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The Activity of PCBs in Sediments and Water from Lake Calumet and Waukegan Harbor

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Abstract

Techniques were developed to measure the activity (fugacity; escaping tendency) of semi-volatile organic compounds, PCBs in this case, in water and sediment samples. The techniques were applied to samples from Lake Calumet and Waukegan Harbor. Knowing the activities of the PCBs in the samples permitted the following to be determined: (1) the thermodynamic sediment/water partition coefficient, K_d; (2) the direction of movement of compounds between the sediments and water; (3) the expected PCB concentrations in the water at equilibrium with the sediments; (4) the amount of PCBs evaporating per year from these bodies of water; and (5) an average partition coefficient for the PCBs present in each sediment sample, K_d*.

The PCB activities found in the sediment and water samples from these two locations were very different, as expected. The K_ds for individual PCB congeners were an order of magnitude or more higher for the Lake Calumet sediments. Significantly, the two samples from slip #3 in Waukegan Harbor, those closest to the past PCB discharge, showed the lowest average K_d (K_d*) - the highest relative activity of the samples measured. There is considerable variability in the ratio of the concentration of the PCBs in the sediments to their activities, indicating that the PCB concentration is a poor estimator of partitioning (and toxicity due to equilibrium toxicity) for these samples.

The dissolved concentrations (activities) found in the Lake Calumet samples indicated that they were close to equilibrium with the sediments. Calculations based on the water concentrations indicate that net transfer to the air is occurring from both locations, with an estimate loss of 1.4 kg/yr from Lake Calumet and 0.25 kg/yr from Waukegan Harbor (about 0.04 kg/yr from the contaminated slip #3). The water samples from Waukegan had much lower activities than the bulk sediments. The results also indicated that the composition of the surficial sediments in Waukegan Harbor is different from that of the bulk sediment samples collected.

An unexpected finding was that the sediments collected from the vicinity of the PCB discharge to Waukegan Harbor were quite depleted in PCB congener #18, relative to congener #17 and other PCB congeners present. The reasons for this relative depletion are not known, but the absence of #18 now serves as a marker for the sediments in this area.

X

Executive Summary

In dealing with inorganic materials in water, the concept of activity is firmly established. The concept says that the effective presence of a substance, say a hydrogen ion, is related to its chemical activity, not to its concentration. For instance, if one takes two containers with a liter of water in each, and adds one mole of a weak acid, say acetic acid, to one and a mole of a strong acid to the other, the concentration of acid in each is 1.0 mole/liter. However, the effectiveness of those solutions as acids is determined by the activity of the hydrogen ion, the pH of the solution. In this case, the hydrogen ion activity in the solution of the strong acid will be close to one mole/liter. However, the hydrogen ion activity in the solution of the weak acetic acid will be only about $2 \cdot 10^{-3}$ moles/liter. *While the total acid concentrations in these two solutions are the same, the effective acidities — the activities of the hydrogen ion, are almost three orders of magnitude different!*

Unfortunately, this concept of chemical activity (fugacity; escaping tendencies) has not been applied to other substances. But, in order to determine the direction and rate of movement of compounds between phases by partitioning, the activity of the compounds in the phases of interest needs to be known. The activity of a compound is the same in all the phases which are at equilibrium. Thus, for an air/water/sediment system in equilibrium, determining the activity of a compound in one phase (air is the easiest) gives the activity in all of the other phases. This permits the calculation of dissolved concentrations in the water, the sediment/water partition coefficient (K_d) for each of the compounds on the sediments, the estimation of fluxes, and toxicity that is related to the activities.

In this project, techniques involving equilibrium partitioning to the gas phase were developed to determine the activity of semi-volatile organic compounds in water and sediment samples. The method for the water samples involved equilibrating the water sample with air in a 1.2 m vertical packed column with counter-current air and water flows. For sediments, nitrogen saturated with water vapor was slowly passed over pulverized, dehydrated sediments, and mixed with glass wool in a 1 m thermostated tube.

In this study, useful and interesting results from most of the samples were obtained from the fugacity determinations. The concentration and activity of the PCBs in the Lake Calumet samples were much less than in the Waukegan Harbor samples and, with one exception, the activities of the sediment and water samples from each of the locations were within an order of magnitude. The consistently different results for the samples from these two quite different sites are some evidence for the validity of the techniques applied here. The results also demonstrate that the sediments are an important control on the PCBs concentrations in the water, particularly for these shallow waters.

From the activity of the PCBs found in the water samples, the amount of PCBs evaporating could be estimated. These results indicate that about 1.4 kg/yr of PCBs were evaporating from Lake Calumet and about 0.25 kg/yr from Waukegan Harbor. These loss rates constitute a significant mechanism for Lake Calumet. Contrary to the notion that materials get 'bound-up' or sequestered by sediments, these results demonstrate that surficial sediments can be an actively participating part of the aquatic environment.

What could have happened to these bodies of water, is that higher inputs resulted in the accumulation of PCBs (and other compounds) in the sediments. With the decline of these inputs, the activity of these compounds in the sediments is now higher than in the environment (as represented by the air and water concentrations), and the sediments are returning to equilibrium by partitioning PCBs into the water, and from there into the air.

The relationship between fugacities and PCB concentrations is shown in Figure 10, page 42. There is some relationship, but it is certainly not a direct, linear one (slope = 1.0). There are also a number of significant outliers. The techniques developed in this project permitted measurements to be made to test the hypotheses that concentration is a reasonable surrogate for activity. The relationship, as shown on Figure 10, is poor, and there are a number of significant outliers. Thus, the use of concentrations in place of fugacities can not be expected to give good results. Figure 10 clearly demonstrates the need to use fugacities when considering the solubility, air partitioning and toxicities of semi-volatile organic compounds in the environment.

Chapter 1. Introduction and Background

Organic toxic materials associated with sediments can be mobilized in two ways. Particles carrying the toxic materials may be resuspended, or the toxic materials can dissolve in the water. The particulates and dissolved materials then will be transported with the water, and volatile compounds can evaporate.

This project focuses on the equilibrium partitioning process that leads to sediment-bound compounds dissolving, and the transport and fate of these dissolved materials in the water column. Because partitioning can be an important mechanism for exposing organisms in the food chain to toxic organic compounds, it is also considered (Clayton *et al.* 1977; Connolly *et al.* 1988; Mackay and Hughes 1984).

When two or more phases are in contact, chemical molecules will exchange or partition between them until equilibrium for each of the compounds in all the phases is reached. At equilibrium, the activity of the material is the same in each phase. Thus, the transport of a compound by partitioning between phases is a function of the activity of the compound in each of the phases. While equilibrium is not attained in many environmental situations, it is the driving force for the movement of dissolved and vapor phase compounds between phases in the environment. The resuspension of particulates from sediments and their transport in the environment and interaction with organisms is also a very important process, but it is not being considered here.

A problem in dealing with toxic materials is that while the activity of a compound controls its partitioning and toxicity due to equilibrium partitioning, the presence of these compounds is usually discussed in terms of concentration. Also, enforcement standards and maximum permitted levels of toxic materials are, unfortunately, most often written in terms of concentrations (e.g., materials containing more than 50 ppm PCBs are considered hazardous materials, regardless of the matrix). It is true that for similar matrices, the activity is proportional to the concentration, but, in general, there is not a direct relationship between them.

One of the reasons activities are not widely used is that they can be much more difficult to determine than concentrations. For instance, non-polar organic compounds with low water solubilities tend to associate with particulates. Enrichment factors of these compounds on particles, compared to water, can be a factor of a million or more. For the very dilute solutions of these compounds that occur in natural water systems, their activity is proportional to the amount dissolved, i.e., to the amount present in the water as free, uncomplexed molecules. It is usually easy to filter a solution and determine the total concentration of compounds in the filtrate. However, this measurement usually over-estimates the dissolved concentration of non-polar compounds since some small particles may also pass through the filter. Because of the high enrichment factor of non-polar organics on these particles, the total concentration of non-polar organic compounds in a filtered solution may be significantly higher than the dissolved concentration of these compounds in the same solution.

For instance, the activity of a compound in water is directly proportional to its dissolved concentration, not to the easily measured filtered concentration. But, because small particulates pass through filters, and the small particles can contain significant amounts of material, the true dissolved concentration of compounds can be difficult to determine. This is the major problem in determining the dissolved concentration of trace organic compounds in phases rich in organic matter, such as sediments, where the enrichment factors on the particles can be 10^6 or more.

Fugacity is another way of describing the chemical activity of a compound. It is the tendency of a compound to partition between two or more phases (Thibodeaux 1979; Mackay 1979; and Mackay and Paterson 1981) and is proportional to the vapor pressure of the compound. For compounds with a measurable vapor pressure, fugacity provides a framework that permits the activity of compounds to be determined in most phases. Fugacity, being equal to the activity of a compound, is the thermodynamic driving force behind the movement of compounds between phases. For instance, if the fugacity of a compound in water is known, its tendency to evaporate and partition into air or other phases, is also known. Also, if a compound is present in several phases and the phases are at equilibrium with respect to that compound, then the fugacity (f has units of pressure, Pa) of the compound is the same in each of the phases:

$$f_a = f_w = f_s = f_x \qquad (1)$$

where f_a, f_w, f_s, and f_x are the respective fugacities in the air, water, sediment and any other phase (surface film; algae; *etc.*) in equilibrium with them.

The implication of this is that if the fugacity can be determined in one phase, it will be known for all phases that are in equilibrium.

The relationship between fugacity and concentration is:

$$f=C/Z \qquad (2)$$

where f is the fugacity with units of pressure (Pascals; Pa), C is the concentration (mol/m^3), and Z is the fugacity capacity (mol/(Pa•m^3). Z is related to the solubility of a compound in the phase, and can differ greatly for different phases. Fugacity is usually determined from the concentration using a known or estimated Z (Mackay and Paterson 1981). However, there are few useful methods for directly determining values for Z.

In this project, advantage will be taken of the fact that the fugacity of a gas phase sample can be determined in a straight-forward manner, and if it is in equilibrium with other phases, then the fugacity in those phases is also known (eq. 1):

$$f_a = f_w = f_s = f_x = C_a/Z_a = C_w/Z_w = C_s/Z_s$$

For the gas phase, the Z_a = 1/RT, and the C's are the concentrations in the respective phases and the Z's are the fugacity capacities for the different phases. Thus the fugacity of a compound in the gas phase is directly proportional to the gas concentration:

$$f_a = C_a/Z_a = C_a/(1/RT) = C_aRT \qquad (3)$$

where C_a (mol/m^3) and Za are the concentrations and fugacity capacities of the compound in air, R is the gas constant (8.31 Pa•m3/(mol•°K) and T is the temperature (°K). At 20°C:

$$f_a = 2.43 \cdot 10^3 \cdot C_a \qquad (4)$$

For water, Z_w = 1/H, where H is the Henry's Law constant. For sediments, $Z_s = (\rho \cdot K_d)/H$ where r is the density of the sediment (kg/l), and K_d is the thermodynamic sediment water partition coefficient (l/kg).

$$f_w = HC_w \qquad (5)$$

$$f_s = HC_s/(\rho \cdot K_d)$$

If water, air and sediment samples are in equilibrium, then the fugacities are the same:

$$f_a = f_w = f_s = C_aRT \tag{6}$$

and:

$$HC_w = C_aRT; \quad C_w = C_aRT/H \tag{7}$$

$$HC_s/(\rho \cdot K_d) = C_aRT; \quad C_s = C_aRT\rho K_d/H \tag{8}$$

In this project, the fugacity of the compounds of interest in sediment and water samples will be determined by equilibrating the samples with air, and determining the fugacities in all of the phases from the measured air concentrations (Eq. 6). The concentration of the compound present as dissolved molecules in solution can then be calculated using equation 7.

It is also of interest to estimate the amount of PCBs evaporating from Lake Calumet and Waukegan Harbor. The flux of a compound across the air/water interface can be calculated as the product of the fugacity difference between the two phases, a mass transfer coefficient, K_{ol} (Mackay *et al.* 1986), and the fugacity capacity (1/H) for water:

$$\text{Flux} = K_{ol}\,(f_w - f_a)/H \tag{9}$$

K_{ol} is dependent on the Henry's Law Constant, temperature, the molecular weight of the compound, the presence of a surface microlayer and the wind speed. K_{ol} is now usually calculated using a two-film resistance model (Liss and Slater 1974):

$$K_{ol} = \frac{1}{K_w} + \frac{RT}{HK_a} \tag{10}$$

where K_w and K_a are the mass transfer velocities (m/s) for the air and water phases.

A number of measurements have been made of K_w under ambient conditions. In order to estimate the net evaporation of PCBs from Lake Calumet and Waukegan Harbor, appropriate estimates of K_w, K_a, and meteorological information will be obtained from the literature and used with appropriate values of H and T for the calculations.

The partitioning of materials into water from sediments is usually investigated (see review by Karickhoff 1984) by determining the partition coefficient (K_p) of the compound of interest between the sediment and water phases. The K_p for a compound is the ratio of the concentration of the compound in the sediment (g/kg), divided by the concentration of the compound (g/l) in water in equilibrium with the sediment. K_p varies with the structure of the compound, the composition of the sediment, and the methods used to determine it.

