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# HALOGENATED HYDROCARBONS IN WASTEWATERS: KNOWNS AND UNKNOWNS

Many of the halogenated hydrocarbons revealed by gas chromatography to be present in southern California municipal wastewaters have not been identified and are not yet being routinely measured. In view of the established toxicity and possible carcinogenicity of this class of compounds to a wide variety of organisms, we have initiated studies to learn more about their identity, concentrations, and behavior. We have also extended our investigation of the distributions of five chlorinated benzenes in effluents and continued our efforts to inter-calibrate the measurement of DDT and PCB residues with the three largest dischargers of municipal wastewater in the Bight. These studies suggest that measurements of only DDT's and PCB's—which generally make up most of the "total identifiable chlorinated hydrocarbon" concentrations monitored by coastal dischargers in compliance with California's Ocean Plan (State of California 1972)—probably account for less than 1 to 2 percent of the actual concentration of total halogenated hydro-carbons in municipal wastewater.

During the summer and winter of 1976, we collected replicate 1-week composites of two to six dally grab samples of final effluent from the five largest dischargers of municipal wastewater to the Southern California Bight. The samples were analyzed using solvent extraction methods described by Young et al. (1976) and electron-capture gas chromatography techniques described in the article in this report entitled "Chlorinated Benzenes in Palos Verdes Flatfish." Resultant concentrations of detectable chlorinated benzenes and DDT and PCB residues are presented in Table 1. Corresponding estimates of annual mass emission rates to the ocean are listed in Table 2. Total DDT and 1242 PCB and 1254 PCB concentrations measured in replicates of these 1-week composites by the sanitation district laboratories of Los Angeles County, Los Angeles City (Hyperion), and Orange County are presented in Table 3.

To investigate the presence and approximate concentration of the more volatile halogenated hydrocarbons, we have employed a gas-purging technique. These volatile synthetics, often termed the low-molecular-weight halogenated hydrocarbons (LMHH), are swept out of an aqueous sample with a stream of helium dispersed by an air stone and trapped on a 15-cm-long, 3 percent SE-30 column at room temperature. When the purging is complete,

the SE-30 column is rapidly heated to 200 C, and the sample is flashed onto the gas chromatography column (2-m long, 2 mm ID, Chromosorb 101). Detection of the LMHH is accomplished with a Coulson detector.

A chromatogram of a grab sample of Hyperion's 5-mile effluent is shown in Figure 1; the sample was purged about 15 minutes after it was taken. The peaks are tentatively identified and roughly quantitated. The Chromosorb 101 column used did not separate some of the volatile chlorinated hydrocarbons, and there was no confirmation by different columns and/or mass spectrometry; therefore, positive identification is not yet possible. However, as the detector response is directly proportional to the number of chlorines (or halogens) present in a compound, the quantifications shown are probably accurate to within a factor of two, even though the identification may not be correct.

Figure 1 also shows a chromatogram obtained from a replicate of the Hyperion grab sample that was purged after it had been stored at room temperature for 7 days in a capped glass bottle. The greatly reduced profile of signals indicates that the normal collection and com-position procedures undoubtedly lead to significant losses of the LMHH from such samples. Thus, new techniques of on-site extraction and preservation are needed for this class of synthetic organics.

Figure 2 is a chromatogram of purged tap water from the City of El Segundo, location of the Project's head-quarters and trace organics laboratory. The tentative identifications and approximate quantifications of peaks are indicated. Peak 4 in this figure was most probably caused by a haloform produced during chlorination of the City's water supply. Haloforms have the general formula of $CHX_3$, where X is F (fluorine), Cl (chlorine), Br (bromine), or I (iodine).

The results presented in Tables 1 and 3 indicated generally satisfactory agreement in the quantifications of 1242 PCB, 1254 PCB, and total DDT by the Project and the Los Angeles County and Orange County laboratories. However, it should be noted that the regular 1976 monitoring data for PCB's in the effluent of Los Angeles County's Joint Water Pollution Control Plant (JWPCP) have been too low by one or two orders of magnitude because of an error in data reduction; the agency is now making efforts to correct this error in present analyses and in past data. Also, we note that some of the results of the Hyperion laboratory appear questionable in comparison with our PCB wastewater analyses, which have been previously confirmed within a factor of 2 by two university laboratories. For example, although Hyperion's quantifications of 1242 PCB and 1254 PCB in the sample of 5-mile outfall effluent are 8 to 10 times as large as the Project's values, their value for 1242 PCB in the 7-mile outfall sludge effluent is only one-tenth as large as the Project's. However, the values for 1254 PCB and total DDT in the sludge effluent obtained by the two laboratories agree within a factor of 2. Previous inter-calibrations with the San Diego sanitation district lab-oratory have indicated that their monitoring data on the chlorinated hydrocarbons in their

effluent are not yet reliable. A similar gap in useful monitoring data for these compounds exists in the case of the Oxnard treatment plant discharge.

