CHANGES IN THE AMOUNT AND PROPORTIONS OF DDT AND ITS METABOLITES, DDE AND DDD, IN THE MARINE ENVIRONMENT OFF SOUTHERN CALIFORNIA, 1949–72

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ABSTRACT

This paper is about the contamination of the ocean and its biota off southern California by the pesticide, DDT. The accumulation of DDT and the changes in proportions of DDT and its metabolites in the ocean are described for the years 1949 to 1972 especially as they are reflected in the myctophid fish, *Stenobrachius leucopsarus*. This time period was characterized by continuous dumping of DDT wastes into the ocean by a large manufacturer of DDT and the cessation of this dumping in 1970. Aspects and implications of the pesticide pollution problem in the marine environment are discussed.

In January and May 1970, the Fishery–Oceanography Center, La Jolla, Calif., collected samples of fish off southern California and Baja California as their part in a survey of chlorinated hydrocarbon (CHC) pesticides in marine fishes by the U.S. fish and Wildlife Service Bureau of Commercial Fisheries (now the National Marine Fisheries Service). Each sample consisted of the livers of several specimens of a single species from one locality. The samples were sent to the Environmental Protection Agency Laboratory at Gulf Breeze, Fla., for analysis.

The results (Duke and Wilson, 1971) showed that off southern Baja California 9 samples (170 fish) contained an average of 0.14 parts per million (ppm) wet weight of DDT and its metabolites; in Sebastian Vizcaino Bay (central Baja California) 3 samples (29 fish) averaged 1.2 ppm; along the southern California coast south of Oceanside and at two offshore banks 15 samples (179 fish) averaged 13 ppm; in Santa Monica Bay 8 samples (65 fish) averaged 370 ppm. Two samples (26 fish) of Pacific hake, *Merluccius productus*, taken by a Russian trawler off northern California and Oregon averaged 2.7 ppm, and fish sampled farther to the north by the Seattle Laboratory contained less than 1 ppm or no detectable DDT residues in the livers. The highest levels of DDT and its metabolites were found in the Los Angeles area with DDT levels declining greatly in samples taken to the north, south, and offshore from Los Angeles.

Previous pesticide residue surveys of marine birds and fish (Keith and Hunt, 1966; Risebrough et al., 1967; Risebrough et al., 1968) had been confined primarily to central California and did not reveal the extent of DDT pollution in the ocean off Los Angeles. Risebrough et al. (1967) reported one sample of northern anchovy, *Engraulis mordax*, taken off Los Angeles that contained 12.7 ppm DDT and its metabolites compared with additional samples of anchovies and three other species of fish taken north of Los Angeles to San Francisco that ranged in DDT residue content between 0.2 and 2.8 ppm.

In the spring of 1969, Keith, Woods, and Hunt (1970) investigated the breeding pelican, *Pelecanus occidentalis*, colony on Anacapa Island, about 35 nautical miles west of Santa Monica Bay, and found extensive reproductive failure caused by thin-shelled eggs which broke under the brooding pelicans. They found that the contents of a composite sample of many broken eggs contained 1,818 ppm DDT residues (lipid basis) while nine intact eggs averaged 1,215 ppm. They also sampled pelican eggs from three breeding colonies in the Gulf of California and found DDT residues averaging 58, 61, and 105 ppm. Jehl (1970) sampled pelican eggs from Los Coronados Islands, about 95 nautical miles south of Anacapa. These contained 810 ppm DDT residues. At San Martin Island 250 nautical miles south of Anacapa, egg residues were 192 ppm.

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More recent data (Southern California Coastal Water Research Project, 1971)[2] for the *p,p'*DDE content of the mussel, *Mytilus californianus,* show that two samples taken on the Palos Verdes Peninsula, near Los Angeles, contained 61 and 151 ppm of *p,p'*DDE while samples taken at a greater distance from Los Angeles declined greatly to between 0.3 and 3 ppm at San Diego, Point Conception, and on the farther outlying islands.

Burnett (1971) determined DDT residues in samples of the sand crab, *Emerita analoga,* from 19 locations along the coast between northern Baja California and San Francisco. Only in those crabs from the Los Angeles area did he find values greater than 1 ppm (up to 7.2 ppm). The DDT values fell off rapidly north and south of Los Angeles and averaged about 0.1 ppm at most of these locations.

These results of the above studies demonstrate that geographical proximity to Los Angeles was accompanied by greatly elevated levels of DDT and its metabolites in marine organisms.

High DDT residues in marine life in the ocean off Los Angeles had an adverse effect on the fishing industry. In June 1970, canned jack mackerel, *Trachurus symmetricus,* shipped from Los Angeles was condemned by the U.S. Food and Drug Administration in New York for high DDT content (13 ppm). The FDA had set a maximum tolerance of 5 ppm on fish products. In the following year jack mackerel was withheld from distribution by the packers, and jack mackerel and Pacific bonito, *Sarda chiliensis,* were condemned by the FDA in the Los Angeles area. In December 1970, the FDA seized about 8,000 lb of white croaker, also called kingfish, *Genyonemus lineatus,* that had been caught near Los Angeles. These contained 19 ppm DDT residues.

While the fishing industry was unable to pinpoint any particular area of heavy DDT contamination of pelagic fish off southern California, it seemed to be fairly well defined for the more sedentary bottom dwelling species. Although the total DDT in the flesh of the Santa Monica Bay fish samples taken in May 1970 ranged from 12 to 57 ppm, about 30 nautical miles away at Farnsworth Bank on the west side of Santa Catalina Island, DDT in the flesh of a sample of sculpin, *Scorpaena guttata,* and in flesh samples of four species of rockfishes, *Sebastes* spp., had a range of only 0.23 to 0.49 ppm; and, a sample of white croakers taken off Oceanside, 40 nautical miles south of Los Angeles, contained only 0.61 ppm of DDT residues in the flesh.

The pelagic fish were not good indicators of the source of pesticide contamination because they are much more migratory than the bottom dwelling species, and the area in which they are caught is not necessarily the area in which they were contaminated. Even though this would also mean that their exposure to heavy contamination would be of shorter duration than for bottom fishes living in these areas, they still built up high concentrations of DDT in the flesh because pelagic fish tend to store fat throughout the body rather than in the liver as do bottom dwelling, more sedentary species. The DDT residues are stored in the fats, and the distribution of the total body load of DDT residues in the fish is roughly related to the distribution of fat.

Although we have no flesh sample analyses from pelagic fish to illustrate this point, concentrations of DDT were found to be two to six times higher in the livers of samples of four different species of bottom dwelling fish taken in 1970 along the coast between San Diego and Oceanside than they were in the livers of a sample of jack mackerel from the same area, and seven to 19 times higher than in the livers of a sample of Pacific sardine, *Sardinops sagax,* taken in San Diego Bay at about the same time. And even among bottom fish taken from the same area at the same time, those that have more oil in the flesh seem to carry relatively more of the total DDT load in the flesh. For five species of bottom dwelling fishes taken from Santa Monica Bay in 1970, there is an inverse relation between the ratio of DDT in the liver to DDT in the flesh and the percent of oil in the flesh as given in Table 1.

Because of the prevalence of winds from the Pacific, and the concentration of agriculture in the inland valleys, we considered it unlikely that the heavy DDT contamination in the ocean off Los Angeles was caused by airborne pesticide residues. Surface runoff was also an unlikely source. Southern California's arid climate, the damming of rivers, the large population and importation of water have resulted in a condition in which the annual discharge by sewers into the ocean is at least twice the average annual surface runoff of

[2]Southern California Coastal Water Research Project, 1971. Comments on the policy for water quality control proposed by the State Water Resources Control Board. Presented at the State Water Resources Control Board public hearing, San Diego, Calif., 2 Dec. 1971, 27 p.

TABLE 1.—Relation between ratio of DDT in liver to DDT in flesh and percent of oil in flesh of five species of bottom dwelling fishes from Santa Monica Bay in 1970.

Species	Number of fish	Total DDT		Ratio of DDT	Percent oil in flesh
		Liver (ppm)	Flesh (ppm)	Liver:flesh	
Bocaccio, *Sebastes paucispinis*	9	590	12	49:1	1.4
Starry rockfish, *S. constellatus*	5	1,030	57	18:1	1.8
Vermilion rockfish, *S. miniatus*	10	163	16	10:1	2.2
Dover sole, *Microstomus pacificus*	13	63	13	5:1	3.6
Sablefish, *Anoplopoma fimbria*	10	103	23	4:1	6.0

water. The "rivers" of southern California are its sewers, and the two largest of these, in the 400 million gallons (1.51 million m^3) per day class, are the outlets of the Hyperion treatment plant that serves the city of Los Angeles and those of the White Point treatment plant that serves Los Angeles County.

The Hyperion plant empties into the head of an underwater canyon in the northern half of Santa Monica Bay, and the White Point plant empties into the ocean off Palos Verdes Peninsula. Fish samples that showed very high DDT residues came from southern Santa Monica Bay about midway between the two sewer outfalls.

The County Sanitation Districts of Los Angeles County (CSDLAC) began a monitoring program to test for CHC pesticides in its sewerage system in December 1969 (Carry and Redner, 1970). They found that very high concentrations of DDT were present in the sewer system. In March 1970, they began to sample the sewer trunk lines in order to pinpoint the sources of DDT input into the sewer system.

They soon discovered that the source of most of the DDT pollution was the Montrose Chemical Corporation, a major manufacturer of DDT, located in the city of Torrance. Los Angeles Times staff writer, John Dreyfus, reported (7 October 1970), after interviewing a Montrose official, that at that time, Montrose was the only manufacturer of DDT left in the United States, and that it accounted for two-thirds of the world's sales of DDT.

The CSDLAC found that water samples taken from the sewers immediately upstream from Montrose contained 34 parts per billion (ppb) of DDT and its metabolites (DDD and DDE) in a flow of 25.3 million gallons (95.8 thousand m^3) per day or 7.2 lb (3.27 kg) of total DDT per day, while samples taken immediately downstream contained 2,950 ppb in a flow of 26.6 million gallons (100.7 m^3) per day or 654 lb (297 kg) of total DDT per day (Carry and Redner, 1970).

