

## DDT AND ITS METABOLITES IN THE SEDIMENTS OFF SOUTHERN CALIFORNIA

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### ABSTRACT

To assess the degree of DDT contamination in the marine sediments off Los Angeles, 103 stations in the Pacific Ocean off southern California were sampled in July and August 1971 for DDT and its metabolites, DDD and DDE. Heavy contamination of bottom sediments in this area was expected because of large amounts of DDT that have entered the ocean through the Los Angeles County sewer system as waste from a DDT manufacturing plant.

From the data acquired, it was estimated that there were about 200 metric tons of DDT, DDD, and DDE in the sediments in an area of 14 square nautical miles near the sewer outfalls and 300 metric tons in the entire 911 square nautical mile area sampled. The heaviest concentrations of total DDT were distributed in the relatively shallow-water area on the Palos Verdes shelf to the northwest of the sewer outfalls in the general direction of the current flow.

Metabolism of DDT was inhibited in deepwater sediments. Ratios of DDE to DDT were low, and DDT was more abundant than DDE at some stations. In sediments from shallow-water stations, DDE exceeded DDT by more than 10 times.

The bottom of the ocean off Los Angeles, Calif., has been very heavily contaminated with the pesticide DDT owing to the discharge of wastes from a DDT manufacturing plant into the Los Angeles County sewer system over a period of about 20 yr ending in 1970 (MacGregor 1974).

The amount of DDT which entered the ocean through the Los Angeles County sewer system was estimated at 250 kg/day. Following the cessation of DDT discharges by the manufacturer, the amount entering the ocean dropped to 45 kg/day in December 1970 and to 11 kg/day in October 1971. Most of these later discharges resulted from sewer cleaning operations which stirred up old deposits of DDT in the sewer lines. The discharges resulting from the cleaning operations were primarily DDD and DDE, metabolites of DDT, while the earlier discharges were primarily DDT.

Because there has been a great deal of speculation about the fate of DDT and other toxic chemicals released into the environment by man (Woodwell et. al. 1971; National Academy of Sciences 1971), this investigation was undertaken to determine the areal distribution and fate of these chemicals in the bottom sediments in the ocean off Los Angeles.

### MATERIALS AND METHODS

The bottom sediments were sampled from a grid of 103 stations between lat. 33°30' and 33°58' N and long. 118°00' and 118°44' W (Figure 1). The stations were designated by four-digit numbers, the first two indicating minutes north

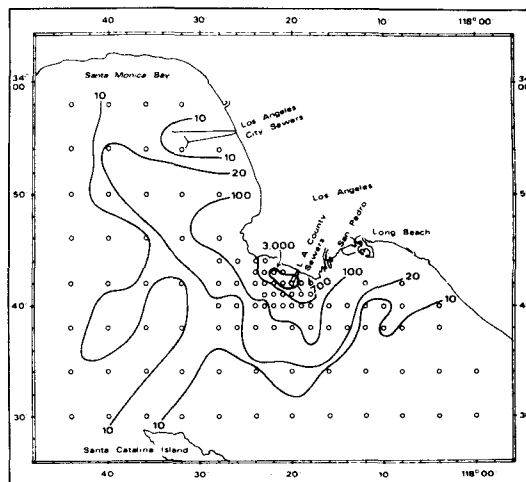


FIGURE 1.—Distribution of total DDT in milligrams per square meter of bottom in the sediments of southern California. Total DDT ranged from 6,600 mg/m<sup>2</sup> of bottom at station 43-22 to 0.12 mg/m<sup>2</sup> at station 30-08.

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of lat. 33°N and the second two indicating minutes west of long. 118°W.

The samples were taken aboard the National Marine Fisheries Service RV *David Starr Jordan* between 26 July and 3 August 1971. The Shipek bottom sampler was used to obtain the samples of sediment. This device obtains a block of material equal to 400 cm<sup>2</sup> of bottom sediment to a depth of about 10 cm, or slightly more, in soft mud or to a depth of half as much or less in coarse sand.

Two samples were taken at each station in order to obtain an estimate of sampling error. The vessel was allowed to drift while the samples were being taken, so the sample pairs were taken in only approximately the same location. However, agreement in the various parameters between samples from the same station was good.

The samples were placed in aluminum foil-lined containers of approximately the same size as the sampling bucket and were quick-frozen. They were stored in a freezer until removed for analysis.

In most samples, DDT was confined to the top 2 or 3 cm of the sediment. At most of the stations where the sampler sampled to 10 cm, and at all of the stations where it sampled to a lesser depth, it appeared that all of the DDT under the 400 cm<sup>2</sup> had been sampled. In this study, therefore, DDT concentrations are given as the weight of DDT per unit area of bottom to a depth of 10 cm. In a few areas of rapid sedimentation, where the sampler sampled to about 10 cm depth, there were still significant amounts of DDT below 10 cm. Estimates for the amounts of DDT below 10 cm are based on core samples taken by other investigators in this area.