Determining K_p for sediments involves equilibrating the sediment with water and then determining the concentrations of the compounds of interest in the water and on the sediments. The difficulty in obtaining accurate values for K_p is in determining the water concentrations. What is in solution is usually defined and measured as what passes through a 0.45 µm filter. A number of studies have now shown that a significant proportion of the organic materials that go through such filters are on small particles (Hoffmann *et al.* 1981; Means and Wijayaratne 1982; Baker *et al.* 1986). Thus, the determination of the concentration of a compound in the filtrate of a sample equilibrated with sediments will normally give a result higher than the amount actually dissolved. The differences can be substantial for compounds that have very low water solubilities and have high affinities for organic micro-particulates. Many of the hazardous organics are in this category.

However, a number of careful measurements have been made of K_p for a variety of compounds and sediments. Methods for estimating K_p, based on these results, are now available. For non-polar compounds with low water solubilities, a widely used method is based on assuming that the compounds are preferentially associated with the organic carbon component of the sediment, and that the relative tendency of the compound of interest to partition between water and a non-polar phase is related to how it partitions between 1-octanol and water. This octanol/water partition coefficient, K_{ow}, is determined in laboratory equilibrations.

A widely used method of calculating K_p for a sediment is described by Karickhoff (1984), and uses the following two relationships:

$$K_p = K_{oc}/OC; \qquad (11)$$

where:

$$\log K_{oc} = A \log K_{ow} + B$$

where OC is the fraction organic carbon in the sediment, and A and B are empirically derived constants.

While Karickhoff describes K_p in thermodynamic terms, in practise it is an empirical measurement based on a number of assumptions that all organic carbon is alike; linearity in the equations, equilibrium conditions, *etc.* Fugacity provides an alternative and direct method to determine K_d, the thermodynamic K_p (Yin and Hassett 1986). Equilibration of the sediment sample with air, and determining the fugacity of the compounds of interest in the air also gives their fugacity in the sediments (Equation 1). From this, the K_d can be calculated from Equation 12 or 13:

$$f_s = HC_s/(\rho \bullet K_d); \quad K_d = HC_s/(\rho \bullet f_s) \qquad (12)$$

For C_s in units of wt/wt, the density of the sediment, ρ, is implicitly incorporated in the C_s term. Thus:

$$K_d = HC_s/f_s \qquad (13)$$

By determining the fugacity of the vapor in equilibration with a sediment, the fugacity of the sediment and the K_d for the sediment are obtained.

A complication in dealing with PCBs is that they are mixtures of a number of different chemical compounds, each with its own physical properties. Although they occur together, they dissolve, evaporate, react and partition according to their own individual properties. Thus each chlorobiphenyl compound, or congener, will have its own K_d in each sediment sample. An average K_d, K_d*, can be calculated for a sediment sample, for instance, by summing the PCBs in the water and dividing by the sum of the PCBs in the sediment. However, such a K_d* is like a team batting average, it gives some overall idea of the activity of the sediment, but it gives no information about the subjects of interest, i.e.,the individual compounds. Thus comparing K_d* values for different sediments should be done cautiously, realizing that the K_d for most of the compounds present is different from the K_d* for the sediment. The K_d* then is a function of the sediment and the physical properties of the PCBs, but also of the composition of the PCBs.

The emphasis to date in quantifying the exposure risk of toxic and hazardous materials has been on the concentration of the toxic materials present. Unfortunately, in many cases concentrations may have little relationship to activity. If the route of exposure is by partitioning, then the hazard is related to the activity. Thus the fugacities determined for the compounds measured in this project should be a direct relative measure of their toxicities by bioaccumulation. (Clayton *et al.* 1977; Mackay and Hughes 1984; Connolly and Pedersen 1988).

Chapter 2. Sampling and Measurement Procedures

Water

Water samples were collected from the shore and through the ice of Lake Calumet, and from a boat dock in Waukegan Harbor. The shore samples from Lake Calumet were collected from some convenient off-shore rocks on the west shore of the Lake several hundred meters south of the Pullman Creek (LC-2B) inlet. The samples from Waukegan Harbor were collected from a boat dock that extends about half way across the north slip. This dock is approximately at the site where the PCB discharge to the harbor historically occurred, and is about midway between WH-1 and WH-3 on Figure 1.

Most of the samples from Lake Calumet and Waukegan Harbor were collected from beneath the surface in clean, one gallon (4 l) glass bottles. The samples from beneath the ice in Lake Calumet and Waukegan, and the winter samples from Waukegan Harbor (the docks were raised about five feet above the water surface during the ice season) were collected by drawing water through a 3/8 in. (0.95 cm) clean copper tube into a one or five gal. (19 l) clean glass container. The water was drawn into the bottles by using an air pump to withdraw air from the bottle.

The water was equilibrated with air by passing the water and a clean air stream, counter-currently through a glass column. This equilibration column was a glass tube 1.5 m. long, 4 cm. i.d.., with 1.2 m. of its length packed with copper scouring pads, mounted vertically. The copper sponge increased the amount and residence time of the water in the column, and increased the surface area for equilibration (see Figure 2). A different column equilibration technique has recently been reported by Fendinger *et al.* 1988.

The water sample was contained in a 19 l. carboy. Air pressure was used to force it through a clean 0.25 in. (.63 cm.) copper tube to a spray head at the top of the column. The metal spray head had several small holes drilled in it from which the water sprayed on the column. The air entered the bottom of the column through a Florisil tube, and exited at the top through a Florisil tube that stripped the air of the compounds that partitioned out of the water. The water exited the column through a stopcock at the bottom. The stopcock was set to keep some water in the column to prevent air loss. A typical water sample consisted of 70 l. for Lake Calumet (three large bottles and several small ones), and 19 l. for Waukegan Harbor (see Table 6).

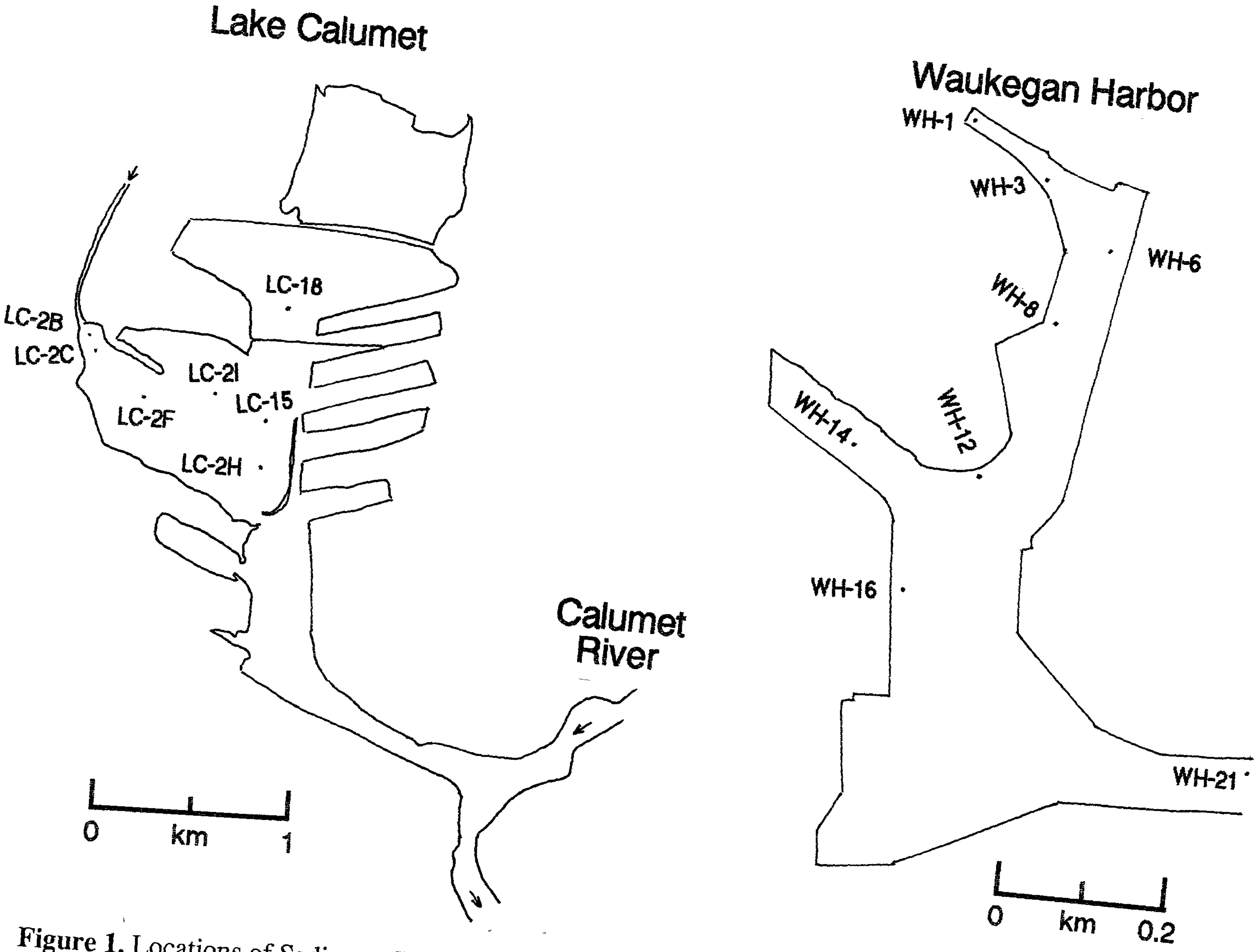

Figure 1. Locations of Sediment Sampling Sites.

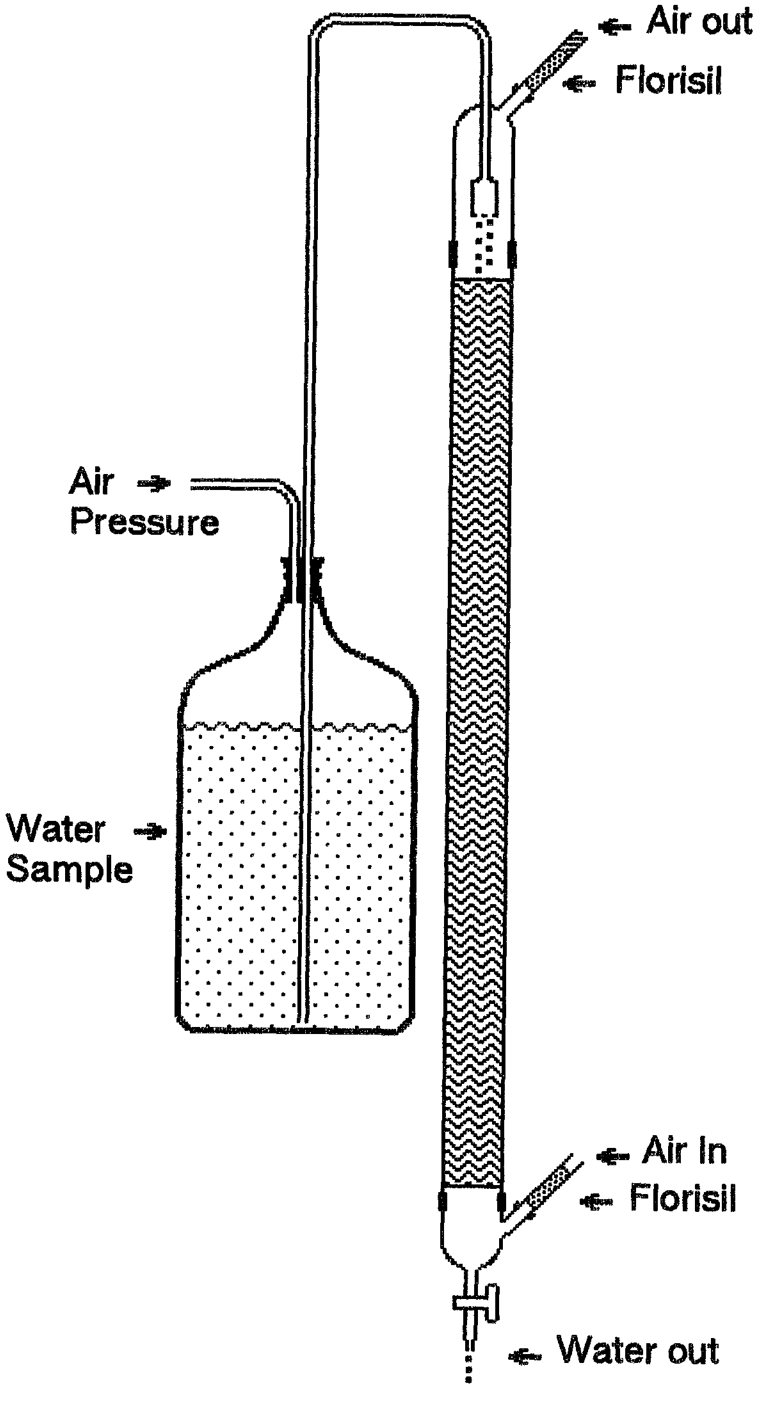

Figure 2. Water Equilibration Set-up.