In April 1970, Montrose began hauling most of its processing wastes to a storage area, which caused a considerable drop in CHC entering the CSDLAC disposal plant. However, in May 180 lb (81.6 kg) per day CHC, of which 150 lb (68.0 kg) was DDT and its metabolites, were still found to be entering the White Point plant. The primary source of this was found to be the sewer trunk line serving Montrose Chemical Corporation. Because the composition of the total DDT sampled, 14% DDT, 48% DDD, and 38% DDE, was different from the Montrose effluent previously sampled, 74% DDT, 5% DDD, and 21% DDE, CSDLAC personnel concluded that the primary source of pollution was from old deposits in the sewer lines.

Between 11 December 1970, and 1 July 1971, 567,000 lb (257,000 kg) of deposits, of which 7,700 lb (3,500 kg) were total DDT, were removed from the interceptor system that served Montrose (Redner and Payne, 1971). The cleaning of this section of the sewer lines also stirred up old deposits which were washed down into the sewerage disposal plant, resulting in an increase in total DDT entering the plant. By October 1971, the total CHC entering the disposal plant had decreased to 60 lb (27 kg) a day of which 28 lb (13 kg) was total DDT and the remaining 32 lb (14 kg) polychlorinated biphenyls (PCB).

Since March 1971, an average of 22,000 gallons (83.3 m^3) a day of alkaline waste from the Montrose plant has been trucked to the Sanitation District's landfill on Palos Verdes Peninsula, and another 700 gallons (25.9 m^3) of acid waste has been trucked to a quarry. The alkaline waste was found to contain about 3,000 ppm of total DDT (Redner and Payne, 1971) or about 550 lb (250 kg)

per day. The acid waste was not tested, but if the concentration of DDT was similar to that in the alkaline waste, it would amount to an additional 175 lb (79 kg) of DDT residues per day.

The average inflow of DDT into the White Point sewerage plant during December 1969 through March 1970 was estimated at 652 lb (296 kg) per day. The amount measured in the sewers at the Montrose plant was 647 (293 kg) per day. The amount trucked out as alkaline waste only was estimated at 550 (250 kg) per day. Considering the difficulties in sampling such large volumes of material and the fact that the samples were taken in different localities at different times, there is remarkable agreement among them.

It is difficult to determine just how much DDT finally was pumped into the ocean after treatment at the sewerage plant. Some of it was undoubtedly removed in grit, grease skimming operations, and in dried sludge.

At the Hyperion treatment plant (city of Los Angeles), the digested sludge is pumped into the ocean, although some of it, at least in the past, has been used for fertilizer. The DDT input into the Hyperion plant was estimated to be on the order of 0.6 lb (0.27 kg) a day (tests by Hyperion personnel cited in Los Angeles Times, 7 October 1970) so, insofar as the DDT input into the ocean is concerned, it has had little impact. The White Point treatment plant has never discharged its sludge into the ocean (Terry Hindrichs, Southern California Coastal Water Research Project, pers. commun.) except during a short period of heavy rains in 1955. Until 1959, digested sludge was spread on nearby fields to air dry. Since 1959 a centrifuge has been used to partially dry sludge. The resulting cakes have been used for fertilizer or landfill.

CSDLAC personnel were unable to get reliable estimates of the DDT content of their effluent into the ocean until December 1970 (Carry and Redner, 1970), long after Montrose stopped dumping most of their wastes. Nine samples that they took from the effluent into the ocean in December showed that the average total CHC entering the ocean was 130 lb (59 kg) a day. The influent into the sewerage disposal plant in December had a load of 153 lb (69 kg) per day. The influent samples were taken after the grit chambers so any CHC removed in grit would not have been included. If we assume that sludge removal accounted for a 15% loss of CHC in December 1969 through March 1970, between influent (average 652 lb or 296 kg per day) and effluent into the ocean, then, the ocean discharge would have been about 552 lb (250 kg) per day of CHC for these months. This is about 100 short tons (91 metric tons) per year or about 10 times the amount of pesticides estimated to be carried into the Gulf of Mexico each year by the Mississippi River (Butler, 1969).

Montrose received a permit to dump its wastes into the CSDLAC sewer system in 1953, but it had been dumping for a few years before that according to company personnel. The continuous dumping of large quantities of DDT wastes into the ocean at a single point over a period of about 20 yr presented an unparalleled opportunity to study the effects of DDT on the ocean environment. Unfortunately the one-time opportunity to take advantage of the situation was not fully realized until some time after the dumping had stopped, and no large-scale coordinated investigation was undertaken to exploit this ecological windfall.

An investigation of pesticide pollution of the marine environment was initiated at the Fishery Oceanography Center (FOC), La Jolla, in 1970. Personnel at FOC have collected samples of bottom muds, fishes, and other biological samples primarily from the ocean off Los Angeles in order to study the effects of heavy DDT pollution in the marine environment.

Collections of marine organisms taken for other purposes, some dating back to 1949, were available for study. Most of the present paper is based on DDT levels found in specimens from one of these collections of a myctophid fish, *Stenobrachius leucopsarus*, found in the ocean off southern California in an attempt to trace the historical buildup of DDT and its metabolites in the marine environment as reflected in this species.

MATERIALS

The California Cooperative Oceanic Fisheries Investigations (CalCOFI) has taken plankton samples over an extensive area off California and Baja California since 1949. These samples were obtained over a predetermined pattern of stations in order to determine the species present, their numbers, and their distribution. The most intensive sampling took place during the 1950's; during the 1960's the number of CalCOFI cruises was reduced considerably.

All fish and fish eggs are routinely sorted out of the collections for identification. About 600

specimens of the myctophid fish, *S. leucopsarus*, that had been sorted from the plankton collections, were selected for this study to give best areal and temporal coverage.

Initially a few plankton samples, which were available in much greater quantity, were tested for pesticides. However, the plankton species composition varied in time and with locality, and it was felt that the samples might not be comparable. The plankton samples also appeared to contain both Aroclor 1242[3] and Aroclor 1254 (polychlorinated biphenyls (PCB) manufactured by Monsanto Corporation) while the myctophids generally contained only Aroclor 1254 in quantity. Plankton samples can include man-produced debris that contains relatively large amounts of CHC or other organic chemicals which interfere with analysis, while individual myctophids are relatively free of such material. Myctophids do not undergo any more horizontal movement than other plankton organisms, and, if they use their motility at all, at least in the coastal waters, it is probably to maintain position over the deeper basins. In addition, they tend to contain more pesticide than the invertebrate constituents of the plankton with which they are taken, and they are convenient material to work with.

The myctophids tested for pesticide residues ranged in standard length (SL) from 14 to 77 mm. They are apparently short-lived fish. Fish of the year can be followed through their first year and into their second by length-frequency distributions (Figure 1). Most of the myctophids tested appeared to be comparable in DDT content to other fish taken at the same time and place, but the amounts in smaller fish were erratic. Some

[3]Reference to trade names does not imply endorsement by the National Marine Fisheries Service, NOAA.

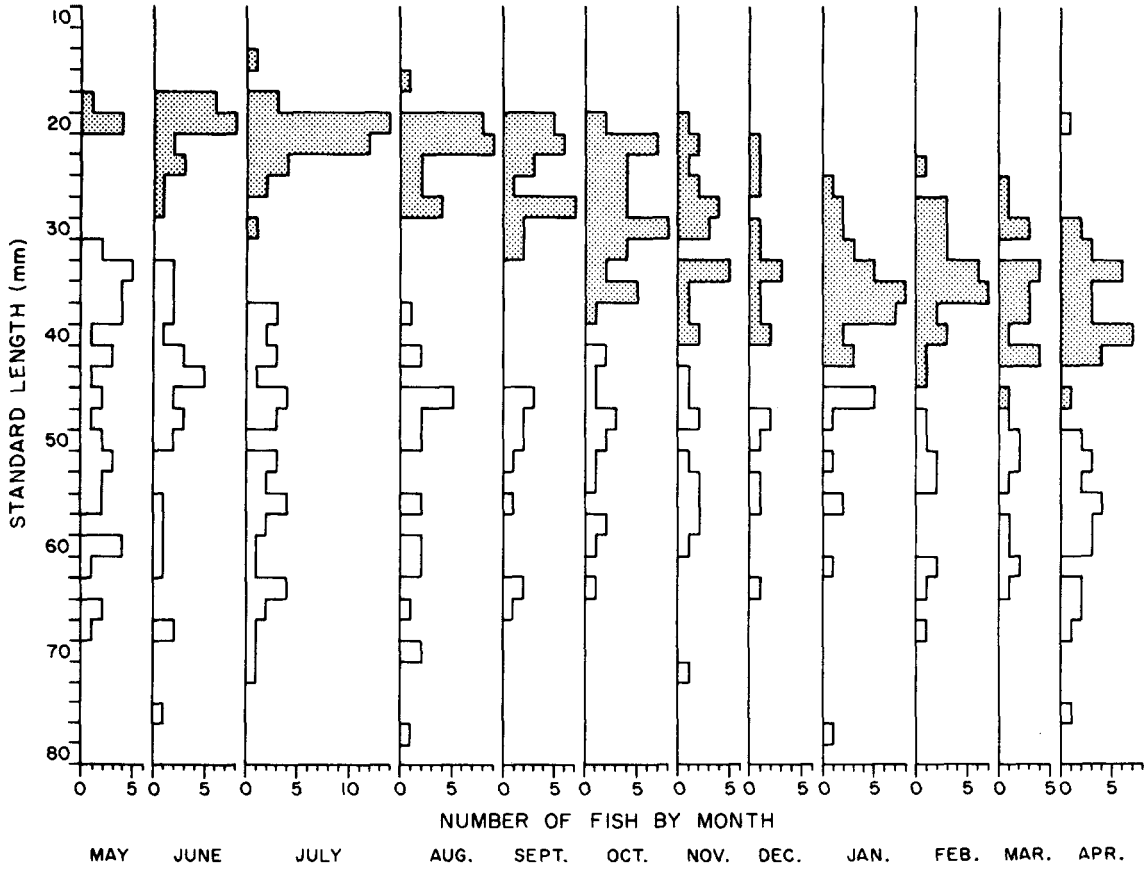


FIGURE 1.—Length-frequency distribution of *Stenobrachius leucopsarus* by month. Shaded area is entering year class.

were comparable to larger fish, while others contained less DDT than might be expected in larger fish taken at the same time and in the same locality.