The bottom sediment samples were thawed and blended in a 1-gallon Waring<sup>2</sup> commercial blender. Before blending, small stones were removed from the few samples that contained them. Some samples contained a few small molluscs or brittle stars, but these were not removed. Measured amounts of distilled water were added to some of the drier (sandy) samples to facilitate blending.

A sample of 15 to 20 g of blended sediment was weighed onto a watch glass, dried to constant weight, and reweighed to obtain percent water in the sediment. This gave an index of bottom type

ranging from 30 to 40% water for coarse sand to 60 to 70% water for fine silt.

A second sample weighing about 30 g was weighed into a 1-pint Mason jar for DDT determination. About four or five times as much Na<sub>2</sub>SO<sub>4</sub> was weighed into the jar as a drying agent. The sediment and Na<sub>2</sub>SO<sub>4</sub> were mixed using a stainless steel spatula, and the mixture was frozen. A cutting assembly was fitted to the jar, and the frozen mixture was thoroughly blended to a powder using an Osterizer blender.

About 5 g of the powder was weighed into a tared, large disposable pipet (Matheson super pipet) plugged with glass wool. The powder was extracted into a 15-ml graduated centrifuge tube with 5 ml of hexane and 5 ml of acetone. The extract was evaporated to dryness and redissolved in 1 ml of hexane. This sample was eluted through a super pipet filled with activated alumina (McClure 1972) using enough hexane to obtain a 6-ml sample.

This sample was reduced or increased in volume as required and injected into a model 402 Hewlett Packard gas chromatograph (GLC) with a Ni<sup>63</sup> electron capture detector. The 6-foot glass column contained 4% SE-30/6% QF-1 on 100/120 mesh Supelcoport.

There was evidence of a polychlorinated biphenyl, Aroclor 1254, in all samples, but the DDT peaks were so dominant in the chromatograms that they generally obliterated any traces of other chlorinated hydrocarbons within their range. Only the six peaks representing the ortho-para and para-para forms of DDE, DDD, and DDT were quantified. "Total DDT" is used to designate the sum of these six analogs.

## RESULTS AND DISCUSSION

Fifty-five correlations were obtained for 11 parameters to determine various DDT relationships. The 55 correlations were obtained for all 103 stations (Table 1, values above 1.000 correlation diagonal) and for 76 stations leaving out those 27 stations having total DDT readings greater than 100 mg/m<sup>2</sup> (Table 1, values below 1.000 correlation diagonal). For 100 observations a correlation coefficient of 0.254 indicates a probability of 0.01. Logarithms were used for total DDT and distance from outfall, arithmetic values for the other nine measurements.

There is a very high negative correlation between log total DDT and log distance from the

<sup>2</sup>Reference to trade name does not imply endorsement by the National Marine Fisheries Service, NOAA.

TABLE 1.—Correlation coefficients for 11 parameters relating to DDT and its metabolites in bottom sediments off southern California. Values above 1.000 correlation diagonal are for 103 stations. Values below diagonal are for 76 stations leaving out those 27 stations having total DDT readings greater than 100 mg/m<sup>2</sup>. For 100 observations, a correlation coefficient of 0.254 indicates a probability of 0.01.

Parameter	Log total DDT	Log distance from outfall	Depth	Sample weight	% H <sub>2</sub> O in sample	$\rho, \rho'$ DDD $\rho, \rho'$ DDT	$\rho, \rho'$ DDE $\rho, \rho'$ DDT	$\rho, \rho'$ DDE $\rho, \rho'$ DDD	$\rho, \rho'$ DDE $\rho, \rho'$ DDE	$\rho, \rho'$ DDD $\rho, \rho'$ DDD	$\rho, \rho'$ DDT $\rho, \rho'$ DDT
Log total DDT	1.000	-0.871	-0.253	0.221	0.157	0.142	0.144	0.281	-0.040	-0.272	-0.334
Log distance from outfall	-0.604	1.000	0.228	-0.095	-0.147	-0.032	-0.043	-0.238	0.016	0.332	0.334
Depth	0.078	-0.036	1.000	0.643	0.771	-0.443	-0.512	-0.572	0.315	0.168	0.095
Sample weight	0.245	0.041	0.761	1.000	0.743	-0.265	-0.341	-0.332	0.190	0.036	-0.151
% H <sub>2</sub> O in sample	0.095	0.002	0.921	0.756	1.000	-0.315	-0.390	-0.396	0.228	0.019	-0.013
$\rho, \rho'$ DDD/ $\rho, \rho'$ DDT	0.123	0.066	-0.418	-0.268	-0.325	1.000	0.909	0.297	-0.168	-0.194	0.556
$\rho, \rho'$ DDE/ $\rho, \rho'$ DDT	0.100	0.040	-0.492	-0.366	-0.416	0.907	1.000	0.446	-0.208	-0.171	0.463
$\rho, \rho'$ DDE/ $\rho, \rho'$ DDD	0.060	-0.075	-0.535	-0.418	-0.487	0.268	0.408	1.000	-0.289	-0.043	-0.011
$\rho, \rho'$ DDE/ $\rho, \rho'$ DDE	0.190	-0.234	0.296	0.225	0.248	-0.151	-0.196	-0.273	1.000	0.021	0.113
$\rho, \rho'$ DDD/ $\rho, \rho'$ DDD	-0.129	0.275	0.106	0.090	0.059	-0.177	-0.151	0.023	-0.024	1.000	0.130
$\rho, \rho'$ DDT/ $\rho, \rho'$ DDT	-0.154	0.167	0.006	-0.127	0.025	0.630	0.537	0.084	0.068	0.060	1.000