The data listed in Table 1 are in agreement with a conclusion reported last year—that the sum of the measurable DDT and PCB residues (which make up most of the effluent monitoring total identifiable chlorinated hydro-carbon values) are generally an order of magnitude below the level of total chlorinated benzenes in these municipal wastewaters (Young and Heesen 1976). In addition, our recent pilot studies of the Hyperion 5-mile effluent (whose 350-mgd flow accounts for about one-third of the municipal wastewater discharged to the Bight) suggest that the level of LMHH is one order of magnitude above that of the chlorinated benzenes, and two orders of magnitude above that of the DDT/PCB residues generally reported to regulatory agencies as total identifiable chlorinated hydrocarbons. Although, we have obtained some information on the accumulation of the chlorinated benzenes in flat-fish around the JWPCP outfalls (discussed elsewhere in this report), we do not yet know anything about the fate or effects of the LMHH compounds, which may well dominate municipal wastewater inputs of toxic halogenated hydro-carbons to the Southern California Bight.

## REFERENCES

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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. Mean 1976 chlorinated hydrocarbon concentrations (µg/liter) measured in 1976 municipal wastewaters by Coastal Water Research Project chemists.***

| | p-DCB | o-DCB | 1,2,4-TCB | 1,3,5-TCB | HCB | Total Chlorinated Benzenes | 1242 PCB | 1254 PCB | Total DDT |
|---|---|---|---|---|---|---|---|---|---|
| Los Angeles County (JWPCP) | | | | | | | | | |
| Summer | 12.0 | 9.1 | 3.6 | 0.05 | 0.30 | 25 | 3.3 | 0.86 | 2.5 |
| Winter | 7.2 | 7.3 | 1.8 | 0.03 | 0.30 | 17 | 0.98 | 0.26 | 2.6 |
| Los Angeles City | | | | | | | | | |
| 5-Mile | | | | | | | | | |
| Summer | 0.4 | 0.3 | 2.9 | 0.04 | 0.003 | 3.6 | 0.09 | 0.17 | 0.053 |
| Winter | 4.8 | 2.6 | 0.76 | <0.01 | 0.001 | 8.2 | 0.11 | 0.09 | 0.056 |
| 7-mile | | | | | | | | | |
| Summer | 7.4 | 5.5 | 100 | <0.8 | 1.1 | 120 | 8.9 | 12.4 | 1.6 |
| Winter | 100 | 41 | 43 | <0.1 | 0.11 | 180 | 11 | 9.4 | 4.7 |
| Orange County | | | | | | | | | |
| Summer | 4.3 | 3.0 | 0.18 | 0.01 | 0.08 | 7.6 | 6.3 | 0.66 | 0.05 |
| Winter | 5.8 | 4.3 | 0.76 | <0.01 | 0.07 | 11 | 0.65 | 0.26 | 0.20 |
| San Diego City | | | | | | | | | |
| Summer | 2.2 | 0.5 | 0.16 | 0.007 | 0.006 | 2.9 | 0.46 | 0.19 | 0.01 |
| Winter | 5.8 | 2.5 | 0.25 | <0.01 | <0.001 | 8.6 | 1.7 | 0.95 | 0.11 |
| Oxnard | | | | | | | | | |
| Summer | 10.5 | 9.0 | 0.89 | 2.2 | 0.040 | 23 | 0.37 | 0.17 | 0.09 |
| Winter | 7.0 | 3.4 | 0.27 | <0.01 | 0.0005 | 10.7 | 0.011 | 0.065 | 0.12 |

*Each seasonal value based on two replicate samples of 1-week composites.

