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DEPOSITION OF DDE AND POLYCHLORINATED
BIPHENYLS IN DATED SEDIMENTS
OF THE SANTA BARBARA BASIN

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Deposition of DDE and Polychlorinated Biphenyls in Dated Sediments of the Santa Barbara Basin

Abstract. Analysis of dated oceanic sediments from the Santa Barbara Basin of the Southern California Bight has shown that deposition of polychlorinated biphenyls (PCB) began about 1945 and that DDE [1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene] first appeared in sediments deposited about 1952. Concentrations of both show a progressive increase through 1967; estimated deposition rates (in grams per square meter per year) in 1967 of DDE and PCB were 1.9×10^{-4} and 1.2×10^{-4} , respectively.

Examination of dated marine sediments deposited in basins of the southern California coastal zone has shown that the present flux of both lead and mercury into the sediments exceeds that of the 19th century. In the Santa Barbara Basin, west of Santa Barbara and southeast of Point Conception, the anthropogenic lead flux is estimated to be twice that deriving from natural sources. The increase of the mercury flux into the Santa Barbara Basin began about 1900; the present anthropogenic input is estimated to be equivalent to the natural input (1). Both lead and mercury are rapidly precipitated into sediments upon entry to the marine environment from rivers or waste-water outfalls (2, 3). In oceanic areas remote from these outfalls, a significant but as yet undetermined fraction of the flux into the basin sediments is assumed to derive from aerial fallout (1, 4).

We report here on the deposition of two groups of synthetic organochlorines in the sediments of the Santa Barbara Basin. Both the DDT (5) compounds, principally *p,p'*-DDE (5), and the polychlorinated biphenyls (PCB) have become significant components of the marine food webs of southern California. It has been found that DDE frequently constitutes more than 0.1 percent of the fat of fish-eating birds such as the brown pelican (*Pelecanus occidentalis*) and of sea lions (*Zalophus californianus*).

Both DDE and PCB are associated with a high incidence of premature births among these sea lions, and DDE accounts for most if not all of the increased variance in the calcium carbonate content of the thin shells of eggs of the fish-eating birds (6). The high concentrations of both DDE and PCB encountered in these and other marine ecosystems suggest that the rates of degradation in the marine environment are slow; however, deposition in the sediments provides a pathway for the removal of these pollutants from the marine biomass and for the

reduction in their residues as input decreases.

The varved anaerobic sediments of the Santa Barbara Basin present an opportunity to determine the rate of deposition of these chlorinated hydrocarbons in the sediments within an absolute time framework. The laminations observed in the sediment are a direct response to the seasonal rainfall of the southern California region. The low oxygen content of the bottom waters of the basin excludes burrowing organisms and permits the preservation of the fine sediment structure. The accuracy of the overall time framework derived by the counting of the varves has been confirmed by the correspondence of rainfall and sedimentation patterns (7) and by ^{210}Pb and $^{228}\text{Th}/^{232}\text{Th}$ radiometric age measurements (8, 9).

Core 265 (32°12'N; 120°02'W, 595 m) was selected for the chlorinated hydrocarbon study. It was obtained with a box corer, designed to operate with the ship's wire slackened and to penetrate slowly into the sediment. The closing arms of the corer were directly attached to the collecting box, allowing a tight seal and minimizing disturbance during recovery and handling. Upon retrieval, the box and core were quickly frozen and placed in cold storage. Later the frozen core was extruded and cut into longitudinal slabs from which x-radiographs were obtained. These radiographs were used to construct varve pattern templates which allowed the sectioning of the frozen slabs into bulk subsamples representative of a specific set of years. The slab analyzed was cut from the central part of the core and sectioned, and subsamples were stored in glass jars, sealed with aluminum foil, both of which had been thoroughly washed with acetone known to be free of contaminating substances.

