

ENRICHMENT OF PCBS IN LAKE MICHIGAN SURFACE FILMS¹

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ABSTRACT. *The processes of exchange of PCBs and related organics at the surface of large bodies of water such as the Great Lakes are unavoidably linked to the unique properties of surface films. We have observed a 3 to 8 fold enrichment of PCB over underlying water in surface film samples taken from Lake Michigan with a Garrett screen sampler. The particle association of the PCBs was highest in the microlayer, averaging 50% compared to 20% on particles in the subsurface water and less than 5% in the air. The PCBs in the samples were identified as Aroclor 1254 and Aroclor 1242. The percentage composition of the two Aroclors varied between the air and the water as follows: the air was 30.2% Aroclor 1254 and the water (microlayer plus subsurface) was 57.6% Aroclor 1254.*

INTRODUCTION

Active research on surface microlayers has been going on for about 20 years. These studies have coincided with man's awareness of the manifold problems associated with hydrophobic man-made pollutants. The popular concept is that microlayers, as concentrators of hydrophobic substances, have an important role in the cycling of such materials. For example, the microlayer should enhance photolytic decomposition and mediate the air/water exchange of hydrophobic pollutants. However, except for some descriptive studies, little has been done to quantify or scale these processes. There are some excellent reviews of microlayer research (Liss 1975, Slinn *et al.* 1978, MacIntyre 1974) which briefly deal with the organic pollutant question. It is the intent of this paper to discuss the data currently available on surface microlayer concentrations of organic pollutants and describe some recent Lake Michigan data.

A few scattered values are available for surface microlayer enrichments of various organic pollutants (PAH—Strand 1978; petroleum hydrocarbons—Marty and Saliot 1976). However, the most extensive data base for pollutants in microlayers is on PCBs and DDT (Table 5 in Bidleman *et al.*

1976). Most of the data confirm that there is an enrichment of the PCBs and pp-DDT in surface microlayers worldwide. The bulk of the literature is from the marine environment, with only a few data points for freshwater systems. Eisenreich *et al.* (1978) reported 85-832 ng/L of DDT in foam collected from Lake Mendota, Wisconsin, and Elzerman (1976) reported finding 245 ng/L of PCB in microlayers from Lake Michigan in 1974. The corresponding concentrations for subsurface water in each of these reports were less than 1 ng/L for the DDT and 22 ng/L for the PCB.

With this background of information on chlorinated hydrocarbon concentrations in microlayers, we embarked on a study of Lake Michigan surface waters to develop some information on PCB levels in the air/water boundary region. This seemed especially important considering reports that significant input of PCBs was occurring from atmospheric deposition via rainfall (Murphy and Rzeszutko 1977, Strachan and Huneault 1979). Another goal of this study was to separate the PCBs into a dissolved and particulate component in each of the strata, air, microlayer and near surface water, and finally to attempt to characterize the Aroclor makeup of the PCBs identified.

MATERIALS AND METHODS

The samples were collected from the University of Michigan Research Vessel Laurentian during three

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separate sampling cruises. The cruise tracks and dates are recorded in Figure 1. On each of these cruises, samples of air were collected while underway and samples of surface microlayer and subsurface water were collected while on the designated stations. The air was sampled by drawing air first through a precleaned glass fiber filter for particulate removal followed by a series of pre-extracted polyurethane foam plugs for vapor phase removal of high molecular weight chlorinated hydrocarbons (Billings and Bidleman 1980). The suction pump was a General Metals high volume air pump equipped with an extension tube 25 cm long by 7.5 cm in diameter which contained the plugs and an 8" X 10" glass fiber filter holder. Air flow for the collection averaged 0.5 m³/min and the sample times varied from 3–7 hr for each of the samples (i.e. samples of air totaling 76–224 m³).

A Garrett screen sampler was used for collection of the microlayer samples (Garrett 1965). A surface slick was not always visible during sampling; this was especially true for October 1979 and April 1980 when rough seas made visual observations difficult. The average microlayer depth sampled was calculated to be 228 μ m. The samples were phase separated into particulate and dissolved components by filtering with Gelman glass fiber filters (Type A-E). The filtrate from these samples was placed in empty 1-gallon pesticide grade solvent bottles and extracted with 200 mL of pesticide grade methylene chloride by rolling the bottles on a Jar-mill roller (Christensen *et al.* 1979). The methylene chloride in these samples was poured off into 1-L bottles capped with Teflon[®] inserts and transported to the lab for analysis. The filters from the above samples were folded face inward, wrapped in aluminum packets, and frozen until analysis. For subsurface collection of water a 2-1/2 gal glass carboy was immersed approximately 1 m below the lake surface and allowed to fill. These samples were filtered through 142-mm-diameter glass fiber filters. The filtrates were collected in 5-gal carboys where they were solvent extracted by stirring with 1.6-L volumes of pesticide grade methylene chloride. The methylene chloride extracts were siphoned into empty pesticide grade solvent bottles and returned to the lab for subsequent analytical workup.