This variation in pesticide content appeared to be related to the "fat" content (hexane extractable portion of the fish) of the specimens. The fat content of the fishes (Figure 2) increased very rapidly and with considerable variation to 30 mm length, 6.5% fat of the dry weight of the fish in an 18-mm specimen to 42.5% in a 29-mm specimen) where it began to level off. In mature fish the fat is about 49% of dry weight and 16% of wet weight. There is no apparent seasonal fat cycle. For comparison of DDT in time and space, only myctophids 30 mm or longer were used.

METHODS

The myctophids used in this study were preserved in Formalin which had no apparent effect on the pesticides to be analyzed. The specimens were measured and weighed and placed in tared disposable pipets that had been plugged with glass wool at the small end, or for larger fish in similarly prepared glass tubing of appropriate size. The fish were dried in an oven at 65°C to constant weight and reweighed to obtain dry weight. Each fish was macerated in the tube and extracted into a 15-ml graduated centrifuge tube with 10 ml of hexane. The remains of the fish in the pipet were dried and reweighed to obtain the weight of material extracted.

The extract in the centrifuge tube was mixed to uniformity, and an aliquot equal to 20 mg or less of fat removed. This was reduced in volume if necessary and passed through an activated alumina column as described by McClure (1972). The cleaned up sample was again reduced in volume if necessary and injected into a model 402 Hewlett Packard gas chromatograph (GLC) with a Ni^{63} electron capture detector. The 6-foot glass column contained 1.5% OV-17/1.95%QF-1, on 100/120 mesh Supelcoport.

DDT gets its name from its former chemical designation, *p,p'*-dichlorodiphenyltrichloroethane. The current chemical designations for DDT and its metabolic products mentioned in this paper are:

p,p'-DDT	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane
p,p'-DDD (TDE)	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane
p,p'-DDE	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene
p,p,'-DDMU	1-chloro-2,2-bis(*p*-chlorophenyl)ethylene
Kelthane (Dicofol)	1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol

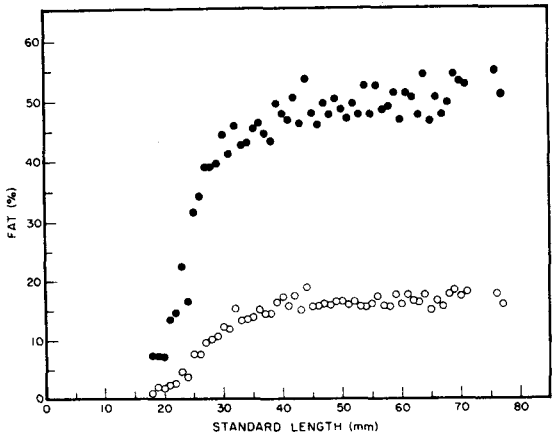
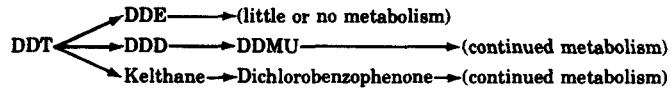


FIGURE 2.—Increase in percent fat with increase in length for *Stenobrachius leucopsarus*. Dark circles equal fat as a percent of dry weight; open circles, as a percent of wet weight. Fat equals hexane extractable substances. Pesticide values for fish less than 30 mm standard length (SL) were not used because of the greater variation in these values than in larger fish in which fat content was more stabilized.

For the ortho-para isomers of DDT, DDD, DDE, and DDMU substitute 2(*o*-chlorophenyl)-2-(*p*-chlorophenyl) for 2,2-bis(*p*-chlorophenyl). In this paper total DDT includes *p,p'*DDT, *o,p'*DDT, *p,p'*DDD, *o,p'*DDD, and *p,p'*DDE. While *o,p'*DDE and *p,p'*DDMU are present, although not as major constituents of the fish samples, both have the same short retention times on the column used and are interfered with by a number of other unknowns as tends to be true of anything having a shorter retention time than *p,p'*DDE in these samples; therefore they were omitted because of the difficulty in identification and quantification. Kelthane was also omitted because it breaks down on this column (Morgan, 1967) to a material that has a low response and an even shorter retention time than DDMU.

For the purposes of this paper we assume that DDT is metabolized (O'Brien, 1967; Morgan, 1967; Menzie, 1969) as follows:



Since we have no measurements of Kelthane, the scope of this paper includes only the measurement of the metabolism of DDT to DDE and DDD. As mentioned earlier, the effluent from the Montrose plant was already partly metabolized (Carry and Redner, 1970). In seven samples taken between 14 August and 24 November 1970, the total DDT portion of the effluent contained 74% (range 62–84) of DDT, 5% (3–7) of DDD, and 21% (9–35) of DDE. During this period the effluent contained 2 lb or less of DDT per day. The proportions of DDT, DDD, and DDE at the time when dumping was 650 lb (295 kg) per day were 73:2:25.

At the beginning of this investigation some pesticides were separated on other columns to confirm the identification of DDT and its metabolites. Additional confirmation was obtained by dehydrochlorinating samples with alcoholic KOH which converts DDT and DDD to their respective ethylene derivatives, DDE and DDMU, but does not change the PCB, Aroclor 1254.

Because there are so many possible sources of variance to the estimates of pesticide content, we cannot obtain a precise measure of this error. Based on the least accurate measurements made in the course of analysis, the standard error of the amount of pesticide in a sample should be about plus or minus 10%. The error may be increased by shortcomings in methodology and by the presence of other peaks that interfere with those to be quantified. At low pesticide values the error increases, and it may be more like plus or minus 100% at values on the order of 10 ppb. However, the absolute error is only a few parts per billion also and makes little difference when values that differ by orders of magnitude are being compared.

In the myctophid samples, Aroclor 1254 seemed to be the only substance that contributed peaks on the chromatogram of any significance which could interfere with quantification of the DDT series. Six Aroclor 1254 peaks span the retention time range of *p,p'*DDE, *o,p'*DDD, *o,p'*DDT, *p,p'*DDD, and *p,p'*DDT (Figure 3). In all the marine samples examined, *o,p'*DDT and *o,p'*DDD are present in either very small quantities or not detectable at all unless the samples contain very large quantities of *p,p'*DDT or *p,p'*DDD. In the myctophid samples, Aroclor 1254 seems to maintain its integrity very well. There is no apparent selective breakdown of its components, and the pattern of peaks from myctophid samples containing this PCB and very little pesticide closely resemble the Aroclor 1254 standard (Figures 3 and 4).

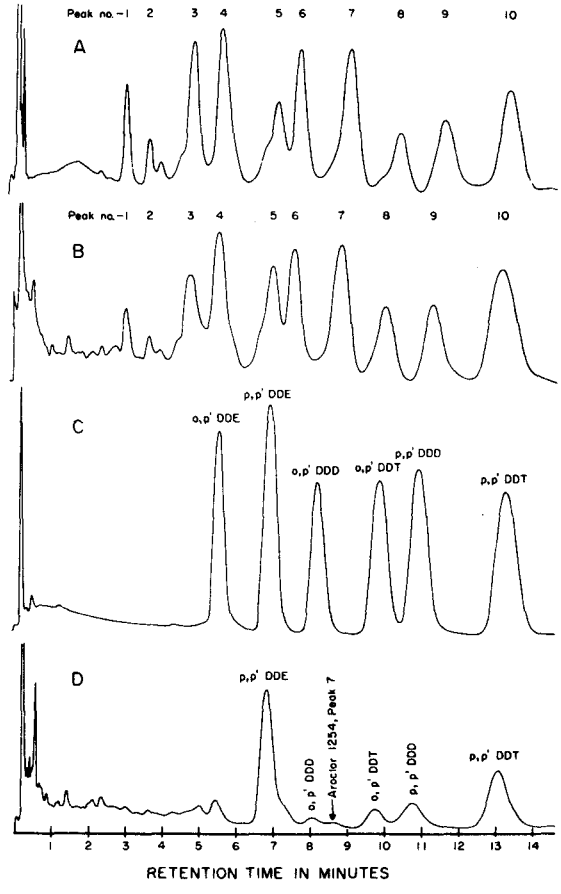


FIGURE 3.—A. Aroclor 1254 standard; column: 1.5% OV-17/1.95% QF-1, 100/120 mesh Supelcoport. B. Sample of two *Stenobrachius leucopsarus* each 20 mm standard length (SL) taken in July 1951, at CalCOFI station 70.100. About 0.54 ppm Aroclor 1254 with peak no. 5 increased slightly by 0.2 ppm DDE and peak no. 10 by 0.3 ppm DDT. Less highly chlorinated Aroclor peaks no. 1, 2, and 3 may be breaking down in the environment; more highly chlorinated peaks (no. 4 through 10) tend to maintain their integrity of pattern. Same column as A. C. Standard of six DDT analogs. Same column as A. D. Sample of a 33-mm *S. leucopsarus* taken in November 1955 at CalCOFI station 83.40. This sample contains 2.3 ppm total DDT. Because of the high DDT content of this sample, it was not concentrated as much as sample B. It probably contains at least half as much Aroclor 1254 as sample B. Same column as sample A.

