in species in the northern hemisphere with biocoenetic equivalents in the Antarctic. Concentrations of industrial chlorinated hydrocarbons such as the polychlorinated biphenyls in the antarctic biota have been one to several magnitudes lower than those in biocoenetic equivalents in the northern hemisphere. If levels of a particular metal recorded in the antarctic species were equivalent to those of a related species in the northern hemisphere, it would appear that both levels were "natural". A difference in concentrations comparable to the differences observed in chlorinated hydrocarbon levels would imply anthropogenic input to the northern hemisphere populations.

Results

Levels of silver, cobalt, lead, cadmium, chromium, nickel, mercury, copper and zinc were determined in breast muscle, liver and bone of four populations of petrels; the Snow Petrel (Pagodroma nivea) restricted to the pack ice zone of Antarctica, the Ashy Petrel (Oceanodroma homochroa) resident in coastal California waters and two populations of Wilson's Petrel (Oceanites oceanicus). One population of Wilson's Petrel breeds in the Antarctic Peninsula and winters in

the North Atlantic during the northern summer, the other breeds on the opposite side of the antarctic continent, and presumably winters in the Australian region. The distributions of copper and zinc showed no significant geographical or species variation. Silver, cobalt and lead were present in low concentrations and no marked variation in the [illegible] populations examined was apparent. Differences in the levels of [illegible] cadmium, chromium, nickel and mercury may have resulted from anthropogenic input. The differences, however, were relatively small and may have resulted from a combination of differences among species and geographical factors (Anderlini et al., 1972). [illegible]

Examination of levels of these metals in tissues of the Brown Pelicans inhabiting coastal waters of California and Florida showed no differences, with the exception of mercury which was several times [illegible] higher in the Florida samples (Connors et al., 1972). [illegible] Florida showed no [illegible]

Two populations of Common Terns were examined for heavy metal contamination (Ag, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn). One population is marine, on Long Island Sound; the other is a freshwater population breeding on Lake Ontario. Abnormalities had been noted in both [illegible] tion populations, although different abnormalities were found in each [illegible] ion colony. No differences were detected in the levels of these metals in bone, breast muscle, liver or kidney between the two populations [illegible] (Connors et al., 1975). [illegible] were detected in the levels of these metals in [illegible] bo[illegible]

Breast muscle and livers of known age Sooty Terns (Sterna fuscata) from the tropical Atlantic were analyzed for Cu, Zn, As, Se, Hg, Fe, Mn, Sr, Cr, Pb, Ni and Cd by X-ray fluorescence or Zeeman-effect atomic adsorption. No increases in metal concentrations with [illegible], Hg, Fe, Mn, Sr, Cr, Pb, Ni and Cd by X-ray fluorescence or Zeeman-effect atomic adsorption. No increases in metal concentrations with

age of the birds was detected after age of 3 years, indicating that fluxes of these elements into the terns had reached equilibrium with metabolic processes that excrete them (P. G. Connors, W. Robertson, S. A. Jacobs and R. W. Risebrough, unpublished data). The mercury: selenium correlation found in marine mammals (Koeman et al., 1973 Martin et al., in press) was not found in this species, suggesting that marine birds and mammals detoxify mercury and/or selenium in different ways.

In collaboration with other laboratories, tissues of aborting female sea lions and their premature pups (cf. below) and a series of female sea lions giving normal birth, and their pups, collected in 1972 on San Miguel Island, California, were analyzed for a series of heavy metals and trace elements, as well as for chlorinated hydrocarbons. No differences in metals were found between the two groups of animals with the exception of selenium, bromine and mercury which increased with age; they also increased in equimolar ratios, suggesting the existence of a molecular complex, containing selenium, mercury and bromine which functions either to detoxify the methyl mercury present in the fish upon which the sea lions feed, or to detoxify the selenium present with the mercury in fish. No evidence of anthropogenic input to the levels of metals and trace elements in the sea lion population of Southern California was found (Martin et al., in press). Thus, a terminal carnivore dependent upon fish in an area of the sea known to receive high inputs of heavy metals from the atmosphere and from wastewater outfalls in the Los Angeles area does not appear to contain elevated levels of these metals. This observation reinforces the conclusions of other studies of the distribution of metals and trace elements in marine

mammals carried out in collaboration with other laboratories that anthropogenic contributions to the burden of heavy metals and non-essential trace elements at this level of marine food

A chromatogram showing a saponified extract of the Gentoo Penguin is shown in Figure 9. The profile is similar to that of the saponified extract of antarctic snow (Figure 4), except that proportions relative of PCB compounds are changed somewhat and the/amount of DDE is reduced compared to that in the snow. The change in the ratio of total DDT:PCB from the snow to the penguin might result from 1) preferential degradation of p,p'-DDT to polar derivatives during passage through the food chain, or 2) direct input of PCB from the atmosphere to the sea with only a fraction of PCB scavenged from the atmosphere by precipitation.

