

THREE-PHASE PARTITIONING OF HYDROPHOBIC ORGANIC COMPOUNDS  
IN GREAT LAKES WATERS

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ABSTRACT

Great Lakes waters were freshly collected, inoculated with radiolabelled hydrophobic organic compounds and, after equilibration, separated into particle bound, dissolved organic matter bound and freely dissolved phases. In these ambient suspended matter (0.2-5 ppm) and dissolved organic carbon (1-6 ppm) media, the freely dissolved phase generally dominates and the amounts associated with dissolved organic matter rarely exceeds 5% for most compounds. Solubility controls the constituent distribution between particle bound and freely dissolved but plays a much smaller role in mediating the binding to dissolved organic matter. Differences observed in the binding to dissolved and particulate organic matter support the need to consider the distribution of constituents among three phases. Although the concentration and composition of the substrate changes significantly, there is no apparent seasonal effect on the distribution of compounds among the three phases in the Great Lakes.

Introduction

In lakes and estuaries, the partitioning of hydrophobic organic contaminants (HOC) onto particles followed by settling and eventual incorporation into the sediments is commonly the major internal process controlling the residence time and concentration of these compounds in the water column. Over the past few years, several laboratory studies have examined the role of partitioning and phase distribution in the behavior and fate of contaminants in aquatic ecosystems. Partitioning to particles has been shown to be inversely proportional to log solubility of the HOC (1) and to the log of particle concentration (2,3) and proportional to the organic carbon content of the particulate matter (4).

Investigators have recently reported that HOC forms an association with the spectrum of materials operationally defined as dissolved (5-7) including very fine colloidal particles

along with truly dissolved organic matter (DOM). The extent of partitioning of HOC to particulate or dissolved organic matter largely determines the behavior and fate of these constituents and also apparently affects their bioavailability to various aquatic organisms (8,9)

A perceived shortcoming of most laboratory phase distribution studies is the use of artificial media, usually with grossly elevated particle concentrations. Since concentration of particulate matter affects the HOC distribution (2,3) the results of these experiments are difficult to extrapolate back to ambient conditions for most aquatic systems. In addition, the substrate usually used in reported studies are sediments, not the particulate matter mixed within the water column.

In the present study, freshly collected Great Lakes waters were inoculated with a suite of radiolabelled HOC and were phase separated after equilibration to measure the freely dissolved HOC concentration and the HOC associated with particles and dissolved organic matter. The study was designed to examine the effect of the seasonal change in ambient conditions as well as differences in ambient conditions among the Laurentian Great Lakes on the phase distribution of HOC.

#### Methods

Raw water for most of this study was collected in 10 L Niskin bottles from a depth of 5 m at 3 stations in Lake Michigan. The stations were located approximately 5, 16 and 36 km offshore Grand Haven, Michigan with respective water depths of 24, 75 and 100 m. The water was placed in two precleaned, sample water rinsed, brown gallon bottles and stored at 4°C prior to inoculation (maximum of 5 days storage). Samples representing offshore waters (stations at least 40 km offshore) were collected from a depth of 5 m from Lakes Michigan, Superior, and Huron in early July after stratification was well established.

Three 2 L aliquots (nearshore) or two 3 L aliquots (offshore) were filtered through prewashed, preweighed 47 mm diameter glass fiber filters (Gelman AE). The filters were dried at 90°C, re-equilibrated with room temperature and humidity and reweighed along with controls. The difference in weights represented our operationally defined total suspended matter (TSM). Coefficients of variation for TSM measurements were less than 5%.

Three 250 ml aliquots were filtered through precombusted (4 hrs @ 400°C) 25 mm glass fiber filters (Gelman AE), that were analyzed for particulate organic carbon (POC) by the wet combustion method (10). Coefficient of variation for POC were also less than 5%. Dissolved organic carbon (DOC) was measured on 5 ml aliquots of the POC filtrate by the same procedure with similar precision.