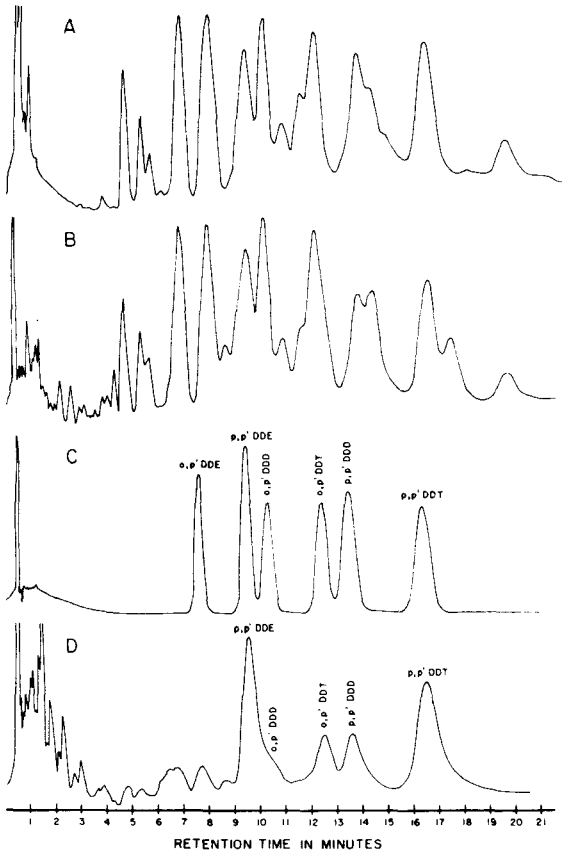


FIGURE 4.—A. Aroclor 1254 standard; column: 4% SE-30/6% QF-1, 100/120 mesh Supelcoport. B. Sample of a 28-mm *S. leucopsarus* taken in November 1955 at CalCOFI station 83.55. Aroclor 1254, 4.2 ppm; pesticides not measured. Same column as A. C. Standard of six DDT analogs. Same column as A. D. Sample of one 37-mm *S. leucopsarus* taken in March 1954 at CalCOFI station 85.45. 1.0 ppm total DDT. Same column as A.

It is apparent (Figure 3) that the seventh of the Aroclor peaks is not interfered with by the DDT series. The two ortho–para prime peaks bracketing it are generally small or absent. Therefore, it may be used to correct the DDT series for PCB interference and to quantify the Aroclor 1254.

An estimate of peak area, peak height times width at one-half peak height, was used in quantification. Increasing chart speed makes it possible to measure the width more accurately. Peak area rather than peak height is a more accurate measurement of the combined effects of two CHC when their retention times are about the same. Because GLC operating conditions may change gradually during a sample run, one pesticide standard was injected for every two samples so that each sample would have an adjacent standard for quantification.

To correct the areas of the combined peaks of the DDT series and Aroclor 1254 to the area representing pesticide only, we let X equal the area of each peak at the respective retention time of each of the DDT series and Y equal the area of Aroclor peak no. 7. Then for our operating conditions and Aroclor standard, the areas allotted to the components were:

Combined peaks	Area of Aroclor	Area of DDT series
*p,p'*DDE + Aroclor no. 5	0.24*Y*	*X* – 0.24*Y*
*p,p'*DDD	0	*X*
*o,p'*DDT + Aroclor no. 8	0.54*Y*	*X* – 0.54*Y*
*p,p'*DDD + Aroclor no.9	0.73*Y*	*X* – 0.73*Y*
*p,p'*DDT + Aroclor no. 10	0.95*Y*	*X*– 0.95*Y*

An estimate of Aroclor 1254 was obtained by multiplying the area of the no. 7 Aroclor peak by 12.3 and quantifying against the area of the *p,p'*DDE standard, or multiplying by 9.6 and quantifying against the area of the *p,p'*DDT standard. The subtractive corrections for the DDT series were confirmed in part for a few samples by calculating values both before and after dehydrochlorination with alcoholic KOH.

In a few samples taken far from the sewer outfall and in the earlier years, Aroclor 1254 was high enough to mask out the DDT residues except for slight increases in some peak areas (Figure 3). In such cases the pesticides were present in such small quantities that it made no appreciable difference in the overall results what small values were assigned to them. The illustrated example is an extreme case of masking.

In most of the samples the DDT residues dominated the PCB peaks and over the range of the six pesticide standards (Figure 3), only peaks no. 6 and 7 of Aroclor 1254 were evident. If DDT residues were high, peak no. 6 was evident as a widening of the base of the *p,p'*DDE peak (Figure 3).

RESULTS AND DISCUSSION

The pattern of CalCOFI stations from which the samples were obtained extends across the north flowing coastal countercurrent out into the south flowing California Current cutting across the counterclockwise eddy or eddies that develop between the two currents. At a depth of 200 m the

California Current is usually farther offshore than at the surface (Wyllie, 1966). In April and May this current moves inshore eliminating the countercurrent at the surface and sometimes at 200 m. When the California Current is offshore, the surface countercurrent develops; when it moves onshore, the surface countercurrent is absent although the southern California eddy usually persists.

The currents, and consequently the distribution of the sewer discharge, are influenced locally by such factors as the configuration of the coast, the presence of islands, the topography of the ocean floor, and the short range effects of winds and tides.

The total DDT data for the myctophids were divided into four time periods, and the average DDT value determined for all specimens taken at each station, or combined stations if they were very close together, for each time period (Figures 5-8). The total DDT content of the fish tended to be high near the sewer outlet and decreased away from the outlet. Total DDT values increased with the passage of time.

Total DDT for the purpose of this discussion consists of DDT, DDE, and DDD. Although total DDT content in the myctophids increased with time, this did not hold true for each of the three constituents. DDT increased for a few years until metabolism and dispersion equalled input and then leveled off. DDD acted in a similar manner but at a lower level. Most of the increase in total DDT after the first few years was caused by the increase in the persistent metabolite, DDE. The

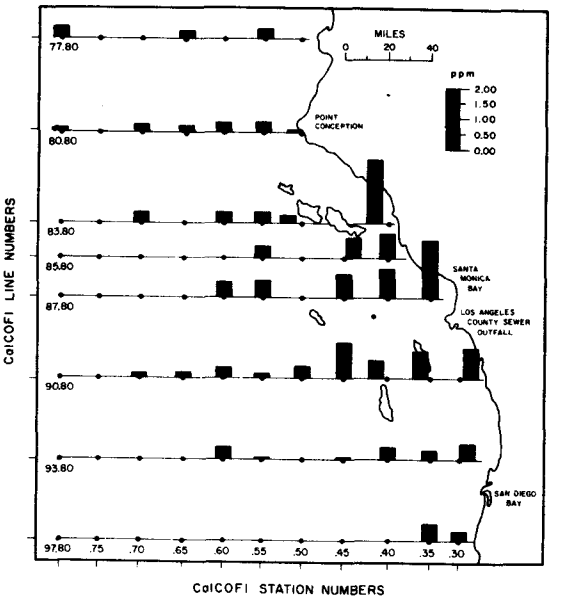


FIGURE 6.—Average total DDT at CalCOFI stations off southern California for the 4 yr 1953–56.

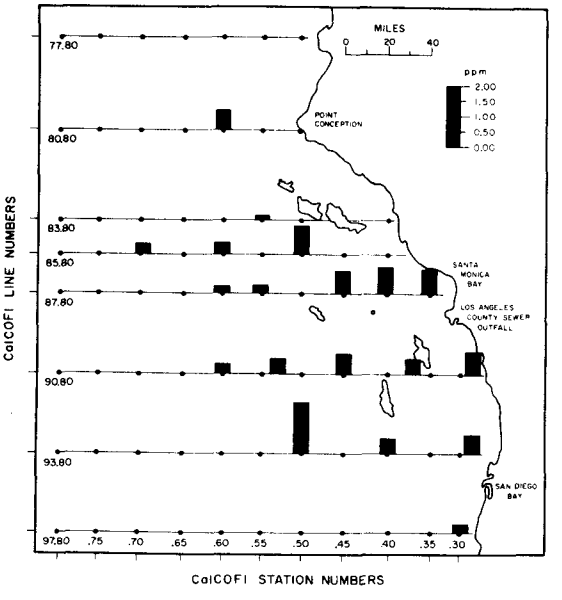


FIGURE 5.—Average total DDT at CalCOFI stations off southern California for the 3 yr 1950–52.

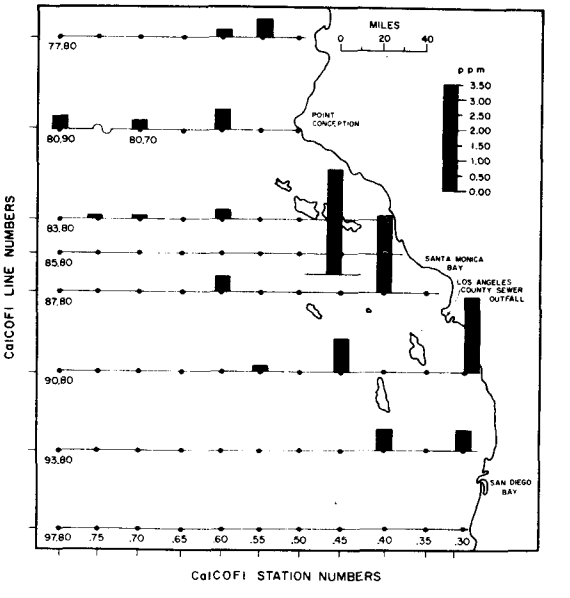


FIGURE 7.—Average total DDT at CalCOFI stations off southern California for the 4 yr 1957–60.

