# Input of Polychlorinated Biphenyls into California Coastal Waters from Urban Sewage Outfalls

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Polychlorinated biphenyls (PCB) are widespread pollutants in the California coastal waters and, among the pollutants identified in marine fish and birds, are second in abundance only to the DDT compound p,p'-DDE(1,2,3). The sources of this PCB are largely unknown, nor are any data available that might indicate the rates of accumulation of these compounds in the coastal environment. Although PCB is isolated from environmental samples with the same techniques used for chlorinated hydrocarbons of insecticide origin (4,5), the existing monitoring programs in the United States do not report PCB, although the national monitoring programs established in Sweden and Great Britain for marine fish include PCB among the pollutants measured (6,7). Since continued accumulation of PCB in the coastal waters would pose a threat to the future utilization of marine food resources in California, it is clearly important to determine the major sources of input of PCB into the sea and to monitor these sources on a routine basis.

PCB was detected in all samples of rainwater obtained over a 12-month study in Great Britain from 7 stations (8). Aerial fallout, therefore, is clearly one source of PCB in the sea although at the present time its relative importance has not been determined. Aliphatic chlorinated hydrocarbons identified in surface waters of the north Atlantic derive from barge dumping of waste products of the vinyl chloride industry (9). PCB therefore might also be introduced to the sea as a component of waste materials dumped from barges. Duke et al. (10) have traced PCB contamination of Escambia Bay, Florida, to an industrial plant on the Escambia River. Two papers from Europe have recently reported the presence of PCB in sewage. Ahling and Jensen (11) found PCB in sewage sludge from Sweden, and Holden (12) estimated that approximately a ton of PCB a year is entering the Clyde estuary in Scotland as a component of crude sewage sludge and that an equivalent amount enters the estuary of the Thames in sewage sludge.

Over a billion gallons of waste water from urban sewage systems in California enter the sea each day (Table 1). Concentrations of mercury in marine organisms have been found to be higher in the vicinity of sewage outfalls (13), and it has been concluded that the source of the majority of the DDT residues in the highly polluted marine environment of southern California is the effluent from the DDT manufacturing factory in Los Angeles (14). This effluent is ultimately discharged into the sea at

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White Point, the outfall of the Los Angeles County Sanitation Districts Joint Water Pollution Control Plant in Harbor City. When we examined samples of this effluent for DDT compounds (14) we also found substantial amounts of PCB, similar in composition to a mixture of the commercial preparations Aroclor 1242 and Aroclor 1254. In this paper we report on the PCB detected in outfalls from 9 sewage treatment plants that discharge waste to the sea in California, including San Francisco Bay.

The more highly chlorinated PCB molecules are very resistant to degradation by fire or microorganisms (15) and because, like the chlorinated hydrocarbons of insecticide origin, they possess a high partition coefficient between water and lipids of marine organisms, a substantial fraction of the PCB entering the sea in sewage can be expected to enter marine food chains. Average PCB concentrations in the lipids of thin-shelled eggs of the Brown Pelicans (Polecanus occidentalis) were 210 ppm in 65 broken eggs from Anacapa and 266 ppm in 28 broken eggs from the Coronados (16), indicating a significant contamination of the marine food chains in southern California with PCB.

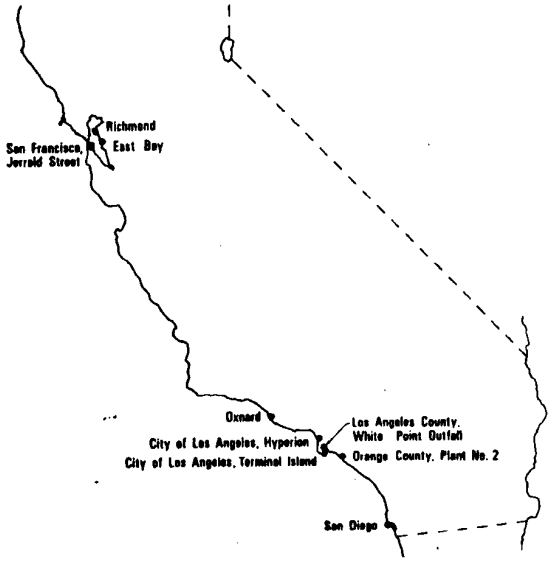


Figure 1. Locations of treatment plants sampled.



