CHLORINATED HYDROCARBONS IN MARINE ECOSYSTEMS

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ABSTRACT

Polychlorinated biphenyls, chlorinated hydrocarbons which are extensively used in industry and agriculture, are now widely distributed in marine ecosystems of the Pacific Ocean. Birds contain higher concentrations of these chemicals than fish; tissues of the peregrine falcon have contained the highest amounts which have so far been recorded. The polychlorinated biphenyls have not yet been detected in samples of airborne particulates but their observed distribution in the sea indicates that they are dispersed by wind currents and that their fallout pattern is similar to that of the DDT compounds. Their effects upon natural populations, including man, are as yet unknown. Among the chlorinated hydrocarbon "pesticides," DDE is accumulating in significant amounts in marine food chains and is also present in highest concentrations in marine birds, especially the procellariiform species. Its distribution indicates that coastal areas are not the primary sources of contamination. A quantitative approach to the problem of aerial transport of chlorinated hydrocarbons to the sea has been made by analyzing the airborne particulates which contribute to marine sedimentary deposits. The results obtained to date indicate that wind transport can account for the observed distribution of DDT compounds in California waters and that the amount of chlorinated hydrocarbons entering the tropical Atlantic as fallout from the Northeast Trades is comparable to that entering the sea from a major river system.

REPORT

THE ACCUMULATING EVIDENCE that no part of the world is now free of "pesticide" residues, the products of atomic explosions, or of a variety of industrial pollutants has induced subtle but profound changes in our concept of our position in the global ecosystem and in our individual conceptions of remoteness and isolation. There has never been any question that local ecosystems could be irreversibly changed by the introduction of synthetic

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chemicals, whether these introductions be purposeful or incidental. Since the sea, however, is the dominant feature of the worldwide ecosystem, interpretations of environmental contamination in terms of local ecosystems, whether terrestrial or aquatic, may therefore be misleading. The accumulation of significant amounts of several pollutants in marine organisms, pollutants which are nonpolar and therefore water-insoluble but lipid-soluble, not only elicits an uncertainty about the long-term utilization of the sea as a source of human food, but has suddenly raised the question of the ultimate survival of a number of species of sea birds. These species comprise a very large fraction of the world's wildlife and doubts about their future would have been considered preposterous and untenable only three or four years ago.

Perhaps because fish kills have provided the most dramatic evidence of insecticide contamination, distribution studies in the United States and elsewhere have frequently consisted of monitoring the residue levels in major river systems (2, 7). In spite of the low solubility of chlorinated hydrocarbons in water (4), their tendency to pass into the vapor phase and to leave the region of application (1, 5, 6, 17, 22), their persistence in soils despite drainage (3, 14, 24), and their presence in very low concentrations in some streams draining areas of intensive application (23), large amounts of these stable persistent pesticides are transported to the sea by way of rivers with high silt contents. Thus, the Sacramento and San Joaquin rivers, which drain the Central Valley of California, one of the most heavily pesticided areas of the world, annually bring about 1,900 kilograms of chlorinated hydrocarbons into San Francisco Bay (2, 27), and the Mississippi contributes about 10,000 kg to the Gulf of Mexico (7, 27).

When the Institute of Marine Resources began a study of the distribution of chlorinated hydrocarbons in marine fish, we expected to find, therefore, much higher levels in the fish from San Francisco Bay than in the fish from the Pacific Ocean (30). The data of Table I-I, however, show that collections of the Northern anchovy and of the English sole from the coastal waters contained as much as or in two instances significantly more total DDT residue than did the collections from San Francisco Bay. Total DDT

TABLE I-I

DDT RESIDUES* IN COLLECTIONS OF NORTHERN ANCHOVY (*ENGRAULIS MORDAX*) AND ENGLISH SOLE (*PAROPHRYS VETULUS*) FROM SAN FRANCISCO BAY AND CALIFORNIA COASTAL WATERS

