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## **INPUTS OF DDT AND PCB**

For several years, the Project has conducted an EPA-sponsored study of the routes by which synthetic chlorinated hydrocarbons enter the Southern California Bight. Our work has focused on the pesticides DDT and Dieldrin and two industrially important polychlorinated biphenyls (PCB's), Arochlors 1242 and 1254. We have attempted to quantify the amounts of these substances in municipal and industrial wastewaters, vessel antifouling paints, surface runoff, and aerial fallout; we have also estimated the amounts entering and leaving the Bight via ocean currents.

The study was completed this year, and the results (summarized in Table 1) are discussed here.

### **MUNICIPAL WASTEWATERS**

Municipal wastewater discharge has been the dominant route by which total DDT, Dieldrin, and 1242 and 1254 PCB enter the Bight, particularly in the early years of our study.

Our mass emission estimates for municipal wastewater were usually based on replicate 1-week composites collected from the five major southern California treatment plants during two different seasons of each year. Together, these plants account for approximately 95 percent of the municipal wastewater discharged to the Bight.

Source control and use restrictions appear to have resulted in significant reductions in municipal wastewater discharges of the synthetic organics over the past 3 to 4 years. The greatest decrease was in the amount of DDT residues discharged via Los Angeles County's Joint Water Pollution Control Plant (JWPCP) outfalls off the Palos Verdes Peninsula. Termination of the dominant industrial input to this sewer system in the spring of 1970 resulted in an approximate 95 percent reduction in total DDT emissions between 1971 and 1975. In addition, PCB levels in this effluent have decreased by an order of magnitude since 1972.

### **INDUSTRIAL DISCHARGES INTO HARBORS**

Most of the industrial wastewaters released directly to marine waters of southern California are discharged into San Pedro and San Diego Harbors. The discharges to these

harbors also represent a wide variety of industries; thus, we were able to study a number of different types of industrial effluents by surveying the two harbors. More than 20 discharges into San Pedro Harbor, and approximately 10 discharges into San Diego Harbor, were investigated. To ensure accurate sampling, we enlisted the assistance of the government agencies holding jurisdiction over the various discharge areas to be sampled.

Estimates for overall industrial inputs to the two harbors were obtained by calculating flow-weighted concentrations of detectable chlorinated hydrocarbons in up to six types of effluents. These values were then multiplied by the total flows of each of these classes of industrial wastewaters into the harbors to obtain estimates of annual mass emission rates. Our results have provided no indication of significant discharges of chlorinated hydrocarbons to marine water from the industrial effluents studied.

#### VESSEL ANTIFOULING PAINTS

Polychlorinated biphenyls are reported to have been used extensively as a plasticizer in paints before such use was banned in this country in 1971. In 1973, we surveyed most of the drydock or haulout facilities serving naval, commercial, or recreational vessels in San Pedro and San Diego Harbors, as well as those serving recreational vessels in Newport Harbor and Marina del Rey, the two largest small-craft anchorages in the Bight. Our objective was to obtain a representative picture of antifouling paint usage in southern California. We obtained samples of the approximately 40 brands of antifouling paint most commonly used at these facilities, as well as data on the number of craft in each harbor and the quantities of these paints applied annually.

1242 PCB or 1254 PCB was detected in only 7 of the 28 wet paint samples analyzed; median values for the two substances were 0.3 mg/liter (range: <0.01 to 18 mg/liter) and 0.7 mg/liter (range: 0.02 to 28 mg/liter), respectively. An estimated 300,000 liters of antifouling paint are applied annually to vessels in marinas and harbors of the Bight. By combining these values, we obtained an estimated upper limit of 0.3 kg for PCB annual usage in southern California anchorages. Upper limit values for total DDT were an order of magnitude lower.

Sixteen samples of antifouling paint scrapings collected from drydock facilities were also analyzed. Most of the PCB concentrations measured were less than 20 ppm. However, four samples yielded total PCB concentrations of 270, 3,300, 56,000, and 150,000 ppm, respectively. Furthermore, the two highest concentrations of 1254 PCB that we found in the

dried samples (approximately 5 and 15 percent on a dry weight basis) correspond with an observation by Dr. V. McClure,\* who found that a paint chip collected in a zooplankton trawl in 1970 contained approximately 10 percent PCB.

Our survey revealed that, on the average, the density of antifouling paints used in southern California is about 1.5 dry kg/liter. Therefore, if such paints did contain 10 percent PCB in the past, an application rate of 300,000 liters/year would correspond to a PCB usage of 45,000 kg/yr. Antifouling paints are designed to slough off with time, and an estimated 5 to 10 percent of the old paint removed from vessel bottoms is believed to be carried back to the harbor waters. Thus, although the actual PCB concentrations in paints used in southern California before the ban are not known, and despite the fact that we do not know what fraction of such materials is actually released to the water, these observations point to the possible importance of antifouling paints in the past as a source of PCB to the coastal marine environment.

