

INPUTS OF CHLORINATED BENZENES

During the course of our EPA-sponsored investigation into levels of chlorinated pesticides and PCB's in major municipal wastewaters of southern California, several other chlorinated compounds of potential concern were uncovered. The first was hexachlorobenzene (HCB), which was tentatively identified in our spring 1974 samples by R. Risebrough and B. de Lappe (Bodega Marine Laboratory). Subsequently, this material was repeatedly detected in our laboratory in semi-annual analyses of final effluents by electron-capture gas chromatography. The total body of data—results obtained over a 2-year period with four different chromatograph columns in two different laboratories--indicate that HCB is present in local wastewaters at levels one to two orders of magnitude below those measured for PCB. This is important in view of the growing concern about HCB in the environment.

However, at the suggestion of Professor J.D. Isaacs (chairman of our Consulting Board), we also sought and found four other chlorinated benzenes in municipal wastewaters. These substances—para-dichlorobenzene (p-DCB), ortho-dichlorobenzene (o-DCB), 1,2,4-trichlorobenzene (1,2,4-TCB), and 1,3,5-trichlorobenzene (1,3,5-TCB)—have received almost no attention in ocean pollution studies. Yet the results from our two 1975 seasonal surveys (Table 1) suggest that all except the last occur at concentrations that are at least an order of magnitude above those of HCB and comparable with observed PCB levels.

In view of the uncertainty in identifying compounds by electron-capture gas chromatography retention times alone, we sought confirmation of the presence of these chlorinated benzenes by mass spectrometry. During January 1976, relatively large grab samples of three effluents were collected, and several replicate sets of subsamples extracted and processed.

One set of these samples was analyzed with the electron-capture method at our laboratory, according to the same procedure used in the earlier analyses of chlorinated benzenes in wastewater. Two other sets were submitted to California Analytical Laboratories in Sacramento, California, and the EPA Environmental Research Laboratory in Athens, Georgia, for analysis by mass spectroscopy. Confirmation of all of the chlorobenzenes under consideration except 1,3,5-TCB was obtained at the Sacramento laboratory on the joint basis of

retention time and corresponding detection of the molecular ions of the compounds. The presence of DCB in all three samples and TCB in one (Hyperion sample) was also confirmed by the Athens laboratory.

Table 2 presents a quantitative comparison of the independent analyses of the wastewater samples by the Project and California Analytical Laboratories. With the exception of the DCB levels in the Hyperion sludge sample, the agreement between the two sets of data is most satisfactory. Thus, it appears that our identification of chlorinated benzene contamination of southern California municipal wastewater in general has been confirmed, although further work is needed to establish typical levels in individual cases.

To examine the importance of surface runoff as a source of chlorobenzenes to the coastal ecosystem, we conducted a preliminary survey of the Los Angeles River during a major storm in 1976. Our previous studies have shown this channel to be the single most important route of chlorinated hydrocarbon input via runoff to the Bight. Twelve samples collected during a rainstorm in early February were obtained with an all-metal, depth-integrating sampler and analyzed. The mean net concentrations (\pm one standard error) of total DDT, 1254 PCB, and 1242 PC3 were 0.34 ± 0.06 , 0.49 ± 0.09 , and less than 0.18 pg/liter, respectively; these values, which were two orders of magnitude above the blank corrections, were similar to results obtained in previous studies of Los Angeles River storm runoff. The chlorobenzenes observed occurred at considerably lower levels; thus, the individual extracts were combined into a single composite, which was reanalyzed and found to contain 0.05 pg/liter p-DCB, 0.01 pg/liter o-DCB, 0.005 pg/liter 1,2,4-TCB, 0.004 pg/liter 1,3,5-TCB, and less than 0.001 μ g/liter HCB. Because the corresponding blank corrections were almost as large as these net values, we consider them to be only order-of-magnitude estimates. However, it does appear that storm runoff contains concentrations of chlorobenzenes considerably lower than those for total DDT and total PCB.

In view of these results, and the fact that we have found surface runoff to be a less important source of DDT and PCB compounds than municipal wastewater, it appears that urban runoff probably makes an insignificant contribution of chlorinated benzenes to the Southern California Bight.

As mentioned earlier, we have found that dry aerial fallout is an important source of total DDT and 1254 PCB to the Bight. Recently, we conducted a pilot study of the importance of airborne chlorobenzene inputs, using our dry-ice-cooled collector. Five stations (Santa Barbara, El Segundo, La Jolla, Santa Catalina Island, and San Clemente Island) were selected; the stations lay on two transects that were parallel and roughly perpendicular to the coast and represented much of the area sampled so intensively in our

previous fallout studies.