Species *Locality, Date*	*Number*	*Mean Wt* *(g)*	p,p'-DDE†	*Total DDT*- ppm†
Northern Anchovy				
San Francisco Bay	17	12.4	0.21	0.59
July 29, 1965		(6-22)	±0.05	±0.11
San Francisco Bay	29	4.0	0.11	0.33
November 4, 1965		(2-5)	±0.05	±0.04
Monterey	30	26.5	0.68	0.90
November 30, 1965		(21-35)	±0.19	±0.22
Morro Bay	29	25.9	0.45	0.74
June 16, 1965		(19-33)	±0.12	±0.22
Port Hueneme	15	11.6	2.44	3.04
February 24, 1966		(2.8-21.5)	±0.77	±1.00
Terminal Island	44	11.7	10.2	14.0
Los Angeles, June 25, 1965		(6.5-20)	±2.1	±1.9
English Sole				
San Francisco Bay	18	14.3	0.14	0.55
July 29, 1965		(5-35)	±0.02	±0.07
San Francisco Bay	33	17.3	0.13	0.55
November 4, 1965		(7.5-53)	±0.03	±0.12
San Francisco lightship	15	253	0.12	0.19
December 1, 1965		(175-306)	±0.03	±0.04
Monterey	15	195	0.53	0.76
February 15, 1966		(89-262)	±0.13	±0.16

*From R. W. Risebrough, D. B. Menzel, D. J. Martin, Jr., and H. S. Olcott, in preparation. DDT residues include the two isomers of DDT, p,p'-DDT and o,p'-DDT and their metabolic derivatives: p,p'-DDE, o,p'-DDE, p,p'-DDD and p,p'-DDMU.

†Wet-weight parts per million, means, standard errors, 95% confidence limits.

concentrations were highest in the collection from waters off Los Angeles, but anchovies from the Channel Islands area off Port Hueneme also contained significantly more residue than the anchovies of San Francisco Bay. Since no major river system enters the Pacific Ocean from southern California the source of the DDT could not be agricultural drainage waters. Similarly, the data of Table I-II, which sets forth the distribution of total DDT residues and of polychlorinated biphenyls in several collections of marine fish, including shiner perch from San Francisco Bay, hake, jack mackerel and English sole from the coastal waters of California, bluefin and yellowfin tunas from waters off Baja California and Central America, and skipjack tuna from South America and the

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TABLE 1-II
DDT* AND POLYCHLORINATED BIPHENYL (PCB) RESIDUES IN MARINE FISH†

Species, Locality, Date	Number	Mean Wt. (g)	Total DDT ppm	p,p'-DDE %	PCB	DDT/PCB
Northern Anchovy						
Terminal Island June 25, 1965	44	11.7 (6.5-20)	14.0 ±1.9	83	1.0	14
Shiner Perch						
San Francisco Bay October 20, 1965	14	5.5 (4-8)	1.0 ±0.1	28	1.2	0.8
San Francisco Bay October 20, 1965	10	26.7 (10-48)	1.4 ±0.3	35	0.4	3.5
San Francisco Bay November 4, 1965	15	15.3 (8-49)	1.1 ±0.1	38	1.2	0.9
English Sole						
San Francisco Bay July 29, 1965	18	14.3 (5-35)	0.55 ±0.07	25	0.11	5
San Francisco Bay November 4, 1965	33	17.3 (7.5-58)	0.55 ±0.12	24	0.11	5
San Francisco lightship December 1, 1965	15	255 (175-366)	0.19 ±0.04	53	0.05	4
Monterey February 15, 1966	15	195 (89-262)	0.76 ±0.16	70	0.04	19
Jack Mackerel						
Channel Islands November 22, 1965	31	81.8 (45-141)	0.56 ±0.10	57	0.02	28
Hake						
Puget Sound January 29, 1966	22	281 (135-550)	0.18 ±0.05	23	0.16	1.1
Hake						
Channel Islands February 24, 1966	6	384 (61-872)	1.8 ±1.1	68	0.12	15
Bluefin Tuna‡						
[illegible] muscle	7	—	0.56 ±0.21	45	0.04	14
L[illegible]	9	—	0.22 ±0.15	45	0.04	6
Yellowfin Tuna						
Liver§	13	—	0.07 ±0.02	13	nd¶	>7
Liver‡	13	—	0.62 ±0.19	30	0.04	15
Skipjack Tuna						
Liver††	3	—	0.057	23	0.1	0.6
Body Muscle††	13	—	0.051 ±0.014	18	nd	>30
Liver‡‡	25	—	0.056 ±0.023	11	nd	>30
Liver§§	12	—	0.029 ±0.009	21	nd	>20

*[illegible] (1960). Concentrations in [illegible] weight, ppm, steam, standard [illegible]

†Northern anchovy (*Engraulis mordax*), shiner perch (*Cymatogaster aggregata*), English sole (*Parophrys vetulus*), Pacific jack mackerel (*Trachurus symmetricus*), hake (*Merluccius productus*), bluefin tuna (*Thunnus thynnus*), yellowfin tuna (*Thunnus albacares*), skipjack tuna (*Euthynnus pelamis*).

