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}Th/^{232}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 Nanograde (Mallinkrodt) hexane for 14

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

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

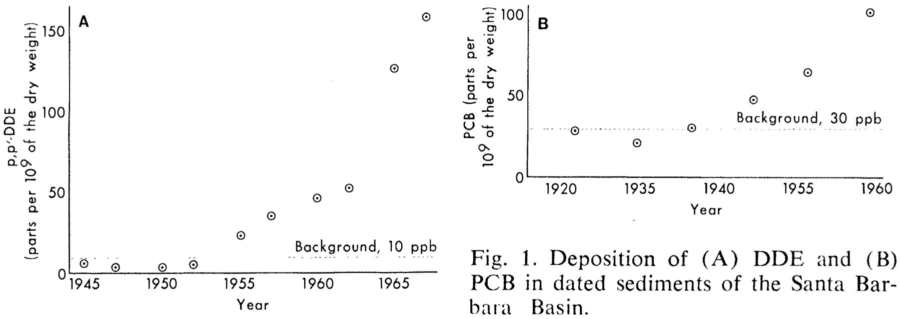

Fig. 1. Deposition of (A) DDE and (B) PCB in dated sediments of the Santa Barbara Basin.

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 g per cubic centimeter of deposit) times (0.39 cm/year) times $(10^4\ \mathrm{cm^2/m^2}) = 1.9 \times 10^{-4}\ \mathrm{g\ m^{-2}\ year^{-1}}$. The rate of PCB deposition during the same time interval is $1.2 \times 10^{-4}\ \mathrm{g\ m^{-2}\ year^{-1}}$. 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 $8 \times 10^{-5}\ \mathrm{g\ m^{-2}\ year^{-1}}$. 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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5. Abbreviations: DDT, 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane; *p,p′*-DDE, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene; *p,p′*-DDD, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; *p,p′*-DDMU, 1-chloro-2,2-bis(*p*-chlorophenyl)ethylene.
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Curvature Detectors in Human Vision?

McCollough (*1*) showed that a striking aftereffect was produced by adaptation for several minutes to a vertical grating of black and orange stripes alternating with a horizontal grating of black and blue stripes. Black and white test gratings with retinal orientations similar to those of the adapting patterns were tinged with colors opposite to the adapting colors. She ascribed these effects to "color adaptation of orientation-specific edge-detectors."

Riggs (*2*) has observed similar effects with patterns of curved lines. Fig. 1, A and B, shows his stimuli. The observer views lines that are concave up in green light and lines that are concave down in red light, always keeping his gaze near the center of each pattern (Fig. 1A). The test pattern (Fig. 1B) then appears pink on concave-up lines and green on concave-down lines. Adaptation to weakly curved lines produces aftereffects that are most vivid on patterns with sharper curvature. Riggs postulates curvature detectors, which prefer strong curvature.

McCollough's simpler idea (the oriented-line hypothesis) can explain these effects. While looking at the center of the adapting patterns, the retina to the right of gaze is exposed to green lines of positive slope and red lines of negative slope; the retina to the left of gaze is adapted to the opposite condition. The McCollough effect is, in fact, specific to retinal locus (*3, 4*). Now, with gaze at the center of the test pattern (Fig. 1B), concave-up lines appear pink due to adaptation to green lines of positive slope to the right of gaze and negative slope to the left of gaze. Similarly, concave-down lines appear green. The experiments I describe here show that this hypothesis accounts for Riggs' observations.

High-contrast adapting patterns (Fig. 1A) were projected from the rear on a diffusing screen in magenta light (Wratten 34a filter) and green light (Wratten 53 filter). These colors (*4*) produce very strong McCollough effects. The mean luminance was approximately 140 millilamberts. The test patterns were high-contrast prints viewed in white fluorescent room light. All patterns were about 5.5° wide, as were Riggs'.

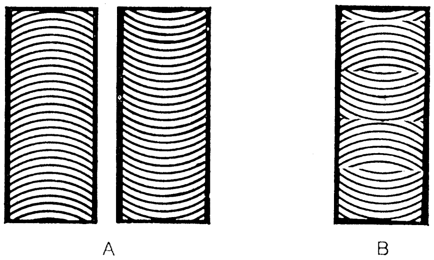

Fig. 1. (A) Adapting patterns viewed in magenta light and green light. These patterns have a radius of curvature of 4.5° when the patterns subtend about 5.5° across. (B) Test pattern with a radius of curvature of 4.5°. [Courtesy of L. A. Riggs]

Three observers adapted for 20 minutes to the concave-up pattern in green and the concave-down one in magenta; the patterns were interchanged every 10 seconds. The observer scanned up and down the vertical midline of each pattern. With gaze at the center of the test pattern (Fig. 1B), concave-up lines appeared pink and concave-down lines green. But, with gaze about 1° beyond the left or right edge, the colors definitely reversed—concave-up lines now appeared green and concave-down lines pink. Riggs observed that the colors did not reverse when gaze was moved somewhat off the midline. The oriented-line hypothesis predicts that the colors will appear weaker as gaze moves off the midline, but the clearest color reversal will occur only when gaze falls about 1° beyond the edges of the pattern. No reversal is expected even when gaze is as much as 1.5° from the midline. The concave-up lines will still predominantly stimulate regions to the right of gaze with lines of positive slope and regions to the left of gaze with lines of negative slope, and the concave-down lines will have the opposite effect. (These properties may be seen by sliding a tracing of Fig. 1A across Fig. 1B.)

Riggs observed that each panel of the test pattern (concave-up or concave-down lines) appeared pink or green throughout. This spread of color along contours within each panel, especially to the horizontal tangents of the curves, reflects a general property of the McCollough effect (*4*), and does not support the curvature detector hypothesis in particular, contrary to Riggs' argument.

Truly curvature-specific adaptation was not observed here. Three observers adapted for 20 minutes as described above while fixating a single point on a horizontal train of lighted points that moved leftward across the adapting patterns at approximately 1.5° per second. The train subtended 20° centered on each pattern, and the observer tracked repeatedly from far right to far left. Two other observers adapted for 1 hour to the opposite color condition, and the patterns were interchanged between each track from right to left. No aftereffects were seen. Every