Radiolabelled compounds (Table I) were all greater than 97.9% pure as determined by thin layer chromatography in combination with liquid scintillation counting. The radiolabelled compounds in methanol carrier were inoculated (in triplicate sets) into 50 ml Pyrex centrifuge tubes and the methanol was evaporated under a stream of nitrogen. Raw lake water (50 ml) was then added, the tubes capped (with an aluminum foil liner) and rotated (8 rpm) for three days at approximately 25°C. Time to apparent partitioning steady state had been previously measured to be less than 36 hours and the amount inoculated to be within the linear portion of the sorption isotherm for all of these compounds (11).

Table I. Solubilities and inoculations of the HOC used in this study.

<u>Compound</u>	<u>Code</u>	<u>uMol Inoculated</u>	<u>Solubility uMol</u>
[ <sup>14</sup> C] 4-Monochlorobiphenyl	MCB	0.005	4.3
[ <sup>3</sup> H] Pyrene	Py	0.059	0.74
[ <sup>14</sup> C] 2,2',5,5' Tetra chlorobiphenyl	TCB	0.031	0.055
[ <sup>14</sup> C] DDT	DDT	0.0080	0.010
[ <sup>14</sup> C] 2,2',4,4',5,5',HCB	HCB	0.0020	0.0026
[ <sup>3</sup> H] Benzo(a)pyrene	BaP	0.0008	0.0020

Five fractions (a through e, described below) were collected from each replicate to calculate phase separation. First, the mixture was vacuum filtered (25 mm filter, stainless steel screen support) through a pair of glass fiber filters. The top filter (a) collected our operationally defined particulate matter and adsorbed some dissolved HOC, the bottom filter (b) was presumed to adsorb an equal amount of dissolved HOC and was counted to correct both the particulate and dissolved fractions. This filter correction was generally small and never greater than 5% of the total recovered HOC. After the 50 ml had been filtered, 5 ml of distilled deionized water was added to the centrifuge tube, shaken and filtered in an effort to remove residual particles from the tube. The two filters were (individually) placed in glass scintillation vials. Two ml of water (c) were removed from the filtrate and placed in a scintillation vial to count the freely dissolved plus dissolved organic matter associated HOC. Ten ml of filtrate were taken up in a 10 ml gas-tight syringe to which a Waters C-18 reverse phase Sep Pak was then attached. Six ml were pushed through the Sep Pak (at approximately 0.25 ml/sec) as a rinse, then 2 ml, representing the DOM bound HOC (d), were passed through the Sep Pak into a scintillation vial. The vacuum filter flask was emptied of filtrate and the filtering apparatus reassembled without a filter. It was rinsed with approximately 10 ml of distilled deionized water and drained. Finally 12 ml of scintillation cocktail (Research Products International 3a70b) were used to wash the filtering apparatus (e) and collected for

counting. This fraction was generally small for the more soluble HOC, but increased to approximately 10% for the least soluble compounds used and all calculations included a correction for this sorption to glass. Summarizing, the five fractions to be counted were:

- a) Particle associated HOC + HOC sorbed to filter
- b) HOC sorbed to filter
- c) HOC freely dissolved + HOC associated with DOM
- d) DOM bound HOC
- e) HOC sorbed to filtering apparatus

The activity of each fraction was measured on a Packard 460C liquid scintillation counter. Samples were corrected for quench using the external standards ratio method after subtracting background. Counting errors were less than 1% for all fractions and were not included in subsequent calculations. HOC recovery, calculated as part of the data reduction program, ranged from 86 to 107% of the inoculation for the 219 experiments.