‡[illegible], Baja California, Aug. 29, 1965.

§[illegible] Galapagos Archipelago, Nov. 6, 1965.

¶[illegible] less than 0.01.

[illegible] W, 8° N, Aug. 23, 1965.

[illegible] 1965.

[illegible] November and December, 1965.

[illegible] ber 1, 1965.

Central Pacific, show that almost all total DDT residue levels fall within the range of 0.2 and 2.0 parts per million (ppm), wet weight, including those in the bluefin and yellowfin tunas which are offshore, pelagic species. Only the yellowfin tuna from the Galapagos region and the skipjack tuna contained lower total DDT residues. In contrast, among the freshwater fish from California collected and analyzed by the California Department of Fish and Game and the Bureau of Sport Fisheries and Wildlife, only one, a channel catfish, contained DDT concentrations higher than 2.0 ppm. Eight values fell within this range and four fell below (21). In Wisconsin the majority of fish analyzed by the Wisconsin Conservation Department in 1965 contained fewer than 0.2 ppm total DDT residue (33). Moreover, fish from a stream in Wisconsin which drained an orchard where chlorinated hydrocarbons had been intensively applied over the years contained lower amounts of chlorinated hydrocarbon residues than did these marine fish from the Pacific Ocean (23). These combined observations indicate that it is very unlikely that chlorinated hydrocarbons in marine fish have originated only in coastal waters contaminated by local agricultural runoff.

Nor can contamination by agricultural runoff account for the DDT distribution among the various species of seabirds. A skua from Antarctica (32), shearwaters from both the Atlantic and Pacific Oceans (29, 39), and black petrels nesting on islands in the Gulf of California (28) have been found to contain higher residue levels than those of the vast majority of birds from America and Great Britain. Shearwaters and petrels breed on remote islands and otherwise spend their entire lives at sea. They do not dive for fish but feed primarily upon organisms obtained at or

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near the surface, the component of the marine ecosystem which receives aerial fallout and which because of its unique physical-chemical properties could be expected to retain temporarily the water-insoluble chlorinated hydrocarbon components.

Observations that chlorinated hydrocarbons do not accumulate indefinitely in soil but reach a steady state value and that they rapidly disappear after application to ponds and marshes must therefore be considered in a somewhat broader context.

The polychlorinated biphenyl (PCB) peaks had long been evident in chromatograms of extracts of marine fish and birds but remained unidentified until late in 1967. An unhatched egg and tissues of peregrine falcons contained exceptionally high amounts of the unknown compounds. Since the peregrine is now extinct as a breeding species in the eastern United States, having declined rapidly for unknown reasons in the late fifties and early sixties, and the West Coast population is greatly reduced, considerable effort was made to identify them. These attempts remained unsuccessful until reports appeared from Sweden (36) and from Great Britain (19) that PCB had been identified in wildlife with the use of mass spectrography and gas-liquid chromatography, respectively. The published chromatogram (19) was very similar to those which we had obtained from the peregrine falcon extracts.

The polychlorinated biphenyls occurring in the environment are assumed to be industrial pollutants. They are used extensively in industry as plasticizers and in the manufacture of paints, resins, electrical insulators and other products; they have been applied with insecticides, and can be purchased in railway car amounts. Since they are very stable, resist degradation, have small but finite vapor pressures, are insoluble in water and highly soluble in lipid, it is inevitable that they should be concentrated in biological systems. Their chemical structure is in some respects similar to that of several chlorinated hydrocarbon insecticides such as DDT and the benzene hexachlorides, so that it is to be expected that they would behave similarly in their movements through ecosystems. They are highly toxic to man when inhaled as vapors (12, 31), and the more heavily chlorinated components have greater toxicity. No tolerance limits have been set for human food supplies, and their carcinogenic properties remain to be determined; but they are now present in concentrations as high as 1 ppm on a wet-weight basis and several times higher on a lipid-weight basis in species of fish which are used as human food. At the present time it is not entirely clear how the PCB enter the environment, but presumably they are introduced into the atmosphere as vapors during manufacturing processes, when high temperatures increase vapor pressure, by gradual volatilization over a period of time, or when materials containing them are incinerated.