Spike and recovery experiments of the methylene chloride extraction procedure were carried out using C¹⁴-labelled trichlorobiphenyl and C¹⁴-labelled hexachlorobiphenyl. Recovery of the two PCB isomers averaged 82% for the carboy extraction method. Procedural blanks were analyzed for

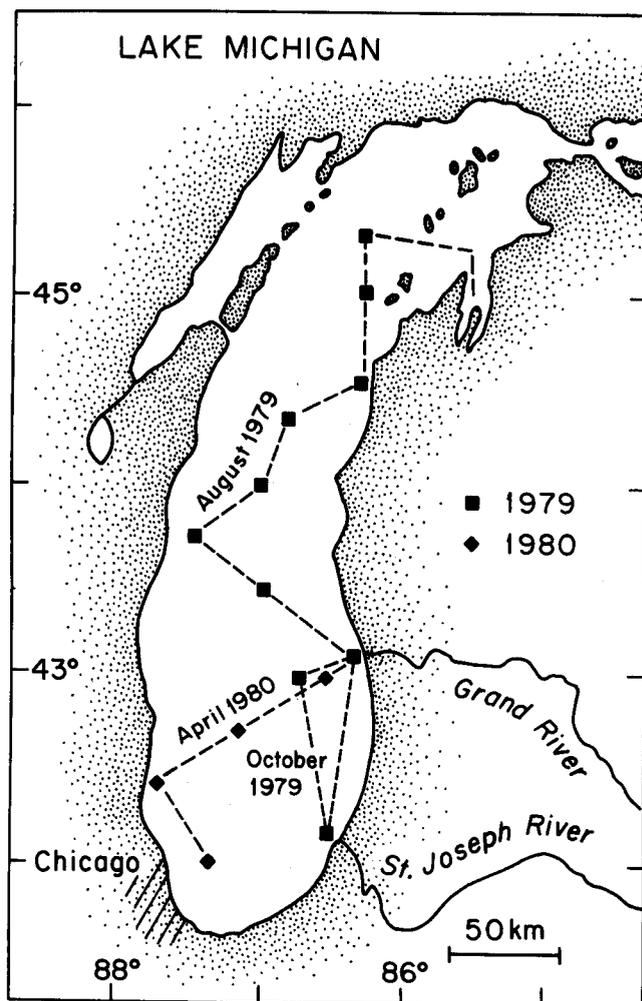


FIG. 1. Cruise track and sampling stations for collection of air and surface water samples for PCBs in Lake Michigan.

each of the collection and extraction procedures. Extreme care had to be taken to ensure against sample contamination due to low levels of PCB present in the samples. It was discovered that our greatest source of contamination could be avoided by minimizing sample contact with laboratory water. Because of this problem, we did not use water in our procedural blanks. The method was to extract empty sample bottles and unused filters which were returned from the field. The values quantified from these blanks were used to correct the results for each of the sample types. In most cases, these values were less than 1/2 the sample result. The coefficient for variation of the blanks was less than 0.20. Achieving low limits of detection was especially stressed in this study. Control of

this variable was achieved by increasing the sample volumes and carefully controlling contamination of the samples. For the surface microlayer samples, the limit of detection was 2 ppt for each of the Aroclor mixtures, and for the subsurface water sample it was 1 ppt for each Aroclor type. For the air, the limit of detection was 0.1 ng/m³.