Concentrations in the three defined phases were calculated as:

$$C_f = \text{freely dissolved contaminant concentration (ng/ml)} \\ = (\text{fraction c} - \text{fraction d}) + 2 * \text{fraction b} + \text{fraction e}$$

$$C_p = \text{particle associated contaminant concentration (g/g TSM)} \\ = (\text{fraction a} - \text{fraction b}) / \text{TSM}$$

$$C_b = \text{complexed contaminant concentration (g/g DOC)} \\ = \text{fraction d} / \text{DOC}$$

where

TSM = total suspended matter (g/ml)

DOC = dissolved organic carbon concentration (g/ml)

In order to calculate the HOC mass distribution in the water samples, the following mass balance model was used:

$$T * C_T = C_f * W + C_p * \text{TSM} + C_b * \text{DOC} \quad (1)$$

where

$C_T$  = total contaminant concentration (ng/ml)  
= inoculation

$T$  =  $W + \text{TSM} + \text{DOC}$

W = TSM and DOC free water (g/ml)

[In all cases considered,  $1.001 > W > 0.999$  and is set equal to 1 for convenience]

Define:

$$K_d = C_p/C_f \quad (2)$$

$$K_{oc} = 100 \cdot K_d / (\% \text{ Organic C of TSM}) \quad (3)$$

$$K_b = C_b/C_f \quad (4)$$

Substituting (2) and (4) into (1)

$$\begin{aligned} T \cdot C_T &= W \cdot C_f + K_d \cdot C_f \cdot \text{TSM} + C_b \cdot \text{DOC} \\ &= C_f \cdot [1 + K_d \cdot \text{TSM} + K_b \cdot \text{DOC}] \end{aligned}$$

Fraction free

$$F_f = \frac{C_f}{C_t} = [1 + K_d \cdot \text{TSM} + K_b \cdot \text{DOC}]^{-1} \quad (5)$$

Fraction DOC bound

$$F_b = \text{DOC} \cdot K_b \cdot F_f \quad (6)$$

Fraction particle bound

$$F_p = \text{TSM} \cdot K_d \cdot F_f \quad (7)$$

## Results

A total of 73 water samples were analyzed in this study. Ten surface (nearshore only) samples covering the period from April 19 to December 10, 1984 and 11 sets of surface samples at all three stations from January 22 to December 7, 1986. Surface samples from other lakes constituted the remainder of the set. The water samples covered a wide range in ambient TSM (0.2 - 5.0 ppm), DOC (0.83 - 5.8 ppm) and POC (TSM of 2.0 - 42 %). Data reduction from each of these collections yielded information on the equilibrium phase distribution of the suite of inoculated compounds. An example of these results from our May 7, 1986 collection, presented as correlations of the log of distribution coefficients with the log of the solubility of the inoculated contaminants (Figure 1), illustrates the previously identified correlation of sorption to compound solubility (1) along with a much weaker correlation for binding with DOC ( $K_b$ ) for compounds that range over 4 orders of magnitude in solubility.

The regressions of  $K_{oc}$  vs. water solubility previously reported (1,4) are shown on the same panel. The lines are nearly parallel, with the results generated in this study having the

highest  $K_{oc}$  values of the three sets of data. Since our ambient TSM concentration was an order of magnitude or more lower than the other studies, these results support the idea that HOC phase distribution is a function of both particle concentration and the characteristics of the substrate organic matter. The values for  $K_b$  are considerably smaller and the slope (importance of solubility) is much smaller than for the particle association relationship.