Los Angeles County sewer outfalls ( $r = -0.871$ ). Values ranged from 6,600 mg of total DDT/m<sup>2</sup> of bottom near the sewer outfalls to about 1 mg/m<sup>2</sup> at more distant stations.

The distribution of DDT was modified somewhat by currents which tended to deposit the DDT along the coast and to the northwest more than to the east (Figure 1). The apparent relation between total DDT and depth results from the fact that the sewers discharge into relatively shallow coastal waters and the sludge tends to remain there. The deeper waters are merely farther from the sewer outfalls and the areas along the coast favored by the currents.

McDermott et. al. (1974) took sediment samples from the Palos Verdes shallow-water shelf area in the vicinity of the sewer outfalls only. Their tables A-1 and A-4 give total DDT in parts per million dry weight from gravity core samples taken in 1972. I have contoured their data (Figure 2B) for the top 10 cm of sediment to compare with the 1971 data (Figure 2A) which has been converted to parts per million dry weight. Their 1973 data in their table A-5 represents parts per million dry weight of total DDT in the top 5 cm of Shipek samples taken in the same area (Figure 2C). In each of the 3 yr the patch of sediment representing more than 100 ppm. total DDT tends to retain its integrity fairly well as an oblong area stretching to the northwest of the sewer outfalls. The contours representing 10 to 100 ppm. seem to be expanding somewhat to the northwest and in 1973 to the southeast also.

At the Los Angeles County sewage disposal plant, most of the solids are removed by centrifuging, but the supernatant is pumped into the ocean along with the water from the settling

tanks. This reduces the amount of particulate matter being discharged into the ocean. Nevertheless, quantities of relatively DDT-free particulate matter have been deposited on the Palos Verdes shelf since dumping of DDT into the sewer system was stopped. In time this could cause a change in the DDT profile of the sediments.

On the other hand, most of the shallow inshore areas along this section of coast tend to have sandy bottoms, and the silt bottoms in the vicinity of the sewer outfalls would appear to be unstable artifacts. Storms, tides, and currents could remove or deposit layers of bottom silts in this shallow-water area and further change the DDT profiles.

Based on the paired samples taken in 1971, the variation within a sampling area for one sample would be roughly plus 100% minus 50% at a one standard deviation level. For an average for two samples it would be plus 70% minus 40%. This could account for the differences in the distribution of total DDT for the 3 yr. However, the similarities are much more striking than the differences.

High sample weight and high water content both indicate samples containing more silt, while lower weights and lower water content indicate samples containing more sand. Both of these measurements are related to depth, with the bottom in deep basins tending to be fine silt while shallow areas tend to be sandy. This tendency is masked in shallow-water areas where there are sewer outfalls which deposit large quantities of fine material in the shallower waters. This is indicated by the improvement of the correlation coefficients from 0.643 to 0.761 for sample weight and from 0.771 to 0.921 for percent water with