The commercial PCB preparations are mixtures of compounds which differ in the degree of chlorination. Of these, those having the following retention times relative to p,p′-DDE on DC-200 and QF-1 columns have been detected in marine fish and birds:

DC-200: *1.25*, *1.48*, *1.75*, 2.05, 2.41, 2.50, 2.90, 3.41, 3.88, 5.53
dieldrin: 1.00; p,p′-DDD: 1.27; p,p′-DDT: 1.68

QF-1: 1.10, *1.33*, *1.40*, 1.65, *1.72*, 2.14, 2.59, 3.23, 3.88, 4.84
dieldrin: 1.49; p,p′-DDD: 1.75; p,p′-DDT: 1.91

The retention times of three of the principal peaks are italicized. Similar values for the DC-200 column have been reported from extracts of seals from the North Atlantic (18). Because of the similarity of retention times, it is evident that large amounts of PCB will interfere with the determination of p,p′-DDD and p,p′-DDT on DC-200 columns and with p,p′-DDD on QF-1 columns. Conversely in many extracts the PCB content can be determined only after DDD and DDT have been removed by saponification with alcoholic KOH. In the absence of the microcoulometric detector, the quantitative measurements of the PCB compounds were made as follows: it was assumed that each produces the same peak height with the electron capture detector as the same amount by weight of p,p′-DDE. After summing the contributions of the individual peaks, the total was multiplied by 4.2. Use of this factor in measurements of standard solutions yielded results which agreed with the predicted values. Through the kindness of Mr. [illegible] microcoulometric determinations were made of a standard solution and of a peregrine extract. The values con[illegible] by the electron capture method. Take toxa-

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phene, but unlike DDT the PCB compounds are not destroyed by nitration (13, 23).

Concentrations of the chlorinated hydrocarbons, both DDT and PCB, tend to be an order of magnitude higher in marine birds than in fish (Tables I-II, I-III, and I-IV). Unlike the DDT compounds, PCB levels are relatively higher in San Francisco Bay. Since Caspian tern eggs from San Francisco Bay and San Diego Bay have similar DDT and PCB contents, it is likely that the "pesticide" ecologies of the two bays are similar. Few data on PCB levels in freshwater and terrestrial organisms have so far been accumulated, but three fish, a white crappie, a black crappie, and a blue gill from Clear Lake contained 0.004, 0.003, and 0.005 ppm PCB, respectively. It is not clear how much of these low amounts of PCB resulted from fallout, from local contamination, or were brought to the lake by migrant species. White-tailed kites, a species which accumulates low chlorinated hydrocarbon residues as a result of its position in the local ecosystem, contain low PCB concentrations, but a Cooper's hawk from San Diego, a species which preys upon terrestrial land birds, contained 6 ppm (28). PCB is therefore present in the terrestrial environment but its movements through food chains remain completely unknown.

As shown in Tables I-III and I-IV, it is evident that PCB is widely distributed among marine food birds which are the terminal carnivores of a complex mesh of food chains in the sea. Sooty and slender-billed shearwaters are pelagic species which breed in New Zealand and Australia, respectively, and which spend the southern winter in the northern Pacific. Rhinoceros auklets and ancient murrelets breed on the coasts of British Columbia and Alaska whereas kittiwakes, fulmars and red phalaropes breed in Alaska and the Canadian Arctic. All of these specimens were collected off California, so that it is not clear how much DDT and PCB the birds had ingested on their breeding grounds. PCB is, however, present in resident species in remote areas of the Gulf of California, and was found in eggs of brown pelicans resident in the Gulf of Panama (28). It could not be detected in five eggs of the Adelie penguin brought from Cape Crozier, Antarctica and kindly made available for analysis by Dr. R. E. Feeney (28). The total DDT

content of the eggs, however, was low, and the ratio of total DDT to the maximum detectable amount of PCB was within the range of the ratios recorded in other species (Tables I-III and I-IV).