The analytical procedure applied for each of the samples was to isolate the PCBs from the other coextracted residues, e.g. pesticides, fats, etc., and detect their presence by electron capture gas chromatography. To accomplish these steps the following procedures were applied. The dissolved fractions from the water collections were extracted in the field as already described. The remaining samples (the air samples made up of foam plugs and filters, and the water sample filters) were Soxhlet extracted with an acetone hexane (1:1) mixture. Each sample was cycled a minimum of 100 times. The sample extracts were treated by various methods to place them in solvents appropriate for their cleanup by alumina column chromatography (Christiansen *et al.* 1979). For the dissolved water extracts, this involved boiling off the lower boiling methylene chloride with hexane as a "keeper." For the extracts containing acetone, an aqueous phase partitioning step was used to remove the acetone. For cleanup, these hexane extracts were concentrated to 1 to 2-mL volumes by Kuderna Danish evaporative concentrators and eluted through Activity III alumina (Christiansen *et al.* 1979). The eluate from this step was again concentrated and fractionated by silicic acid chromatography to isolate the PCB from other potential interfering compounds (Bidleman *et al.* 1978). The PCB fractions were analyzed on a Varian 3700 Gas Chromatograph equipped with pulsed Ni⁶³ electron capture detector cells. The samples were chromatographed using a 2 mm i.d. X 1.8 m glass column packed with

1.5% SP-2250/1.95% SP2401 on 100/120 mesh Supelcoport (Supelco Inc., Bellefonte, PA). The instrumental conditions were: injector temperature 220°C, oven temperature 190°C, detector temperature 350°C, and a nitrogen flow of 55 mL/min. A comparison of the samples to several Aroclor mixtures revealed that none of them precisely matched any one Aroclor. However, a mixture of Aroclor 1242 and 1254 provided the best match. The concentration of the PCBs in the samples was calculated by comparison of peak heights of sample peaks to matching peaks in the standards. Peaks in the samples which matched in retention times but which appeared out of proportion to the fingerprint pattern of the Aroclor mixtures were not used for quantitation.

RESULTS

The concentration of PCBs measured in the air averaged 2.8 ng/Kg (3.1 ng/m³) (Table 1). This level was representative of the concentration found on all of the cruises shown in Figure 1. The surface microlayer concentration of PCB (particulate plus dissolved) averaged from 15.7 ng/L to 22.0 ng/L in all the collections (Table 1). As expected, there was definite enrichment of PCBs in the microlayer over the subsurface water which averaged 2.88 ng/L for August 1979 and 5.66 ng/L for April of 1980. The particulate portion of the microlayer samples generally represented more than half of the total PCB measured, except for the sample in April 1980, Table 2. This is in contrast to the particle and dissolved association of PCB in the subsurface water in which only 17 to 24% of the total measured PCB was found on the particles. With the large area covered in the sampling (both open lake and near shore, Figure 1) it was considered likely that geographical differences in concentration might

TABLE 1. Average PCB measurements in microlayer, air, and water for Lake Michigan.

| | Date | Number of Samples | Average PCB Concentration (ng/kg) | Range (ng/kg) |
|----------------------|--------------|-------------------|-----------------------------------|---------------|
| Air | August 1979 | 5 | 2.8 | 0.84 - 4.6 |
| Surface Microlayer | August 1979 | 12 | 15.70 (±12.28)* | 3.30 - 47.2 |
| | October 1979 | 5 | 21.4 (±17.02) | 8.42 - 50.13 |
| | April 1980 | 11 | 22.0 (±8.91) | 10.30 - 41.54 |
| Subsurface (1 meter) | August 1979 | 8 | 2.88 (±3.37) | 1.11 - 11.18 |
| | April 1980 | 4 | 5.66 (±1.12) | 4.67 - 7.14 |

*The quantity in parentheses represents the standard deviation of the means.

TABLE 2. Average relative distribution of PCBs in the air, microlayer, and water samples collected from Lake Michigan.

| | Date | Percentage of Total PCB Identified as Aroclor 1254 | Average Percentage of PCB on the Particles |
|----------------------|--------------|--|--|
| Air | August 1979 | 30.3 | <5 |
| Surface Microlayer | August 1979 | 54.4 | 66 |
| | October 1979 | 58.0 | 51.6 |
| | April 1980 | 54.7 | 30.0 |
| Subsurface (1 meter) | August 1979 | 62.0 | 23.6 |
| | April 1980 | 65.9 | 17.4 |

appear in the data. However, no significant correlations could be found. This could be a fault of the limited data available.

The relative amount of Aroclor 1254 in the total PCB measured (Aroclor 1242 plus Aroclor 1254) was lowest in the air samples, i.e., 30%, Table 2. For the water and microlayer samples, the percentage of Aroclor 1254 in the samples varied from 54.4% to 65.9%.