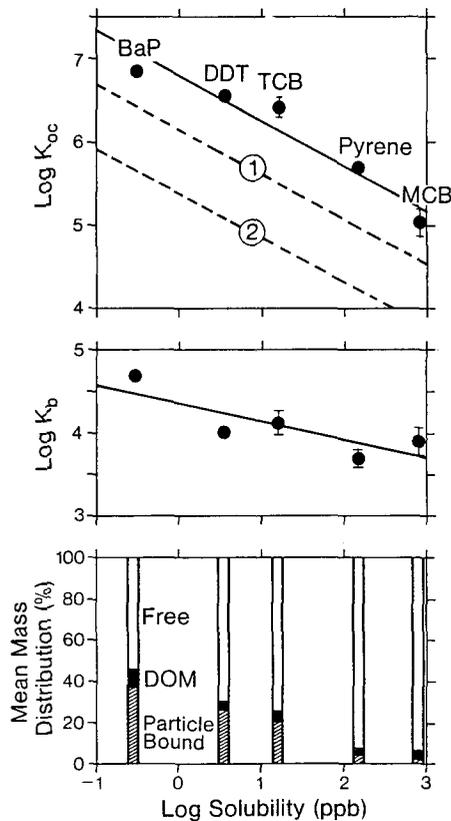


Figure 1. Log  $K_s$  vs. log solubility (ppb) for sample collected May 7 at the 36 Km offshore Lake Michigan station (TSM = 1.8 mg/L; POC = 0.058 mg/g TSM; DOC = 2.9 mg/L). In the upper plot, the data (+ 1 SD) and the solid regression line are from this work. The 1 and 2 represent the regression results of (4) and (1) respectively; the slopes are not significantly different. The slope of the  $K_b$  data is much smaller than for  $K_{oc}$ . The compound phase distribution is in percent of total recovered.

The distribution of the inoculated contaminants among particle bound, DOC bound and freely dissolved phases are also illustrated in Figure 1 for the May 7 samples. The mean values of the log  $K$  were used in these calculations. There is a systematic decrease, from 39 down to 1.4 percent of the compound, in the particle bound category as solubility increases. The fraction of each constituent bound to the DOC is less than 10% of the total.

Each of the 73 water samples yielded this type of information. With triplicates analyzed for each compound-water pair, the maximum number of samples for any compound was 219, although substitutions (eg. HCB for DDT) resulted in a lower number for several compounds. The entire data set of partition coefficients was best described by a log normal distribution. After the data were log transformed, statistics for the entire set were calculated (Table II). The HOC distribution coefficient between particulate matter and

Table II. Statistics on Distribution Coefficients

	BaP	HCB	DDT	TCB	PY	MCB
Log Kp (x)	5.78	5.74	5.57	4.93	4.76	3.83
(s)	0.33	0.24	0.36	0.42	0.52	0.49
Log Koc (x)	6.66	6.76	6.36	5.83	5.65	4.71
(s)	0.40	0.30	0.31	0.40	0.46	0.50
Log Kb (x)	4.57	4.42	4.26	3.88	3.76	4.02
(s)	0.38	0.39	0.44	0.53	0.39	0.71
n	217	71	114	192	218	154

x = mean of log transformed data

s = 1 standard deviation

water (mean Kd, Koc) exhibits a two order of magnitude range for the compounds studied. The slope of the log Koc vs log solubility (-0.57) is not significantly different from those previously reported (1,4) and illustrated in figure 1. For these calculations, the solubility has units of mg/Kg to conform to the cited studies. Subsequent calculations use umol units for solubility. The HOC association constant with DOC (Kb) shows much lower values with a range of only one order of magnitude and is not as well behaved as the particle data.

A synthesis of the mass distribution of HOC among the three phases for all of our experiments (figure 2) shows that in all cases most of the compound was in the freely dissolved phase, with only a small fraction associated with the DOC. About 40% of the least soluble compounds, BaP and HCB were particle associated. This distribution is similar to measurements of ambient PCB in waters collected from these lakes (12-15). As the compound solubility increased, the fraction associated with particulate matter decreased. For all compounds studied, the amount associated with DOC was small and did not change systematically with solubility.

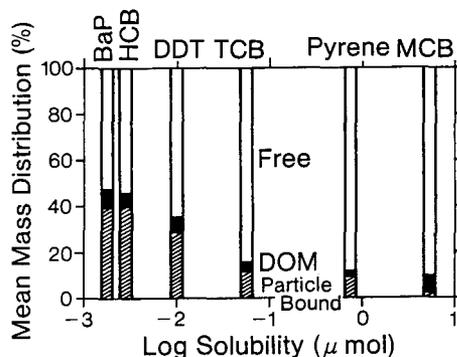


Figure 2. Mean HOC mass distribution among the three defined phases for all of the experiments. The hatched area represents particle associated HOC, the dark area represents HOC associated with dissolved organic matter and the remainder represents the freely dissolved portion of the HOC.