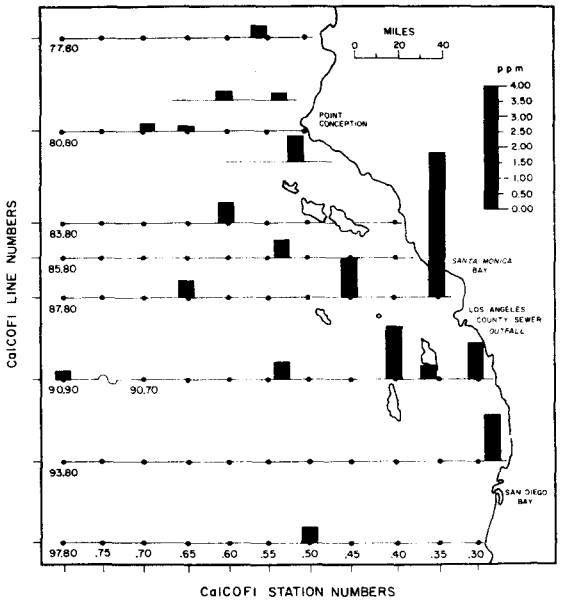


FIGURE 8.—Average total DDT at CalCOFI stations off southern California for the 6 yr 1961–66.

increase in *p,p'*DDE relative to *p,p'*DDT for the years 1950-51 through 1965-66 in the myctophids was:

Year	*Ratio of DDE to DDT*
1950–51	0.33:1.00
1952–53	0.36:1.00
1954–55	0.69:1.00
1956–57	1.06:1.00
1959–60	1.14:1.00
1961–62	2.02:1.00
1963–64	2.39:1.00
1965–66	3.96:1.00
(1970)	(4.74:1.00)
(1972)	(8.80:1.00)

These data show a 12–fold increase in the amount of DDE relative to DDT from 1950–51 to 1965–66. The ratio for the fish taken in 1970, 65–70 nautical miles southeast of the sewer outlet (in La Jolla Canyon) indicates a continuing increase in the ratios, although there were only two fish in the sample. The 1972 sample, consisting of only five myctophids, was taken west of Santa Catalina Island and about 25–30 nautical miles south southwest of the sewer outfall about 2 yr after the dumping of DDT into the sewer system had stopped. The high ratio may reflect in part continued metabolism of DDT without replenishment.

Because there are no data on the amount of DDT discharged into the ocean through the White Point sewer outfall each year, I have assumed that it was constant and discharged continuously throughout the year. Under these circumstances the amount of DDE (and DDD) entering the marine environment should gradually have increased in the earlier years until the input of DDT equalled the amount of DDT metabolized, when the input of DDE (and DDD) would also be constant. This is indicated by the initial slower increase in ratios of DDE to DDT.

If we assume that the same amount of pesticide is released into an environment each year and that it is released continuously throughout the year we may empirically represent the accumulation of the pesticide in the environment by the formula

$$Y = K(1 - S^X)$$

in which Y equals the amount of pesticide accumulated at the end of X years; K equals the maximum amount of pesticide that could be accumulated by the organism under the prevailing conditions; and S equals the "survival" rate of the pesticide for 1 yr.

In some of the years from 1949 to 1966, CalCOFI cruises were limited, and fewer samples were taken. Also the fish were not uniformly sampled with respect to distance from the sewer outfall in each of the years. But, by averaging the *p,p'*DDE content of all fish taken in each year and grouping years by twos, a rough indication of the increase in *p,p'*DDE was obtained to compare with theoretical values of the formula, $Y = K(1 - S^X)$ (Figure 9).

The almost linear increase in *p,p'*DDE indicates that its metabolism is very low. In fact, metabolism in this case would include *p,p'*DDE lost by removal from the area under study, and, therefore, the data indicate that very little was lost from this area during the years in which dumping occurred.

Because of the apparent lack of metabolism of *p,p'*DDE, this metabolite of *p,p'*DDT should give the best picture of areal and temporal buildup of a CHC in the ocean as a result of the sewer discharge.

Data on *p,p'*DDE content of the myctophids, year of capture (with 1949 equal to year 1), and distance in nautical miles from the sewer outlet to the place of capture were fitted to the formula:

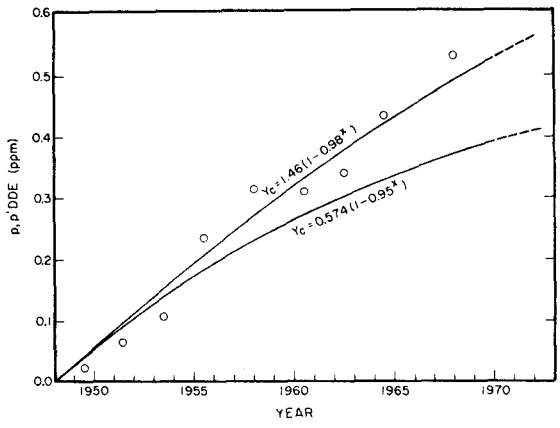


FIGURE 9.—Increase in *p,p'*DDE in the ocean off southern California, 1949–70. The points are averages of all stations combined in 2-yr groupings. Because the same patterns of stations were not run each year, myctophids were not obtained from the same stations or the same number of stations each year. Also pesticide concentrations were more dependent on distance from the point source of contamination than on year. This makes the coarse grouping of data necessary when increase in DDE with time only is considered. The two theoretical lines are computed to the formula $Y_C = K(1-S^X)$, in which Y_C = computed value of *p,p'*DDE, K = value at which metabolism, excretion, and dispersal of DDE equals input, S = survival of DDE for 1 yr, and X = year with 1949 considered as year no. 1. The data indicate that *p,p'*DDE is very stable. For the 98% survival curve, which more closely fits the data, 90% of the equilibrium value would not be attained for 114 yr.

$$\log Y = \log a + b \log X + c \log X'$$

in which Y = calculated value of DDE in parts per billion, X = distance from sewer outfall in nautical miles, and X' = year. The data were grouped for greater ease of computation and to minimize individual variations which tend to distort the actual values transformed from log–log calculated values if not minimized by averaging.

The values determined for the above equation are:

log a	3.054
b (distance)	−1.062 (SE 0.057)
c (year)	1.423 (SE 0.122)

The correlation coefficients are:

multiple	0.978
partial (b)	−0.829
partial (c)	0.522

all of which are significant at P of less than 0.001.

The computed lines did not fit the data for 1949, 1950, and 1951 very well. These years were left out of the calculations because the input of DDE was rising relatively rapidly at this time and did not begin to stabilize until about 1953. Also in these earlier years, the influence of the sewer discharge of pesticide extended out to only about 100 nautical miles from the outfall. In the following years the influence of the sewer discharge increased rapidly to between 300 and 400 nautical miles from the outfall before becoming indistinguishable from the ocean background. Although there are no extensive data for any one station throughout the period under study, we can now calculate values for a theoretical station 20 nautical miles from the sewer outfall from the DDE–time–distance formula and in conjunction with the observed changes in ratios among the various DDT analogs, obtain a description of the metabolism of DDT in the marine environment as reflected in the myctophid fish, *S. leucopsarus*.

Because *o,p'*DDE was not quantified, we used only *p,p'*DDE, *p,p'*DDT, and *p,p'*DDD in the ratios. In more than 300 myctophids 30 mm or longer in standard length in which the above three constituents and *o,p'*DDT and *o,p'*DDD were measurable, *o,p'*DDT and *o,p'*DDD averaged 22.3% of *p,p'*DDT and *p,p'*DDD. In samples of commercial DDT that were tested *o,p'*DDT averaged about 25% of *p,p'*DDT.

From the calculated values of DDE and ratios of DDE to DDT, we can calculate that at our theoretical 20 mile station DDT accumulates in the fish up to 1.077 ppm when input equals metabolism. From this we may calculate that:

$$Y_t = 1.077(1 - 0.708^X)$$

in which Y_t equals calculated *p,p'*DDT and X equals the year with 1949 equal to year 1. From the values obtained (Table 1, Figure 10) we may recalculate values for DDE. These values remain essentially the same as those calculated from the DDE–time–distance formula for the later years but make allowances for lower input from DDT for the earlier years if we use the formula:

$$2.046Y_e = 0.368X - 1.077 + 1.077(0.708^X)$$
$$\text{or} \quad Y_e = 0.180X - 0.526 + 0.526(0.708^X)$$

in which Y_e = calculated *p,p'*DDE and X equals the year and in which we assume that there is no further metabolism of DDE.

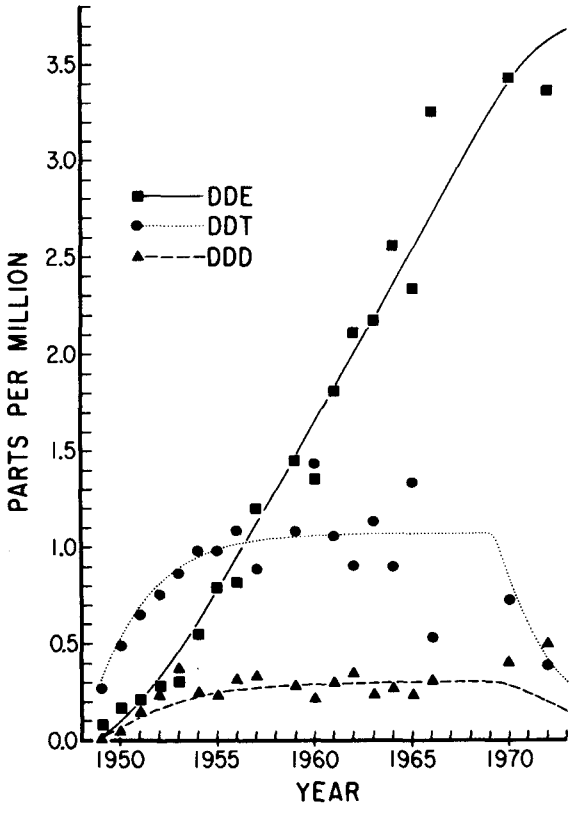


FIGURE 10.—Trends of *p,p'*DDE (squares), *p,p'*DDT (circles), and *p,p'*DDD (triangles) in the ocean off southern California, 1949–72, at a theoretical station 20 nautical miles from the point source of pesticide contamination. Computed lines show persistant DDE increasing until dumping of DDT wastes ceased in 1970. Both DDT and DDD increase for several years and then level off when metabolism, excretion, and dispersion equal input. Points are based on calculated total value of the three analogs distributed among them on the basis of the observed ratios of the three analogs to each other for each year. The 1972 ratios were affected by sewer cleaning operations that caused large quantities of DDD to enter the ocean.