The results of this survey are summarized in Table 3. These data show that the rates of total DDT and 1254 PCB input exceed those for the chlorinated benzenes by one to three orders of magnitude. The typical fallout rate for HCB (1 ng/sq m/day) was less than 1 percent of the median value measured for total DDT or 1254 PCB. In contrast, the estimated total quantity of HCB collected from the vapor state of air samples by a special sampler was approximately 10 to 25 percent of the total DDT collected. Thus, it appears that, because they are more volatile than the DDT and PCB compounds, the chlorinated benzenes are much less likely to be carried from the atmosphere to the coastal plain or waters of the Bight via dry particulate fallout.

The chlorinated benzenes are used extensively in industry. Approximately 13 percent of the benzene consumption in the United States between 1955 and 1961 was for production of chlorobenzenes (Hardie 1964). Both p-DCB and o-DCB are manufactured in very large quantities. The International Agency for Research on Cancer (1974a and b) reports 1972 production figures in this country of 35 million kg and 28 million kg, respectively; in contrast, 20 million kg of DDT was produced in the United States in 1971. 1972 combined DCB production in Western Europe and Japan was 30 million kg and 27 million kg, respectively. Over 90 percent of the p-DCB consumed in the U.S. is used in products that function through vaporizing, such as moth repellent, mildew retardant, and space deodorizer. The common application of p-DCB in deodorant cakes in public urinals probably accounts for the relatively large concentrations measured in municipal wastewaters. Results of a recent study on p-DCB in fat tissue of Toyko residents are consistent with our observations that this substance is a widespread and relatively important urban contaminant; the average concentration found in 34 samples was 2.3 ppm (the value for PCB was 2.1 ppm), and levels measured in the blood were about three times the corresponding PCB concentrations (Morita and Ohi 1975).

Ortho-dichlorobenzene is used in cleaning solvents for engine parts, heat transfer media, rust proofing and degreasing agents, solvents for lacquers and resins, dye intermediates, and insecticides. The trichlorobenzenes have been used as solvents of oil-soluble dyes and grease, dielectric fluids, lubricative oil additives, and termite exterminators. A liquid mixture sold in the United Kingdom contained approximately 85 percent 1,2,4-TCB, 7 percent 1,2,3-TCB, and small amounts of 1,3,5-TCB, dichlorobenzene and tetrachlorobenzene. This high ratio of 1,2,4- to 1,3,5-TCB is consistent with that observed in our southern California municipal wastewaters. The tetrachlorobenzenes are reported to have few industrial applications (Hardie 1964).

In years past, hexachlorobenzene has received considerable

attention as an environmental contaminant; a recent report from the National Academy of Sciences (1975) concludes that this synthetic organic is a pollutant of special concern. Its use as a fungicide in seed treatment resulted in wild-life losses in the Netherlands, and accidental consumption of HCB-treated wheat in Turkey caused 3,000 to 5,000 cases of porphyria, a metabolic disturbance. Approximately 7,000 kg were used as a grain fungicide in 1971, principally in the western U.S.; apparently, this is the only production data available. However, HCB has been detected in poultry and meat from 20 states, and 20,000 cattle were quarantined in Louisiana in 1972 when the 0.3 ppm action guideline for meat was exceeded. Concentrations of 1 and 6 ppm have been measured in human fat tissue samples from Australia and Germany. It is reported that HCB is also produced as a by-product in the manufacture of many chlorinated hydrocarbons, such as perchloroethylene and carbon tetrachloride. If the amount of HCB produced by this process were equivalent to 0.1 percent of the total production of the low-molecular-weight hydrocarbons, yearly production would exceed 1 million kg. Thus, industrial wastes may be the major source of HCB to the environment.

In view of the emphasis which the National Academy of Sciences report has placed on HCB as a potential pollutant, and the fact that the concentrations of HCB we have measured are relatively low compared to those of several other chlorinated benzenes, it seems useful to further compare these compounds. The 1974 Toxic Substances List (U.S. Department of Health, Education, and Welfare 1974) reports the following values for median lethal oral doses to rats:

Compound	Lethal Oral Dose (mg/kg body wt.)
Benzene	3,400
Chlorobenzene	2,910
Para-dichlorobenzene	500
1,2,4-Trichlorobenzene	756
1,2,4,5-Tetrachlorobenzene	1,500
Hexachlorobenzene	3,500
p,p'-DDT	113
p,p'-DDE	880
p,p'-DDD	400
Arochlor 1232	4,470
Arochlor 1254	500

In addition, in chronic toxicity tests with rats, o-DCB was found to be considerably more toxic than p-DCB to the liver, one of the organ systems most affected by animal exposure

to chlorobenzenes (Reid et al. 1973). These data suggest that p-DCB, o-DCB, and 1,2,4-TCB, three of the most abundant chlorinated hydrocarbons found in our municipal wastewaters, may be as important as other hydrocarbons of present concern.