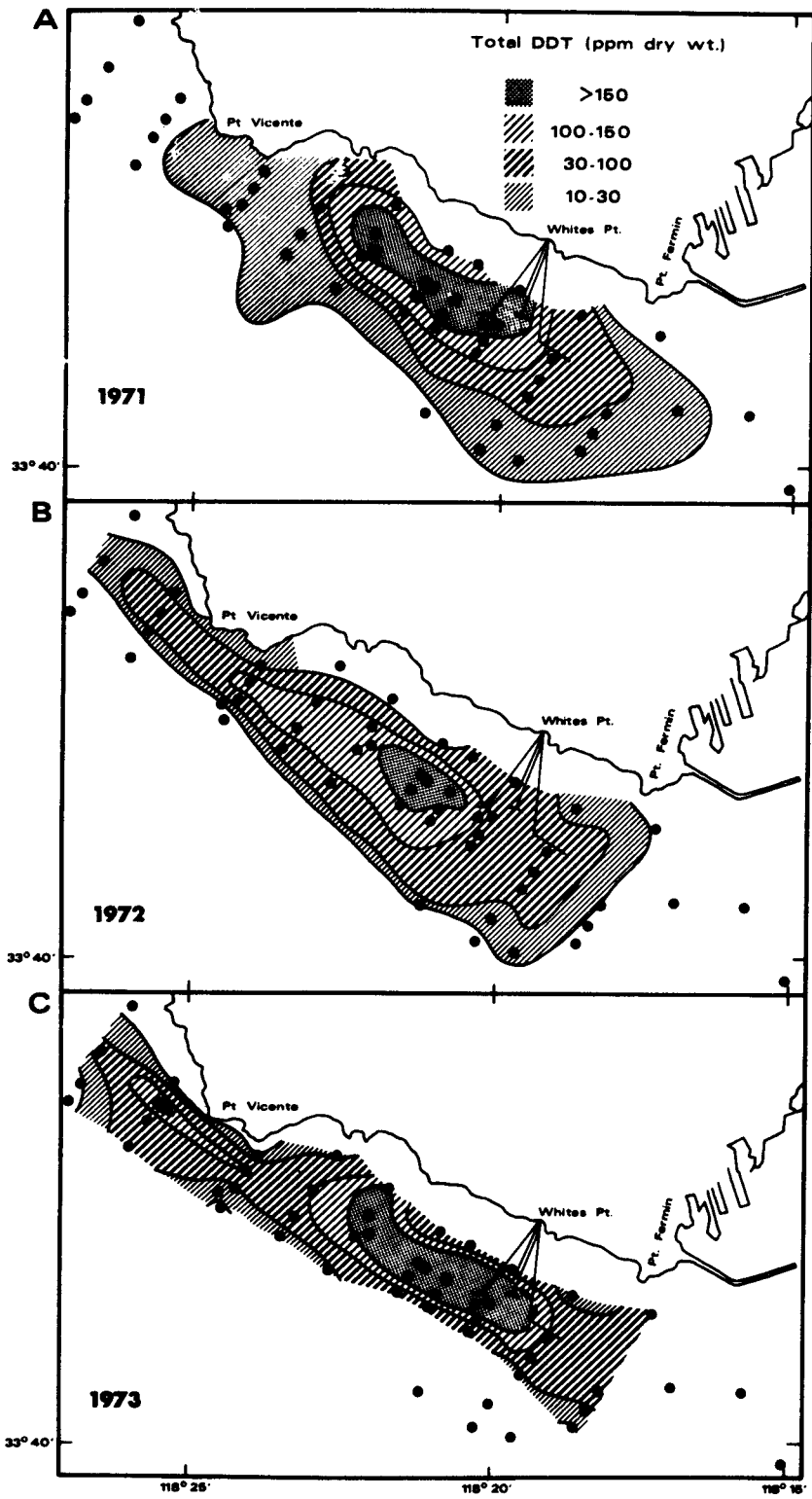


FIGURE 2.—Total DDT (parts per million dry weight) in the bottom sediments off Palos Verdes in the vicinity of the Los Angeles County sewer outfalls. A. Shipek samples (present paper); B. top 10 cm of gravity cores (McDermott et al. 1974); C. top 5 cm of Shipek samples (McDermott et al. 1974).

depth when the 27 stations of heavy sewer deposition in shallower waters are omitted.

The very high correlation coefficient (0.909) between  $p,p'$ DDD/ $p,p'$ DDT and  $p,p'$ DDE/ $p,p'$ DDT shows that when metabolism of DDT to DDD is high, metabolism of DDT to DDE is high also. These high rates of metabolism are negatively correlated with depth. Actually, they are more probably associated with some of the conditions prevailing at depth in the ocean off Los Angeles. The deep areas sampled tend to be anaerobic, and it is probably the lack of oxygen and colder water that determines the low rate of metabolism. The high correlations of the ratios with sample weight and percent water are secondary effects of the correlations of these two factors with depth.

The high negative correlation between  $p,p'$ DDE/ $p,p'$ DDD and depth indicates that metabolism of DDT to DDE is favored over metabolism to DDD in shallower waters. However, the positive correlation of  $p,p'$ DDE/ $p,p'$ DDD with  $p,p'$ DDD/ $p,p'$ DDT (0.297) as well as with  $p,p'$ DDE/ $p,p'$ DDT (0.446) supports the conclusion that metabolism to both metabolites is much greater in shallow aerobic waters than in deep anaerobic waters. Actually, much more DDT is probably metabolized to DDD than to DDE under all circumstances prevailing in the study area, but the DDE is much more persistent than the DDD and accumulates to a greater degree while DDD is further metabolized to DDMU and other metabolites.

There was at least 10 times as much DDE as DDT in the bottom sediments from stations along the coast of the study area, while 10 stations in deeper waters north of Santa Catalina Island had less DDE than DDT in the bottom samples (Figures 3, 4). DDD tended to follow somewhat the same pattern (Figure 5).

At the 10 stations the average total DDT was 19.9 mg/m<sup>2</sup>, of which 60% was DDT, 19% DDD, and 21% DDE. Mean depth was 341 fathoms (623 m) and the total area represented by the 10 stations was 111 sq nautical miles containing an estimated 5.74 metric tons of total DDT.