The operating conditions were chosen so that the air residence time would be more than four times the air/water exchange half-life estimated from the reported K_{ol}. The water flow rate was chosen such that less than 10% of the dissolved compounds with H = 20 Pa•m^3/mol (similar to the PCBs) were stripped during passage through the column. The residence times in the column were ≈90 sec. for water and ≈45 sec. for air. The column was operated with water flows of ≈7 l/hr and air flows of ≈100 l/hr. A greater proportion of compounds with higher HLCs would partition into the air (which could deplete the water), while a smaller proportion of those with a lower HLC would do so. The air and water flow rates, temperatures of equilibrations and volumes of air and water used for each sample are listed in Table 6.

After a sample was run, the water inlet head was replaced with a condenser, and the column and column packing were cleaned by refluxing acetone and then hexane through the column. The copper inlet tube for the water was rinsed with acetone.

The total concentration of PCBs in each of the water samples was determined as described in the analysis section. The sample analyzed typically involved seven liters of water from Lake Calumet or two liters of water from Waukegan Harbor.

An uncontrolled source of error in the experiment was the temperature of the equilibration. The sample was usually in the lab for 18 hours or more before the sample was run. Since the water passed through about 2 m of 0.25 in. copper tubing and then through the column, all at room temperature, we assumed that the equilibration was done at room temperature, about 23 ± 2°C. The Henry's Law constants used were for 20°C. Assuming the HLC doubles for a change in temperature of 10°C (Burkhard *et al.* 1985), the air concentration measured will be higher than calculated by about 20%. The results shown in Table 4 are corrected for this bias.

Several different experiments and kinds of experiments were tried to check the accuracy of the results from the water equilibration experiments. On a number of occasions a measured volume of a water solution of a single chlorobiphenyl compound, 2,2',5,5'-tetrachlorobiphenyl (IUPAC congener #52) was added to the water sample several hours or more before the equilibrations were begun. The idea was that congener #52 would equilibrate with the particles in the solution and would partition like the PCB congeners already present. The experiments using the added congener #52 showed an increase in the percent dissolved of this congener of 10-20% compared to experiments without added #52. This difference was not large, but was consistent. It indicates that the added congener #52 was relatively more volatile than the #52 present in the sample. The most reasonable explanation for this is that the added #52 did not completely equilibrate with the particulates. However, the #52 in these experiments did show reduced volatility over what would have been expected if no particulates had been present.

Finally, a solution of Aroclor 1254 was prepared in deionized, organic-free water by adding a solution of the PCBs in acetone and stirring the water overnight. The amounts used were low but comparable to the Lake Calumet samples. The water was equilibrated with air and the amount calculated to be dissolved was compared to that found from an analysis of the water. The calculated amount included the correction for the temperature of the equilibration. Ninety percent of the expected amount was found. This was within the experimental limits of the experiment.

This experiment demonstrates that the PCB compounds behave as expected in the absence of sediment particles. The results from this experiment, and the ones with congener #52 described above, indicate that the air/water equilibration methods worked as anticipated.

Sediments

Sediment samples were collected with a Ponar dredge on sampling trips in Nov., 1986, and April, 1987 by the research groups participating in the Lake Calumet and Waukegan Harbor projects. The sediment samples were mixed to homogenize them, and then each was subsampled for the different projects. The samples then should represent the volume-weighted composition of the upper 5-10 cm of the sediments sampled. Portions of some of the sediment samples were obtained for this project (see maps on Figure 1).

An air/sediment equilibration method was developed to determine the fugacity of the PCBs in these samples. It involved packing a long glass tube with sediments, and passing nitrogen slowly through the tube to allow the PCBs in the sediments to equilibrate with the gas. In order to get rapid and efficient equilibration between the sediment and gas phases, a large surface area was needed. It was decided to dehydrate the sediment, and pack the tubes with a mixture of pulverized sediment and glass wool to maximize the surface area and the permeability of the sediments for the equilibrations.

Portions of the sediments were dehydrated over Calcium Chloride in a dessicator. The sediments were not air dried or dried in an oven in order to minimize the loss of volatile materials. No attempt was made to thoroughly dehydrate the sediments, and the Calcium Chloride was typically quite moist when the dehydrating was terminated.

The dehydrated sediments were mixed with cleaned glass wool and packed into sections of glass tubing ≈1 cm i.d. Similar volumes of sediment and glass wool were used to pack about 1.1 m of the tube. The sediment-containing tube was mounted in a larger tube which formed a water jacket. Water from a 20°C constant temperature bath was passed through the water jacket to control the temperature during the equilibration. See Figure 3.

Sediments contain a variety of binding sites on which molecules can be adsorbed. The binding sites differ in their shape, polarity and affinity for molecules. It is possible that thorough dehydration of the sediments would remove some of the bound water molecules from active sites and then these sites could bind more strongly to the organic molecules. This would change the PCB fugacity compared to the wet sediments. To avoid or minimize this problem, the nitrogen gas used to equilibrate with the sediments was saturated with water vapor at 20°C. If there were no irreversible changes in the sediment upon dehydration, the sediments should then have been hydrated by the water-saturated gas, and the adsorbed molecules should have behaved as if the sediments were suspended in water.

Several experiments were run to check on the effects on the PCB concentrations in the gas phase due to using dehydrated sediments. In two of these experiments, several measurements were made using dry nitrogen on dessicator-dried sediments, and then the nitrogen was saturated with water and additional measurements were made. There was little difference in the gas phase PCB concentrations before and after using the water-saturated air with the dehydrated sediments.

In addition, two tubes were packed with dehydrated sediments (WH-3). One sample was dehydrated in the normal manner, the other was more thoroughly dehydrated using phosphorus pentoxide as the dessicant. Several experiments were run using dry nitrogen. Then the nitrogen was saturated with water and additional runs were made. The amounts found in the vapor

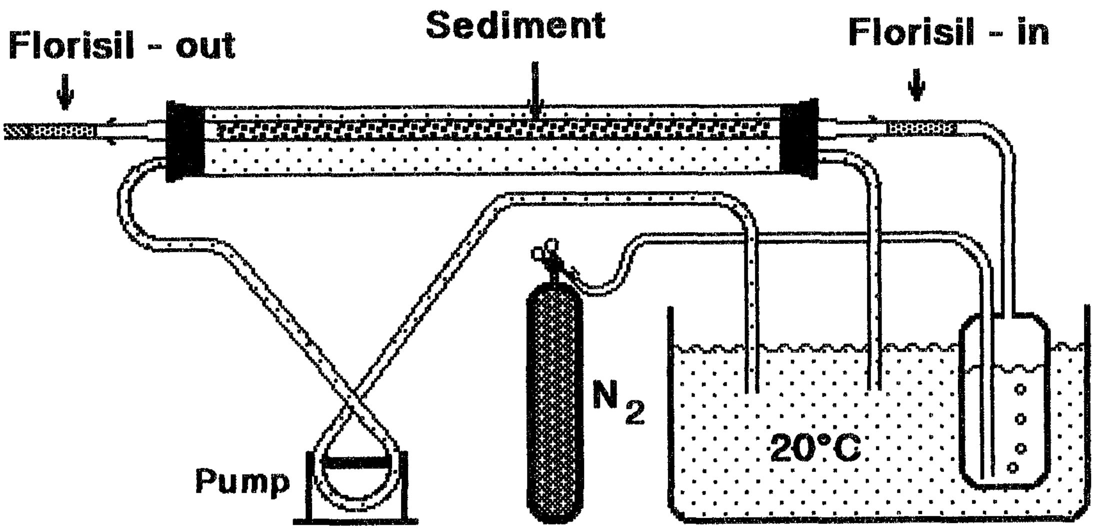

Figure 3. Sediment Equilibration Set-up.

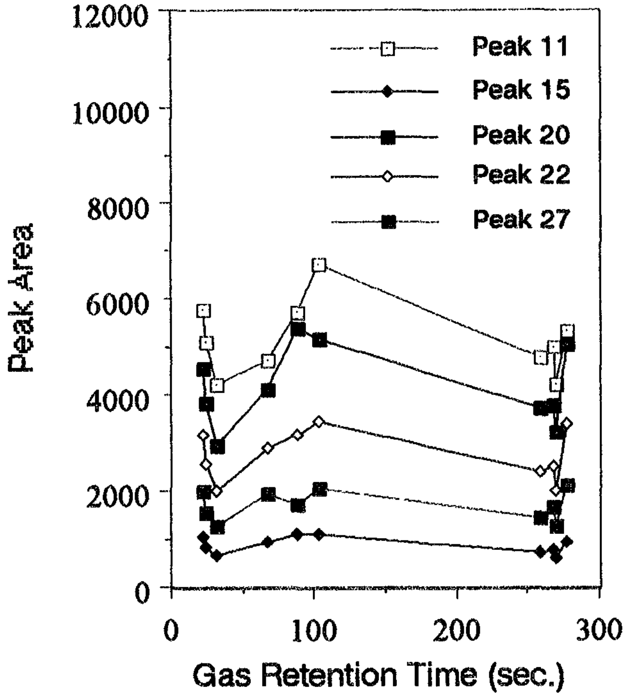

Figure 4A. Peak Area vs. Flow Rate.

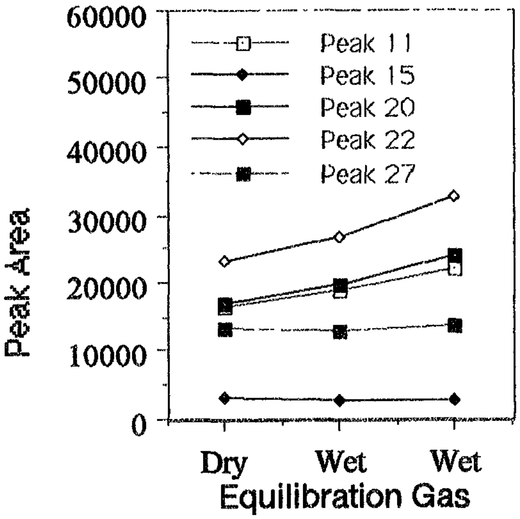

Figure 4B. Dry vs. Wet Equilibrations.

phase were quite similar for both tubes, for both the dry and water-saturated runs, Figure 4B.

Finally, a slurry of fresh sediment (undried) was placed in a 1.4 m column (2 cm dia.) and clean air was bubbled through the column to equilibrate with the sediments. Within a factor of 2, the PCB concentrations found in the air were the same as those found in the dehydrated sediment equilibration experiments (0.3 - 0.6 $\mu g/m^3$ for WH-3).

The gas passed through a Florisil containing tube on entering the column to remove any impurities present, and through a similar Florisil tube at the end of the column to collect the compounds that partitioned into the gas. The residence time of the gas in the column was typically about 3 min. To check whether the sediment equilibration experiments were at equilibrium, a number of experiments were done at different gas flow rates. This permitted a check on whether the PCB concentrations found in the gas phase were a function of the gas retention time in the tube.The results from one set of these experiments are shown in Figure 4. It can be seen that even at retention times much longer (20 min.) than those used in the experiments (3 min.), the PCB concentrations in the gas phase did not increase. The flow rate and gas volume collected in each of the experiments are shown in Table 2.

Analysis

All solvents used to process samples in the project were pesticide grade. Solvents distilled from glass were frequently used to rinse the apparatus. The Florisil™ was activated by baking at 600°C and storing at 130°C. The chlorinated organic compounds were determined in the dehydrated sediment samples by extraction in a soxhlet extractor with hexane and methylene chloride. The extracts were chromatographed on Florisil. The fractions eluted with hexane and hexane + 20% methylene chloride contained the compounds of interest.

The chlorinated organic compounds were determined in the water samples by extracting them with methylene chloride (Alford-Stevens 1985). About 0.3 l of methylene chloride was added to a 1 gal (4 l) bottle containing the water to be extracted. The bottle was capped and shaken vigorously several times. The methylene chloride was separated from the water by using a separatory funnel. The extracts were dehydrated, concentrated, the solvent changed to hexane, and the sample cleaned-up by chromatography on Florisil, as above, and analyzed.

The Florisil tubes from the water and sediment equilibration experiments were eluted with hexane, and then 20% methylene chloride in hexane, the extracts concentrated and the PCBs determined with GC as described below.

Non-polar chlorinated organic compounds measured in this project were separated by gas chromatography. In the early part of the project a 30 m, wide-bore (0.75 mm), bonded-phase (DB-5) capillary column was used with a Tracor MT-220 GC. Detection was by a Ni^{63} electron capture detector. Peaks were integrated using a digital electronic integrator (Supergrator-3); the peak retention times were determined relative to internal standards of 1,3,5-tribromobenzene (TBB) and octachloronaphthalene (OCN). Compounds were identified by comparing them to the retention times of standards run under identical conditions. The PCBs were quantified by first determining the response factors for 54 of the resolved peaks in the PCB chromatogram. These response factors were then applied to the appropriate PCB peak in the chromatogram of the sample to determine the amount of PCBs in each peak present. These amounts were summed to give the total amount present.