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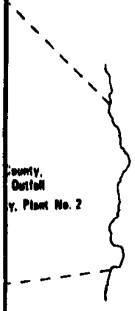

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## Methods of Collection and Analysis

The locations of the nine sewage treatment plants sampled are shown in Figure 1.

1) The City of Richmond Water Pollution Control Plant was sampled at 10 a.m. on December 18, 1970. This plant serves most of Richmond, including one of the most heavily industrialized regions of the Bay Area. The sewage is secondarily treated by the activated sludge method and discharged at the foot of Garrard Avenue into San Francisco Bay. The digested sludge is not released into the bay.

2) The East Bay Municipal Utility District (EBMUD) Water Pollution Control Plant in Oakland was sampled at 10 a.m. on December 16. This plant serves Albany, Berkeley, Emeryville, Oakland, Piedmont and Alameda and discharges primary treated wastewater and digested sludge into San Francisco Bay halfway between the east tollgate and Yerba Buena Island. The flow varies widely during the year depending on the amount of rainwater intrusion into the sewage system during the winter months. We sampled during an interval between two storms.

3) The City of San Francisco Southeast Sewage Treatment Plant was sampled at 12 noon on December 16. This plant serves the industrial area of San Francisco and discharges primary treated wastewater into San Francisco Bay off the Army Street terminal. Since storm and sewer drains are not separated, flow varies greatly from day to day, depending on the rainfall.

4) The City of Oxnard Waste Water Treatment Plant was sampled on December 9 at 11 a.m. It serves the city of Oxnard and discharges primary treated wastewater 6500 ft. offshore into the Pacific Ocean.

5) The City of Los Angeles Hyperion Treatment Plant was sampled on December 10 at 8:30 a.m. This plant has two outfalls; the first discharges combined primary (70%) and secondary (30%) treated wastewater into Santa Monica Bay five miles off Playa Del Rey and the second discharges digested sludge (diluted to 1% solids) seven miles offshore. Most of the sewage is from domestic sources.

6) The Joint County Sanitation Districts of Los Angeles County Water Pollution Control Plant was sampled at 3 p.m. on November 9 at the White Point outfall. This plant serves that part of the County of Los Angeles excluding the City of Los Angeles, Pomona, and cities to the north, but including Long Beach, Torrance, and other heavily industrialized areas. This plant discharges primary treated wastewater and digested sewage into the Pacific Ocean five miles off the Palos Verdes Peninsula at White Point.

7) The City of Los Angeles Terminal Island Treatment Plant



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was sampled at 1 p.m. on December 10. This plant serves the Wilmington and Terminal Island areas, processing mostly industrial waste. It discharges primary treated wastewater and digested sludge into the Pacific Ocean 200 feet off Terminal Island.

8) The County Sanitation Districts of Orange County Treatment Plant No. 2 was sampled at 3 p.m. on December 10; this district serves most of Orange County. The wastes from Plant No. 1 are pumped to this plant, where the two wastewaters are combined, chlorinated and discharged 7000 ft. offshore into the Pacific Ocean. The effluent sampled was mostly primary treated wastewater (15 million gallons a day receives secondary treatment) with some digested sludge overflow.

9) The City of San Diego Point Loma Waste Water Treatment Plant was sampled at 9 a.m. on December 11. This plant serves the City of San Diego and surrounding communities. It discharges primary treated wastewater into the Pacific Ocean 11,450 ft. off Point Loma.

All samples were taken from sewage outfalls at sites closest to the points of entry into the sea. All were one-liter grab samples collected in one-gallon glass jugs purchased from the California Glass Corp., 2098 Oakdale Ave., San Francisco. Prior to departure from Berkeley, the sample bottles were tested for possible contamination by substances that would subsequently interfere with the analyses. 100 ml of Nanograde hexane (Mallinckrodt Chemical Co.) were placed in the bottles, which were shaken vigorously; the hexane was then concentrated to about 10 ml, and 10 microliter aliquots were injected into the gas chromatograph. No peaks were present on the chromatograms that would have interfered with the determination of either PCB or any of the DDT compounds.

