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INPUTS OF DDT PCB, AND TRACE METALS FROM HARBORS

Past Project research into marine inputs of poly chlorinated biphenyls (PCB) and copper from vessel antifouling paints has shown that southern California harbors are potential sources of these contaminants to the coastal marine ecosystem. PCB has been used extensively in antifouling paints and hydraulic fluids. Similarly, quantities of copper in the paints are relatively large (approximately 600 g/1), making harbors a potential source of this trace metal, with an input roughly one-third that of municipal wastewaters. Therefore, with the support of the California Cooperative Fisheries Investigations, we studied the discharges of two chlorinated hydrocarbons (1254 PCB and total DDT) and three trace metals (chromium, copper, and nickel) from San Pedro, Newport, and San Diego Harbors.

During fall 1974, water was collected from the entrance of each harbor every 3 hours over a 12-hour interval. In San Pedro Harbor, the sampling location was the western opening of the breakwater. Collection periods were chosen to coincide with the largest tidal range of the month. To establish the actual tidal flow over the sampling intervals, a current meter was installed midway between the surface and bottom just inside the entrance of each harbor.

CHLORINATED HYDROCARBON RESULTS

Extremely low levels of chlorinated hydrocarbon were observed, with concentrations generally falling in the range of 1 to 15 parts per trillion (1 pptr = 1×10^{-9} g/1). The precision obtained at these low levels was most satisfactory—replicate values generally agreed within 1 to 2 pptr. Figure 1 illustrates the resultant concentrations of total DDT and 1254 PCB, and also volumetric flow, found over the sampling interval at San Diego Harbor.

For each harbor, we combined individual sample concentrations with the corresponding volume of seawater that flowed during the 3-hour period beginning 1-1/2 hours before each sampling to obtain the amount of both chlorinated hydrocarbons that was transported. The sum of these individual mass transports was divided by the total flow, disregarding direction, for the entire 12-hour period to obtain the flow-weighted mean concentrations for the three harbors (Table 1).

On the average, the highest DDT concentrations were found in the San Pedro Harbor entrance; values ranged from 6 to 12 pptr. In contrast, the average levels found in San Diego Harbor were 10 times lower, ranging from 0.2 to 1 pptr. The results from the Newport Bay survey (values ranging from 1 to 18 pptr) also indicated relatively high concentrations of total DDT. The highest levels coincided with the outflow of back-bay water.

At the San Diego Harbor entrance, we observed the strongest tidal currents (Figure 1). The 1254 PCB concentrations peaked at the end of the outflowing cycle in a manner similar to the total DDT concentrations in Newport Harbor. The concentrations of 1254 PCB measured at the Newport entrance (flow-weighted mean: 19 pptr) were significantly greater than those found at the other two harbors (.the flow-weighted mean concentrations from San Pedro and San Diego Harbors were both approximately 2 pptr).

TRACE METAL RESULTS

Figure 2 illustrates the concentrations of chromium, copper, and nickel measured at the entrance to San Diego Harbor. Table 1 presents the flow-weighted mean concentrations for these trace metals at all three harbors. The values observed for copper and nickel fall within the ranges reported in the literature for southern California seawater, which are 0.4 to 9.0 and 0.4 to 2.5 ppb, respectively. Concentrations of chromium in southern California seawater are not yet available; however, typical worldwide values range from 0.2 to 0.6 ppb. Our values generally fell within this range.

Chromium values tended to be higher in San Diego Harbor: The flow-weighted mean concentration of 0.6 ppb was three times higher than either Newport or San Pedro Harbor values. Chromium values increased as the water entered the San Diego Harbor. In Newport Harbor seawater, the level of chromium remained relatively constant throughout the semidiurnal tidal cycle.

The highest flow-weighted mean concentration of copper (3.0 ppb) was observed in Newport Harbor seawater. This value was 2 to 3 times higher than the concentrations found in water collected at San Diego and San Pedro Harbors. Copper levels peaked at the end of the outflowing cycle at both the San Diego and Newport Harbor entrances.

The flow-weighted mean concentration of 0.9 ppb for nickel in Newport Harbor was approximately one-half that found in the other two harbors. Nickel measurements remained relatively constant during the entire 12-hour water sampling period in both San Diego and Newport Harbors.

NET TRANSPORT OF CONTAMINANTS

The relatively short duration of these studies, and the extremely low concentrations measured, permitted only order-of-magnitude calculations to be made for net transport of these chlorinated hydrocarbons and trace metals in and out of the three harbors. However, we obtained upper limit estimates, which are listed in Table 2; positive values indicate a net annual transport through the channel to the coastal ecosystem.

These results illustrate the very small differences between concentration levels of chlorinated hydrocarbons in the outflowing and inflowing tidal phases. An extrapolation of the data to an annual basis indicated net transports of less than 25 kg/yr total DDT through any of the three harbor entrances. Corresponding analysis for 1254 PCB indicated annual net transports into the harbors of less than 50 kg/yr.