#### Seasonal Behavior, Offshore

A total of 19 surface water samples were collected from stations at least 10 km offshore in southern Lake Michigan and used in these experiments. The TSM concentration and characteristics changed significantly throughout the year (figure 3a,b). During the thermally unstratified period (Jan-May), materials are resuspended from underlying sediments and are distributed throughout the water column (16). Stratification begins in the late spring (May-June) accompanied by a maximum in primary productivity (17), and the particulate organic matter content reaches a high of 87% of the particle pool. With the completion of stratification the epilimnion is effectively isolated from underlying waters and the water column is cleared as detritus sinks out of the epilimnion. Beginning in August and lasting through early October, calcium carbonate precipitates in the warm surface waters of Lake Michigan (as well as Ontario and Huron), producing a new population of rapidly settling particles (18,19). The measured composition of the TSM used in these experiments ranged from 2% to 72%  $\text{CaCO}_3$ . Among the consequences of this annual whitening event is a minimum amount of suspended matter in the epilimnion (20) in late October and November. In the late fall, as the lake overturns, resuspended sediment materials begin to reappear in the increased TSM.

Examining the equilibrium phase distribution of inoculated HOC in these waters, we found that for the least soluble compound examined (BaP) an average of 52% was in the freely dissolved phase (Figure 2). Most of the remainder (40%) was associated with particulate matter, with only a small amount associated with DOC. The mean particle distribution coefficients,  $K_d$  ( $6.03 \times 10^5$ ) and  $K_{oc}$  ( $4.57 \times 10^6$ ) were much larger than that measured for DOC ( $K_b = 37,200$ ). Seasonal trends were not apparent for any of the three distribution coefficients, nor for the phase distributions. For BaP, as well as the other 5 compounds used in this study, the values

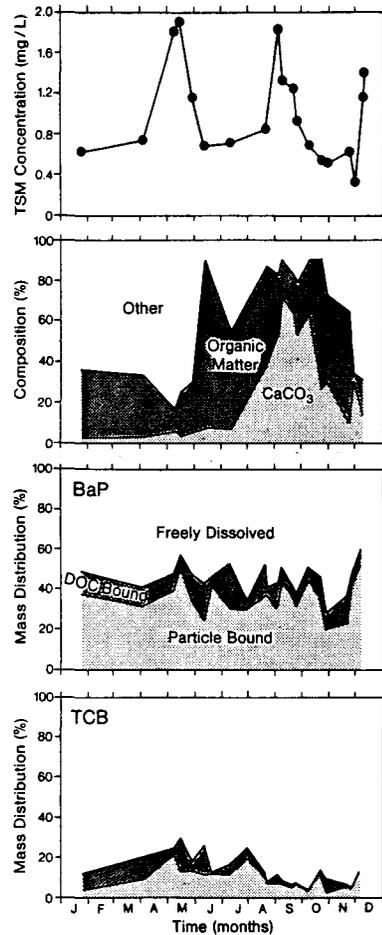


Figure 3. a. Total suspended matter concentration for the offshore station surface water samples. The two peaks are spring resuspended matter and CaCO<sub>3</sub> respectively.

b. Composition of the TSM. The lightly shaded region represents CaCO<sub>3</sub> and ranges from 2 to 72% of the TSM. The darker area represents the particulate organic matter (= 2 x POC). The remainder of the material is composed of clays, silicious material, etc.

c. Seasonal mass distribution of BaP in these water samples. Considering the changes in particle concentration and composition above, the distribution is remarkably constant. The lightly shaded region is the fraction of BaP associated with particulate matter. The darker area represents the material associated with DOC and the remainder is freely dissolved.

d. Seasonal distribution of TCB. Areas denoted as above.

of  $K_{oc}$  had a larger variability than  $K_d$  (Table II). Although somewhat noisy, the distribution of BaP among the three measured phases (Figure 3c) remained remarkably consistent throughout the year and did not correlate with the changes in particle composition. There was no significant correlation between the  $CaCO_3$  concentration and any of the BaP distribution coefficients.