**Table 2. Estimated 1976 mass emission rates (kg/yr) of chlorinated hydrocarbons to the Southern California Bight via municipal wastewater discharges.**

| | Los Angeles County | Los Angeles City | | Orange County | Point Loma | Oxnard |
|---|---|---|---|---|---|---|
| | | 5-mile | 7-mile | | | |
| p-DCB | 4,680 | 1,290 | 310 | 1,270 | 650 | 140 |
| o-DCB | 4,000 | 720 | 130 | 920 | 240 | 100 |
| 1,2,4-TCB | 1,320 | 900 | 410 | 120 | 30 | 10 |
| 1,3,5-TCB | 20 | 10 | 3 | 3 | 1 | 20 |
| HCB | 150 | 1 | 3 | 20 | 1 | 1 |
| Total CB | 10,170 | 2,920 | 860 | 2,330 | 920 | 270 |
| 1242 PCB | 1,040 | 50 | 60 | 880 | 180 | 3 |
| 1254 PCB | 270 | 60 | 60 | 120 | 90 | 2 |
| Total PCB | 1,310 | 110 | 120 | 1,000 | 270 | 5 |
| Total DDT | 1,240 | 30 | 20 | 30 | 10 | 2 |

**Table 3. Concentrations (µg/liter) of PDB's and total DDT measured in 1976 municipal wastewaters by treatment plant laboratories.***

| | 1242 PCB | 1254 PCB | Total DDT |
|---|---|---|---|
| Los Angeles County | | | |
| Summer | 3.7 | 0.62 | 2.3 |
| Winter | 2.5 | 0.80 | 3.3 |
| Los Angeles City | | | |
| 5-Mile | | | |
| Summer | 0.7 | 1.8 | – |
| 7-Mile | | | |
| Summer | 0.9 | 21 | 2.5 |
| Orange County | | | |
| Summer | 4.65 | 0.25 | 0.034 |
| Winter | <0.20 | 0.53 | 0.13 |

*Splits of 1-week composites analyzed by the Project and reported in Table 1.

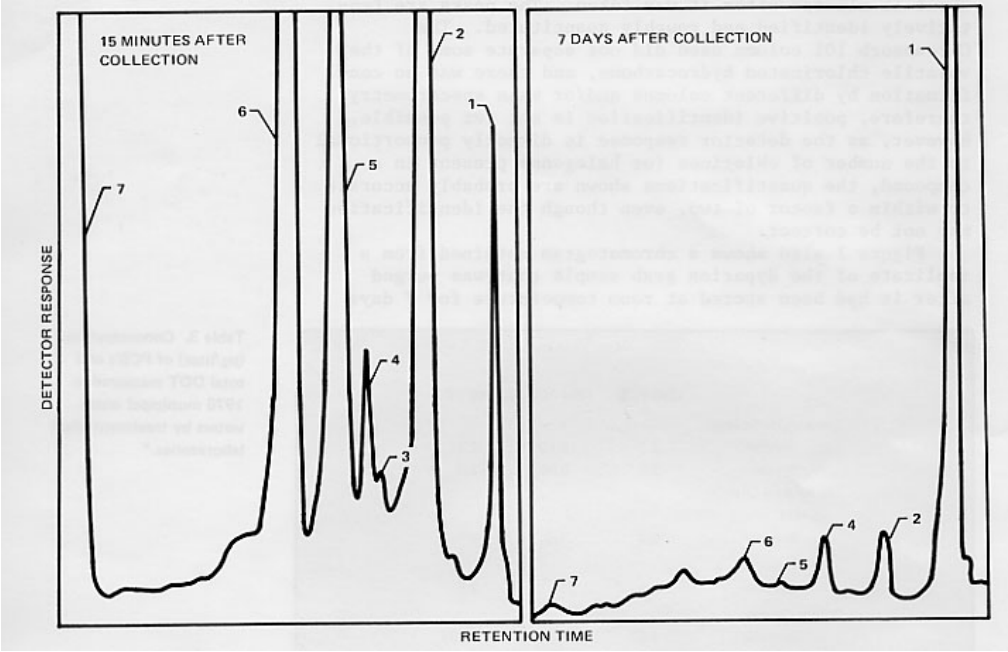


**Figure 1. Gas chromatograms of Hyperion 5-mile effluent 15 minutes and 7 days after the sample was collected; recorder attenuations were the same for both chromatograms. Peaks are tentatively identified as (1, 2, and 3) unknown, (4) chloroform, (5) ethylene dichloride and/or carbon tetrachloride and/or 1,1,1-trichloroethane, about 25 ppb, (6) trichloroethylene, about 38 ppb, and (7) 1,1,2-trichloroethane, about 114 ppb.**