Immediately after the samples were taken, 75 ml of a 15% solution of ethyl ether in hexane was added to the glass jugs, and the jugs were shaken vigorously for two minutes. Degradation through microbial action was thereby arrested and chlorinated hydrocarbons were concentrated in the organic solvent fraction rather than absorbing to glass. Composite collecting equipment used for continuous sampling of sewage effluents for pollutants may contain plastic tubing (either nalgene or tygon), and glass, which can be expected to absorb a considerable fraction of the chlorinated hydrocarbons present in the original samples. The plastic could contribute substances that interfere with the determination of the polychlorinated biphenyls. We consider the instantaneous extraction procedure which we have employed superior to the techniques which permit samples to remain a day or even a week without treatment.

Upon return to the laboratory, each sample was drained into a 2000 ml separatory funnel, the solvent being permitted to separate from the aqueous layer. The aqueous layer was drawn into a second separatory funnel and the extraction process



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repeated. The 75 ml of 15% ethyl ether in hexane used for this extraction was first poured into the collecting jug for a second rinse. The organic solvents were combined and passed through 3 in. of anhydrous sodium sulfate (tested first for purity from interfering substances) topped by a layer of cotton (refluxed with acetone in a soxhlot apparatus until free of interfering substances). This was followed by two rinses with small volumes of hexane. The extract was concentrated with a rotary evaporator to about 15-20 ml. The concentrated extract was passed through 4 in. of florisil (14 g) topped by 3/4 in. of anhydrous sodium sulfate. The column had been washed with 75 ml of hexane. PCB and DDT compounds were eluted with 200 ml 0.9% anesthetic (Squibb) ethyl ether in hexane.

Aliquots of concentrated extracts were injected into a Microtek 220 gas chromatograph equipped with a nickel-63 electron capture detector. A 3% QF-1 column on Chromosorb W, 80-100 mesh, acid-washed and DMCS treated, was used. Nitrogen was used as a carrier and purge gas. Flow through the column was 95 ml/min., and flow through the purge was 45 ml/min. Column temperature was 190°, injection port temperature was 230°, and detector temperature was 250°.

Several extracts were given additional cleanup through fuming sulfuric-acid-celite columns (17) or by saponification. The latter consisted of refluxing (for 1/2 hr.) a portion of the concentrated extract in hexane in 95 ml of 95% ethyl alcohol to which 5 g potassium hydroxide, dissolved in a minimum amount of water, had been added. Several of the extracts contained materials that produced peaks that emerged early and disappeared with saponification. They are believed to be sulfur (11).

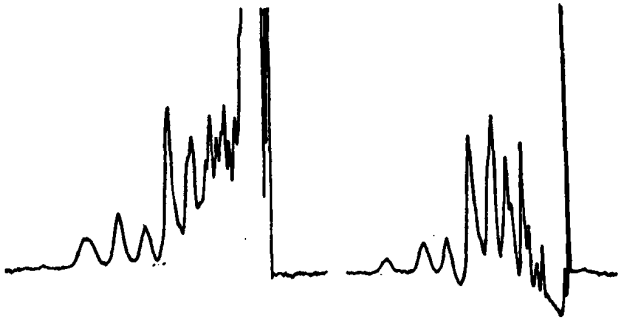


Figure 2.



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Most of the DDT values obtained consisted of maximum values of the predominate compound p,p'-DDE, since peaks with retention times similar to that of DDE were present in many extracts. Identification of p,p'-DDD and o,p'-DDD in the White Point effluent was confirmed by saponification, which converted these compounds to their respective olefin derivatives (14).

PCB was identified by the presence of profiles on chromatograms identical to those of one of the commercial PCB preparations. Thus, the chromatogram of Hyperion sludge is virtually identical to that of Aroclor 1254 (Figure 2). Other chromatograms were identical, except for minor peaks, to chromatograms of Aroclor 1242, mixtures of Aroclor 1242 and 1254, or of Aroclor 1260. PCB was quantified by direct comparison with standard preparations of these commercial mixtures. The profile of PCB peaks was unchanged by either saponification or passage through the acid-celite column.