HCB and DDT are next in the order of solubility. The PCB congener (IUPAC # 153) has been reported as relatively abundant in Lake Superior (21). The distribution coefficients and phase distributions that we measured for the HCB were very similar for those measured for BaP. For DDT, an average of 65% was present in the freely dissolved phase, while only 6.5% was associated with the DOC. As with BaP, there was no seasonal trend or relationship with the POC or  $CaCO_3$  concentration for either compound.

The next two compounds used in our experiments, TCB (IUPAC #52) and pyrene are significantly more water soluble, and this is reflected both in the lower values of the distribution coefficients and the increased amount of compound in the freely dissolved phase (figure 3d). The amount associated with DOC averaged only 4 and 2% respectively. The amount of TCB associated with DOC was approximately twice as high in the winter-spring as later in the year. Other than that, there was no indication of any seasonal trend in the phase distribution or any relationship with POC or  $CaCO_3$ .

The most soluble compound examined was 4-MCB (IUPAC # 3). An average of 90% of this compound was in the freely dissolved phase, and only 1.2% was associated with particles. As with the TCB, the fraction associated with DOC was somewhat higher in the early part of the year, otherwise no seasonal trend was seen.

During late June to early July, surface water samples were collected from mid-lake locations in Lakes Michigan, Huron and Superior. The TSM ranged from 0.20 (Superior) to 1.7 (Michigan) mg/L (Figure 4). Compound phase distributions in these offshore waters were similar to those discussed above. The largest difference was for BaP, where the particle association dropped from an average of 39% in Lake Michigan down to an average of 19% of the total for the low TSM Lake Superior samples. Although the TSM in Lake Superior is a factor of 10 less than the nearshore Lake Michigan concentration, the fractions associated with the three measured phases only varied by a factor of two. This was the result of high  $K_d$  values at these very low TSM concentrations. In all cases the dissolved organic matter played a small role, a maximum of 6% of the BaP was associated with DOC in Lake Superior waters and all other compounds were less than 5% DOC associated.

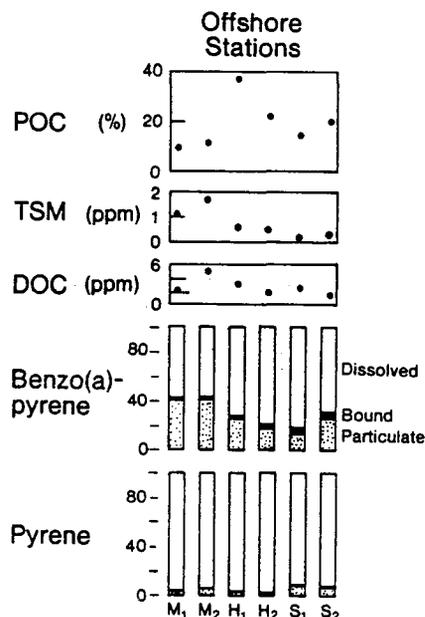


Figure 4. Particle characteristics and HOC phase distribution for mid-lake surface waters. M1 and M2 are were in southern and northern Lake Michigan, H1 (northern) and H2 (southern) Lake Huron, S1 (eastern) and S2 (central) Lake Superior. All stations were greater than 40 Km offshore.

#### Seasonal Behavior. Nearshore

Over the course of the study, 17 water samples were collected at the nearshore station where larger variations in particle concentrations and characteristics were expected than those observed offshore. Measured concentration of suspended matter ranged from 0.7 to 3.7 ppm and the organic carbon content of these solids (POC) ranged from 2 to 28%, with the lowest values during the spring and fall when there appeared to be an increase in sediment resuspension. The dissolved organic carbon had a maximum of 5.47 ppm and for the rest of the collections remained between 2 and 4 ppm. In only 3 of these 17 samples were any of these values outside the range of TSM, DOC or POC measured at the offshore location, and this was less then by a factor of 2. Comparing the means of the distribution coefficients or mass distributions at the nearshore site and the previously described offshore site on a compound by compound basis, no significant difference ( $P < 0.1$ ) was observed. These data sets were combined for subsequent analysis.