#### SURFACE RUNOFF

Our surveys of chlorinated hydrocarbon inputs to the Bight via surface runoff revealed that, during 1972-73, the Los Angeles River storm runoff carried an order of magnitude more total DDT and total PCB than that of any other channel. Further, of all the southern California channels, the major channels in the Los Angeles Basin contributed the majority of chlorinated hydrocarbons input in both storm and dry-weather conditions:

	<b>Storm Flow</b>	<b>Dry Weather Flow</b>
Los Angeles Basin Channels		
Total DDT	83%	81%
Total PCB	92-98%	75-84%
	93%	96%

Mass emission rates of chlorinated hydrocarbons for all southern California channels surveyed in Water Year 1972-73 are presented in Table 2. This summary illustrates that, although dry-weather flow constituted almost 20 percent of the total surface runoff volume during the year, it carried only about 2 percent of the total DDT, 7 percent of the Dieldrin, and 3 percent of the 1254 PCB. Thus, it appears that storm runoff is the dominant mode of surface runoff inputs of these synthetic organics to the Bight, and that the Los Angeles Basin is the principal source region.

## AERIAL FALLOUT

It is difficult to determine the amounts of contaminants deposited from the air directly into the ocean's mixed layer because of the problems in positioning samplers at an adequate number of stations throughout the study area. Fortunately, the Southern California Bight contains a number of islands that can serve this purpose. In our study, we used a collection technique developed by Dr. McClure. The technique involves a clean glass plate, which is sprayed with a 5:1 mixture of hexane and mineral oil and exposed to dry fallout for a specified period. The mineral oil is then collected with a teflon scraper and analyzed. Replicate plates 0.1 sq m in area were exposed for about 1 week at an elevation of about 4 meters on structures at thirteen coastal and five island stations between Point Conception and the U.S./Mexico border.

Two 13-week surveys were conducted in summer 1973 and spring 1974. During both surveys, net flux values for total DDT generally ranged between 40 and 200 ng/sq m/day; values for 1254 PCB were usually between 50 and 150 ng/sq m/day. Values at certain coastal stations at the edge of the Los Angeles Basin were higher. As described in last year's annual report, much larger values were measured around a major DDT manufacturing plant and one of its land-fill disposal sites.

During a third survey in fall 1974, values for total DDT were three times higher and 1254 PCB levels were two times higher, on the average, than the summer and spring levels. These results probably reflect the fact that the fall and winter seasons in southern California are characterized by desert winds (Santa Ana conditions), which occur periodically and transport the polluted air of the Basin out over the Bight.

We have used the median net flux value for total DDT and 1254 PCB measured at each sampling site during each of three surveys to calculate the inputs of these substances into the Bight under non-Santa Ana and Santa Ana conditions. We first calculated the inputs into the sectors shown in Figure 1. These sectors comprise an inner and an outer coastal zone, each almost 400 km in length and 50 km in width. (There were few stations in the outer zone; thus the input estimates for this area are considerably less reliable than those for the inner zone.) Table 3 presents monthly mass fallout rates, by sector, for the periods actually sampled. These data were then used to estimate the annual mass fallout rates, by sector, based on different wind conditions. Overall annual input rates of total DDT in non-Santa Ana and Santa Ana conditions are estimated to be 1,200 and 3,800 kg/yr, respectively; the corresponding input rates for 1254 PCB are 1,500 and 2,500 kg/yr, respectively. In

southern California, Santa Ana conditions generally occur about 3 months out of the year. By applying respective weighting factors of 0.25 and 0.75 to the Santa Ana and non-Santa Ana condition values, we obtained estimated annual inputs of 1,800 kg/yr for both total DDT and 1254 PCB to the study area via dry aerial fallout. (Rainfall is so infrequent in this region that its overall effect on fall-out rates is judged to be negligible.)

Our data show that the highest flux and input values for both chlorinated hydrocarbons generally occurred in the sectors off Los Angeles and Orange Counties and centered around the Palos Verdes Peninsula (Sectors F and G, Figure 1.) This portion of the coastal plain of southern California is most affected by air pollution. The 4,500-sq-m area comprising the three sectors between Zuma Beach and Newport Beach (only approximately 10 percent of the 40,000-sq-km study area) received approximately 27 percent of the total DDT input and 20 percent of the measured PCB input. Thus, we find a pattern similar to that for surface runoff: The central basin appears to be the single most important source of DDT and 1254 PCB transported via the atmosphere to the waters of the Bight.

To estimate whether or not there have been any important changes in the aerial input rates of total DDT or 1254 PCB to the Bight over the last 3 years, we conducted a detailed resampling of the Newport Beach site during spring 1976. This station was selected because of the relatively low variability of its summer 1973 and spring 1974 values and because Newport Beach is situated at the southern edge of the Los Angeles/Orange County Basin, just downwind of the major population centers found to be the dominant coastal source of chlorinated hydrocarbons to the atmosphere. Seven pairs of replicate samples were collected; the results, and the values for 1973 and 1974, were:

	Median Fallout Rate, Newport Beach (ng/sq m/day)			Ratio 1976 to 1973
	Summer 1973	Spring 1974	Spring 1976	
Total DDT	214	219	158	0.74
1254 PCB	111	114	97	0.89

This analysis revealed that there has been a statistically significant ( $p < 0.05$ ) decrease in the input of DDT residues to the coastal waters via dry aerial fallout since 1974; however, the rate of decrease at Newport Beach has been relatively low, averaging about 10 percent per year. An even lower annual decrease rate of about 5 percent was

measured for 1254 PCB, and this decrease was not significant ( $p < 0.20$ ).