In all three surveys, the estimated net transport for metals was generally outgoing. However, except for copper and nickel in San Diego Harbor seawater, this transport was less than 10 percent of the municipal wastewater input from the adjacent submarine discharges. The estimated annual inputs of copper and nickel from San Diego Harbor to the adjacent coastal waters were 9 and 12 metric tons, respectively.

SUMMARY AND CONCLUSIONS

Extremely low levels of chlorinated hydrocarbons were observed in harbor seawater. Values obtained from San Pedro, Newport, and San Diego Harbors generally fell within the range of 1 to 15 pptr. The highest DDT concentrations were found in the western San Pedro Harbor entrance and were 10 times higher than levels measured in San Diego Harbor. These differences are consistent with those reported last year for DDT in harbor mussels; median values for the two harbors were 380 and 30 μg/wet kg (ppb), respectively. The highest levels measured at Newport

Harbor coincided with the outflow of back-bay water. We believe that our measurements are typical of the maximum DDT transport from the sedimentary reservoir of these tidal flats in the Newport Bay estuary.

At the San Diego Harbor entrance, the 1254 PCB concentrations peaked at the end of the outflowing cycle. This suggests a source of 1254 PCB in the inner region of San Diego Harbor, with possible net transport to the coastal waters. We previously reported that the mussels in all three harbors had significantly higher concentrations of 1254 PCB than those in nearby open coastal areas. The greatest difference was observed in the San Diego region, where the median value of 30 ppb in specimens from inside the harbor was six times that for mussels of the same species collected outside. The levels of 1254 PCB measured at the Newport Harbor entrance were significantly higher than levels found at the other two harbors. This could be due to large quantity of estuarine detritus observed being carried to the sea during the sampling period.

Chromium values increased as the water entered San Diego Harbor, which could imply a source of this metal outside the harbor; however, the adjacent submarine outfall on Point Loma discharged chromium at a level that was one-fifth the trans-port rate projected from these measurements. In view of the difficulties encountered in measuring these very low concentrations of chromium in water, the differences observed probably are not significant. Newport Harbor chromium values remained relatively constant throughout the sampling period. Preliminary results for chromium in digestive glands of mussels from inside and outside both these harbors are consistent with these findings. In San Diego, the values for the coastal specimens were higher by a factor of 1.5; in Newport, the values in mussels collected both along the outer coast and inside the harbor were fairly uniform.

Copper levels peaked at the end of the outflowing cycle at both San Diego and Newport Harbors, indicating potential inner harbor sources for this metal. Again, a similar pattern was reflected in the harbor mussels. The average concentration of copper in inner San Diego Harbor mussels was twice that for specimens collected along the adjacent coast; in mussels from inner Newport Harbor, it was several times higher. The nickel measurements remained relatively constant during the entire 12-hour water sampling period in both harbors. This uniformity of nickel levels also appeared in the mussels collected from both areas.

Extrapolating the data to obtain annual net transports of chlorinated hydrocarbons indicated that the harbors would not be an important source of either total DDT or 1254 PCB. Similarly, only San Diego Harbor would be an important source of trace metals and only of copper and nickel. The estimated annual inputs of these metals from San Diego Harbor to the adjacent coastal waters were 0.6 and 1.7 times the corresponding discharges from the Point Loma municipal wastewater outfall.

On the basis of total emissions, the harbors generally appear to be relatively unimportant sources of coastal contamination for the trace metals studied. However, as is discussed in a following section, concentrations of copper and nickel in the dissolved fraction of water collected at the harbor entrances usually exceeded those measured in the wastewater plume near the Whites Point submarine outfalls. As trace elements are believed to be most toxic in the dissolved state, harbors may be equal to or greater than adjacent municipal outfalls in importance as sources of these metals in biologically-available forms in the water column of the coastal ecosystem.

Table 1. Flow-weighted mean concentrations of chlorinated hydrocarbons (ng/l) and trace metals (µg/l) in harbor seawater, 1974.

	San Pedro Harbor	Newport Harbor	San Diego Harbor
Chlorinated Hydrocarbon			
Total DDT	7.4	8.3	0.5
1254 PCB	1.5	19	1.8
Trace Metal			
Chromium	0.2	0.2	0.6
Copper	0.9	3.0	1.8
Nickel	2.0	0.9	1.8

Table 2. Estimated maximum daily transport of seawater (10^8 liters) chlorinated hydrocarbons (g), and trace metals (kg) in outflowing and inflowing tidal currents at three harbor mouths.