BIOLOGICAL EFFECTS OF MARINE POLLUTANTS

Studies of pollutant transfer to the marine environment are "relevant" if levels found are related to those which damage a component of the marine ecosystem. Thus, input fluxes may be considered in relation to potentially harmful levels in the marine environment. As indicated above, there is as yet no evidence for harmful effects of heavy metals and trace elements to marine birds and mammals. Apparently high mercury levels have been recorded in eggs of the White-tailed Eagle (Haliaetus albicilla) in the Baltic (Henriksson et al., 1966), but eagles in this area also contain excessively high levels of organochlorine compounds (Jensen et al., 1972), probably accounting for the population decline of the species in this area. A decline in the reproductive success of the White-tailed Eagles breeding in Schleswig-Holstein has been attributed to DDE (Koeman et al., 1972).

Premature pupping of the California Sea Lions (Zalophus californianus) was first observed in the Channel Islands area of Southern California in the late 1960s (DeLong et al., 1973) and

Figure 9. Chromatogram of saponified extract of a Gentoo Penguin egg, Doumer Island, Antarctic Peninsula, January, 1975. 3% OV-1 column, Gas Chrom Q.

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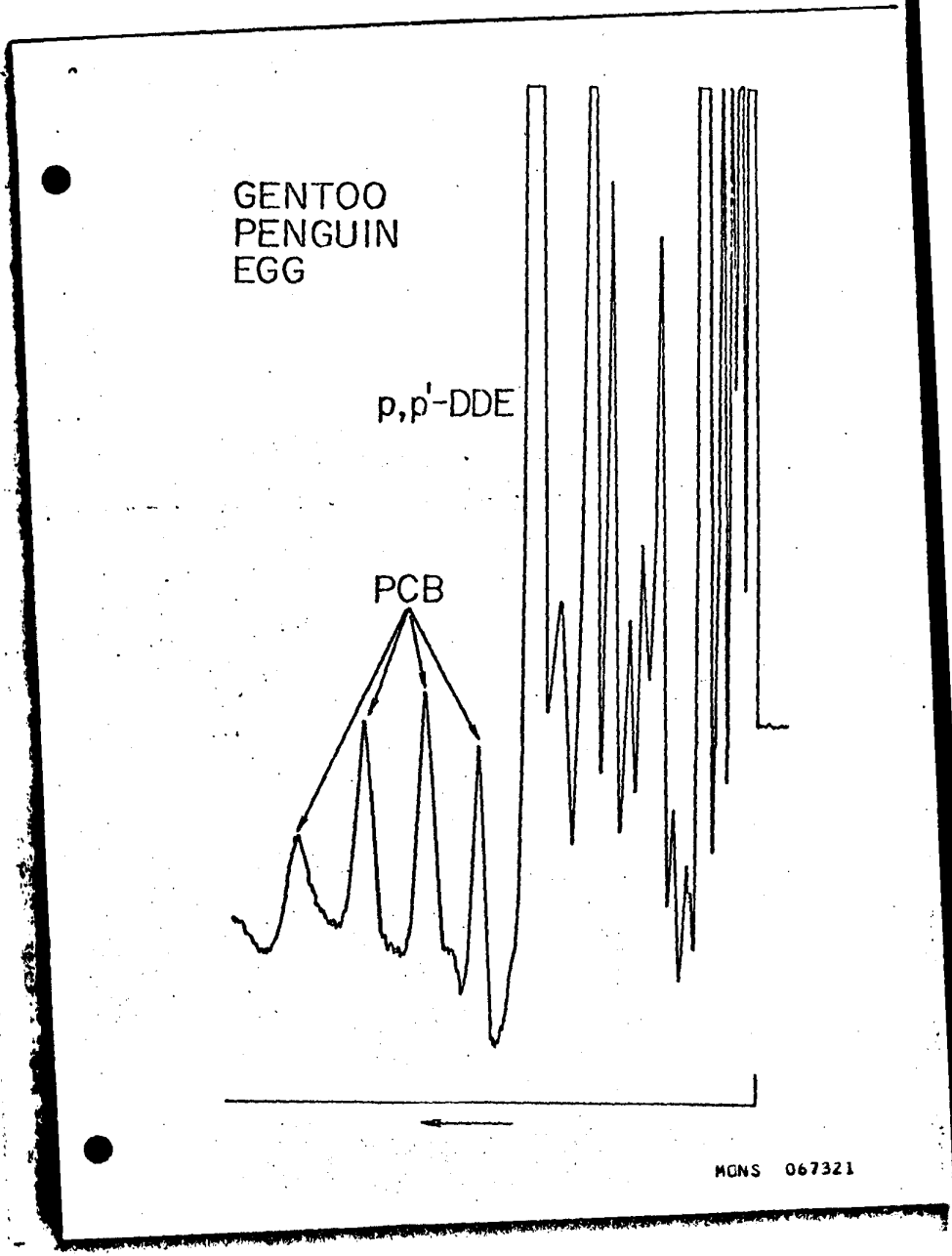
GENTOO
PENGUIN
EGG
p,p'-DDE
PCB
MONS 067321