## CONCLUSIONS

In the past, submarine discharge of municipal wastewater has been the dominant source of chlorinated hydrocarbons such as DDT, Dieldrin, and 1242 and 1254 PCB to the Southern California Bight. Dieldrin inputs have been of only second-order importance compared to those of DDT, and other chlorinated pesticide inputs have been insignificant. PCB contamination of these wastewaters is ubiquitous; in contrast, DDT inputs have been completely dominated by industrial wastes released by a single pesticide manufacture to Los Angeles County's sewer system.

Control of this input to JWPCP in 1970 has reduced the submarine introduction of DDT-contaminated particulates by more than 95 percent since 1971. PCB emissions (mostly 1242) via submarine outfalls have decreased by an order of magnitude since 1972, possibly as a result of the 1971 restriction of PCB usage to closed systems.

Neither direct industrial discharges nor antifouling paints now appear to be significant sources of chlorinated hydrocarbons to the Bight. However, past use of PCB in the paints may have constituted a major input to the marine ecosystem, which the 1971 restriction apparently has now controlled.

Surface runoff has made only second-order contributions of chlorinated hydrocarbons to the Bight, almost all from storm flow. The Los Angeles Basin has been the major source region, constituting approximately 85 to 95 percent of the individual inputs of total DDT, Dieldrin, and total PCB via runoff.

Since 1974, dry aerial fallout has been the dominant route by which total DDT is transferred from southern California to the coastal ecosystem; for 1254 PCB, this situation may have existed even earlier. However, 1242 PCB, a relatively volatile mixture, appears to have occurred at lower levels than 1254 PCB in aerial fallout and recent surface runoff. During 1975, the greatest inputs of 1242 PCB were still being carried via municipal wastewater discharge.

The manufacture of DDT in Los Angeles County, and losses from past landfill deposits of resultant wastes, may be contributing significantly to coastal inputs of this contaminant via aerial fallout. In contrast, PCB inputs to the atmosphere appear to be much more diffuse. Fallout rates of both contaminants in this region are slowly decreasing.

**Table 1. Estimated annual inputs of chlorinated hydrocarbons (kg/yr) to the Southern California Bight via six routes**

Route	Total DDT	Dieldrin	1242PCB	1254
Municipal wastewater				
1971	21,600	-	-	-
1972	6,490	100	≥19,200	≥260
1973	3,920	≤280	≥1,900	1,510
1974	1,580			
1975	1,270			
Industrial discharge, 1973-74	40	10	≤70	30
Antifouling paint, 1973	<1	-	<1	<1
Surface runoff				
1971-72	100	20	100-170	90-110
1972-73	320	65	0-550	250-280
Aerial fallout, 1973-74	1,800	-	-	1,800
Ocean currents, 1973	≤7,000	-	-	≤4,000

**Table 2. Chlorinated hydrocarbon inputs to the Southern California Bight via storm and dry-weather runoff, 1972-73.**

	Storm (kg/yr)	Dry Weather (kg/yr)	Total (kg/yr)	Dry Weather (% of Total)
Volume (10 <sup>6</sup> cu m)	570	130	700	19
Total DDT	310-320	7	320-330	2
Dieldrin	62	5	67	7
1242 PCB	0-520	0-30	0-550	-
1254 PCB	240-270	7-8	250-280	3
Total PCB	240-790	7-38	250-830	1-15

**Table 3. Chlorinated hydrocarbon inputs (kg/mo) to the Southern California Bight via dry aerial fallout, 1973-74.**

Sector*	Non-Santa Ana Conditions				Santa Ana Conditions Oct-Nov 74	
	Jul-Sep 73		Feb-Apr 74		Total DDT	1254 PCB
	Total DDT	1254 PCB	Total DDT	1254 PCB		
A	3.1	4.8	3.2	3.7	8.1	6.0
B	4.7	6.5	6.2	5.7	13	12
C	5.3	7.6	9.2	6.1	25	15
D	7.1	9.2	11	7.2	29	17
E	9.2	7.0	8.3	11	17	13
F	7.0	5.2	6.4	8.3	17	12
G	10	6.8	15	9.2	52	26
H	7.6	8.2	6.4	6.2	34	16
I	5.3	7.0	4.8	4.5	22	12
J	3.7	6.0	5.3	5.7	8.3	9.2
K	2.3	4.3	3.4	4.7	11	9.2
Total, inner sectors	65	73	79	72	240	150
L	18	52	22	53	83	60
Total Outer sectors	18	52	22	53	83	60
TOTAL	83	125	100	125	320	210

\*Sectors are shown on Figure 1.

**Figure 1. Collection stations and sectors used to calculate chlorinated hydrocarbon inputs to the Southern California bight via dry aerial fallout.**