TABLE I-III
DDT* AND PCB RESIDUES IN MARINE BIRDS† AND IN THE PEREGRINE FALCON***

Species, Locality, Date	*Total DDT‡ ppm*	*% DDE*	*PCB*	*DDT/PCB*
Cassin's Auklet§	5.8	98	0.16	36
Ancient Murrelet¶	0.75	90	0.15	5
Fulmar**	0.41	76	0.08	5
Fulmar**	3.4	89	0.34	10
Red Phalarope††	0.78	79	0.10	8
Rhinoceros Auklet‡‡	2.7	97	0.36	8
Slender-billed Shearwater§§	32.0	92	2.1	15
Sooty Shearwater¶¶	12.3	94	1.2	10
Sooty Shearwater¶¶	10.3	86	0.9	12
Peregrine Falcon***				
Breast muscle, second year female, migrant from Arctic	104	99	22	4.5
Breast muscle, immature California	13	99	10.5	1.2
Breast muscle, adult female, California	112	98	109	1.0

*From Risebrough *et al.* (29) and Risebrough, Kirven and Herman (28).
†Entire bird analyzed, except peregrine falcons.
‡Includes p,p'-DDT, p,p'-DDD, p,p'-DDE, p,p'-DDMU, p,p'-DDE; ppm, wet weight.
§*Ptychoramphus aleuticus*, adult female, Farallon Islands, April, 1966.
¶*Synthliboramphus antiquus*, Monterey Bay, Nov. 1, 1966.
**Fulmarus glacialis, Monterey Bay, Nov. 1, 1966.
††*Phalaropus fulicarius*, Monterey Bay, Nov. 1, 1966.
‡‡*Cerorhinca monocerata*, Monterey Bay, Nov. 1, 1966.
§§*Puffinus tenuirostris*, Monterey Bay, Dec. 12, 1966.
¶¶*Puffinus griseus*, Monterey Bay, Nov. 1, 1966.
***From Risebrough, Kirven and Herman (28).

The ratios of total DDT to PCB appear to cast some light on the distribution and fallout patterns of the chlorinated hydrocarbons. In San Francisco Bay species, including two wintering peregrine falcons, Caspian terns, Western gulls and shiner perch, the ratio tends to be close to unity. Analyses of Western gull eggs [illegible] to those reported in Table I-IV show that eggs from San Francisco Bay contained more PCB than eggs from the Farallon Islands, 27 miles west of the Golden Gate Bridge, which in turn contained more PCB than eggs from Baja California (28).

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TABLE 1-IV
DDT AND PCB CONTENT IN EGGS OF SEVERAL BIRD SPECIES

Species, Locality	Number	Total DDT* micrograms	p,p'-DDE %	PCB* micrograms	DDT/PCB
Brandt's Cormorant† (*Phalacrocorax penicillatus*)					
Farallon Islands	17	326	91	115	2.9
Pelagic Cormorant (*Phalacrocorax pelagicus*)					
San Mateo Co. Calif.	2	128 (125-130)	90	62 (48-75)	2.1
Murre					
Uria aalge					
Farallon Islands	6	1945 (952-3621)	96	558 (364-1010)	3.5
Pigeon Guillemot					
Cepphus grylle					
Farallon Islands	1	110	95	20	5.5
San Mateo Co.	1	105	91	62	1.7
Cassin's Auklet					
Ptychoramphus aleuticus					
Farallon Islands	2	147 (127-167)	97	15 (12-18)	10
Western Gull					
Larus occidentalis					
Farallon Islands	1	423	95	118	3.6
San Mateo Co.	1	235	94	112	2.1
San Francisco Bay	1	458	87	480	0.95
Black-crowned Night Heron					
Nycticorax nycticorax					
San Francisco Bay	1	541	89	330	1.6
	1	869	99	24	36
Caspian Tern					
Hydroprogne caspia					
San Francisco Bay	2	1269 (1216-1322)	89	805 (660-950)	1.7 (1.3-2.0)
San Diego Bay	5	1430 (991-2430)	88	1010 (550-1600)	1.4
Forsters Tern					
Sterna forsteri					
San Diego Bay	2	655 (593-732)	89	114 (91-137)	5.8
Least Petrel					
Halocyptena microsoma					
Baja California	2	30 (23-37)	84	3.1 (1.2-5.0)	10
Peregrine Falcon†					
Falco peregrinus					
Baja California	1	4850	97	471	10

*Total micrograms.
†Samples pooled for PCB analysis. p,p'-DDE content ranged from 63 to 120 micrograms.
‡From Risebrough, Kirven, Herman, Reiche, and Olcott (28).