The GC used for all the sediment analyses and most of the water samples, was a Hewlett-Packard 5890 GC, with an electron capture detector, and a 30 m, .25mm, .25 µm DB-5 bonded phase, capillary column. The data were collected and reduced with a HP 3393A integrator. Identification was by retention time compared to a mixture of Aroclor standards. Quantitation was by the internal standard method using chlorobiphenyl compound #204 as the internal standard, and trichlorobiphenyl compound #30, TBB and OCN as additional time reference peaks. Individual response factors, calculated from a mixture of standards whose absolute composition has been determined (Mullin 1985; Mullin *et al.* 1984), were used for each of the resolved PCB peaks. Standard mixtures were run daily to check retention times and response factors. The recovery of the PCBs from the Florisil traps for the sediment experiments was corrected by the addition of standards to the unextracted collection tubes.

Besides the quantification measurements, the patterns of the PCB compounds in the spectra were checked. The PCB patterns in the starting samples were determined. In the partitioning to the air, the more volatile congeners would preferentially evaporate giving a PCB pattern relatively enriched in the lower molecular weight congeners. Given the composition of one of the mixtures, the composition of mixtures in equilibrium with it can be calculated (Murphy *et al.* 1987). In all cases, the composition of the mixtures fit with that expected.

Chapter 3. RESULTS

Sediments

Measurement and calculations were done by individual PCB congener for each of the water and sediment samples analyzed. A summary of the results obtained from each of the sediment samples tested is shown in Tables 1 and 2. Total PCBs are shown. Details of the Tables are discussed in the text.

Table 1. SUMMARY OF SEDIMENT RESULTS.

	$[PCB]_s$ mg/kg (dry)	$[PCB]_a$ $\mu g/m^3$	f_s Pa	K_d* l/kg	$[PCB]_w$ ng/l	OC[&] frac.	#18/#17 Ratio	K_{oc} x10^{-6}
WH-1	20.	9.4	8.2E-05	2.2E+04	92	0.0034	0.11	6.5
WH-3	380.	307	3.1E-03	1.1E+04	35,000	0.015	0.014	0.73
WH-6	11.	1.1	1.1E-05	8.9E+04	120	0.040	0.24	2.25
WH-8	43.5	2.0	2.1E-05	18.0E+04	240	0.048	0.55	3.75
WH-12	30.	0.12	1.0E-06	270.0E+04	11	0.050	1.6	54
WH-14	12.	2.3	2.2E-05	4.8E+04	250	0.037	0.28	1.3
WH-16	9.8	0.18	1.8E-06	48.0E+04	20	0.036	0.77	13
WH-21	0.36	0.053	5.4E-07	5.9E+04	6	0.016	0.73	3.7
Average				*44.8E+04 ±205%*		*0.037*	*0.56*	*10.7 ±18*
(less WH-12)				*12.7E+04 ±130%*			*0.38*	*4.5 ±4.2*
LC-2B	1.1	0.004	2.9E-08	3.4E+06	0.3	0.048	1.43	70.8
LC-2C	3.6	0.026	2.3E-07	1.4E+06	3.0	0.045	1.48	31.
LC-2F	0.4	0.003	2.8E-08	1.3E+06	0.3	0.025	1.17	65.
LC-2H	0.24	0.30	2.8E-06	7.6E+03	32	0.030	1.61	0.25
LC-2I	0.16	0.003	2.5E-08	5.7E+05	0.3	0.025	1.70	23.
LC-15	0.6	0.010	9.2E-08	5.8E+05	1.0		0.99	
LC-18	1.6	0.016	1.4E-07	1.0E+06	1.6		1.11	
Average				*1.2E+06 ±92%*		*0.036*	*1.35*	*38.±30*

[&] Waukegan results from Risatti, 1988; Lake Calumet results from Ross *et al.* 1988.

The measured total PCB concentrations for the sediments are shown in column 2. The total PCB concentration of the vapor in equilibrium with the sediments is shown in column 3. The fugacity (equation 3) found for each sample is in column 4.

Table 2. Summary of Experimental Parameters for Sediment Sample Equilibrations.

Sediment Name	Amount Used gm	Air Retention Time minutes	Nitrogen Used m3	Recovery %
LC-2B	18.42	2.76	0.914	
LC-2C	38.45	3.29	2.045	58.2
LC-2F	99.50	3.25	2.050	93.4
LC-2H	83.83	2.80	2.020	65.1
LC-2I	81.94	3.18	1.850	45.3
LC-15	78.60	2.32	2.010	80.7
LC-18	64.93	2.41	1.870	56.2
WH-1	23.89	6.23	0.0043	70.8
WH-3	5.41	2.51	0.0067	45.9
WH-3	5.41	3.15	0.0042	61.5
WH-3	5.41	17.35	0.0022	57.8
WH-3	5.41	17.60	0.0106	61.1
WH-3	5.41	27.74	0.0056	75.2
WH-3	5.41	22.71	0.0075	51.8
WH-3	5.41	2.22	0.0070	42.0
WH-6	13.89	2.97	0.0252	
WH-6	13.89	3.93	0.4440	85.6
WH-8	17.83	2.77	0.1400	91.1
WH-8	17.83	2.50	0.2910	45.5
WH-8	17.83	42.30	0.1220	37.4
WH-8	17.83	3.35	0.0930	51.6
WH-12	12.78	2.89	0.5010	95.8
WH-14	23.47	1.40	0.4900	52.5
WH-16	62.39	2.24	1.4900	66.5
WH-21	81.39	2.50	1.8100	47.5

The K_d* was calculated for each of the sediments using equation 12, the total PCB concentration of the sediment (column 2), the average H (23 ±10 Pa•m^3/mol), and the total fugacity of the PCBs in the sediments (column 4). The results are shown in Table 1, column 5. The values found here ranged from $1.1 \cdot 10^4$ for WH-3 to $3 \cdot 10^6$ for WH-12 and LC-2B. As discussed in the introduction section, the K_d* is only an average and most of the individual congeners will have different K_ds. For instance, the K_d* for WH-3 is $1.1 \cdot 10^4$ while the individual K_ds range from $4 \cdot 10^3$ to $3 \cdot 10^6$. The K_d* is biased toward the K_ds of the congeners in the vapor, the low molecular weight congeners.

The calculated concentration of dissolved PCBs in water ($[PCB]_w$) in equilibrium with these sediments is shown in column 6. These are calculated from Equation 7 using the fugacities in column 4 and the average H value. They range from 35 µg/l for WH-3 to 0.3 ng/l for LC-2I, a range of 10^5. The range is a function both of the different compositions of the sediments (more soluble PCBs were present in the WH samples) as well as the range of PCB concentrations found. To the extent that biota accumulate PCBs from the environment by partitioning (Connolly and Pedersen 1988; Clark *et al.* 1988), the fugacities (Column 4) or the projected dissolved concentrations should be a direct measure of the toxicity of the sediments due to PCBs.

Since the concentration of the PCBs in the water in equilibrium with the sediments was not measured, a K_{oc} as usually determined, is not available. However the thermodynamic K_d* calculated from the sediment (column 5) can be divided by the percent total organic carbon (OC; column 7) to give a K_{oc} in the samples. This value is shown in column 9.

The two lowest K_d*s in Waukegan Harbor are for sediments WH-1 and WH-3, the two closest to the PCB discharge. Of these, WH-3 & WH-12 seem to be anomalous. Compared to the other WH samples, WH-3's relative fugacity is much higher than its PCB concentration would indicate. This results in its much lower K_d*. Conversely, WH-12 has the highest K_d* and highest Congener #18/#17 ratio for any of the WH samples. The high K_d* could reflect a different sediment type than is present in the rest of the harbor (though the %OC is typical of the other samples, perhaps the type of the OC in this sample is different from the OC in the other samples). The very different #18/#17 ratio suggests that the PCBs in this sample are from a different source than the PCBs found in the remainder of the harbor.

The results on WH-3 are of great importance to the hazard of the sediments in the Harbor, as this sample *represents the area of highest [PCB] in the harbor, and most of the mass of the PCBs in the harbor.* In addition to the results shown in Tables 1 and 2, two additional sediment equilibration tubes were prepared from the WH-3 sediment sample. The measured fugacities were within experimental error of the results in Table 1. The results for the WH-3 sample are further highlighted in Table 3 and Figure 5.

The results for each of the individual PCB congeners which were present in both the sediment and vapor samples, for two of the sediment samples are shown in Tables 3 (WH-3) and 4 (LC-2C) (the individual congener data for the other samples may be obtained from the authors, or from the Hazardous Waste Research and Information Center). The fugacity of the individual congeners is calculated from their vapor pressures using Eq. 6. These results are in Tables 3 and 4, column 3, and in Figures 5B and 6B. The K_ds (column 6) were calculated using Eq.13, the fugacites and C_s found, and the H for each congener (Burkhard *et al.* 1985; Murphy *et al.* 1987)

As in the Aroclor mixtures, there is a lot of variability in the amounts of individual PCB congeners present within each sample, and between the two samples. The discharges from Waukegan harbor are reported to have been a mixture of Aroclors 1242 and 1248, both consisting predominantly of congeners containing five or fewer chlorines. This can be seen in a plot of the composition of the PCBs *vs.* the elution order of the congeners from the GC for WH-3 (Figure 5B). The plot of the amounts *vs.* GC retention time is used rather than a plot *vs.* IUPAC congener number because the retention time is principally a function of the vapor pressure of the congener. Since the results to be compared are vapor pressures, fugacities and dissolved water concentrations, the GC retention time should give a more useful ordering of them. Also shown for comparison on Figure 5, are a GC of a mixture of PCB standards (Figure 5A), and a GC of a Waukegan Harbor sediment sample (WH-21; Figure 5C) from close to the harbor mouth, a location remote from the PCB discharge to the harbor.

The PCBs in LC-2C reflect a greater diversity of sources, and their composition shows larger proportions of the higher molecular weight compounds (Figure 6A). This is part of the explanation for the high K_d* for LC-2C compared to the K_d*s for the Waukegan sediments, though the K_ds for specific congeners are still an order of magnitude or more, higher for LC-2C than for WH-3. The Lake Calumet data are more typical of environmental

Table 3. MEASUREMENTS AND FUGACITY CALCULATIONS ON WH-3.

IUPAC Number	$[PCBs]_{air}$ ng/m^3	fugacity Pa	$[PCBs]_{sed}$ ng/g	$[PCBs]_{sed}$ mol/g	K_d l/kg
3	5851	7.4E-05	5242.4	2.8E-08	7.5E+03
4	27642	3.0E-04	8431.8	3.8E-08	3.8E+03
7	3761	4.0E-05	2199.6	9.9E-09	8.8E+03
6	4030	4.3E-05	2969.5	1.3E-08	9.2E+03
8	131045	1.4E-03	95316.0	4.3E-07	8.5E+03
19	19403	1.8E-04	12244.4	4.8E-08	7.9E+03
13	134	1.4E-06	564.6	2.5E-09	5.3E+04
18	403	3.8E-06	659.9	2.6E-09	2.0E+04
17	42687	4.0E-04	45971.6	1.8E-07	1.5E+04
24	6119	5.7E-05	8505.1	3.3E-08	1.9E+04
16	28358	2.6E-04	40839.2	1.6E-07	1.4E+04
25	2284	2.1E-05	7332.0	2.8E-08	5.4E+04
31+28	19104	1.8E-04	55723.2	2.2E-07	3.2E+04
51	2955	2.4E-05	6892.1	2.4E-08	2.9E+04
22	1060	9.9E-06	6305.5	2.4E-08	5.0E+04
45	90	7.4E-07	267.6	9.2E-10	3.7E+04
46	79	6.5E-07	278.6	9.5E-10	3.8E+04
52	776	6.4E-06	2932.8	1.0E-08	3.8E+04
49	1045	8.6E-06	4399.2	1.5E-08	4.9E+04
47	7164	5.9E-05	30134.5	1.0E-07	5.3E+04
44	199	1.6E-06	1114.5	3.8E-09	4.4E+04
37	373	3.1E-06	2932.8	1.0E-08	4.9E+04
100	627	4.6E-06	4765.8	1.5E-08	9.5E+04
63	260	2.1E-06	2786.2	9.5E-09	1.3E+05
74	149	1.2E-06	2228.9	7.6E-09	1.3E+05
70	224	1.8E-06	2896.1	9.9E-09	1.0E+05
95	373	2.7E-06	4061.9	1.2E-08	9.1E+04
91	284	2.1E-06	2712.8	8.3E-09	1.1E+05
84	90	6.6E-07	1055.8	3.2E-09	8.1E+04
101	134	9.9E-07	2060.3	6.3E-09	1.2E+05
99	96	7.0E-07	791.9	2.4E-09	7.3E+04
110	57	3.8E-07	1979.6	5.5E-09	1.5E+05
82	9	6.6E-08	117.3	3.6E-10	6.5E+04
107	18	1.2E-07	1613.0	4.5E-09	2.3E+06
138	12	7.9E-08	1561.7	4.3E-09	4.1E+05
SUM	307000	3.1E-03	377000	1.5E-06	1.1E+04#

#Calculated using Equation (9), the total values for the air fugacity (Pa) and sediment concentration (mol/g), and 23 ±10 Pa•m^3/mol for H.

(The chemical identity and IUPAC names for each of the PCB congeners discussed in this report are listed in Appendix A).