### Discussion

Our procedures allowed us to separate tracer contaminants among three operationally defined phases in a near ambient environment. These contaminants are distributed among a spectrum of substrates that differ in particle size and chemical characteristics, as well as in a truly dissolved state. Since it has recently been shown that only the dissolved compounds are readily bioavailable (8,9) then the factors influencing associations with indigenous substrates are of considerable interest.

Laboratory (3) and field (21) studies of HOC partitioning have reported strong inverse correlations between the log transformed distribution coefficients and substrate concentrations. The cause of this relationship has been described both as an association with an unfilterable colloidal fraction that increases in importance as substrate concentration increases (22) and by increases in particle collision frequency as concentration increases (23,24). Our approach allowed us to examine this phenomena, avoiding the difficulties associated with the measurement of ambient trace contaminant concentrations while still working in the range of ambient suspended matter concentrations and relatively unaltered organic matter.

### Role of TSM, POC and DOC

The relationships between the log of the distribution coefficients ( $K_d$  and  $K_{oc}$ ) and the log of substrate concentration (TSM and POC) were explored for each compound by using a least squares regression. The distribution coefficient for organic matter ( $\log K_b$ ) was similarly treated with respect to the log of the concentration of DOC. The square of the correlation coefficient ( $r$ ) represents the fraction of total variance assigned to the log of substrate concentration (Table III).

Normalizing the particle distribution coefficient by substrate organic carbon ( $K_{oc}$ ) has been used with apparent success in estimating partitioning to elevated concentrations of TSM in sediment-water systems (3,4). However applying this approach to our data resulted in the loss of any significant correlation with TSM concentration for all compounds. A similar result was found (21) for ambient concentrations of PCB congeners in Lake Superior. The freshly collected POC in these studies represent a wider spectrum of organic matter than studies using sedimentary material as substrate. Organic matter that reaches the sediment has presumably been reduced by microbial metabolism in the water column and in the sediments. The  $\log K_{oc}$  does show a strong correlation with the log of the POC for the 4 least soluble compounds. In laboratory experiments where different concentrations of the same sediment are used, the correlation with both TSM and POC is the same. The discrepancy that we observed between the correlation of  $K_{oc}$  with TSM and POC implies that the chemical characteristics of the organic

substrate are critical to its binding capacity. Similar conclusions have been reached for the association of HOC with natural DOC (11,25) and a variety of humic and fulvic acid substrates (26-29). The complexity described above illustrates that we are far from understanding the multitude of processes controlling phase partitioning and subsequent bioavailability.

Table III. Significance ( $r^2$ ) for linear correlations between distribution coefficients and log of the substrate concentration

<u>COMPOUND</u>	Log Kd	Log Koc		Log Kb
	vs	vs	vs	vs
	<u>Log TSM</u>	<u>Log TSM</u>	<u>Log POC</u>	<u>Log DOC</u>
BaP	0.03	0.07	0.22*	0.03
HCB	0.36*	<0.01	0.49*	0.22**
DDT	0.35*	<0.01	0.13**	0.24**
TCB	0.24*	<0.01	0.24*	0.06
Pyrene	0.17**	<0.01	0.04	0.05
MCB	0.14**	<0.01	0.07	0.15**

\* P > 0.99

\*\* P > 0.90

For all compounds examined except BaP, there was a significant relationship between log Kd and log of the ambient TSM. The relationships for HCB was the same and for TCB was different ( $P < 0.01$ ) from those reported (21) in an analysis of ambient PCB distribution in Lake Superior.