From the calculated values of DDT and the DDD:DDT ratios we may estimate values for DDD. From these it appears that DDD accumulates in the fish up to 0.303 ppm where input equals metabolism. From this we may calculate that $Y_d = 0.303(1 - 0.525^X)$. However, this formula is based on a constant input equivalent to 0.189 ppm. The actual input from metabolism of DDT was only 0.028 ppm the first year and increased to 0.181 by the 10th year, and 0.188 by the 20th year. By adjusting for these increasing inputs we obtain accumulative values for DDD, for DDMU, and other metabolites of DDD (Table 2, Figure 10).

The percent distribution of total DDT among *p,p'*DDT, *p,p'*DDE, and *p,p'*DDD did not appear to change in myctophids with distance from the sewer outfall. Therefore the percent distribution which is based on large numbers of fish in most years can be used to prorate the total *p,p'*DDT obtained from the curves to obtain "observed" values of *p,p'*DDT, *p,p'*DDE, and *p,p'*DDD (Table 1, Figure 10). Both the curves and their observed values are based on observed percent changes in the composition of total DDT transformed to ppm values of the three constituents at a theoretical station 20 nautical miles from the sewer outfall.

It should be emphasized that the above description of metabolism is only an indication of what is taking place in the ocean. It neither describes the metabolism of DDT in the myctophid fish nor the metabolism in the marine environment, but rather reflects selective storage of DDT and its environmental metabolites in one species of fish.

Three factors determine the amount of CHC found in myctophid fishes: 1) The CHC present in the fish's environment during its brief life span; 2) the selective absorption of CHC through the gills and the ingestion of selected food particles; 3) and the selective storage, metabolism and excretion of CHC. Factors 2 and 3, above, should remain constant for each generation of fish. Therefore, the changes in composition of total DDT probably reflect changes occurring in the environment. However, the percent composition found in the myctophids may not represent the percent composition in the environment because of the selective nature of intake and excretion.

Some of the DDT was changed to DDE and DDD before entering the ocean. Sixteen samples of sewer discharge from the Montrose Chemical Corporation taken between 14 August 1970, and 12 May 1971, averaged 74%DDT, 20%DDE, and 6%DDD (Redner and Payne, 1971). Although these samples represented discharges averaging less than 0.5 lb (0.23 kg) a day, samples taken earlier in 1970 when dumping was estimated at 640 lb (290 kg) per day also had ratios of 73:25:2. These percent ratios are very much like the 74:23:2 distribution in the myctophids in 1949 and the 70:23:7 distribution in 1950.

Although some DDT was converted to DDD and DDE before it left Montrose, most of the metabolism took place after it was discharged from the plant. This is indicated by the percent distribution of DDT, DDE, and DDD in the myctophids in 1970, 16:75:9, by the bottom fish taken

TABLE 2.—Calculated values of *p,p'*DDT, *p,p'*DDE and *p,p'*DDD and their observed percent distribution in the myctophid fish *Stenobrachius leucopsarus*, at a distance of 20 nautical miles from the point source of pollution in the ocean off southern California for the years 1949 through 1973.

Year	Annual input (ppm)	Accumulated input (ppm)	Calculated accumulated *p,p'*DDT (ppm)	Metabolites of *p,p'*DDT		Metabolites of *p,p'*DDD (DDMU and others excreted or not measured) (ppm)	Accumulated total DDT (ppm)	Observed percent			Concentration based on observed percent		
				Accumulated *p,p'*DDE (ppm)	Accumulated *p,p'*DDD (ppm)			*p,p'*DDT (%)	*p,p'*DDE (%)	*p,p'*DDD (%)	*p,p'*DDT (ppm)	*p,p'*DDE (ppm)	*p,p'*DDD (ppm)
1949 (1)	0.37	0.37	0.31	0.03	0.02	0.01	0.36	74.4	23.3	2.3	0.27	0.08	0.01
1950 (2)	.37	.74	.54	.10	.07	.03	.70	70.0	23.3	6.7	.49	.16	.05
1951 (3)	.37	1.10	.69	.20	.12	.09	1.01	64.0	21.1	14.9	.65	.21	.15
1952 (4)	.37	1.47	.81	.33	.16	.18	1.29	58.5	21.9	19.6	.76	.28	.25
1953 (5)	.37	1.84	.88	.47	.20	.29	1.55	55.9	19.7	24.4	.87	.31	.38
1954 (6)	.37	2.21	.94	.62	.22	.42	1.79	54.8	31.1	14.1	.98	.56	.25
1955 (7)	.37	2.58	.98	.78	.24	.57	2.01	48.9	39.5	11.6	.98	.79	.23
1956 (8)	.37	2.94	1.01	.95	.26	.73	2.22	48.7	37.0	14.3	1.08	.82	.32
1957 (9)	.37	3.31	1.03	1.12	.27	.89	2.42	36.5	49.7	13.8	.88	1.20	.33
1958 (10)	.37	3.68	1.04	1.29	.28	1.07	2.61	No data					
1959 (11)	.37	4.05	1.05	1.47	.29	1.24	2.80	38.4	51.4	10.2	1.08	1.44	.29
1960 (12)	.37	4.42	1.06	1.64	.29	1.42	2.99	47.9	45.1	7.2	1.43	1.35	.22
1961 (13)	.37	4.78	1.06	1.82	.29	1.61	3.18	33.4	57.0	9.6	1.06	1.81	.31
1962 (14)	.37	5.15	1.07	2.00	.30	1.79	3.36	26.9	62.8	10.3	.90	2.11	.35
1963 (15)	.37	5.52	1.07	2.18	.30	1.97	3.55	32.0	61.3	6.7	1.13	2.17	.24
1964 (16)	.37	5.89	1.07	2.36	.30	2.16	3.73	24.0	68.7	7.3	.89	2.56	.27
1965 (17)	.37	6.26	1.07	2.54	.30	2.35	3.91	34.1	59.8	6.1	1.33	2.34	.24
1966 (18)	.37	6.62	1.08	2.72	.30	2.53	4.09	12.9	79.5	7.6	.53	3.25	.31
1967 (19)	.37	6.99	1.08	2.89	.30	2.72	4.27	No data					
1968 (20)	.37	7.36	1.08	3.07	.30	2.91	4.45	No data					
1969 (21)	.37	7.73	1.08	3.25	.30	3.10	4.63	No data					
1970 (22)	.11	7.84	.85	3.41	.29	3.28	4.56	15.9	75.3	8.8	.72	3.43	.40
1971 (23)	.00	7.84	.60	3.54	.25	3.45	4.39	No data					
1972 (24)	.00	7.84	.43	3.62	.20	3.59	4.25	9.0	79.2	11.8	.38	3.37	.50
1973 (25)	.00	7.84	.30	3.68	.15	3.70	4.14	No data					

in Santa Monica Bay in 1970, 8:87:6, and by a bottom sediment sample taken near the sewer outfall in 1971, 6:82:12. Samples of sewer water taken in 1970 that derived their DDT content from sewer sediments had ratios of 14:38:48 (Redner and Payne, 1971).

A few specimens of another myctophid, *Triphoturus mexicanus,* also showed a change in CHC ratios with time. Twenty-one specimens taken between 1950 and 1959 contained an average of 69%DDT, 9%DDD, and 22%DDE, while 12 specimens taken between 1961 and 1970 contained 23%DDT, 15%DDD, and 62%DDE. These fish were taken between Los Angeles and southern Baja California (lat 26°20'N). This species has a more southern distribution than *Stenobrachius leucopsarus,* and therefore the population was less influenced by the sewer discharge.

One might expect that DDE would be more abundant in samples taken farther from the sewer outfall, indicating older deposits, but this is not the case. The proportions are very similar in all samples, even those taken outside of the influence of the sewer. For the fish samples taken in 1969-70 for the survey, the percentages are given in Table 3.

Each sample contained several fish of the same species, and only the livers were tested. Where the pesticide levels were very high, the proportions were remarkably similar among samples. For the eight Santa Monica Bay samples, the DDE ranged from 85.2 to 87.7%, DDD from 5.1 to 6.6%, and DDT from 5.7 to 9.1%.

TABLE 3.—Distribution of *p,p'*DDE, *p,p'*DDD, and *p,p'*DDT in fish samples by area taken, 1969–70.

Location	Number of samples	Percent as DDE	DDD	DDT
Southern Baja California	8	80.6	8.9	10.5
Sebastian Vizcaino Bay	3	74.2	8.8	17.0
Cortez Bank	4	86.5	4.7	8.8
Southern California coast	6	86.0	5.1	8.9
Farnsworth Bank	6	86.9	5.6	7.5
Santa Monica Bay	8	86.6	5.8	7.6

The high proportions of DDE relative to DDT and DDD seem to be typical of fishes, porpoises, and crustaceans in the ocean off southern California (Tables 4 and 5). In six adult pelicans taken on Anacapa Island in 1969 (Keith et al., 1970), DDE made up 99% of the total DDT found in the fat, and 93% in eggs taken at the same time. Lamont, Bagley, and Reichel (1970) tested 10 pelican eggs from the same place and year and found that DDE constituted 96% of the total.

Stout (1968) gives data for 17 samples representing seven species of marine fishes taken off Washington and Oregon. In these, DDE averaged

TABLE 4.—Percent distribution of total DDT and ratio of DDD to DDT in rockfishes and sablefish from Santa Monica Bay. Major dumping of DDT wastes into sewer system stopped in April 1970. Samples of May 1970 and August 1971 are averages of five separate samples each for fat, liver, and flesh. In each of these 15 samples the ratio of DDE to DDT was greater than one.