Table 4. MEASUREMENTS AND FUGACITY CALCULATIONS ON LC-2C.

IUPAC Number	$[PCBs]_{air}$ ng/m^3	fugacity Pa	$[PCBs]_{sed}$ ng/g	$[PCBs]_{sed}$ mol/g	K_d l/kg
3	0.04	5.54E-10	0.36	1.9E-12	7.0E+04
4	0.42	4.56E-09	5.57	2.5E-11	1.6E+05
7	0.33	3.51E-09	2.54	1.1E-11	1.2E+05
6	0.15	1.64E-09	5.25	2.4E-11	4.3E+05
8	2.58	2.77E-08	76.91	3.4E-10	3.5E+05
19	1.05	9.83E-09	12.71	4.9E-11	1.5E+05
18	2.34	2.18E-08	86.50	3.4E-10	4.6E+05
17	1.23	1.14E-08	58.43	2.3E-10	6.5E+05
24	0.25	2.33E-09	10.78	4.2E-11	5.7E+05
16	2.02	1.88E-08	108.21	4.2E-10	5.4E+05
25	0.15	1.42E-09	12.11	4.7E-11	
31	0.98	9.12E-09	125.86	4.9E-10	1.4E+06
28	1.37	1.28E-08	220.75	8.6E-10	1.8E+06
22	0.25	2.33E-09	6.95	2.7E-11	
45	0.40	3.31E-09	23.25	8.0E-11	7.2E+05
46	0.18	1.52E-09	10.11	3.5E-11	5.9E+05
52	1.12	9.20E-09	103.44	3.5E-10	9.2E+05
49	1.20	9.83E-09	141.36	4.8E-10	1.4E+06
47	2.84	2.33E-08	57.89	2.0E-10	2.6E+05
44	1.09	8.93E-09	116.23	4.0E-10	8.5E+05
37	1.25	1.17E-08	85.50	3.3E-10	4.3E+05
41	0.65	5.36E-09	111.77	3.8E-10	1.4E+06
40	0.21	1.70E-09	30.50	1.0E-10	9.8E+05
74	0.01	8.93E-11	50.62	1.7E-10	
70	0.47	3.84E-09	162.31	5.6E-10	2.7E+06
95	1.09	7.99E-09	253.09	7.8E-10	1.9E+06
101	0.58	4.23E-09	69.41	2.1E-10	9.0E+05
99	0.32	2.32E-09	56.04	1.7E-10	1.6E+06
110	1.12	8.23E-09	138.05	4.2E-10	5.4E+05
149	0.12	7.95E-10	47.68	1.3E-10	
118	0.12	8.79E-10	94.85	2.9E-10	
138	0.01	5.78E-11	117.19	3.2E-10	
SUM	26	2.31E-07	2810	9.6E-09	9.6E+05#

#Calculated using Equation (9), the total values for the air fugacity (Pa) and sediment concentration (mol/g), and 23 ±10 Pa•m^3/mol for H.

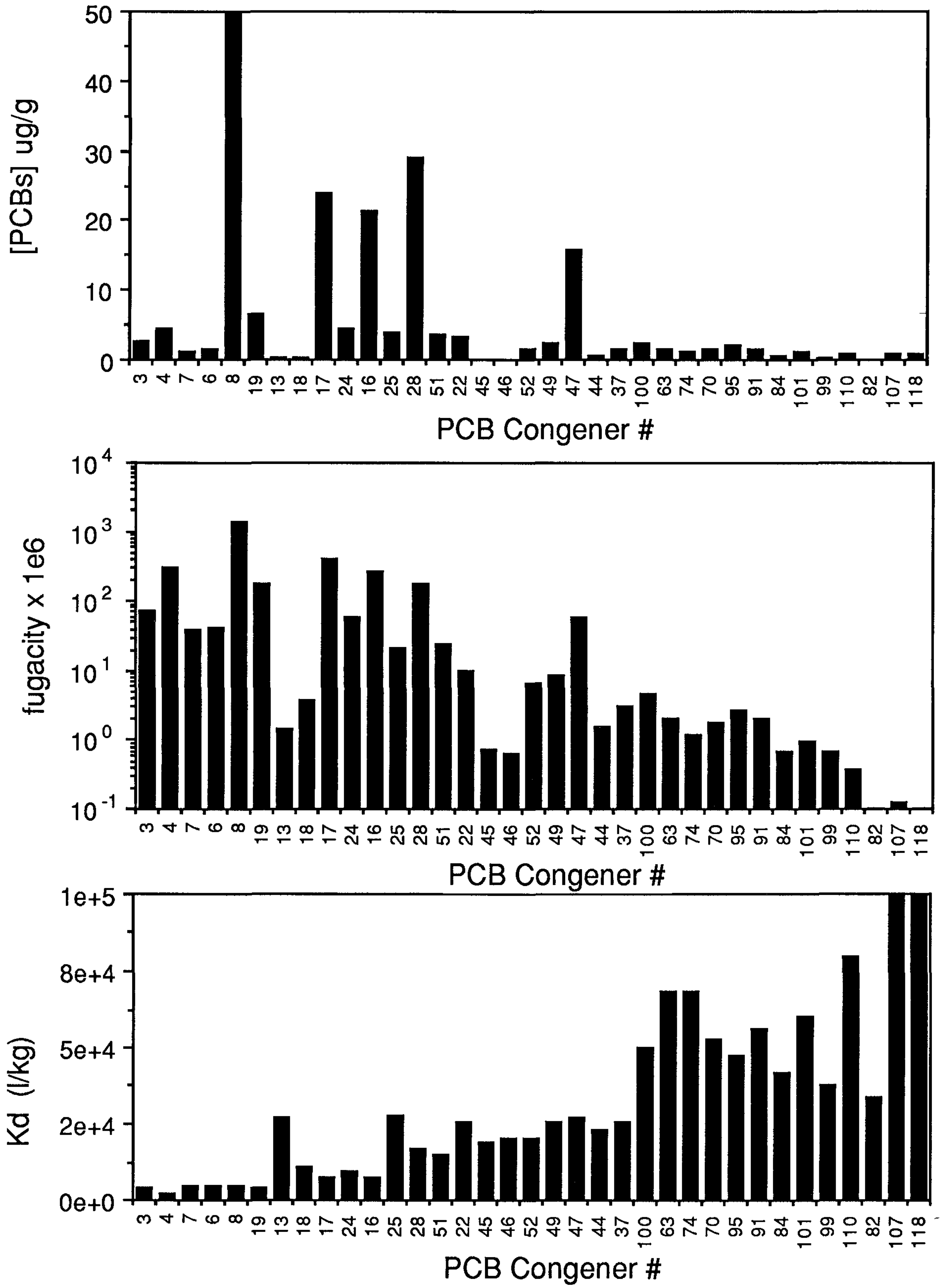

Figure 5. WH-3 Sediment Results.

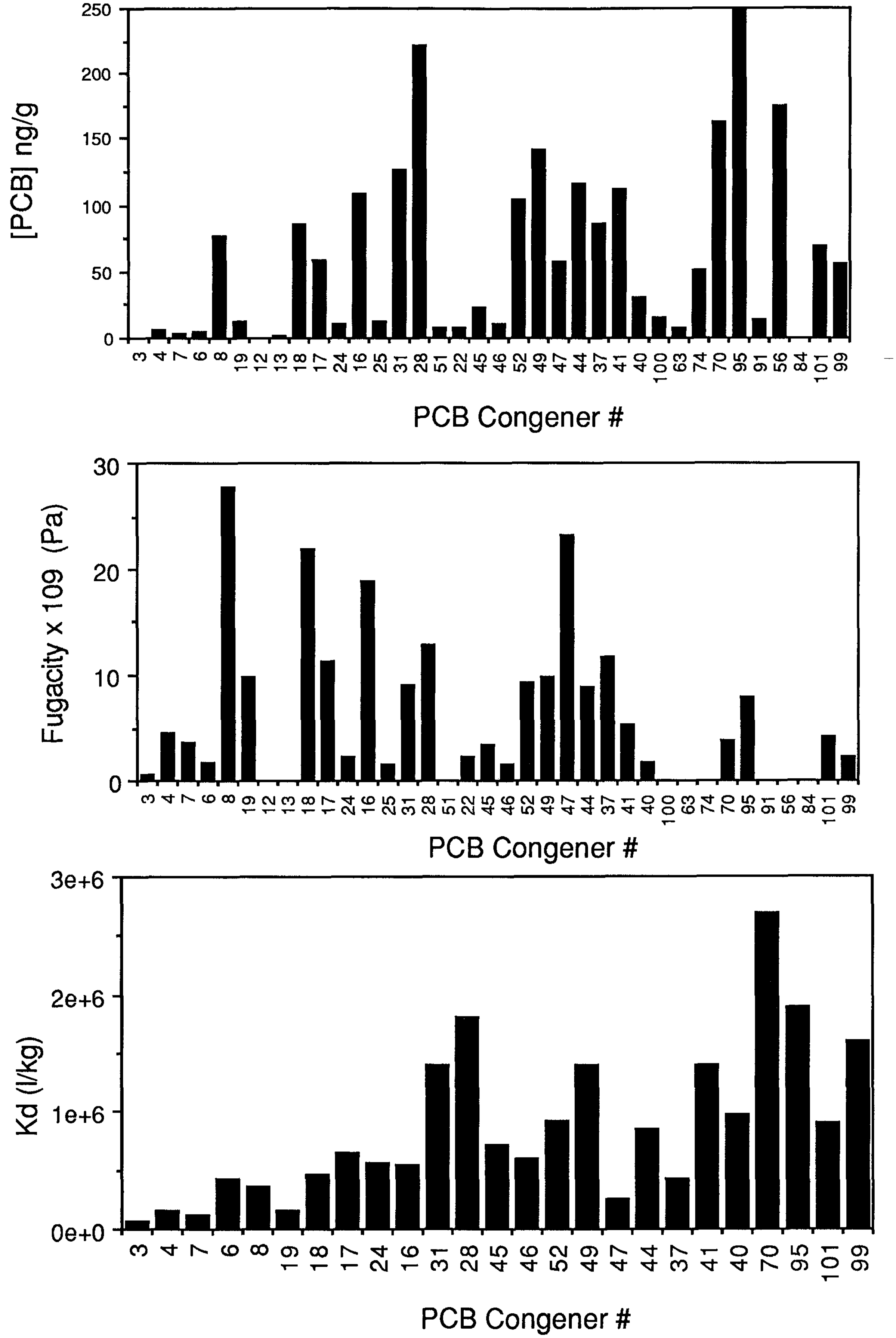

Figure 6. Results for LC-2C Sediment Samples.

samples where the lower molecular weight compounds are present in lower amounts, either due to the composition of the sources, to partitioning into water, or to preferential degradation of the lower molecular weight congeners (Brown *et al.* 1987).

The vapor compositions determined are what you would expect due to partitioning from the sediments. They are relatively enriched in the lower molecular weight, more volatile congeners (Tables 3 and 4, column 2), Murphy *et al.* (1987).

The K_d for each of the congeners in the WH-3 and LC-2C sediments was calculated using Equation 13, and the results are shown in Tables 3 and 4, and in Figures 5C and 6C. As expected, a trend of increasing K_d with increasing GC retention time (higher MW, lower vapor pressure) can be seen in the data for each of the sediments. This is due to the fact that while the vapor pressure of the congeners decreases significantly in going to higher molecular weights, the Henry's Law constant shows little variation for the different congeners. Thus the K_ds show a trend of increasing values with longer retention times. Values of 10^5 to 10^6 (Baker *et al.* 1986) and 10^4 to 10^7 (Brownawell and Farrington 1986) were reported for K_d*s. The K_d*s found here are within the wider range, though at the edges.

There was an unexpected finding in the PCB composition of Waukegan harbor samples. PCB congeners #17 and #18 (the 2,2',4- and 2,2',5-trichlorobiphenyls) elute early from the DB-5 GC column, #18 before #17, and very close together (See Figure 7A). They are important constituents in the Aroclor 1232, 1242, 1248 and 1016 mixtures (Albro *et al.* 1982; Mullin 1985), and are usually present in similar amounts. *The sediments in the area of the PCB discharge (WH-1 & WH-3) to the Harbor had very low #18/#17 ratios* (0.11 and 0.014; Tables 1&2; Figures 5&7B). The average #18/#17 ratio for all of the sediments analyzed from Waukegan was 0.56 (0.38 without WH-12, see discussion). The #18/#17 ratios for the Lake Calumet sediments was about 1.35. The Waukegan Harbor #18/#17 ratio tended to increase as the distance increased from the point of discharge of the PCBs. This probably reflects the incorporation of PCBs from other sources and, at least for WH-21 (#18/#17 = 0.75; Figure 7C), exchange with the open lake. The difference in PCB composition between the area of the discharge, WH-3, and the harbor mouth, WH-21, remote from the discharge can also be seen in Figures 7B and 7C.