Of the two night heron eggs so far analyzed from San Francisco Bay, one had an "ocean" profile: high DDE, low p,p'-DDT and DDD, high DDT/PCB ratio; the other had a "bay" profile, suggesting that the adult females had spent the previous months in different localities. The Caspian and Forster's terns nest side by side on the dikes in San Diego Bay, yet the DDT/PCB ratio is much lower in the Caspian terns, which feed primarily in San Diego Bay and along the coast, than in the Forster's terns, which feed along the brackish and freshwater canals of the Otai River drainage. In the pelagic bird species, in most of the fish from the ocean, and in other specimens from areas remote from sites of application such as Baja California, the ratios of DDT to PCB are of the same order of magnitude and most values are between 5 and 15. If both PCB and DDT were dispersed around the world by the same transport system, their relative concentrations in "remote" areas would very likely be similar. Thus, most of the values obtained for this ratio in birds from a remote area of the Gulf of California are approximately 10 (28). Eggs of the elegant tern, however, a bird which migrates to other regions after the nesting season, had a significantly different ratio. It will therefore be of considerable interest to compare these ratios, and the ratios of either to other chlorinated hydrocarbons, among individuals and species breeding in remote areas of the world. Thus resident species could be compared with migrant species which could in turn be compared with locally raised juveniles before these have left the area.

Global fallout of the radioactive products of atomic experiments such as strontium 90, iodine 131 and cesium 137 is highly dependent upon local precipitation patterns. This is also true of the naturally occurring radioactive nuclides such as lead 210, which is a member of the uranium 238 series and which has a tropospheric residence time of only twenty days (8). It could be expected, therefore, that the fallout of chlorinated hydrocarbons associated with airborne particulate material would follow the same patterns, whether these particles are the original carrier such as dust or soil, or whether they have absorbed chlorinated hydrocarbons originally present in the air as vapors. What is not

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clear is whether nonpolar compounds such as PCB must necessarily become associated with airborne particulates before entering the aqueous part of the marine ecosystem.

A quantitative approach to the problem of aerial transport of chlorinated hydrocarbons over the sea has therefore been made by measuring their concentrations in airborne particulates. These particulates constitute a large fraction of the material entering the sedimentary layers of the sea floor (37) and calculations of their chlorinated hydrocarbon content would therefore permit an estimation of the minimal amount of chlorinated hydrocarbon fallout in the sea. Dust deposits in glaciers, which can be accurately dated with lead 210 (16) have been used in calculating particulate fallout over the sea (37) and will undoubtedly eventually be used also to estimate chlorinated hydrocarbon fallout. To date, nylon mesh screens coated with glycerin have been used to collect marine airborne particulate material. Dust collected on such screens has been shown to collect the mineral talc in concentrations much higher than those expected on the basis of its natural distribution (38). Talc has been extensively used as a diluent for insecticides, and the rate at which it has been deposited on glaciers shows a significant increase after 1940 (38). Analysis of the airborne dust collected from the onshore winds at the end of the Scripps Institution of Oceanography pier in La Jolla showed that insecticides, predominately p,p'-DDT, were present in concentrations ranging from 1 to 81 ppm, with an average value of 18.2 ppm corresponding to 7×10^{-11} grams (g) per cubic meter (M^3) of air (27). By a striking coincidence, analysis of thirty-three samples of particulate material in water of marshes, irrigation canals, streams, rivers and lakes of California yielded an average value of 14.7 ppm with a range from 1.80 to 78.00 (21). The glycerin screen method fractionates against those materials carried on particles less than several microns or which are present as vapors. This value is therefore a lower limit of the amount of chlorinated hydrocarbons in the air. No PCB peaks were observed in the chromatograms of the dust extracts, which were therefore pooled, concentrated and saponified in order to degrade DDT and DDD. PCB was not present in the saponified extracts, and a maximum

concentration of 5 parts per billion (ppb) was calculated for the dust samples, ten thousand times lower than that of the total insecticides (27). Since the ratio of PCB to DDT observed in fish and birds is much higher, it appears that PCB remains in the vapor phase and does not adsorb to particulate matter. Additional work, however, is being carried out in order to clarify this point. We are also collecting dust-free samples from air which has been passed through cold dimethylformamide, which would retain any chlorinated hydrocarbons present in the vapor phase in the air.