## Results and Discussion

The results are presented in Table 1.

At all stations except Oxnard and White Point, p,p'-DDE was the only DDT compound detected. Oxnard samples, which received primary treatment only, contained also p,p'-DDT and p,p'-DDD. The amount of DDT discharged at the White Point effluent, which includes the effluent of the Montrose Chemical Company, the largest DDT manufacturer in the United States, was several orders of magnitude higher than the amounts in other outfalls, including Hyperion, which receives wastes from the City of Los Angeles. Moreover, 14% of the DDT residues in the White Point effluent consisted of ortho-para isomers. These are rare in the environment, but constitute in the order of 15-20% of the manufactured technical product. Therefore, the DDT residues in the White Point outfall did not consist of DDT residues that had circulated through the environment.

Daily outputs of PCB in the order of two kilograms are equivalent to a ton per year. Because of the low solubility of these compounds in water and their high affinity for lipids, a large fraction of the PCB can be expected to pass into marine food chains. The highest output was recorded from Los Angeles County, one of the most industrialized areas of the state. Unfortunately, we were refused permission to collect additional samples at this outfall on December 11, 1970.

Our limited number of samples does not permit more than a rough estimate of total PCB input into the sea from municipal sewage. The results indicate, however, that urban sewage effluent is a significant source of the PCB in the coastal waters and that input should be monitored on a periodic basis.



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Table 1. PCB and DDT compounds in urban sewage outfalls in California

| Sampling Station Flow(mgd)[1] | Sample No. | PCB type | Parts per billion PCB | Parts per billion DDT[3] | Est. Kg/day[2] PCB | Est. Kg/day[2] DDT |
|---|---|---|---|---|---|---|
| Richmond | 1 | ND | --- | 0.040 | --- | 0.005 |
| | 2 | ND | --- | 0.071 | | |
| 21.5 | 3 | ND | --- | 0.068 | | |
| | 4 | ND | --- | 0.063 | | |
| EBMUD | 1 | 1260 | 3.8 | 0.041 | 2.0 | 0.020 |
| | 2 | 1260 | 3.2 | 0.036 | | |
| 155 | 3 | 1260 | 3.6 | 0.041 | | |
| | 4 | 1260 | 3.1 | 0.024 | | |
| San Francisco | 1 | 1260 | 3.8 | 0.020 | 0.6 | 0.003 |
| 31.5 | 2 | 1260 | 5.8 | 0.033 | | |
| Oxnard | 1 | ND | --- | 0.098 | --- | 0.006 |
| 10.0 | 2 | ND | --- | 0.15 | | |
| Hyperion waste | 1 | 1254 | 0.16 | 0.023 | 0.4 | 0.05 |
| water, 340 | 2 | 1254 | 0.37 | 0.057 | | |
| Hyperion sludge | 1 | 1254 | 92.1 | ND | 1.6 | --- |
| 5.0 | 2 | 1254 | 78.5 | ND | | |
| White Point | 1 | Mixt- | 76[4] | 68.1 | 100 | 97 |
| | 2 | ure, | | 96.7 | | |
| 350 | 3 | 1242, | | 67.9 | | |
| | 4 | 1254 | | 58.6 | | |
| Terminal Island | 1 | 1242 | 12.8 | 0.098 | 0.35 | 0.002 |
| 9.3 | 2 | 1242 | 5.8 | 0.029 | | |
| Orange County | 1 | 1242 | 0.21 | 0.071 | 0.18 | 0.030 |
| 130 | 2 | 1242 | 0.64 | 0.058 | | |
| | 3[5] | 1242 | 0.23 | 0.093 | | |
| San Diego | 1 | ND | --- | 0.087 | --- | 0.022 |
| 80 | 2 | ND | --- | 0.055 | | |

1) millions of gallons per day, on day of collection. Information supplied by plant personnel.
2) based on average concentrations
3) includes: p,p'-DDE; p,p'-DDD; p,p'-DDT; o,p'-DDD; o,p'-DDE
4) concentration in pooled samples
5) chlorinated sample



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