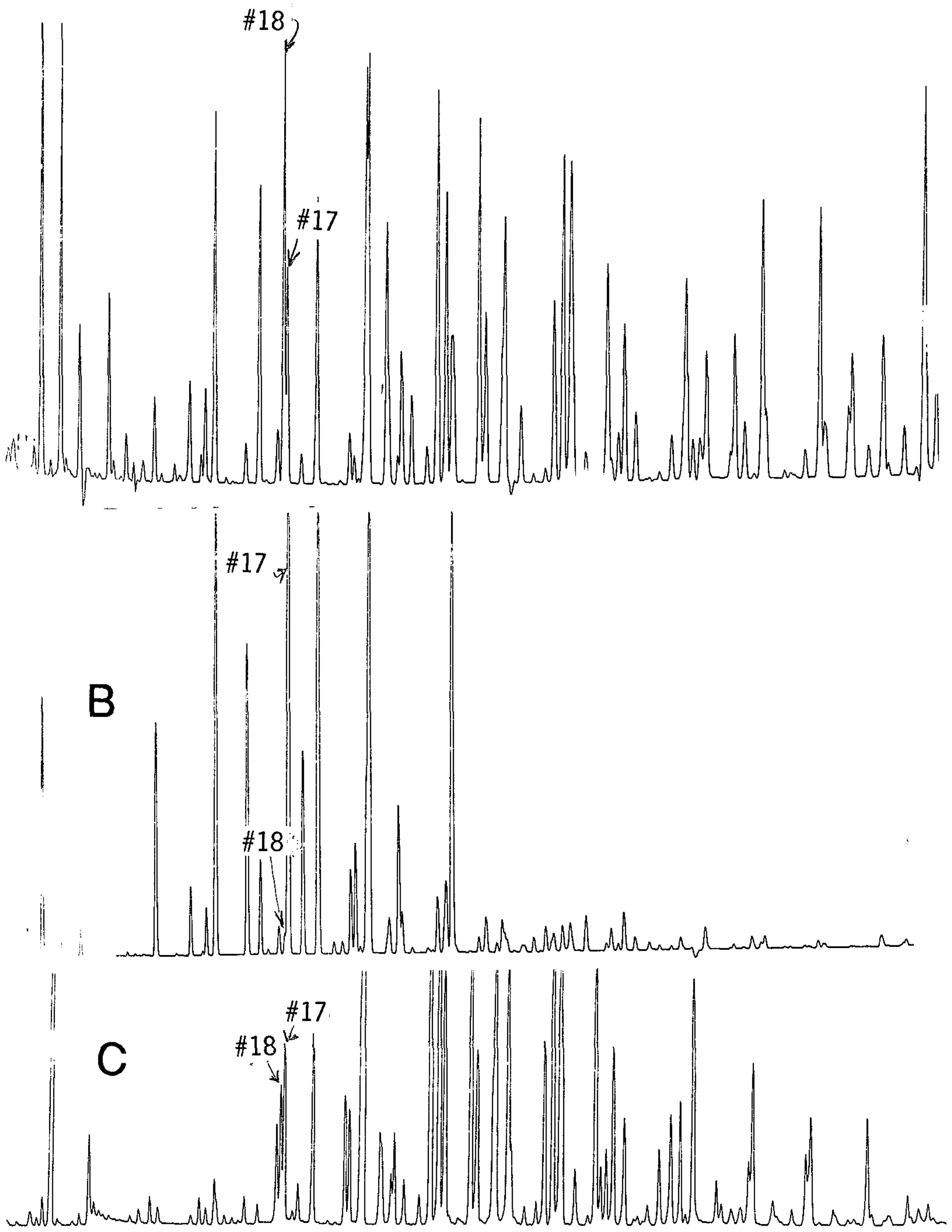

Figure 7. GC chromatograms of Standards (A), and Samples WH-3 (B) and WH-21 (C). These spectra show the absence of peak #18 in WH-3, and the difference between a sample collected close to the discharge site (WH-3) and one remote from it (WH-21).

The reason for the almost total absence of congener #18 is not known, but may be due to degradation. The very high specificity of the loss of this one congener, however, is not supported by observations on PCB degradation in other areas, (Brown *et al.* 1987; Brownawell 1986). It cannot be a loss due to partitioning since the other congeners with close molecular weights have similar physical properties and would be expected to partition in a similar manner. Some batches of Aroclor 1254, in which #17 & #18 are very minor constituents, show a low #18/#17 ratio, but 1254 is not reported to be one of the Aroclors in the hydraulic fluid used by Outboard Marine, and the measured composition of the PCBs in WH-3 confirms that Aroclor 1254 is not a major constituent. In any case the relative absence of congener #18 seems to be a marker for this discharge. It is not known how long congener #18 has been depleted in these sediments.

Karickhoff *et al.* (1979) and others have found that much of the variation in calculated K_p values for sediments can be explained by the organic carbon fraction (OC; Table 1, column 9; Equation 11) of the sediment ($K_{oc} = K_d$ /OC). The correlation between OC and the K_d*s is significant at the 10% level for both the Waukegan Harbor and Lake Calumet sediments. The K_{oc}s show the same trends and outliers as do the K_d*s. They are less variable, however, indicating the OC is one of the variables affecting the K_d*.

Water

The results from these samples are summarized in Tables 5 and 6. The detailed information for the congeners in each of the samples is available from the authors or from the Hazardous Waste Research and Information Center.

Four individual samples were collected from Lake Calumet and equilibrated with air. The first three samples from Waukegan were individual ones. The sample collected on Jan 29th, was equilibrated in duplicate, on Feb. 2, and Feb. 8. Separate samples were collected from 0.1 m and 2.2m depths on March 1.

The samples were equilibrated with air as described. The concentration of PCBs in the air for each of the samples is shown in Table 5, column 2. The sum of the fugacities (vapor pressure in Pascals) for each of the PCB congeners determined, is shown in column 3. The concentration of each PCB congener dissolved in the water in equilibrium with the measured air concentration was calculated using Equation 7 and the H (Murphy *et al.* 1987)

Table 5. WATER SAMPLE EQUILIBRATION RESULTS.

Sample	Air ng/m^3	Fug. Pa	Diss. Calc ng/l	Total Meas. ng/l	Susp. Solids mg/l	Calc. Total	#18* #17
LAKE CALUMET							
Aug. 4, 87	28.3	2.4 E-7	3.	9.5		0.33	1.6
Sept. 9, 87	18.7	1.6 E-7	2.	5.5		0.33	1.5
Jan. 12, 88	106	8.9 E-7	11	2.8		4	1.33
Feb. 25, 88	61	5.2 E-7	6	3.8	9.7	1.6	2.2
AVERAGE	*53.5*		*5.5*	*5.4*		*1.6*	*1.66 ± .38*
WAUKEGAN HARBOR							
Apl. 27, 87	363	3.1 E-6	37.5	58		0.6	0.
Oct. 12, 87	960	9.3 E-6	72	240		0.3	0.36
Nov. 14, 87	322	3.0 E-6	27	92		0.3	0.67
Jan. 29, 88 Feb. 2	440	4.0 E-6	85	23		3.7	0.48
Jan. 29, 88 Feb. 8	200	2.0 E-6	19	34		0.5	0.48
Mar. 1, 88 2.2M	1440	1.4 E-5	110	650	11.4	0.17	0.29
2.2 Sett.				175		0.63	0.29
Mar. 1, 88 0.1M	3030	2.9 E-5	240	2570	17.5	0.08	0.26
Apl. 11, 88 Stir.	1880	1.8 E-5	145	180	13.3	0.65	0.46
Apl. 11, 88 Sett.	1510	1.4 E-5	121	100	9.8	1.2	0.48
Jun. 20, 88 Stir.	2230	1.1 E-5	175	350		.5	0.38
Jun. 20, 88 Sett.	3540	3.2 E-5	250	110		2.2	0.39
AVERAGE	*1447*		*100*	*400*		*0.88*	*0.43 ± .12*
STANDARD							
Aroclor 1254	68		6.2	5.5		1.1	

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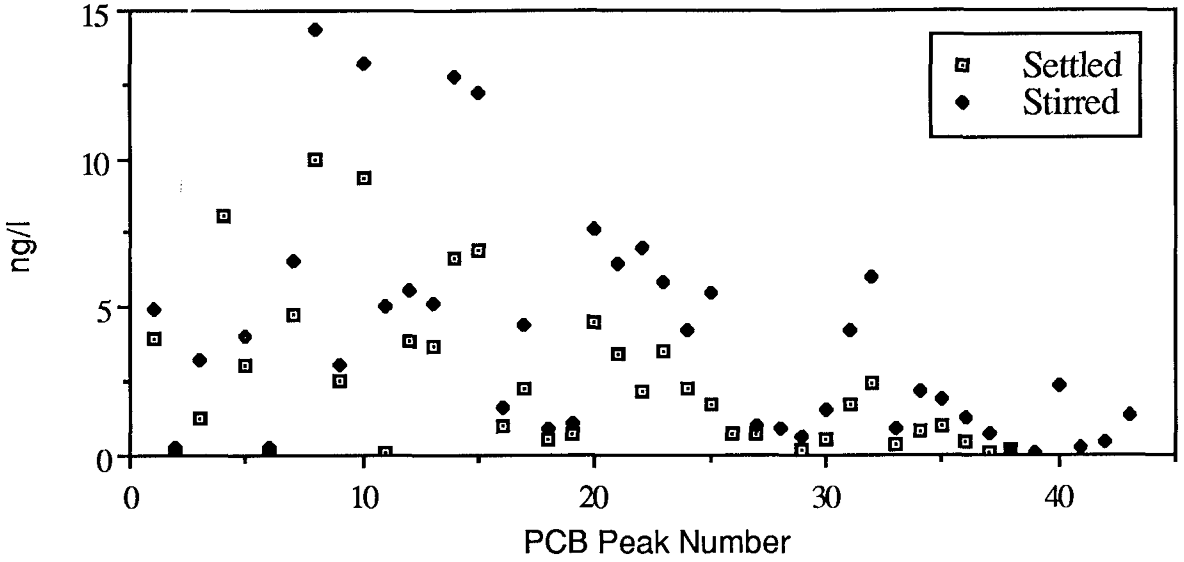
*Ratio of PCB Congener #18 to #17.

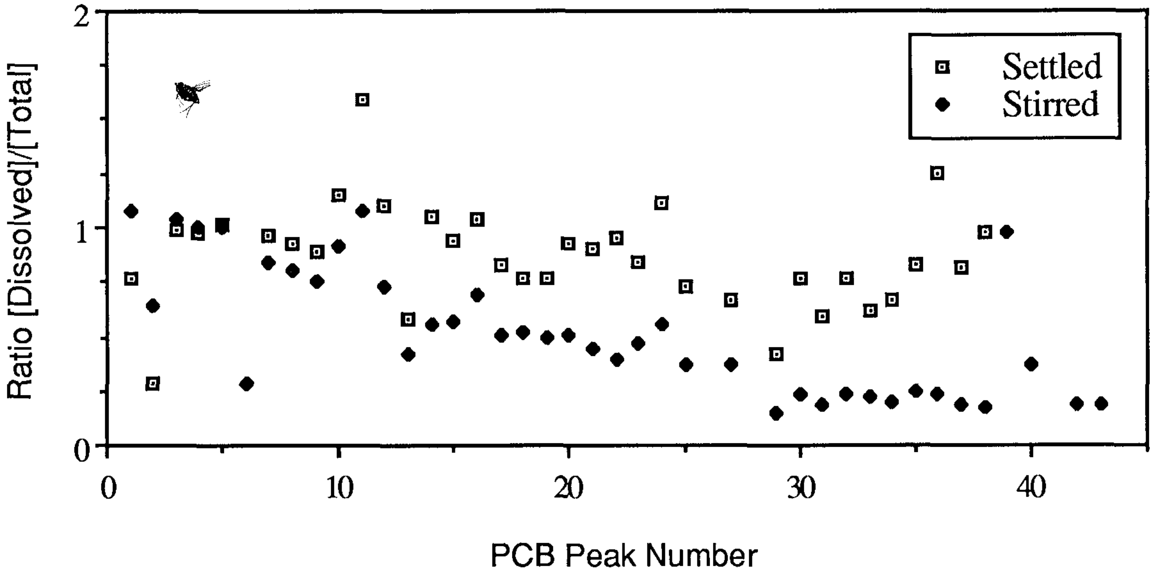
LAKE CALUMET

	-- PCB CONCENTRATIONS --												
	AIR	WATER				Air	Water	Water	Equilibration		FLOW RATES		SEDIMENT
SAMPLE		Calc.	Act.	Calc/Act	TSS	Vol.	Vol.	Anal.	Time	Temp.	Air	Water	[PCB]
	ng/m3	ng/l	ng/l		mg/l	m3	l	l	min	ºC	cc/s	l/m	mg/kg
4 Aug 87	28.3	3.5	9.5	0.4		1.13	84	6.93	507		37.1	0.17	
9 Sept 87	18.7	2.3	5.5	0.4		1.73	84	6.93	851		35.5	0.10	
12 Jan 88	106	13	2.8	5		0.94	54	6.5	583		25.8	0.09	
25 Feb 88	61	7.2	3.8	1.9	9.65	0.39	50	7.05	372	20	17.6	0.13	0.39
AVERAGE	53.5	6.5	5.4	1.93							29	0.123	
WAUKEGAN HARBOR													
27 APL 87	363	37.5	58	0.62		0.74	38	6.93	282		43.7	0.13	
12 OCT 87	960	72	240	0.31		1.73	62	6.5	771		36.1	0.08	
14 NOV 87	322	27	92	0.27		0.78	38	7.1	446		29.3	0.09	
29 JAN 88 2 Feb	440	85	23	3.6		0.23	17.5	6.7	162	12.5	23.3	0.11	
29 JAN 88 8 Feb	200	1.9	34	0.5		0.22	17.5	6.7	163		22.4	0.11	
1 MAR 88 2.2M	1440	110	650	0.18	11.4	0.23	18.5	2.5	220		17.4	0.08	57.0
1 MAR 88 0.1M	3030	240	2570	0.08	17.5	0.22	18.5	0.34	199		18.7	0.09	146.9
11 APL 88 Stir	1880	145	180	0.67	13.3	0.21	17	0.9	114		30.1	0.15	13.5
11 APL 88 Sett.	1510	121	100	0.12	9.8	0.23	16	0.95	148		25.4	0.11	10.2
20 JUN 88 Stir	2230	210	350	0.58	(2.2)	0.14	18	1.9		20			3105
20 JUN 88 Sett.	3540	300	110	2.7	(2.9)	0.1	18	1.85					690
AVERAGE	1447	123	401	0.88	13						27.4	0.11	
STANDARD													
STD	68	8.3	6.5	1.4		0.13	19	0.95	93		23.2	0.20	

Table 6. Summary of Experimental Parameters for Water Sample Equilibrations.