	San Pedro Harbor*	Newport Harbor	San Diego Harbor
Seawater			
Out	406	82	944
In	88	11	483
Sum	494	93	1,427
Chlorinated Hydrocarbons			
Total DDT			
Out	355	79	77
In	414	67	54
Net	-59	12	23
1254 PCB			
Out	54	150	238
In	173	422	304
Net	-119	-272	-66
Trace Metals			
Chromium			
Out	13	2	53
In	1	1	127
Net	12	1	-74
Copper			
Out	47	29	273
In	34	16	248
Net	13	13	25
Nickel			
Out	97	8	268
In	108	7	235
Net	-11	1	33

*Western entrance only

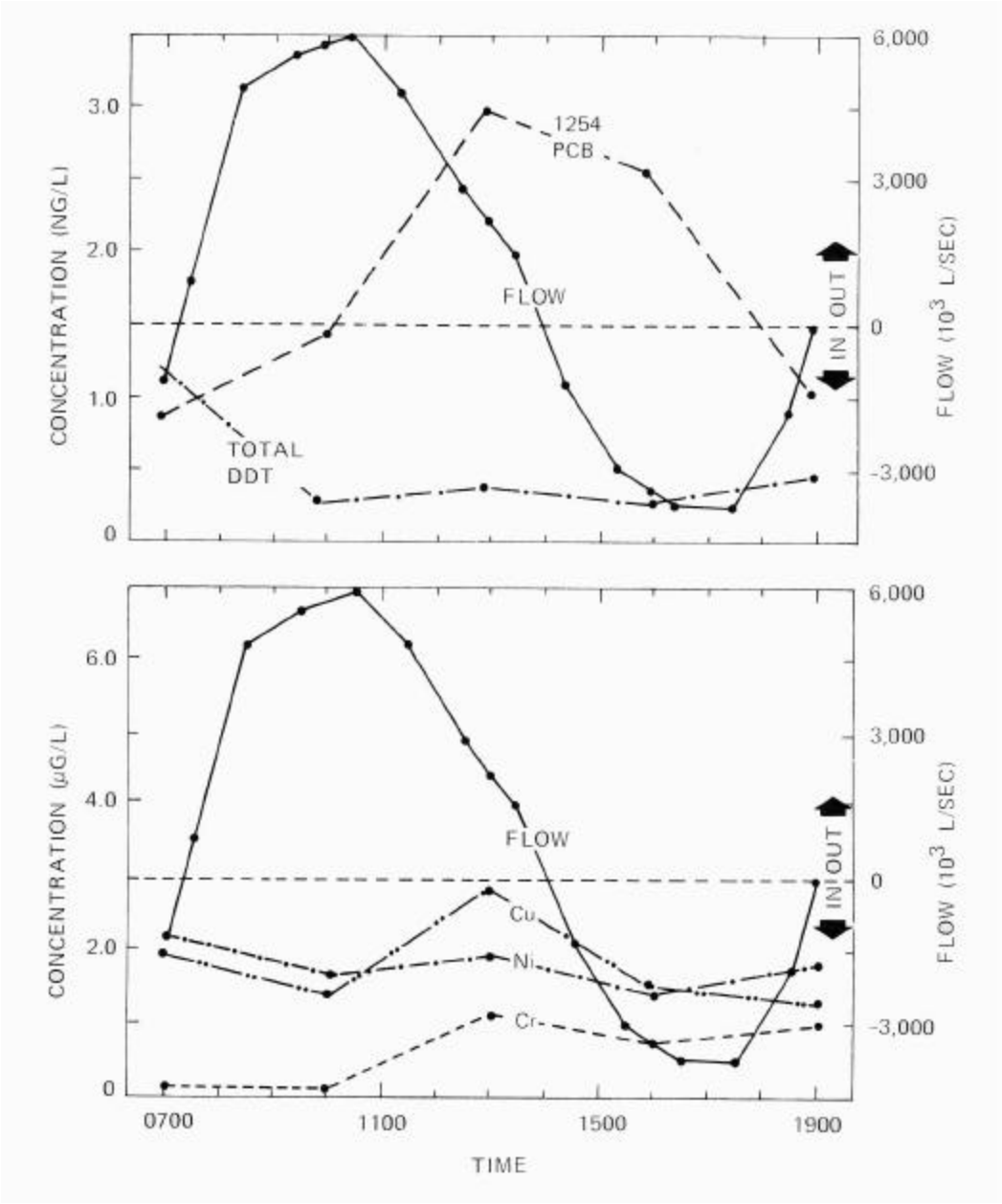

Figure 1. Concentrations of total DDT and 1254 PCB in unfiltered surface seawater collected over a semidiurnal tidal cycle at the mouth of San Diego Harbor, 12 November 1974

Figure 2. Concentrations of trace metals in filtered subsurface seawater collected over a semidiurnal tidal cycle at the mouth of the San Diego Harbor, 12 November 1974.