DISCUSSION

Dry deposition can have a gaseous and a particle deposition component. Atmospheric deposition of particles and gases onto water surfaces has been approached in recent studies from a resistance model standpoint in which the rate limiting step in the transfer sequence has the smallest transfer velocity (Slinn *et al.* 1978, Williams 1980). In the deposition layer, transfer of gases and particles across an interface is governed by molecular diffusion. However, turbulence is the dominant transfer mechanism in layers just above and below the interface (Liss and Slater 1974). For gases, the transfer into or out of the water is dependent on the solubility and reactivity of the species in question. The flux is proportional to the concentration gradient and the rate of transfer is dependent on the overall resistance. An accurate determination of Henry's Law Constant (H) is necessary in predicting the exchange between air and water. If H is small, as in the case of highly soluble, reactive gases, the rate determining step is gas phase controlled whereas, for highly insoluble gases, liquid phase resistance determines the rate of gaseous transfer (Mackay *et al.* 1979; Doskey and Andren 1981). For the deposition of particles, a determination of deposition velocities is necessary to calculate fluxes to the water surface. Slinn and Slinn (1980) predicted that

for particles in the 1 μm size range the deposition velocity is essentially independent of particle size and is equal to the limiting value of atmospheric turbulence.

It is thought that rain is responsible for the major portion of PCB inputs to lakes and large bodies of water (Eisenreich *et al.* 1980, Bidleman *et al.* 1976). Rodhe *et al.* (1980) estimated the concentration of PCB in rain over the Baltic Sea to be 32 ng/L. Murphy has reported concentrations in rain over Lake Michigan to be 119 ng/L (Murphy and Rzeszutko 1977). Murphy and Rzeszutko separated the particulate and dissolved components of rain over Lake Michigan and found 34% to be particulate associated. These values for particulate phase association of PCBs are in the same range as we see in our microlayer samples. PCB distribution on the particulates in the air, however, are much lower (i.e. <5%) than either the microlayer or the subsurface water (Table 1).

Once within the microlayer or subsurface phase, there appears to be a fractionation of the Aroclors present, with a preferential buildup of the higher chlorinated hydrocarbon-containing components (Aroclor 1254) on the particles, Table 2. To estimate the possible enhanced sorption of the Aroclor 1254 mixture over the Aroclor 1242 mixture, the following calculation was carried out for the microlayer and subsurface compartments:

$$R = \frac{\text{Percentage of Total Aroclor 1254 that is Particulate}}{\text{Percentage of Total Aroclor 1242 that is Particulate}}$$

The August and October 1979 data were combined and represent the period of thermal stratification, while the April 1980 data were used for the non-stratified (mixed) determinations. For the surface microlayer particulates there was little difference in the Aroclor partitioning in the stratified condition

($R = 1.16 \pm 0.5$), but in the non-stratified conditions there was a considerable enhancement of 1254 over 1242 (e.g. $R = 2.31 \pm 1.6$). For the subsurface particles, Aroclor 1254 sorption was also favored over 1242 during both stratified and non-stratified periods (e.g. $R = 1.29 \pm 0.38$ for stratified and 1.65 ± 1.5 for the non-stratified periods). A student T-test of the four results showed only the April microlayer results to be significantly different at the 0.05 level of significance. Therefore, the general lack of statistical proof for the results make these findings difficult to interpret. However, the preferential sorption of Aroclor 1254 over 1242 on the particles agrees with theoretical predictions which ascribe higher partition coefficients to Aroclor 1254.

For the April cruise the suspended solids concentrations for each of the samples was determined. The average concentration of particulate material in the microlayer for this period was 2.95 mg/L and 1.57 mg/L for the subsurface water. Using these suspended solids concentrations, it was possible to calculate an empirical partition coefficient (K_p) for the PCBs obtained in these samples. To do this the following calculation was carried out:

$$K_p = \frac{\mu\text{g PCB/L in Particulate Phase}}{\mu\text{g PCB/L in Dissolved Phase}} \times \text{suspended solids concentration}$$

The K_p s resulting from the above calculation were 2.5×10^5 for the microlayer and 1.4×10^5 for the subsurface water. These results compare with the K_p s of 0.4×10^5 to 1×10^5 reported by Pavlou and Dexter (1979) for the marine environment. The fact that the higher K_p value was calculated for the microlayer implies that the particles in this region are more efficient substrates for sorption.

The observed enrichment of PCBs in the microlayer appears to support the importance of the surface microlayer in the overall mass transfer of pollutants through the air/water interface. Our results with PCBs indicate that a significant fraction of hydrophobic pollutants in the microlayers will be associated with particulate material. Therefore, transfer at the air/water interface must take particle cycling into account.

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