correlations were observed between the premature births and the occurrence of high levels of DDT and PCB compounds. In 1972, ten females which had given birth prematurely, their dead pups, ten healthy females, and their pups were collected for pollutant residue determinations and for examination of the presence of disease organisms. As in the previous study, aborting animals had significantly higher DDE and PCB concentrations than did the non-aborting female sea lions; the ratios of DDE to PCB also differed between the two groups. It was postulated that the presence of these high levels of organochlorines lowered the resistance of the animals to a disease endemic in the population, producing the observed premature births (Gilmartin et al., in press).

Extreme shell thinning of eggs of the Brown Pelican (Pelecanus occidentalis) and of the Double-crested Cormorant (Phalacrocorax auritus), in the Southern California coastal area was discovered in 1969 (Risebrough et al., 1971; Gress et al., 1973). Extensive statistical studies of eggs of the Brown Pelican obtained before 1945 and now preserved in museums and of several hundred eggs obtained since 1969 from California, Mexico and Florida has shown that all of the thinning can be attributed to p,p'-DDE (R. W. Risebrough, W. Walker, D. W. Anderson, and R. W. Schreiber, unpublished data). With the decline of DDT input into the Southern California Bight following the change in waste disposal methods of the DDT company in Los Angeles, levels of p,p'-DDE in the Southern California Bight have decreased and the reproductive success of the pelicans has subsequently improved (Anderson et al., 1975).

Dead chicks and unhatched eggs of the Bermuda Petrel

(Pterodroma cahow) were examined to follow up a previous report that a decline in reproductive success of this species, a pelagic feeder in the Sargasso Sea adjacent to Bermuda, was attributed to DDT residues (Wurster and Wingate, 1968). Reproductive success has improved since 1968, but no changes in DDE and PCB levels have been found over the period of the decline and recovery of reproductive success. Moreover, levels of both DDE and PCB were low in comparison to those of other petrels (D. Wingate and R. W. Risebrough, unpublished data).

Peregrine Falcons feeding on marine birds appear to be affected by shell thinning in all areas of their nearly global range so far studied and reproductive success is frequently low (Peakall et al., 1975; Ohlendorf et al., in press; Ratcliffe, 1972). Investigations of pollutant levels in the Peregrine Falcon in Amchitka, Greenland, and coastal Chile showed DDE levels sufficiently high to be associated with shell thinning (White and Risebrough, in press; Walker et al., 1973a; Walker et al., 1973b). An unhatched egg of the related New Zealand Falcon (Falco novaeseelandiae) from the subantarctic Auckland Islands contained DDE residues sufficiently high to cause shell thinning in other species of falcons (Bennington et al., 1975).

Birth defects in a colony of Common Terns (Sterna hirundo) and Roseate Terns (S. dougallii) in Long Island Sound were similar to those caused under experimental conditions by chlorinated dibenzodioxins (Hays and Risebrough, 1972). The possible existence of these and the closely related chlorinated dibenzofurans in marine food webs was postulated.

Mortality of Great Cormorants (Phalacrocorax carbo) along the Netherlands coast and debilitation of Glaucous Gulls feeding on the