The frozen samples were further chilled with liquid nitrogen and freeze-dried with a VirTis lyophilizer over a minimum period of 12 hours. A subsample of approximately 2.5 g was Soxhlet-extracted with 500 ml of Nano-grade (Mallinkrodt) hexane for 14

Table 1. Organochlorine concentrations [parts per billion (ppb) of the dry weight] in dated sediments.

Year	Dry weight analyzed (g)	<i>p,p'</i> -DDE (ppb)	<i>p,p'</i> -DDD (ppb)	PCB (dry weight analyzed) (ppb)
1890	2.61	≤2.5	≤1	
1905	2.72	≤2	≤1	
1917	2.54	≤4	≤2	
		Group A		
1925	2.33	≤10	≤2.9	
1927	2.61	≤10	≤5.0	≤29 (7.52 g)
1930	2.59	≤21	≤5.3	
		Group B		
1932	2.55	≤2.6	≤3.8	
1935	2.67	≤2.5	≤4.8	≤21 (7.86 g)
1937	2.64	≤1.0	≤4.4	
		Group C		
1940	2.61	≤3.7	< 1.0	
1942	2.58	≤3.5	< 1.0	≤31 (7.85 g)
1945	2.66	≤6	< 1.0	
		Group D		
1947	2.35	≤4	≤2.0	
1950	2.69	≤4	≤3.9	49 (7.75 g)
1952	2.71	≤5	≤6.5	
		Group E		
1955	2.55	24	11.9	
1957	2.62	36	9.0	66 (7.90 g)
1960	2.72	47	7.0	
		Group F		
1962	2.65	52	7.5	
1965	2.69	128	11.3	103 (7.05 g)
1967	1.72	160	18.4	

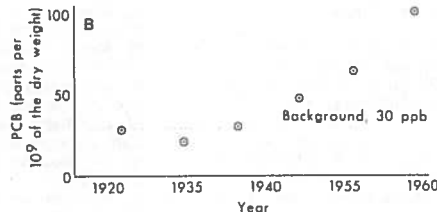
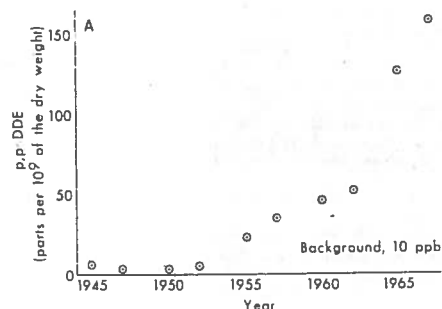


Fig. 1. Deposition of (A) DDE and (B) PCB in dated sediments of the Santa Barbara Basin.

hours. A 10.2-cm column of Florisil (14 g), incubated at 700°C for 5 hours to remove compounds producing interfering peaks, topped by 2.5 cm of anhydrous sodium sulfate, was used for cleanup. Chlorinated hydrocarbons were eluted with 200 ml of 6 percent diethyl ether (Nanograde) in *n*-hexane. Volumes were reduced to 10 ml or less with a three-ball Snyder column for analysis by gas-liquid chromatography. Blanks consisting of 500 ml of *n*-hexane were refluxed in the Soxhlet apparatus for a minimum of 14 hours and then carried through all subsequent steps. These contained less than the equivalent of 5 parts per billion (ppb) of DDE and 30 ppb of PCB in a 2.5-g sample. Concentrations of 10 ppb of DDE and 30 ppb of PCB were assumed to represent the background within the analytical procedure. Since PCB has a lower electron-capture response than an equivalent mass of DDE, samples were combined after analysis for the DDT compounds to determine PCB concentrations, according to the groupings in Table 1.

The profile of the PCB peaks resembled that of Aroclor 1254, which was used as a reference standard. Identification of *p,p'*-DDD (5) was confirmed on the basis of the disappearance of the peak with saponification (10) and the appearance of a peak with the characteristic retention time of the ethylene derivative, *p,p'*-DDMU (5).