A. Total Concentration of PCB Congeners in April 11 Water Samples.



B. Dissolved vs Total PCBs in April 11 Water Samples.

Figure 8. Results for the April 11 Water Equilibrations.

for that congener. The results for each of the congeners were summed, divided by 1.2 (see procedures section) and the results shown in column 4. The total concentration of PCB measured in the water for each of the samples is shown in column 5. The average for the Waukegan samples was 400 ± 742 ng/l (184 ± 192 ng/l less the 0.1 m March 1 sample) and for the Lake Calumet samples it was 5.5 ± 4 ng/l. Based on the discussion in the Introduction (p. 2), the measured dissolved concentration should be higher than the calculated dissolved concentration.

For each congener found in the air, the amount of that congener measured in the water sample was totaled. This total was divided into the total amount calculated to be dissolved (Column 4). The resulting ratio is shown in Column 6. The sum of the total amounts found in Column 5 includes congeners not found in the vapor phase (thus the ratio shown in Column 6 is not necessarily the ratio of column 4 divided by Column 5). The range of this ratio for the Waukegan Harbor samples ranged from .08 to 3.7 (average = 0.93 ± 1.1 ng/l; 0.39 ± 0.2 ng/l for the samples where the ratio was less than 1.0), while the ratio for the Lake Calumet samples ranged from .33 to 4 (average = 1.6 ± 1.7 ng/l).

One-third of the samples collected on April 11, and June 20, were kept stirred, and their fugacity determined within 24 hours. The other two-thirds of each sample was allowed to stand undisturbed in two 5-gal bottles. After two days, the top half of each of the bottles was siphoned off, combined, and equilibrated with air. This is the settled sample. The settled sample should have had the same dissolved [PCB], but lower total [PCB] due to settling out of some of the particulates. Figure 8A shows the total concentrations of each PCB congener in the stirred and settled samples. As expected the concentrations in the stirred sample are higher. Figure 8B shows the amount dissolved ratio (fraction dissolved/1.2)/(measured total) for each congener for the two samples. Most of the PCBs in the settled sample in the water are in solution, while only about 40% of the PCBs in the stirred sample are in solution. For both samples, the percent of the dissolved PCBs decreases with increasing molecular weight. This is what would be expected from their solubilities, where the less soluble preferentially partition to the particles.

An attempt was made to observe the settling out of particles from surface waters, by sampling surface and deep waters in Waukegan Harbor. Water was collected on a cold and windy March 1, 1988 from 0.1 m, and about 2.2 m (about 0.5 m above the bottom). It was anticipated that the 2.2 m samples would be higher in dissolved (closer to the sediments; partitioning) and particulate (resuspension) PCBs, while the 0.1 m sample would be lower in dissolved (evaporation) and particulate (settling) PCBs. In addition to the equilibration experiment, a portion of the 2.2 m sample was allowed to settle, and water from the top half of the bottle was collected after two days and analyzed.

A summary of the results are shown in Table 5. There is no correlation with the expectations. The total concentrations found in the 0.1 m sample were very high, 2,600 ng/l (suspended solids = 17.5 mg/l), while those in the 2.2 m sample were lower, but still high (650 ng/l; SS = 11.4 mg/l) compared to the others collected. The calculated dissolved concentrations found were much lower, 240 and 110 ng/l, but still much higher than those found for other samples from Waukegan Harbor. The windy day could have caused significant resuspension, and explain the high particulate PCB concentrations found.

The drop in the total concentration of PCBs in the 2.2 m sample from 650 ng/l to 175 ng/l on standing, is consistent with most of the particulate PCBs having settled out.

Additional evidence for the high concentration of resuspended sediment particles in the 1 March samples is found in the composition of the PCBs in the samples. As indicated above, the bulk sediments in the area where the water samples are collected are significantly depleted in PCB #18 (2,2',5-trichloro- biphenyl). However, the water samples have #18/#17 ratios of 0.43 ± 0.12, close to the average of 0.38 (Table 5) found for the Waukegan sediments, but not close to the ratios found for the WH-1 & WH-3 sediments adjacent to the water collection site. One explanation is that the water equilibrates only with the surficial sediments. This is supported by the result from the March 1, water samples. Of all the water samples, these had the highest total PCB concentration, the lowest percentage in solution, and the #18/#17 ratios in these samples were the lowest found in the water samples, 0.26 (0.1 m) and 0.29 (2.2 m). All of these results would be explained by greater incorporation into the water of more deeply buried material from the sediments, material in this case with a low #18/#17 ratio from the vicinity of the discharge.

In planning this project, it was expected that quiescent conditions would prevail under the ice cover in winter. It was then expected that the dissolved concentration would increase, reflecting closer approach to equilibrium with the sediments. The dissolved/total ratio was expected to be close to one, reflecting the settling out of suspended solids.

There were two cold spells during the winter of 1987-88 where the temperature was well below freezing for more than a week. Samples were obtained on both occasions from Lake Calumet (12 Jan. and 25 Feb., 1988). In Waukegan Harbor, the wind prevented ice from building up and accumulating during the second cold period. So, only one sample, in duplicate, was collected from Waukegan Harbor (29 Jan., 1988). The analyses for total PCBs in the water for the four samples (Table 5) were the lowest obtained from each site in the project (perhaps indicating low suspended particulates, as expected). Inexplicably, however, three of the four samples showed that the calculated dissolved PCB were higher than the total PCBs in the samples. The only sample which gave an expected result was the duplicate sample from Waukegan that was equilibrated 10 days after collection.

It is difficult to explain why the samples collected during the winter and analyzed soon after collection gave these unexpected results. It can not be due to unusually high temperature during the equilibration, as the temperature of the equilibration of the Feb. 25th Lake Calumet sample was 20°, while that of the Jan 29th Waukegan Harbor sample was 12.5°. A clue may be the portion of the sample collected on Jan. 29th from Waukegan Harbor, allowed to stand at room temperature for 10 days and then equilibrated, showed results similar to those found from the other samples. Perhaps the partition coefficient for the dissolved/adsorbed equilibration is quite temperature sensitive but the equilibration rate is slow (as was found for the congener #52 equilibration experiments previously described). Thus the actual air/water equilibrium experiment was at room temperature between an air phase equilibrating with a water phase at 23°, but the water phase had the composition of that in equilibrium with the sediment phase at (or about) its collection temperature.

Evaporation

A rough estimate can be made of the amount of PCBs evaporating from the surfaces of LC and WH using Equations 9 & 10. The uncertainty in these calculations is quite high, however, and they are made only to show the possible magnitude of the effect.

A value for K_{ol} for Equation 10 needs to be determined for the conditions of the air/water exchange at the two locations. A value of 10^{-3} m/s, as discussed by Mackay and Yuen (1983), will be used for K_a. The value of K_w is a function of the wind speed. This is illustrated in Table 7 where a calculation of an average K_w using an observed wind-speed distribution is shown. The wind-speed frequencies in column 3 are from Midway Airport in Chicago (Sievering *et al.;* 1979), and the K_W values in column 2 for the different wind-speeds were determined for fresh water and marine systems (Liss and Merlivat; 1986). The K_W values are corrected for the lower diffusivity of the PCBs by dividing by the ratio of the square roots of the molecular weights of the PCBs (average = 266) to that of oxygen (Liss and Slater 1974).

The very strong dependance of the K_W on wind speed can be seen in Table 7, and also the very small contribution to the total during low wind conditions, the most common condition. The value of K_W varies by a factor of 100 over the wind speed range listed.

Table 7. Wind-Speed Weighted Mass Transfer Velocity

Wind Speed Range m/s	K_W m/s•10^5	Frequency of Occurrence	K_W per range m/s•10^6
0-3.6	0.033	.38	0.12
3.6-7	0.57	.32	1.8
7-10	1.52	.18	2.7
10-13	2.4	.07	1.7
13-16	3.78	.04	1.5

Weighted average $K_W = \Sigma\ (K_W \cdot \text{freq}) = 8 \cdot 10^{-6}$ m/s

H varies by about a factor of 2 with the structure of the congener, and by about a factor of 10 over the temperature range of 0°C to 20°C (the vapor pressures change by about a factor of 40 over the temperature range, and the solubilities change by about a factor of 4). The average values used in the calculations for H for the congeners found in the water is 2.3 at 0°C, and 23 at 23°C.

The effects of H and K_W on K_{ol} are illustrated on Figure 9. The shaded area show the range of H for the different congeners at 20°C and 0°C. The two X's indicate the values of K_{ol} selected for the calculations (20°C: $K_{ol} = 4.3 \bullet 10^{-6}$; $K_W = 0.8 \bullet 10^{-6}$; H = 23; and 0°C: $K_{ol} = 0.9 \bullet 10^{-6}$; H = 2.3; $K_W = 8 \bullet 10^{-6}$).

For Waukegan Harbor, the average fugacity of the water samples (20°C; Table 5; avg. $[PCB]_W$ = 90 ng/l) was $7.8 \bullet 10^{-6}$ Pa. The air fugacity is based on air concentrations of about 0.5 ng/m^3 (Strachan and Eisenreich 1987) which corresponds to an air fugacity (f_a) of about $0.5 \bullet 10^{-8}$ Pa (0.5 ng/m^3 $\approx 1.8 \bullet 10^{-3}$ mol/m^3 $\approx 0.5 \bullet 10^{-8}$ Pa; Equation 4; R=8.3 m^3 •Pa/(mol •°K); T=293°K), and is

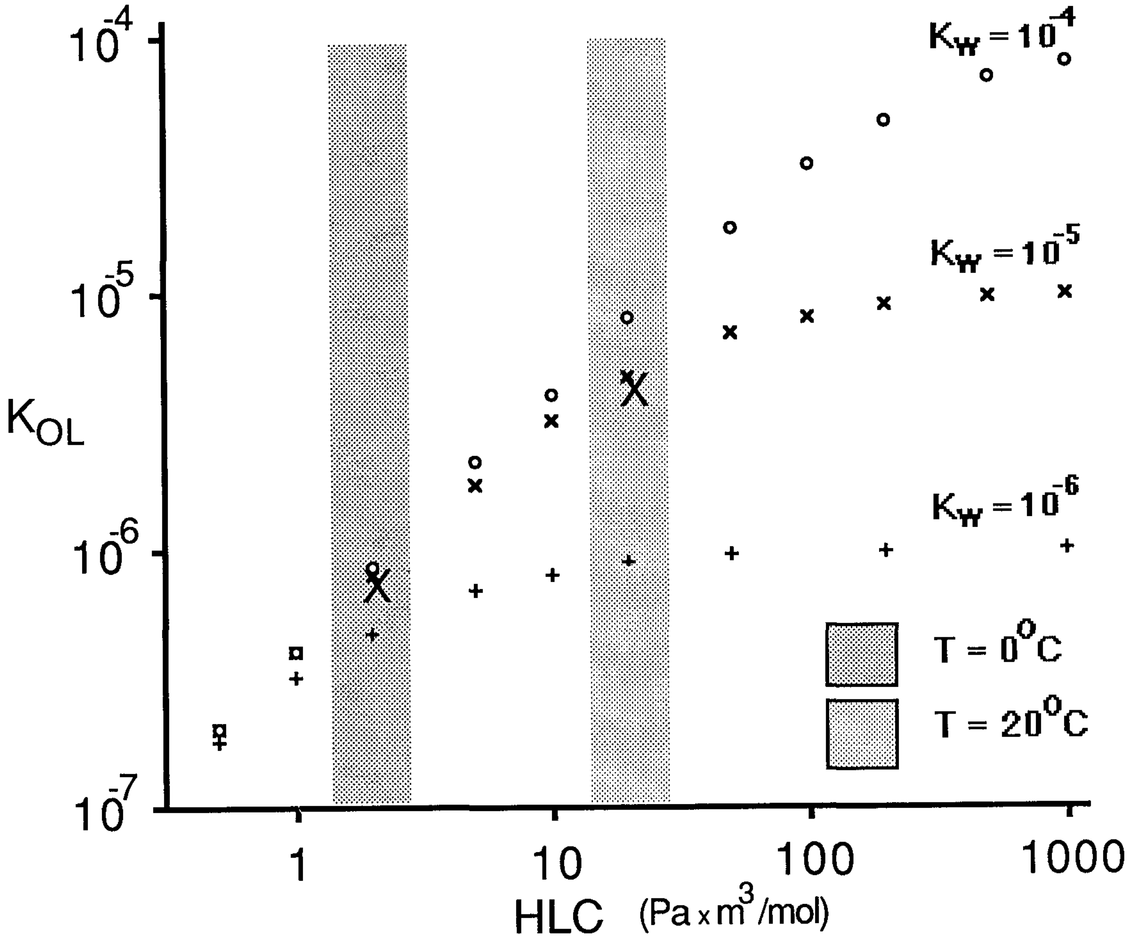


Figure 9. log K_{OL}vs H for different K_Ws and Temperatures

insignificant compared to the water fugacity of $7.8 \cdot 10^{-6}$ atm. The flux (Eq. 9) then is $7.8 \cdot 10^{-6} \cdot 4.3 \cdot 10^{-6} \cdot 1/23 = 1.5 \cdot 10^{-12}$ mol/($m^2 \cdot s$). The average daily mass flux then is the flux, times the area of slip #3 (5700 m^2) times the number of seconds in a day (86,400) which gives $7.2 \cdot 10^{-4}$ mol/d. With an average molecular weight of the volatile PCBs of 266 we get a flux of 0.19 g/d.