Species	Part tested	Total DDT (ppm)	Percent distribution DDE	DDD	DDT	Ratio DDD:DDT
May 1970:						
Sebastes paucispinis	Liver	519.0	86.3	5.6	8.1	0.69:1.00
S. paucispinis	Flesh	11.6	80.6	8.8	10.6	.82
S. miniatus	Liver	162.0	87.0	5.6	7.4	.75
S. miniatus	Flesh	16.0	92.3	trace	7.7	.0?
S. constellatus	Liver	1,026.0	87.7	5.5	6.8	.80
S. constellatus	Flesh	57.2	88.2	5.5	6.3	.86
S. constellatus	Fat	2,588.0	85.0	7.0	8.0	.87
Anoplopoma fimbria	Liver	103.0	87.3	5.8	6.9	.85
A. fimbria	Flesh	23.4	81.2	10.1	8.7	1.15
August 1971:						
S. paucispinis and S. mystinus	Liver	156.0	84.0	10.3	5.7	1.78
A. fimbria	Liver	38.0	84.2	12.9	3.9	4.45
January 1972:						
S. paucispinis	Liver	17.0	78.5	15.5	6.0	2.58
S. paucispinis	Flesh	.20	81.4	12.7	5.9	2.15
S. paucispinis	Fat	115.0	78.8	16.1	5.1	3.15
August 1971:						
Bottom sample	Mud		82.0	72.0	6.0	2.00

TABLE 5.—Distribution of *p,p'*DDE, *p,p'*DDD and *p,p'*DDT in various animals from southern California marine waters. Porpoises found dead on beach north of San Diego, various dates May 1970. Fishes and crustaceans taken in net haul in San Pedro Channel 4 August 1971.

Species	Organ tested	Standard length (mm)	Wet weight (g)	Total DDT (ppm)	Percent as DDE	Percent as DDD	Percent as DDT
Porpoises:							
Lagenorhynchus obliquidens	flesh			84.	92.0	2.3	5.7
Delphinus sp.	flesh			208.	86.5	5.8	7.7
Delphinus sp	flesh			31.	85.0	7.2	7.8
Delphinus sp.	liver			44.	90.7	4.8	4.5
Delphinus sp.	liver			300.	92.0	4.0	4.0
Delphinus sp.	head oil			196.	89.8	2.6	7.6
Delphinus sp.	blubber			497.	88.5	3.4	8.1
Fishes:							
Leuroglossus stilbius	whole	84	5.20	.49	75.9	11.6	12.4
Melanostigma pammelas, eelpout	whole	89	2.40	5.63	87.9	2.7	9.4
Argyropelecus sp., hatchetfish	whole	30	.50	.09	49.5	7.6	42.9
Cyclothone acclinidens	whole	48	.36	2.01	80.7	4.7	14.6
Cyclothone acclinidens	whole	43	.37	.64	76.1	6.9	17.0
Cyclothone acclinidens	whole	47	.39	2.46	83.2	5.9	10.9
Cyclothone acclinidens	whole	38	.18	3.56	89.5	4.5	6.0
Cyclothone acclinidens	whole	34	.15	1.55	84.9	8.5	6.6
Crustaceans:							
Gnathophausia gigas, pelagic mysid	whole		.42	.55	76.7	7.2	16.1
Sergestes sp.	whole		.64	4.38	85.1	6.1	8.8
Sergestes sp.	whole		.38	4.59	82.9	6.1	11.0
Nematoscelis sp., euphausiid	whole		.019	.35	90.3	4.3	5.4
Nematoscelis sp., euphausiid	whole		.043	.26	90.2	3.0	4.9

52% (26–81), DDD 20%, and DDT 28% of total DDT.

Keith and Hunt (1966) list DDT content for samples of mammals, birds, and freshwater fishes taken throughout California. The proportion of DDE tends to be high in categories that include birds of prey and fish eating birds, but varies considerably in their other samples. In their warmwater fish samples and the fish eating birds, white pelican, western grebe, and common egret, DDD is unusually high. This may be because of the former use of DDD as a spray on some California lakes (Murphy and Chandler, 1948; Brydon, 1955; Hunt and Bischoff, 1960).

Following the cessation of DDT dumping into the ocean off Los Angeles in 1970, a change occurred in the DDD:DDT ratios found in fish samples. The five *S. leucopsarus* taken in April 1972 contained 79% DDE, 12% DDD, and 9% DDT. Each of the five specimens contained more DDD than DDT. In the period 1949–70, only 8 out of more than 500 *S. leucopsarus* tested contained more DDD than DDT. The five myctophids taken in April 1972 ranged from 40 to 50 mm SL, indicating that most or all of their growth had taken place since dumping stopped in 1970.

The shift in DDD:DDT ratios also appeared in some other species. The ratios in rockfishes and sablefish, *Anoplopoma fimbria*, taken in Santa Monica Bay in May 1970, indicated that DDT was more abundant than DDD while 15 and 20 mo later the reverse was true (Table 4, Figure 11). The pelagic crustaceans and fish taken in the midwater trawl in August 1971 (Table 5) did not show the increased DDD to DDT ratio as did the bottom fish taken at that time, or the five *S. leucopsarus* taken in April 1972. A mud sample taken in August 1971 (Table 4, Figure 12) about 3 nautical miles from the White Point sewer outfall contained about twice as much DDD as DDT.

The work of Burnett (1971) on DDT residues in the sand crab along coastal California showed that the high ratios of DDD to DDT were a local condition. Twelve samples taken in November 1970 and February 1971 from eight stations on either side of the White Point sewer outfall between 33°22'N and 34°28'N contained more DDD than DDT in all but two samples. The 11 stations north and south of this area all contained less DDD than DDT. The four samples taken closest to the outfall averaged more than three times as much DDD as DDT.

This shift in DDD:DDT ratios was undoubtedly caused by the deposits in the sewer system. CSDLAC cleaning operations started in December 1970, and ended in July 1971. Although large quantities of these deposits were removed directly from the sewers, additional large quantities were moved through the system to the White

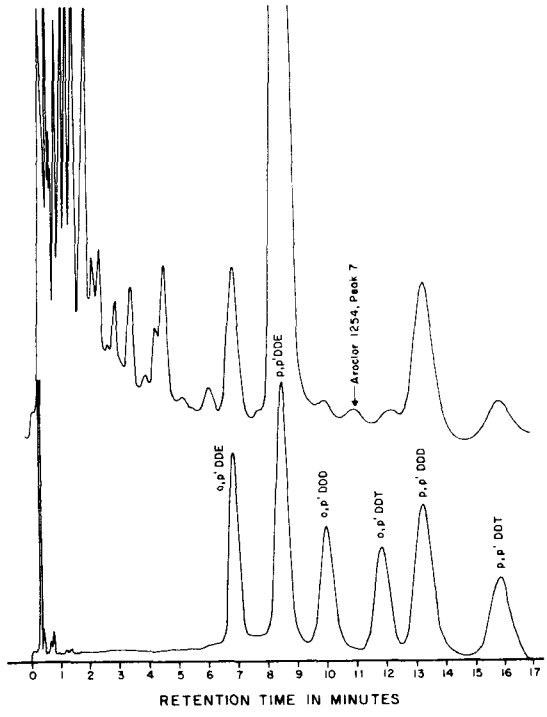


FIGURE 11.—Chromatogram of DDT analog standard and of a fat sample from *Sebastes paucispinis* taken in Santa Monica Bay 7 January 1972. *p,p'*DDE (98 ppm) is off scale. Following cessation of dumping of DDT wastes and flushing out of sewer lines in 1970, *p,p'*DDD (15 ppm) has exceeded *p,p'*DDT (6.1 ppm) in most fish specimens tested. Prior to cessation of dumping and flushing of sewer lines, DDT was almost always present in greater quantities than DDD.

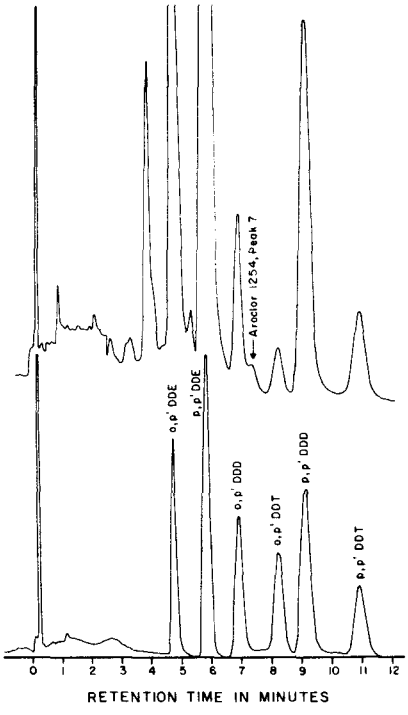


FIGURE 12.—Chromatogram of DDT analog standard and sample of mud from the ocean floor in the Los Angeles area taken in August 1971, 16 mo after most dumping of DDT wastes stopped. DDD greatly exceeds DDT. This may have resulted from the sewer cleaning operations, or it may have been the condition existing before and merely reflect what the biota can excrete more easily. In the *Sebastes* chromatogram (Figure 11), the *o,p'*DDE peak is within the limits of the right proportions to *p,p'*DDE for it to be considered *o,p'*DDE. In the mud sample it is much too high and may be DDMU (a metabolite of DDD) which has the same retention time on this column as *o,p'*DDE.

Point plant and out into the ocean. Sewer water from these deposits contained 48% DDD as opposed to 2–6% in the original Montrose discharges, and although the total amount of DDT and its metabolites was much less than before April 1970, the total amount of DDD entering the ocean appeared to be several times greater than it had been before the dumping stopped in April. This would account for the increase in DDD in the myctophids taken in 1972 rather than the expected decrease indicated by the calculated line (Figure 10, Table 1). A mud sample taken from the ocean floor a few miles from the sewer outfall in July 1971, just after the sewer cleaning operations ceased contained 6%DDT, 82%DDE, and 12%DDD (Figure 12). This compares favorably with the myctophids taken in April 1972, 9:79:12, and the *S. paucispinis* fat samples (Figure 11) taken in January 1972, 5:79:16, and indicates that the fish reflect the values of these analogs in the environment fairly well.

The most noticeable difference between the pesticide metabolites in the fish (Figure 11) and the mud (Figure 12) were the two prominent peaks preceding *p,p'*DDE. The peak at the locus of *o,p'*DDE also may contain DDMU, a metabolite of DDD. The other peak could be a metabolite of Kelthane. However, several dozen additional mud samples tested subsequently did not contain these peaks except for expected amounts of *o,p'*DDE. The mud sample (Figure 12) was run while we were experimenting with methods of determining pesticide content of the mud samples. The subsequent samples were run after we had settled on a different method that gave maximum recovery of DDT, DDD, and DDE without special regard to other CHC. These subsequent mud samples yielded chromatograms almost identical with those of fish and other biological samples from the same general area.