The dust collected at the end of the Scripps pier also contains lead produced by internal combustion engines in concentrations averaging approximately 0.5 micrograms (μg)/m^3 of air. This value is about ten times lower than the mean value found in American cities but is one hundred times higher than that in marine air from the open sea (9, 10). It will be of considerable interest to compare the fallout patterns of the chlorinated hydrocarbons with that of lead produced by internal combustion machines, which can be traced and identified by virtue of its isotope composition.

The winds at the Scripps pier in La Jolla are predominantly landward with an unknown fraction of air from nearby agricultural areas. Although a present shortage of knowledge about air circulation patterns and fallout rates in this region makes it difficult to calculate the amounts of chlorinated hydrocarbons brought to the coastal waters by winds, it seems apparent that such a transport system could account for the unexpected geographical distribution of the DDT compounds in the marine and freshwater fish of California.

The Science Research Council of the United Kingdom had earlier mounted a similar screen on the eastern tip of the island of Barbados in an attempt to collect extraterrestrial dust of meteorite origin. The Northeast Trades at Barbados have blown across 5000 kilometers (km) of the tropical Atlantic, and it was therefore considered highly unlikely that any dust accumulating on the screen could be of continental origin. This assumption was, however, in considerable error since significant quantities of airborne particulate material were collected on the screen which

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upon mineralogical and biological examination proved to be most likely from Africa and Europe. Fallout rates of the dust over the tropical Atlantic and the extent to which it contributed to the bottom sediments were calculated (11). Gram samples were made available to us for analysis. The concentrations of chlorinated hydrocarbons in the dust ranged from less than 1 ppb to 164 ppb, with an average of 41. Knowledge of the fallout rate made possible an estimate of the quantity of insecticides entering the tropical Atlantic between the Equator and 30° N. This figure, a minimum value since the recovery of very small particulate materials was low, was 600 kg/yr, which compares with the value of 1,900 kg entering the San Francisco Bay via the Sacramento and San Joaquin Rivers (27). It cannot be concluded that these insecticides had originated only in Africa; the DDT residues accumulating in the rare Bermuda petrel (39) might have come from any part of the world.

Most of the chlorinated hydrocarbon content of the particulate material in marine air consists of p,p'-DDT. In marine fish and birds, p,p'-DDE is the major component and it would therefore appear that this conversion of DDT to DDE occurs early in the marine food chains. In San Francisco Bay and Puget Sound, DDE constitutes a much lower proportion of the total DDT compounds and DDT and DDD are comparatively more abundant. Similarly, DDE comprises only 22 per cent of the total DDT entering San Francisco Bay in the San Joaquin River (2). In bottom mud where anaerobic conditions might prevail, DDT can be expected to be converted to DDD rather than DDE (20, 35). From mammalian and insect toxicity studies it had earlier been concluded that DDE is relatively harmless. Recent research at the Patuxent Wildlife Research Center, however, has indicated that the toxicity of DDE to birds is much higher than expected and may be about one half that of p,p'-DDT (34). Like p,p'-DDT and other chlorinated hydrocarbons, p,p'-DDE is capable of inducing liver epoxidase enzymes (15). Such enzymes degrade sex hormones and other steroids by hydroxylating them (25) and thereby may affect calcium metabolism. This mechanism would explain how chlorinated hydrocarbons could be responsible for the increasing number of instances of abnormal calcium metabolism in birds. A significant decrease in eggshell weight of several birds of prey in Britain after the Second World War is evidence for a fundamental change in the environment (26). No change in the physical environment which could elicit a physiological effect of this magnitude among several species of birds over a wide area has been recorded. A change in the chemical environment would be manifest only through a change in the chemical composition of the diet. Of the new chemicals introduced into the environment after the Second World War which are ingested and retained by birds, only the organochlorine compounds have as yet been linked with calcium metabolism. No abnormal calcium metabolism has as yet been observed in sea birds, nor has it been looked for.

Application of the persistent biocides and the release of nondegradable waste products into the environment have frequently been justified by arguments that point out that local populations of organisms remain relatively uncontaminated and that, especially in the case of the chlorinated hydrocarbon insecticides, even the persistent compounds disappear with time. It is abundantly clear that these arguments have become misleading, irrelevant, and wrong. Pollutants do go everywhere. Those which are nonpolar, water-insoluble and which have finite vapor pressures will eventually appear in marine food chains. The DDT compounds and the polychlorinated biphenyls have already done so to an alarming degree.

DISCUSSION

RADOMSKI: How were the polychlorinated biphenyls detected in your assay? The commercial compound is a forest of peaks when analyzed. Which of these peaks were present in the analyzed biological material?