A similar calculation for the winter months using: 273°K for the temperature, $K_{ol} = 0.9 \cdot 10^{-6}$, and $[PCB]_w = 90$ ng/l $= 7.8 \cdot 10^{-7}$ Pa, gives a flux $= 1.5 \cdot 10^{-4}$ mol/d (.04 g/d). This is only 20% of the summer value. Assuming the summer and winter values prevail for half of the time, the annual average flux of PCBs from the surface of the north slip in Waukegan Harbor is 0.12 g/d or 0.04 kg/yr.

The large uncertainty in these calculations is the wind speed factor. These calculations assume the same distribution of winds during the warm months as during the cold ones. This is probably not valid. Storms are more frequent on the Lake during the fall, winter and spring, and the circulation of the atmosphere at the water surface is enhanced when the water surface is warmer than the overlying air (fall and winter), and greatly reduced when the air is warmer than the water leading to stable atmospheric conditions. Thus the summer K_{ol} (and PCB exchange) is probably overestimated, while the winter K_{ol} is probably underestimated.

A similar calculation for Lake Calumet (Avg. fugacity of water samples found (Table 5) $= 4.7 \cdot 10^{-7}$ Pa; the fugacity of the air is 1% of that of the water and is neglected; area of the Lake (Demissie *et al.* 1988), 782 ac. $= 3.2 \cdot 10^6$ m^2) yields a mass flux of $2.4 \cdot 10^{-2}$ mol/d or 6.5 g/d. The winter loss, using the same water concentrations, would be 1.35 g/d. The average loss would be 3.9 g/y or 1.4 kg/yr.

Surprisingly, the calculated evaporation loss of PCBs are higher from Lake Calumet than from Waukegan Harbor. This is solely due to the much larger area assumed for evaporation from Lake Calumet. It can be assumed that much more evaporation of PCBs does occur from Waukegan Harbor, but the water samples were collected only from the north slip and thus we have no data from the rest of the harbor to base calculations on. If the concentration of dissolved PCBs averages a factor of five lower in the rest of the harbor, its 30 times greater area means that another .7 g/d (0.26 kg/yr) may evaporate.

The final variable that has a large affect on the air/water transfer rate of these compounds is the Henry's Law constant (H). This is the ratio of the vapor pressure of a compound to its water solubility. Both of these decrease with temperature, but the vapor pressure decreases much faster. At 4°C, the average H (and thus the fugacity; Equation 5) is a factor of 7.2 lower than at 20° (Burkhard *et al.* 1985; Murphy *et al.* 1987). The mitigating factor in this case is that high wind speeds occur with greater frequency during the cold months. Summer *vs* winter wind speed frequencies are not available, but it is anticipated that the overall exchange rates will be higher in the winter.

It is clear from the fugacities of the different phases that the direction of transfer of PCBs is from the sediments to the air in Waukegan Harbor. In Lake Calumet, the sediments and water have similar fugacities, while they are both higher than the air. Thus the net direction of transfer of PCBs is from the water to the atmosphere for both Waukegan Harbor and Lake Calumet. The atmosphere then is serving as a sink for some of the PCBs in the sediments in these bodies of water.

Chapter 4. DISCUSSION

Several factors concerning the composition and interactions of the air, water and sediments complicate the interpretation of these data and need to be discussed. The first is that the sediment samples used are a volume-weighted mixture of the upper 5-10 cm of the specific area of the sediment sampled. The results obtained on these samples could be applicable to effects on the water column from massive resuspension events such as large boats passing and high wind events (See March 1, 1988 results from Waukegan Harbor), and to the toxic effects on benthic organisms in these sediments. But they are not particularly relevant to the water samples collected, since the exchange between the water and the sediment occurs chiefly at the sediment/water interface.

The water gets its PCBs and other contaminants from the surficial sediments, from surface discharges and run-off and from the atmosphere. Pullman Creek, the principal surface water source to Lake Calumet enters about 400 m from the water sampling site. There was a surface-water run-off pipe in the extreme northwest corner of slip#3 in Waukegan Harbor. Water was entering the harbor from it during several of the sampling trips. An analysis of one sample from it showed 200 ng/l PCBs (#18/#17 ratio = 0.93).

The surficial sediments are composed of material from deeper within in the sediments, from other sediments within the area, from particles transported from the main body of water (Lake Michigan or the Calumet River), and from precipitation and particles that have come from the atmosphere. Their composition is then expected to be quite different from the bulk sediment. They are probably close to equilibrium with the water because they are frequently resuspended.

Because they are continually being re-distributed by the water, the surficial sediments are probably more uniform in composition and concentration over an area than are the deeper sediments. The water thus tends to show an average of the concentrations in the sediments it encounters as it moves around and exchanges both dissolved and particulate components.

Also, while the techniques used in this project are based on measurements made at equilibrium, the sediments and water were not, and will not normally be at equilibrium. There are a couple of reasons for this. First, the exchange reactions between the sediments and water are slow compared to the normal flow rates and contact times between the water and particular areas of the sediments. Second, while the water is equilibrating with the sediments, it is also exchanging material with the atmosphere. Certainly in the case of Waukegan Harbor, where the water has a fugacity several orders of magnitude higher than the air, relatively large amounts (compared to what is in the *water*) are being lost to the air. The equilibrium model, however, is still useful as the net transport between the phases is being driven by the differences in activity (fugacity) between the phases and the systems are moving toward equilibrium.

If the sediments were similar except for their PCB concentration, the activity should be proportional to the PCB concentration, (see Equation 2). Figure 10 shows the correlation for these sediment samples. While there seems to be some relationship for the Waukegan sediments (r^2=.563), it is determined chiefly by the outliers. There is no relationship between the PCBs concentration and the fugacity for the Lake Calumet sediments shown (r^2= .001). However, if LC-2H is not included, there is some correlation (r^2= .642). Figure 10 seems to show a reasonable correlation for all of the sediment data (r^2= .656). But it can be seen that there is almost no overlap between the sediments from the different locations and the correlation found is a coincidence.

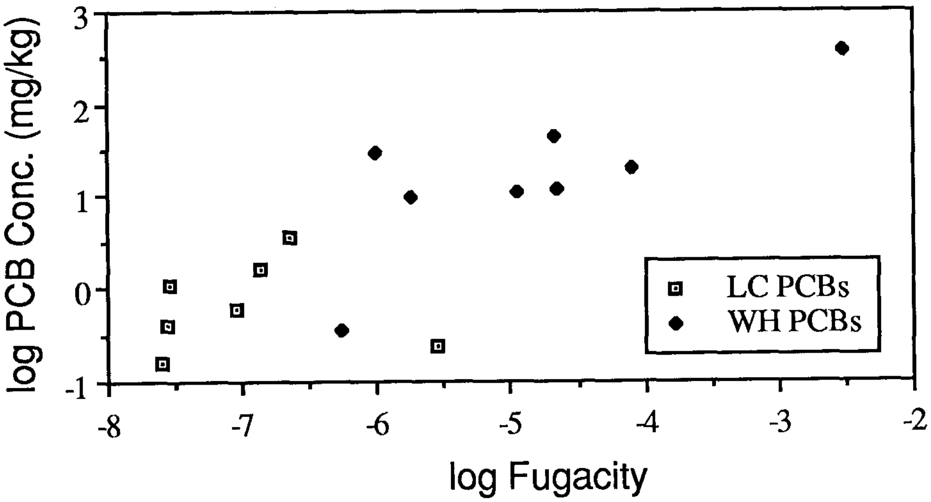


Figure 10. Sediment [PCB] vs. Sediment Fugacities.

Chapter 5. Conclusions

1. Experimental methods were developed to measure the vapor pressure of semi-volatile organic compounds in ambient water and dehydrated sediment samples.

2. These techniques were used to determine the fugacity of PCBs in water and sediment samples (dehydrated for measurements) collected from Lake Calumet (a shallow, natural lake) and Waukegan Harbor (site of past discharges of PCBs) in Illinois.

3. The results found at the two sites were quite different. Besides having higher PCB concentrations than the samples from Lake Calumet, most of the dehydrated sediment samples from Waukegan Harbor had lower partition coefficients (K_d) to water (and to air).

4. There is a net loss of about a kg/yr of PCBs to the atmosphere from the water surface of each of these sites.

5. The surficial sediment most involved in exchange with the water can be very different in composition, and have more spatial uniformity, than the sediment collected using Ponar dredges, or other similar collectors of bulk, surface sediment samples.

6. The K_d* and the ratio of PCB congeners #18 to #17 ratio, indicate that the sediments represented by sample WH-12 are different from the other Waukegan sediments. The K_d* of WH-12 was $2.7 \bullet 10^6$ *vs* an average of $1.3 \bullet 10^5$ for the others, and its #18/#17 ratio is 1.6 *vs* an average of 0.38 ± .3 for the others. The K_d* seems to indicate the sediment material is different while the #18/#17 ratio indicates the source of the PCBs was different.

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Appendix

Identities of PCB Congeners

Table A-1. Identities of PCB congeners.

IUPAC Congener #	IUPAC Name
3	4-Chlorobiphenyl
4	2,2'-Dichlorobiphenyl
6	2,3'-Dichlorobiphenyl
7	2,4-Dichlorobiphenyl
8	2,4'-Dichlorobiphenyl
13	3,4'-Dichlorobiphenyl
16	2,2',3-Trichlorobiphenyl
17	2,2',4-Trichlorobiphenyl
18	2,2',5-Trichlorobiphenyl
19	2,2',6-Trichlorobiphenyl
22	2,3,4'-Trichlorobiphenyl
24	2,3,6-Trichlorobiphenyl
25	2,3',4-Trichlorobiphenyl
28	2,4,4'-Trichlorobiphenyl
30	2,4,6-Trichlorobiphenyl
31	2,4',5-Trichlorobiphenyl
37	3,4,4'-Trichlorobiphenyl
40	2,2',3,3'-Tetrachlorobiphenyl
41	2,2',3,4-Tetrachlorobiphenyl
44	2,2',3,5'-Tetrachlorobiphenyl
45	2,2',3,6-Tetrachlorobiphenyl
46	2,2',3,6'-Tetrachlorobiphenyl
47	2,2',4,4'-Tetrachlorobiphenyl
49	2,2',4,5'-Tetrachlorobiphenyl
51	2,2',4,6'-Tetrachlorobiphenyl
52	2,2',5,5'-Tetrachlorobiphenyl
63	2,3,4',5-Tetrachlorobiphenyl
70	2,3',4',5-Tetrachlorobiphenyl
74	2,4,4',5-Tetrachlorobiphenyl
82	2,2',3,3',4-Pentachlorobiphenyl
84	2,2',3,3',6-Pentachlorobiphenyl
91	2,2',3,4',6-Pentachlorobiphenyl
95	2,2',3,5',6-Pentachlorobiphenyl
99	2,2',4,4',5-Pentachlorobiphenyl
100	2,2',4,4',6-Pentachlorobiphenyl
101	2,2',4,5,5'-Pentachlorobiphenyl
107	2,3,3',4',5-Pentachlorobiphenyl
110	2,3,3',4',6-Pentachlorobiphenyl
118	2,3',4,4',5-Pentachlorobiphenyl
138	2,2',3,4,4',5'-Hexachlorobiphenyl
149	2,2',3,4',5',6-Hexachlorobiphenyl
204	2,2',3,4,4',5,6,6'-Octachlorobiphenyl