Although acute toxicity data for rodents are useful for such comparisons, we need information about long-term effects of low-level exposure to these toxicants on marine organisms. Compounds such as p-DCB have been known for many years to be mitostatic poisons, causing disorders of cell division leading to inhibition of cell wall formation and, consequently, binucleate or multinucleate cells (Biesele 1958). Unfortunately, very little research has been conducted on reproductive inhibition of marine organisms by chronic exposure to such compounds. One study involved the effect of a 24-hour acute exposure of adult brine shrimp (*Artemia salina*) to 10 ppm 1,3,5-TCB (Grosch 1973). Although the survival of the adults exposed to TCB was greater than that obtained with the other organic toxicants, the overall reproductive performance of these adults, which was reduced by about a factor of 10, was the worst observed for the six compounds tested.

Thus, it appears that concern regarding chlorinated hydrocarbons in municipal and other wastewaters, which to date has dealt mainly with the chlorinated pesticides such as DDT and Dieldrin and with the PCB's, should be expanded to cover the chlorobenzenes as well. Attention has recently been focused on HCB, but the data discussed above indicate that other chlorinated benzenes of possible greater importance also are being discharged to our coastal marine waters.

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Table 1. Estimated chlorobenzene concentrations (ug/liter) in major municipal wastewaters, 1975.

	p-DCB	o-DCB	1,2,4-TCB	1,3,5-TCB	HCB	Total Chlorinated Benzene	Total PCB
Los Angeles County (JWPCP)							
Summer	7.4	7.3	8.0	0.2	0.4	21	1.2
Fall	12	12	1.8	0.8	0.2	27	1.6
Los Angeles City							
5-Mile							
Summer	3.4	1.9	5.7	<0.01	0.07	11	0.3
Fall	5.1	4.0	3.1	<0.01	0.01	12	0.4
7 Mile							
Summer	34	30	275	0.9	1.9	340	63
Fall	230	440	130	<0.2	6.8	800	18
Orange County, Summer							
	4.9	2.4	0.3	0.02	0.04	7.7	5.8
San Diego City							
Summer							
	—	2.2	0.23	0.02	0.01	2.5	1.6
Fall							
	0.42	<0.01	<0.01	<0.01	0.01	0.4	1.7
Oxnard							
Summer							
	9.3	4.7	0.9	0.4	0.4	16	0.2
Fall							
	3.1	2.3	0.25	<0.01	0.04	5.8	0.3

Table 2. Municipal wastewater chlorobenzene concentrations (ug/liter) determined by electroncapture gas chromatography and mass spectrometry.*

Method	p-DCB	o-DCB	1,2,4-TCB	1,3,5-TCB	HCB	Total Chlorinated Benzene
Los Angeles County (JWPCP)						
Electron capture	7.6	5.1	0.58	<0.01	0.10	13
Mass spectrometry	7.4	3.3	0.54	—	0.05	11
Los Angeles City (7-Mile)						
Electron capture	90	183	86	0.3	0.45	360
Mass spectrometry	7.8	14	34	—	0.41	56
Orange County						
Electron capture	2.8	1.3	0.08	0.001	0.010	4.2
Mass spectrometry	—	—	—	—	0.007	—

*1-liter subsamples of the Los Angeles City effluent were processed; samples of the other effluents were 10 liters each.

Table 3. Aerial fallout of chlorinated hydrocarbons (ng/sq m/day) off southern California, spring 1976.

	El Segundo*	Santa Catalina Island	San Clemente Island	La Jolla	Santa Barbara	Median
p-DCB	—	—	—	—	—	—
o-DCB	—	<8	27	—	<53	<27
1,2,4-TCB	<20	—	<3	<2	<19	<11
1,3,5-TCB	—	<1	<3	<10	<8	<6
HCB	0.9	1.7	0.1	3.4	0.9	1
Total DDT	640**	73	290	30	820	280
1254 PCB	860	230	98	78	170	170
1242 PCB	<260	<70	<150	<180	<250	<180

*Medians of six collections made during fall 1975.

**The median value measured for Dieldrin was 10 ng/sq m/day.