It appears that most of the pesticide discharged from the Los Angeles County sewer outfalls has been DDT with the exception of the period of sewer cleaning operations in 1970-71 when DDD and DDE predominated (MacGregor 1974). Most of the DDT settles on the bottom close to the outfalls in shallow waters. Once the DDT becomes part of the bottom sediment it tends to stay there

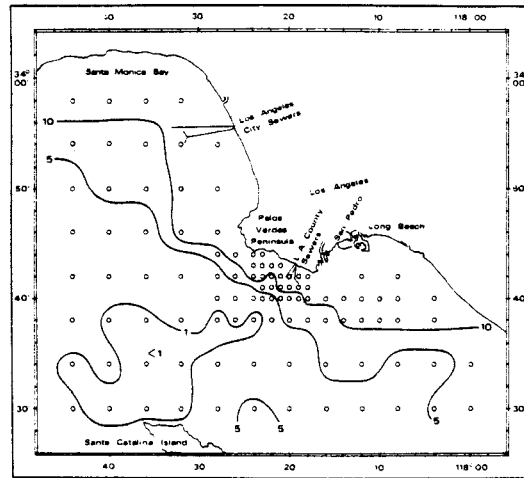


FIGURE 3.—Distribution of ratios of  $p,p'$ DDE to  $p,p'$ DDT. In the shallow waters near shore the ratios exceed 10:1, while in the deeper waters north of Santa Catalina Island the ratios are less than 1:1.

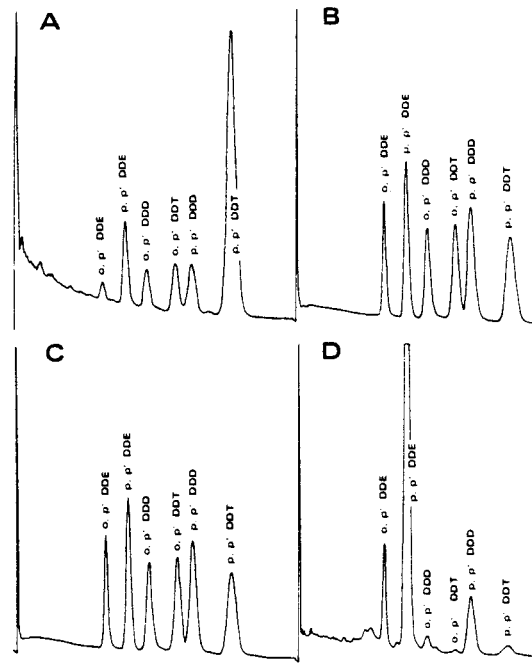


FIGURE 4.—Chromatograms of: A—a deepwater sample (274 m), station 30-40, showing high  $p,p'$ DDT peak, and D—a shallow-water sample (36.5 m), station 40-16, showing a high DDE peak. B and C are standards of the DDT analogs.

and metabolize in place, rapidly in shallower waters and more slowly in deeper waters.

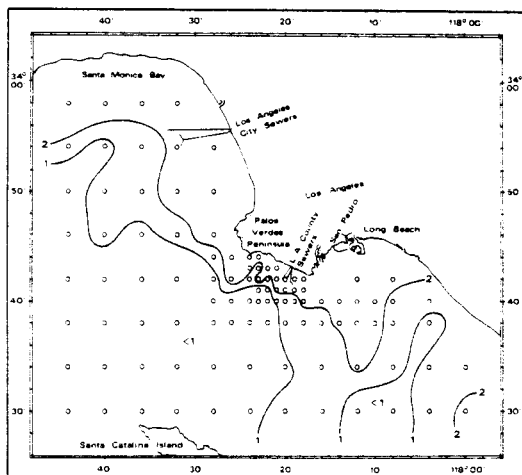


FIGURE 5.—Distribution of ratios of  $p,p'$ DDD to  $p,p'$ DDT. In the shallow nearshore areas the ratios exceed 2:1, while in the deeper waters the ratios are less than 1:1. The higher ratios were probably enhanced by sewer cleaning operations in 1970-71.

The DDT deposits in the deeper waters must have been transported there directly from the sewer outlets before much metabolism could take place. If they had originated from bottom sediments closer to the sewer outfalls and in shallower waters, the DDE content would be much higher. DDE averages about 85% of total DDT in biological material in this area; therefore, most of the total DDT in bottom sediments in the deeper water could not have originated from this source.

For the time series for total DDT accumulation in myctophid fish (MacGregor 1974), DDE was less than DDT from 1949 to 1956, but in the subsequent years DDE became much higher. If the deep water with relatively low DDE had resulted from biological fallout as represented by the myctophids for 22 yr (1949-70), and if there had been no metabolism at depth, the DDE would have been twice as high as the DDT rather than one-third as high.

There is either very little metabolism in deep-water sediments, or there is no metabolism, and the small amounts of DDD and DDE found there are the result of fallout from material metabolized in the better-oxygenated surface and intermediate depths.

In commercial DDT, the ratio of  $p,p'$ DDT to  $o,p'$ DDT is about 4:1 (i.e.,  $o,p'$ DDT is about 25% of  $p,p'$ DDT). The distribution of these latter values for the sediment samples indicate that

$o,p'$ DDT is about what might be expected, while  $o,p'$ DDD is higher and  $o,p'$ DDE is lower (Table 2).