There was also a large decrease between May 1970 and January 1972, in total pesticides in the fish taken in Santa Monica Bay (Table 4). The *S. paucispinis* taken in 1972 were smaller than those taken in 1970 which may account in part for the lower values. The five specimens taken in January 1972, averaged 312 mm total length. Phillips (1964) gives the total length of this species at age 2 as 267 mm and at age 3 as 343 mm. Thus, most of the growth of these specimens had taken place since dumping stopped.

On land where soil has been subjected to DDT spraying for long periods of time, the situation is very different. In New York State vineyard soils (Kuhr, Davis and Taschenberg, 1972) the residues consisted of 73% DDT and 27% DDE after 24 yr of spraying with DDT. In Oregon (Kiigemagi and Terriere, 1972) samples of soil from one orchard contained 80% DDT, 17% DDE, and 3% DDD after 25 yr of spraying, while soil samples from another orchard in a different area contained 78% DDT, 14% DDE, and 8% DDD after 24 yr. Forests in New Brunswick, Canada (Yule, 1973) were sprayed heavily from 1956 to 1967 in which year spraying with DDT ceased. Many samples taken of soils in this area in 1968 contained 92% DDT and 8% DDE. Three years later a second sampling of the soils in the same locality contained 90% DDT and 10% DDE. DDD was present only in trace amounts in both sampling years.

As a general rule soil samples from land areas that have been sprayed with DDT tend to contain a much higher proportion of DDT than DDE or DDD even after many years. This is not necessarily true of the fauna that inhabit the land unless their contamination is the result of recent spraying. Keith and Hunt (1966) give examples of a number of species of mammals and birds in which the proportions of the three analogs vary greatly.

Within some species of birds, which are more wide ranging than mammals, there seems to be remarkable uniformity in the proportions of the three analogs. Martin and Nickerson (1972) tested 125 10-bird samples of starlings from throughout the (48) United States. These samples averaged 91% DDE, 3% DDD, and 6% DDT. Although the total residues ranged from 0.05 to 15 ppm, in only two samples did the amount of DDD exceed DDT, and in only one did the amount of DDT exceed DDE.

The proportions of the three analogs of DDT in the starlings is very similar to the proportions found in the fish taken in Santa Monica Bay in 1970 (Table 4), in the porpoises found dead on the beach in 1970, and the small fishes and invertebrates taken off Los Angeles in the mid-water trawl in 1971 (Table 5). And, in fact, except in cases of recent contamination by DDT, most fauna have tended to approach these proportions in recent years. This is in spite of the fact that soil samples from areas of land that have long histories of spraying with DDT almost without exception contain very high proportions of DDT. From this it would appear that the selective storage, metabolism, and excretion of DDT is somewhat similar for all animals.

When investigators first became aware of the pesticide problem, methods of measuring residues were considerably less refined than they are at present, and few samples were run. Very little work has been done on preserved specimens from these earlier years. But, in view of the similarity in proportions of DDE and DDT in so many different species in recent years, it seems probable that the increase in DDE and the change in ratios of DDE and DDT in *S. leucopsarus* are descriptive of the general change in these analogs that has taken place in the earth's environment.

There was no pattern discernible in the distribution of Aroclor 1254. In 472 myctophid samples taken between 1949 and 1966, the median values of Aroclor 1254 fluctuated around 0.17 ppm and showed no trend with time. Sixty-eight percent of the samples contained less than 0.25 ppm. The only indication of an areal relationship was that while the three stations closest to the White Point sewer outfall, and the city of Los Angeles (CalCOFI stations 87.35, 90.28, and 90.30) constituted only 8% of the total samples, they accounted for 34% (12 out of 35) of the myctophids containing more than 1ppm of Aroclor 1254. However, there were some samples taken 175–200 nautical miles offshore that contained more than 1 ppm, and there were others taken near shore in the Los Angeles area that contained none or traces only. These higher values could result from the myctophids ingesting nondigestible particles of man-made substances either while feeding or accidentally while in the cod end of the plankton net.

In the larger fish taken in the Los Angeles area, the high values of the DDT residues tend to mask the presence of Aroclor 1254. What might be recorded as a trace amount could actually be a rather significant amount in view of the dilute

solutions of sample used in such cases in order to keep the DDT residue recordings on scale.

SUMMARY

1. Between 1949 and 1970, total DDT increased in the ocean off southern California. The major source of this insecticide apparently was wastes discharged into the Los Angeles County sewer system by a major manufacturer of DDT.

2. As measured in the myctophid fish, *Stenobrachius leucopsarus*, *p,p'*DDT and *p,p'*DDD increased for several years until metabolism, excretion, and dispersion equalled input, at which point the content of these CHC stabilized in the fish.

3. The more persistent, less easily metabolized *p,p'*DDE continued to increase in *S. leucopsarus* throughout the time period under study. The amount of *p,p'*DDE decreased with distance from the sewer outfall.

4. During the earlier years the abundance of the other analogs in decreasing order was *p,p'*DDT, *p,p'*DDE, and *p,p'*DDD. During the later period through 1970, the more persistent *p,p'*DDE became more abundant than *p,p'*DDT. Following cessation of dumping, in 1970, *p,p'*DDD became more abundant than *p,p'*DDT in the myctophids and most of the other fish species tested.

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LITERATURE CITED

BRYDON, H. W.
1955. The 1954 control treatment of the Clear Lake gnat *Chaoborus astictopus* D. & S., in Clear Lake, California. Proc. Pap., 23d Annu. Conf. Calif. Mosq. Control Assoc., p. 108–110.

BURNETT, R.
1971. DDT residues: Distribution of concentrations in Emerita analoga (Stimpson) along coastal California. Science (Wash., D.C.) 174:606–608.

BUTLER, P.A.
1969. Pesticides in the sea. *In* F. E. Firth (editor), The encyclopedia of marine resources, p. 513–516. Van Nostrand Reinhold Company, N.Y.

CARRY, C. W., AND J. A. REDNER.
1970. Pesticides and heavy metals. Progress Report, County Sanitation Districts of Los Angeles County, 51 p.

DUKE, T. W., AND A. J. WILSON, JR.
1971. Chlorinated hydrocarbons in livers of fishes from the Northeastern Pacific Ocean. Pestic. Monit. J. 5:228–232.

HUNT, E. G., AND A. I. BISCHOFF.
1960. Inimical effects on wildlife of periodic DDT applications to Clear Lake. Calif. Fish Game 46:91–106.

JEHL, J. R., JR.
1970. Is thirty million years long enough? Pac. Discovery 23(1):16–23.

KEITH, J. O., AND E. G. HUNT.
1966. Levels of insecticide residues in fish and wildlife in California. Trans. 31st North Am. Wildl. Nat. Resour. Conf., p. 150–177.

KEITH, J. O., L. A. WOODS, JR., AND E. G. HUNT.
1970. Reproductive failure in brown pelicans on the Pacific coast. Trans. 35th North Am. Wildl. Nat. Resour. Conf., p. 56–63.

KIIGEMAGI, U., AND L. C. TERRIERE.
1972. Persistence of DDT in orchard soils. Bull. Environ. Contam. Toxicol. 7:348–352.

KUHR, R. J., A. C. DAVIS, AND E. F. TASCHENBERG.
1972. DDT residues in a vineyard soil after 24 years of exposure. Bull. Environ. Contam. Toxicol. 8:329–333.

LAMONT, T. G., G. E. BAGLEY, AND W. L. REICHEL.
1970. Residues of o,p'-DDD and o,p'-DDT in brown pelican eggs and mallard ducks. Bull. Environ. Contam. Toxicol. 5:231–236.

MARTIN, W. E., AND P. R. NICKERSON.
1972. Organochlorine residues in starlings—1970. Pestic. Monit. J. 6:33–40.

MCCLURE, V. E.
1972. Precisely deactivated adsorbents applied to the separation of chlorinated hydrocarbons. J. Chromatogr. 70:168–170.

MENZIE, C. M.
1969. Metabolism of pesticides. U.S. Fish Wildl. Serv., Spec. Sci. Rep. Fish. 127, 487 p.

MORGAN, N. L.
1967. The identification and relative retention times of p,p'-Kelthane and its breakdown product p,p'-Dichlorobenzophenone using GLC. Bull. Environ. Contam. Toxicol. 2:306–313.

MURPHY, G. I., AND H. P. CHANDLER.
1948. The effects of TDE on fish and on the plankton and litoral fauna in lower Blue Lake, Lake County, California. Calif. Fish Game, Inland Fish. Admin. Rep. 48.

O'BRIEN, R. D.
1967. Insecticides. Action and metabolism. Academic Press, N.Y., 332 p.

PHILLIPS, J.B.
1964. Life history studies on ten species of rockfish (genus *Sebastodes*). Calif. Dep. Fish Game, Fish Bull. 126, 70 p.

REDNER, J. A., AND K. PAYNE.
1971. Chlorinated hydrocarbons. Progress Report, County

Sanitation Districts of Los Angeles County, 77 p.

RISEBROUGH, R. W., D. B. MENZEL, D. J. MARTIN, AND H. S. OLCOTT.
1967. DDT residues in Pacific sea birds: A persistent insecticide in marine food chains. Nature (Lond.) 216:589–590.

RISEBROUGH, R. W., P. REICHE, D. B. PEAKALL, S. G. HERMAN, AND M. N. KIRVEN.
1968. Polychlorinated biphenyls in the global ecosystem. Nature (Lond.) 220:1098–1102.

STOUT, V. F.
1968. Pesticide levels in fish of the northeast Pacific. Bull. Environ. Contam. Toxicol. 3:240–246.

WYLLIE, J. G.
1966. Geostrophic flow of the California Current at the surface and at 200 meters. Calif. Coop. Oceanic Fish. Invest., Atlas 4, 288 p.

YULE, W. N.
1973. Intensive studies of DDT residues in forest soil. Bull. Environ. Contam. Toxicol. 9:57–64.