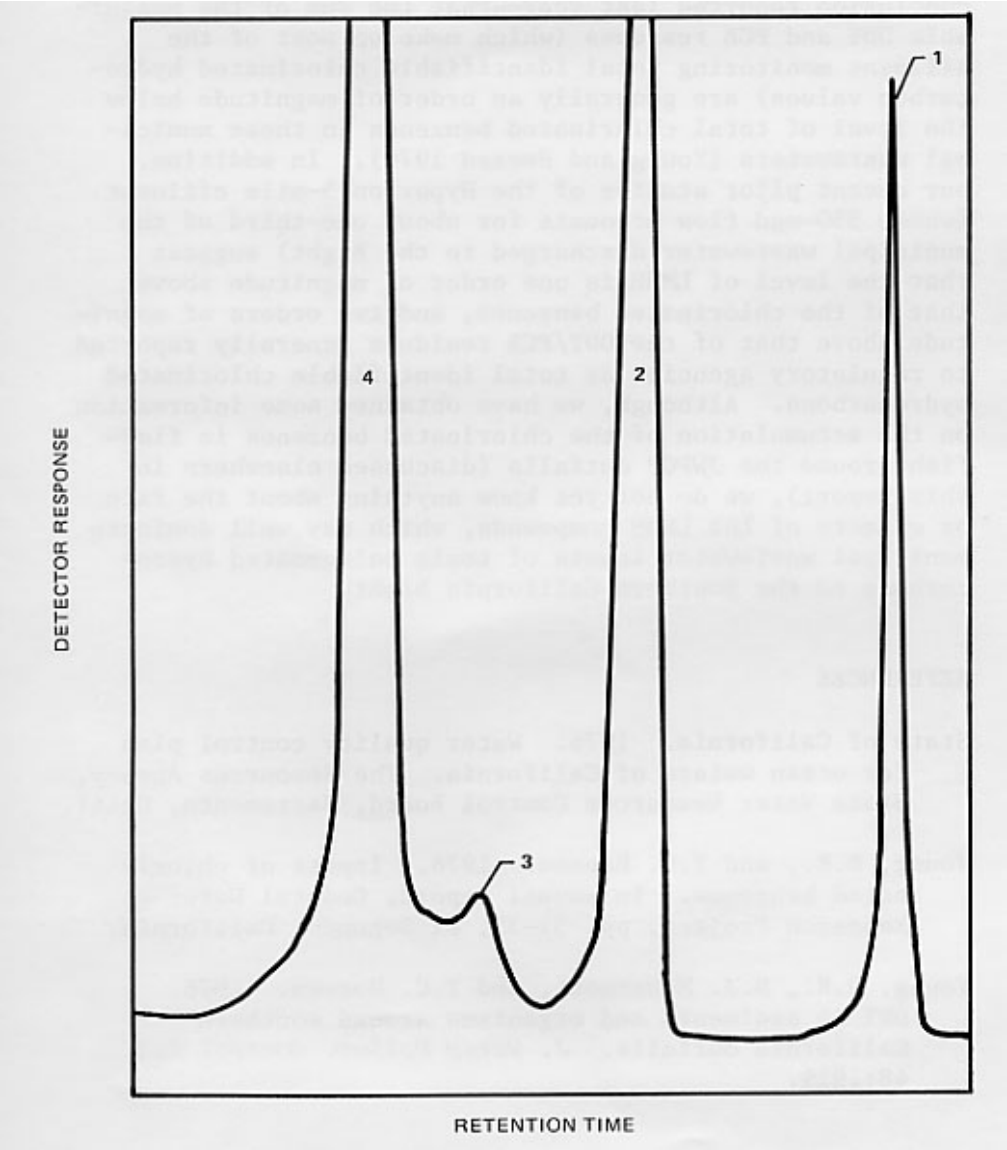


**Figure 2. Gas chromatogram of El Segundo tap water. Peaks have been tentatively identified as (1) unknown, (2) chloroform, about 150 ppb, (3) trichloroethylene, about 2 ppb, and (4) substance with same retention time as 1,2-dichloropropane (about 70 ppb) but probably a haloform.**