RISEBROUGH: There are several commercial preparations which differ in their average chlorine content. Each, however, is a mixture of compounds so that the chromatograms consist of clusters of peaks. The retention times of the peaks identified as PCB in extracts of fish and birds are given in the text. The profile of these peaks most closely matches that of the commercial compound containing 54% chlorine.

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WURSTER: Theoretical considerations would predict a net transfer of chlorinated hydrocarbons from the land areas of the world into the oceanic basins where one would expect them to accumulate, especially considering that their half-life is probably about a decade in the environment. The data that you have from the Pacific Basin indicates that this is occurring. They check well with our data on sea birds in the North Atlantic [Wurster, C. F., and Wingate, D. B.: *Science, 159*:979, 1968].

The interesting thing is that they show the level in those two oceans approaching the level found in some bodies of fresh water and in San Francisco Bay, which drain rather heavily treated areas. Presumably the ocean basins will continue to become still more contaminated. The heaviest contamination of which I am aware in a sizeable lake is Lake Michigan, probably because it flushes only once per century. It serves as an example of things to come in the oceans.

In Lake George, trout fry were not viable after hatching from contaminated eggs containing several parts per million of DDT [Burdick, G. E., *et al.*: *Trans Amer Fish Soc, 93*:127, 1964]. The same thing was observed recently in Jasper National Park, where mortality of fry occurred at a few tenths of a part per million [Cuerrier, J-P., *et al.*: *Naturaliste Can, 94*:315, 1967]. This past spring, fry hatched from contaminated salmon eggs on Lake Michigan but about 20 per cent of them died from DDT poisoning at a time when there should be very low mortality.

It follows that if the contamination level in the world's major fisheries is approaching the levels associated with the collapse of fisheries in some freshwater areas, then we can soon expect a repeat performance in the oceans. What will happen to important fish such as swordfish or tuna? There have apparently been substantial declines in the take of some marine fish; I wonder if some fish are already producing nonviable fry caused by their burden of chlorinated hydrocarbon residues?

RISEBROUGH: My answer can consist only of two additional questions. Who has the responsibility of finding out what might happen to swordfish and tuna, and secondly, who is in fact going to find out what will happen? The answer to the first is clearly

the manufacturers of DDT, dieldrin, PCB or any other persistent compound which ultimately accumulates in the global ecosystems. Unfortunately their major efforts to date in this direction have consisted of writing letters to *Science* which comment upon the relative abundance of robins. As for the second, the inherent limitations of government and international organizations prevent them from taking the initiative. It would appear that the answer must come from cooperative efforts of individual ecologists, naturalists and molecular biologists, perhaps those molecular biologists who are becoming somewhat alienated from the major trends in their field.

BUTLER: Geographic areas have been defined in which DDT levels in marine fish are frequently above 5 ppm in the gonad. In one area of the Gulf of Mexico where we know that reproduction of the speckled trout has declined, we assume that the decline is caused by DDT contamination. There are also indications that contamination with pesticides may be interfering with the reproduction of crabs in California.

HUNT: Did I understand you to say that contamination is greater in the marine ecosystem than it is in the inland water system?

RISEBROUGH: No, but they appear to be approximately equivalent. In the paper written by yourself and J. O. Keith (my reference #21), you reported on the chlorinated hydrocarbons in particulate material in freshwater systems in California. The average level was 14 ppm, and there were thirty-five samples with a range from 1 to 70 ppm. The average value of all samples of airborne particulate material which we collected off the Scripps Pier in La Jolla was 17 ppm with a comparable range from 1 to 80 ppm.

HUNT: Were the animals that live in these two systems also compared? Are you saying that the levels in marine fishes are higher than those in inland fishes?

RISEBROUGH: In the same paper you gave values for chlorinated hydrocarbon concentrations in California freshwater fish. I calculated the residues in whole fish or in flesh and found that these all of these fell within the range of 0.2 to 2.0 ppm, the

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range within which most of the values recorded in marine fish collected off California shores also fall.

HUNT: We have a considerable amount of data on some species, striped bass, for example. The contamination can average as much as 35 or 40 ppm. I would say that certain inland species, particularly the carnivorous fish, would have levels considerably higher than ocean fish.

RISEBROUGH: Yes, of course, but these would reflect local sources of contamination rather than general fallout.

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