In the case of DDT this may mean that  $o,p'$ DDT metabolizes as readily as  $p,p'$ DDT. The two high positive correlations with the parameters indicating high metabolism,  $p,p'$ DDD/ $p,p'$ DDT and  $p,p'$ DDE/ $p,p'$ DDT, may indicate that  $o,p'$ DDT metabolizes more readily than  $p,p'$ DDT under conditions of low metabolism of DDT to DDD and DDE. Both the ratios of  $o,p'$ DDT to  $p,p'$ DDT and  $o,p'$ DDD to  $p,p'$ DDD tend to be high in the bottom sediments north of Santa Catalina Island and in Santa Monica Bay, while ratios tend to be low just south of Palos Verdes Peninsula and in the sandy shallower waters to the east of this area (Figures 6, 7). The association of greater distance from the sewer outfalls and lower total DDT values with high ratios is undoubtedly fortuitous, although the few very high ratios are associated with very low DDT values and probably result from poorer resulting measurements and interfering substances that are no longer completely dominated by DDT at these very low values.

The ratios of  $o,p'$ DDE to  $p,p'$ DDE are greater than 1.00:1.00 for 19 stations. Unlike the other two ratios these high ratios are associated with depth. They also tend to be concentrated in the deeper waters just off the Palos Verdes shelf where the sewer outfalls are located (Figure 8). These apparent high relative values of  $o,p'$ DDE are probably caused by interfering substances, probably DDMU, a metabolite of DDD, which is not being further metabolized under the conditions prevailing at these stations.

TABLE 2.—Frequency distributions of ortho-para isomer as a percent of para-para isomer of DDT, DDD, and DDE in bottom sediments.

Percent	DDT	DDD	DDE
0.0- 5.0	4	0	1
5.1- 10.0	5	0	2
10.1- 15.0	15	0	11
15.1- 20.0	13	7	20
20.1- 25.0	10	8	19
25.1- 30.0	12	16	10
30.1- 35.0	11	24	6
35.1- 40.0	7	16	3
40.1- 45.0	6	9	3
45.1- 50.0	6	9	3
50.1- 55.0	1	1	3
55.1- 60.0	4	4	0
60.1- 65.0	1	1	1
65.1- 70.0	1	0	0
70.1- 75.0	1	1	0
75.1- 80.0	2	0	0
80.1- 85.0	2	0	0
85.1- 90.0	0	0	1
90.1- 95.0	1	1	1
95.1-100.0	0	2	0
>100	1	4	19

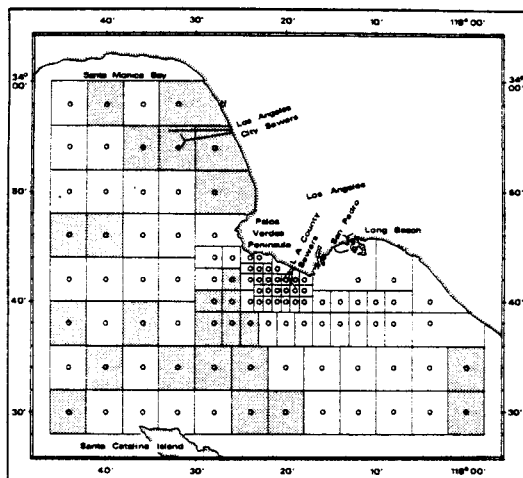


FIGURE 6.—Stations at which the ratio of *o,p'* DDT to *p,p'* DDT was greater than 0.40:1.00.

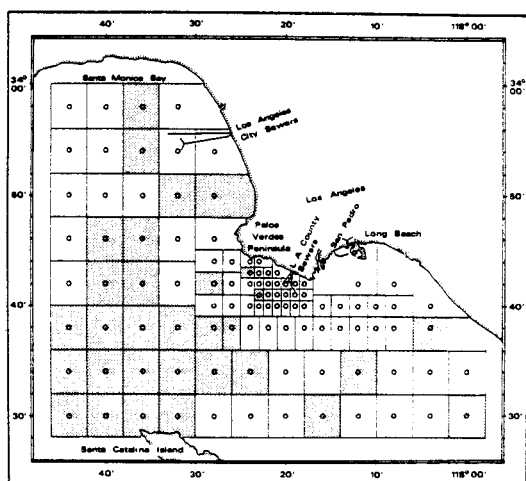


FIGURE 7.—Stations at which the ratio of *o,p'* DDE to *p,p'* DDE was greater than 0.40:1.00.

To estimate the amount of DDT stored in the bottom sediments in the approximately 911 sq nautical miles between long. 117°58' and 118°46'W and lat. 33°18'N and the California coast, represented by the 103 stations, we must assume that each station is representative of its surrounding area. Each pair of samples from each station showed a high correlation for all pairs of parameters. The correlation coefficient for the logarithms of total DDT for paired samples from 94 stations from which two samples were obtained was 0.964 and the standard error of estimate  $\pm 0.321$ .

