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CHLORINATED BENZENES IN PALOS VERDES FLATFISH

Municipal wastewaters discharged into southern California coastal waters contain relatively high concentrations of a newly identified series of chlorinated hydrocarbons, the chlorinated benzenes (CB's). Levels of total CB in the wastewaters typically are an order of magnitude above those of the polychlorinated biphenyls (total PCB), a related class of compounds known to have long-term detrimental effects on a variety of terrestrial and marine organisms (Young and Heesen 1976). Like the PCB's, many of the chlorinated benzenes have been shown to be damaging to liver cells, and one of these synthetic organics, paradichlorobenzene, is known to be a strong inhibitor of mitosis (cell division). During the past year, we have initiated studies to determine the extent to which these synthetic toxicants are accumulated by benthic marine organisms in the regions of municipal wastewater discharge.

The results indicate that the chlorinated benzenes are accumulated by Dover sole to a much smaller degree than are the PCB and DDT compounds. Despite the fact that the estimated 1976 JWPCP mass emission rate for total CB was an order of magnitude greater than that for total PCB or total DDT, the average concentration of total CB in the flatfish livers was at least two orders of magnitude smaller than that for total PCB and at least three orders of magnitude smaller than that for total DDT. Concentrations in muscle tissue revealed a similar pattern. It is clear that the relative values for the current annual input of these three classes of chlorinated hydrocarbons bear no relation to their relative abundances in this benthic indicator organism.

The organism we selected for our initial test was the Dover sole (*Microstomus pacificus*), a flatfish shown by previous Project studies to be abundant around wastewater discharges and to accumulate PCB's and other available chlorinated hydrocarbons to relatively high levels. As part of a program sponsored by the National Oceanographic and Atmospheric Agency (NOAA) and directed by Marjorie Sherwood of the Project, specimens were collected on 5 November 1976 by bottom trawl at a depth of about 150 meters at a station 4 km northwest of Los Angeles County's Joint Water Pollution Control Plant (JWPCP) discharge off the Palos Verdes Peninsula. Six individuals with standard lengths of 150 to 180 mm were randomly selected from the catch and immediately frozen in plastic bags; liver and muscle tissue were subsequently excised under carefully controlled conditions in the Project

laboratory. A 5-gram (wet weight) muscle sample and a 0.5-gram liver sample were then taken from each individual.

In preparation for CB determination, each sample was first covered with acetonitrile and ground in a high-speed blender. The mixture was then filtered and extracted with hexane. The hexane-extractable fraction was cleaned on a Florisil column and injected into a Tracer MT-220 gas chromatograph equipped with ⁶³Ni electron-capture detectors. The gas chromatograph column used was 1.5 percent OV-17 and 1.95 percent QF-1 on 80/100 mesh Gas-Chrom Q. A gas chromatograph oven temperature of 200°C was used in DDT and PCB determinations; hexachlorobenzene (HCB) determinations were made at 150°C, and trichlorobenzenes (TCB's) and dichlorobenzenes (DCB's) were run at 75°C. Quantification of these compounds was accomplished by comparing the sample peak heights on the chromatograms with those of standards. Recoveries were estimated from repeated extractions for the DDT's and PCB's and from spikes of the chlorinated benzene standards; recovery efficiency generally exceeded 90 percent for all compounds except the dichlorobenzenes (recovery of these compounds averaged about 50 percent). Process blanks for the DDT's, PCB's, and HCB generally were less than 10 percent of the gross tissue concentrations, and our results for these compounds have been corrected for blank and recovery efficiency. Values for trichlorobenzenes and dichlorobenzenes were generally very low; thus, only upper-limit estimates of concentrations of these substances (based on gross values) were made.

Results are presented in Table 1. Where actual concentrations were determined, the mean and standard error are given; otherwise, the average upper-limit value is given. For comparison, we have also listed the average of four measurements of these constituents obtained from replicate 1-week composites of JWPCP final effluent collected during both summer and fall of 1976 (discussed in this report in the article entitled "Halogenated Hydrocarbons in Waste-waters: Knowns and Unknowns.") In addition, the table shows the average DDT and PCB concentrations in bottom sediments collected in 1975 from 19 stations on the Palos Verdes shelf.

In recent years, JWPCP inputs of the PCB and DDT compounds have been greatly reduced. Comparison of data from 1972 and 1975 surveys has revealed that, despite the great reduction in inputs, bottom sediment and flatfish muscle tissue concentrations have decreased only slightly in the same 3-year interval, and the changes in the tissue values for both PCB and DDT are very close to those in the bottom sediments (Young et al. 1977). The data in Table 1 illustrate the fact that the 1976 Dover sole tissue concentrations reflect the 1975 sediment values much more closely than the 1976 input estimates. The liver-to-sediment- concentration ratios for 1242 PCB, 1254 PCB, total PCB, and total DDT all fall within the range of 4 to 6, and the muscle-to-sediment-concentration ratios fall within the range of 0.2 to 0.3. In contrast, although the 1976 JWPCP input value for 1242 PCB was four times higher than the value for 1254 PCB, the average liver value for 1242 PCB was one-third that for 1254 PCB.

Thus it appears that the sediment (and possibly also water column) burden of chlorinated benzenes around coastal discharges must be determined if we are to understand the fate and persistence of these relatively volatile synthetic contaminants in the coastal marine ecosystem. This research is now in progress. However, the results obtained to date suggest that despite the recent relatively high inputs of chlorinated benzenes off Palos Verdes Peninsula, levels of these contaminants are relatively low in benthic organisms from this coastal region.

REFERENCES

Young, D.R., and T.C. Heesen. 1976. Inputs of chlorinated benzenes. In Annual report. Coastal Water Research Project, pp. 31-37, El Segundo, California.

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Table 1.Chlorinated benzenes, PCB's, and DDT in municipal wastewaters and in flatfish and sediments from the Palos Verdes shelf.

	JWPCP	Surface Sediment	120000000000000000000000000000000000000	
	Mass Emission	(0 to 5 cm)	Dover sole, 1976**	
Chlorinated	1976	concentration, 1975*	Liver	Muscle
Hydrocarbon	(kg/yr)	(mg/dry kg)	(mg/wet kg)	(mg/wet kg)
o-DCB	4,680		<0.077	<0.007
D-DCB	4,000	N N N 2	< 0,026	< 0.005
1,2,4-TCB	1,320		< 0.016	< 0.005
1,3,5-TCB	20		< 0.004	< 0.001
нсв	150	W. 1972	0.053 ± 0.019	0.002 ± 0.0001
otal CB	10,170		<0.18	<0.02
1242 PCB	1,040	0.98 ± 0.29	4.4 ± 0.9	0.21 ± 0.01
1254 PCB	270	2.4 ± 0.64	13.2 ± 1.8	0.53 ± 0.04
Total PCB	1,310	3.4 ± 0.92	17.6 ± 2.6	0.73 ± 0.04
Total DDT	1,240	41 ± 9.6	250 ± 36	11.3 ± 0.5

^{*}Mean (± standard error) of values for 19 stations. From Young et al. 1977.

^{**}Mean (± standard error) of values for six individuals,