The results of the analyses are presented in Table 1 and in Fig. 1. Conversion of these concentrations, which are expressed on a dry weight basis, to an aluminum basis to correct for the salt content in the interstitial water of surface sediments shows no deviation from the curves depicted in Fig. 1. The deposition of PCB began about 1945, following the rapid increase in PCB use during World War II as electrical insulating fluids, as paint additives, and in a variety of miscellaneous applications which result in the release

of these compounds to the environment (11). Measurable amounts of DDE appear only in the sediments deposited after 1952. We attribute the higher DDE concentrations in the 1930 sample to spurious contamination during collection, storage, or analysis. Neither DDE nor PCB shows any suggestion of a leveling off in the rate of deposition up through 1967.

Koide *et al.* (8) estimate from ^{210}Pb dating a deposition rate of 0.39 cm/year, in agreement with the stratigraphic estimates of 0.4 cm/year. The mass of dry sediment per cubic centimeter of deposition was determined to be 0.3 g. The 1967 DDE concentrations of 160 ppb is therefore equivalent to a deposition rate of (160×10^{-9}) times $(0.3 \text{ g per cubic centimeter of deposit})$ times (0.39 cm/year) times $(10^4 \text{ cm}^2/\text{m}^2) = 1.9 \times 10^{-4} \text{ g m}^{-2} \text{ year}^{-1}$. The rate of PCB deposition during the same time interval is $1.2 \times 10^{-4} \text{ g m}^{-2} \text{ year}^{-1}$. These figures may be assumed to be minimum estimates of the fluxes of these compounds into the overlying waters. The flux of *p,p'*-DDE + *p,p'*-DDD, both of which may derive from *p,p'*-DDT, is approximately twice the atmospheric fallout rate of the DDT compounds in precipitation over Britain during the period from August 1966 to July 1967 (12). The mean concentration of DDT compounds (*p,p'*-DDE + *p,p'*-DDT + *p,p'*-DDD) in rainfall at seven collecting stations in Britain of 80 parts per 10^{12} , assuming an annual rainfall of 100 cm, is equivalent to a deposition of $8 \times 10^{-5} \text{ g m}^{-2} \text{ year}^{-1}$. From global production figures it is known that this value must be considered a maximum estimate of the flux of DDT compounds into oceanic systems from the atmosphere (13). Local sources for most of the DDT compounds in the Santa Barbara Basin are therefore suggested.

The measured deposition rate of DDT compounds in 1967, if typical of

other areas in the Southern California Bight, would represent a total deposition of 10 metric tons per year over an area 200 km by 200 km. This figure greatly exceeds the estimate of 2 metric tons of DDT compounds entering San Francisco Bay from the drainage waters of the principal agricultural areas of California in 1967 (14). The estimated yearly input of DDT compounds from the atmosphere into the Southern California Bight in 1971–1972, after cessation of most DDT use in California, was 2 metric tons (3). The rates of atmospheric fallout during the mid-1960's, when local use of DDT was extensive, may have been several times higher.

Substantially higher concentrations of DDT compounds are present in sediments adjacent to the outfall of the Los Angeles County Sanitation Districts' municipal waste-water treatment plant (3). Input to the sea from that source in 1971 amounted to 19 metric tons (3). A subsurface current, moving northward from the Los Angeles area at a depth of approximately 200 m through the Channel Islands (15), might therefore also be a source of the DDT compounds in the Santa Barbara Basin sediments.

The annual inputs of PCB into the Southern California Bight from waste-water outfalls and from surface runoff in 1970–1971 have been estimated to be 10 and 0.25 metric tons, respectively. Waste-water treatment plants in the Los Angeles–Orange County Basin provided most of this PCB (3).

The high rate of local input of both DDT and PCB compounds into the waters of the Southern California Bight precludes extrapolation to other oceanic areas. Some recycling of chlorinated hydrocarbons from sediments into bottom-feeding organisms can be expected (16), but the concentrations reported in the Santa Barbara Basin suggest that a substantial portion of the chlorinated hydrocarbons entering the sea from diverse sources is being deposited in the sediments.

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