The Shipek sampler took bottom silts only to a depth of about 10 cm and sandy bottoms or shallow sediment deposits to a lesser depth. At all stations except those where bottom deposition was very rapid, as near sewer outfalls, all DDT in the sediments was sampled. Near the sewer outfalls the sample represents only DDT deposits in the top 10 cm of sediment. The total amount of DDT determined for the 911 sq nautical mile sampling area was 217 metric tons in the top 10 cm of bottom sediment. Of this total, 179 metric tons (82%) was DDE, 22 metric tons (10%) was DDD, and 16 metric tons (8%) was DDT. McDermott and Heesen (1974) found that the total DDT in the top 5 cm of sediment consisted of 86% DDE, 11% DDD, and 3% DDT in the area of the Palos Verdes shelf. These somewhat different percentages may have resulted from further metabolism of DDT without replenishment. In addition, the DDE percentages tend to be higher in this area, and the DDD was increased in 1970-71 because of sewer cleaning operations.

The total DDT ranged from an estimated 0.42 kg per sq nautical mile at station 30-08 representing 13.3 sq nautical miles to 28.6 metric tons per sq nautical mile at station 43-22 representing 1.25 sq nautical miles.

Five stations representing 6.24 sq nautical miles or 0.7% of the 911 sq nautical mile area represented by the 103 stations contained 47.3%

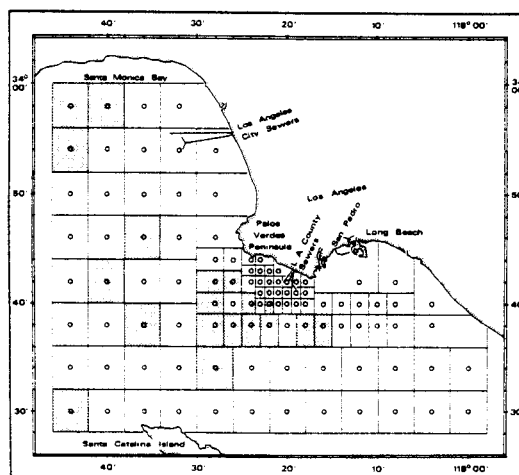


FIGURE 8.—Stations at which the ratio of *o,p'* DDE to *p,p'* DDE was greater than 1.00:1.00. The high apparent *o,p'* DDE values probably were caused by DDMU which has the same retention time as *o,p'* DDE on the column used.

of the total DDT (102.7 metric tons). Sixteen stations representing 18.1 sq nautical miles (2.0% of total area) contained 64.0% (193 metric tons) of the total DDT.

Subsamples taken from the tops and bottoms of the blocks of sediment obtained with the Shipek sampler indicated that most of the pesticide was concentrated in the top strata of the samples except for samples taken in the vicinity of the sewer outfalls where deposition was very rapid. Cores were taken from one sample taken near the sewer outfalls and from a second taken at a greater distance from the outfalls to determine more about vertical distribution of DDT in the sediments (Table 3).

At station 42-36 only *p,p'*DDE was measured because DDT and DDD were not readily measurable in the deeper sediment sections. Half of the DDE was found in the top 2 cm, 81% in the top 4 cm, and 95% in the top 6 cm. At station 42-20, close to the sewer outfall where sewer sediment deposition was heavy, there was very little change in the chlorinated hydrocarbon concentrations at all five depths.

Vance McClure (pers. commun.) has provided me with a plot of the depth distribution of DDT, DDE, DDD, and DDMU found in a box core sample taken about 1 nautical mile west-northwest of the sewer outfall. Subsamples were taken from the core at 3-cm intervals from 0 to 12 cm and at 6-cm intervals from 12 to 36 cm. The pesticide values remained high through 12 cm depth and dropped off rapidly between 12 and 18 cm. DDMU had a deeper distribution than the other three components and increased to a maximum at 9 cm and was still present at 36 cm. DDE was last measured at 24 cm, and DDD and DDT at 18 cm. Excluding DDMU, 72% of the pesticide was found in the column corresponding to the top 10 cm and 28% below that depth. Including DDMU, 67% was in the top 10 cm and 33% below.

If the box core sample is typical of the stations near the sewer undergoing rapid sedimentation, about 30% of the pesticide was missed by sampling only to a depth of 10 cm at these stations. Because these stations near the sewer outfalls contain most of the pesticide, the 217 metric tons of pesticide estimated for the entire area in the top 10 cm could be increased to roughly 300 metric tons as a maximum estimate of total DDT in the area.

In the area of the Palos Verdes shelf only, McDermott and Heesen (1974) estimated that

TABLE 3.—Vertical distribution of DDT in the sediments as determined from core samples taken at stations 42-20 and 42-36.

Core depth (cm)	Stn. 42-20				Stn. 42-36	
	<i>o,p'</i> DDE (ppm.)	<i>p,p'</i> DDE (ppm.)	<i>o,p'</i> DDD (ppm.)	<i>o,p'</i> DDT (ppm.)	Aroclor 1254 (ppm.)	<i>p,p'</i> DDE (ppm.)
0-2	14.6	67.4	10.1	3.1	6.2	0.0233
2-4	19.4	90.7	11.4	3.5	6.0	0.0149
4-6	16.2	84.2	10.1	2.9	4.8	0.0063
6-8	34.8	64.4	13.2	3.5	6.2	0.00180
8-10	34.0	79.1	8.2	2.8	4.8	0.00665

there were 218 tons of total DDT under 62 km<sup>2</sup> of bottom. They calculated that 85% of the total DDT was in the top 12 cm of sediment. If the pesticide is fairly equally distributed in the top 12 cm, about 14% would be in the 10- to 12-cm layer, and the Shipek sampler would sample about 71% of the total DDT.

Sixteen contiguous stations on the Palos Verdes shelf sampled by us in 1971 represented an area of 18.1 sq nautical miles (62.0 km<sup>2</sup>) and a total DDT load of 139 metric tons. If this was only 71% of the total DDT in the area (the load of the top 10 cm only), then the corrected estimate including DDT below 10 cm would be 196 metric tons.

McDermott et al. (1974) using a reduced sampling area of 48 km<sup>2</sup> determined that there were 156 tons of total DDT in their revised sampling area. In this present study the area can be adjusted to 48 km<sup>2</sup> by omitting the effect of 2½ peripheral stations. Estimated total DDT then would be 132 metric tons. However, McDermott et al. (1974, table 5) give estimates of total DDT in the area in 2-cm increments down to a depth of 30 cm of sediments. This table indicates that only about 59% of the total DDT is in the top 10 cm in this area. This would increase my estimate of total DDT to 224 metric tons for the 48 km<sup>2</sup> area.

The available data indicate that there is considerable variation in the depth distribution of total DDT in the sediments on the Palos Verdes shelf. However, the general conclusion that can be drawn from the samples is that there are about 200 metric tons of total DDT in the bottom sediments in the 14 sq nautical mile area (48 km<sup>2</sup>) in the vicinity of the sewer outfalls and another 100 metric tons in the remaining 897 sq nautical miles of the 1971 survey area.

On 27-28 June 1972, 11 mo after the first samples were taken, additional samples were obtained from seven of the original stations. Four of these stations were in deeper water, between 600



and 890 m deep, and 5 to 11 nautical miles from the sewer outfalls. Total DDT remained low in these stations averaging about 30 mg/m<sup>2</sup> of bottom, and the composition was essentially unchanged.

The remaining three stations, in areas of much higher pollution within 1.3 nautical miles of the sewer outfalls and in shallower water, showed some apparent changes in grams per square meter of bottom (Table 4).

TABLE 4.—Changes in composition (in grams per square meter of bottom) at stations 42-21, 43-21, and 42-19 in 11 mo.

Station year	Depth (m)	<i>o,p'</i> DDE DDMU	<i>p,p'</i> DDE	<i>o,p'</i> DDD <i>p,p'</i> DDD	<i>o,p'</i> DDT <i>p,p'</i> DDT	Total DDT
42-21						
1971	119	0.54	3.45	0.53	0.19	4.71
1972		2.09	3.36	0.61	0.23	6.29
43-21						
1971	33	0.46	1.80	0.33	0.14	2.73
1972		0.99	0.80	0.11	0.05	1.95
42-19						
1971	37	0.38	1.78	0.32	0.14	2.62
1972		0.82	0.71	0.16	0.13	1.82
Totals						
1971		1.38	7.03	1.18	0.47	10.06
1972		3.90	4.87	0.88	0.41	10.06

At station 42-21, DDT, DDD, and *p,p'*DDE remained relatively unchanged with a total of 4.2 g/m<sup>2</sup> of bottom in both years, while the *o,p'*DDE-DDMU peak increased by almost four times. At the two shallower stations, 43-21 and 42-19, DDT, DDD, and *p,p'*DDE decreased in 1972 to less than half its value in 1971, while the *o,p'*DDE-DDMU peak more than doubled. These changes could be caused by metabolism, by the addition of sewage deposits that were relatively free of DDT combined with metabolism, or even by the removal of a few centimeters of the deposits in the shallow-water areas without metabolism.

### CONCLUSIONS

Total DDT in the bottom sediments in the ocean off southern California in an area of 911 sq nautical miles was estimated to be between 200 and 300 metric tons. Most of the total DDT was concentrated in a relatively small area with-

in a few miles of the Los Angeles County sewer outfalls.

Total DDT in the top 10 cm of sediment ranged from 6,600 mg/m<sup>2</sup> of bottom near the sewer outfalls to about 1 mg/m<sup>2</sup> of bottom at the more distant stations.

Eighty-two percent of the total DDT was DDE; 10%, DDD; and 8%, DDT. Metabolism of DDT to DDD and DDE was more rapid in shallow waters and apparently very slow or lacking in deep, cold waters that were low in oxygen. Seven samples taken 11 mo later tended to confirm these findings.

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