#### HCB

$$\log Kd = 5.79 - 0.46 \log TSM \quad (\text{this work})$$

$$\log Kd = 5.37 - 0.54 \log TSM \quad (21)$$

#### TCB

$$\log Kd = 5.00 - 0.75 \log TSM \quad (\text{this work})$$

$$\log Kd = 5.33 - 1.08 \log TSM \quad (21)$$

The role of solubility

The log of all three partition coefficients was highly correlated ( $P < 0.001$ ) with the log of contaminant solubility over the four orders of magnitude of compound solubility examined (Table II). The equations for all of the data are:

$$\log K_p = 4.4 - 0.54 \log S \quad r = 0.97$$

$$\log K_{oc} = 5.3 - 0.55 \log S \quad r = 0.97$$

$$\log K_b = 3.9 - 0.19 \log S \quad r = 0.80$$

where the solubility has units of  $\mu\text{mol}$ .

The  $K_{oc}$  slope is not significantly different from others that have been reported (1,4). From a comparison of the slopes for our equations, it is apparent that the binding to DOM is much less a function of solubility than the binding to particles. Further, from the data in Table II, it is apparent that the  $K_b$  vs solubility relationship for MCB is inconsistent with that for the other compounds; its mean  $K_b$  is larger than expected based on solubility, and the variance in the data is large. Removing the MCB data improves the regression ( $\log K_b = 3.6 - 0.31 \log S$ ;  $r = 0.96$ ), and increases the slope significantly, although it is still much smaller than the relationship with particulate matter.

The relationships of the binding of these compounds (with and without MCB) to DOC and POC were also compared to their reported  $K_{ow}$ :

$$\log K_{oc} = 0.90 \log K_{ow} + 0.82 \quad (\text{all data; } r = 0.94)$$

$$\log K_{oc} = 0.72 \log K_{ow} + 1.94 \quad (\text{no MCB; } r = 0.84)$$

$$\log K_b = 0.24 \log K_{ow} + 2.78 \quad (\text{all data; } r = 0.61)$$

$$\log K_b = 0.43 \log K_{ow} + 1.58 \quad (\text{no MCB; } r = 0.72)$$

From these results it is apparent that ambient Great Lakes POC is similar to octanol as a substrate for binding, while the DOC is much less effective.

The relation of  $K_b$  to  $K_{oc}$ 

The use of  $K_{oc}$  is based on the assumption that phase partitioning to particles is in reality partitioning to the organic matter associated with these particles. Because of our limited ability to separate particulate matter from water, some fraction of the contaminant that we

define as bound to DOM is actually associated with fine (< 1  $\mu\text{m}$ ) particulate matter. Is our measurement of binding to DOC simply an extension of the binding to POC, or are there differences which justify the concept of a third phase? If  $K_b$  is an extension of  $K_{oc}$  then a slope of 1 would be expected for a plot of  $\log K_{oc}$  vs.  $\log K_b$  for each compound. Examining the correlations between  $\log K_{oc}$  and  $\log K_b$  for individual compounds shows the slopes increase with increasing compound solubility (Figure 5). There are extreme differences in the  $K_b - K_{oc}$  relationship. MCB, with a slope of nearly 1, behaves as if partitioning to DOC is the same as to POC. At the other end of the solubility spectrum, the slopes for BaP and HCB are not significantly different from zero ( $P < 0.1$ ), indicating that HOC association with the two phases are unrelated. The behavior of the other compounds is intermediate, but the fact that the slopes are different from one another indicates that the compounds are seeing the phases differently. This behavior indicates that for most of the compounds studied, the binding to DOC is different from binding to POC and that an independent third phase is needed to interpret these data.

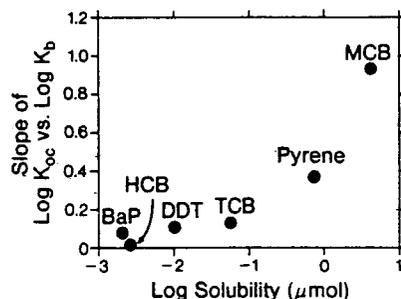


Figure 5. The slope of the  $\log K_{oc}$  vs  $\log K_b$  for each compound with respect to HOC solubility. If  $K_b$  were an extension of  $K_{oc}$  down into the unfilterable size range the slope of  $K_{oc}$  vs  $K_b$  should remain constant at a value of 1. The changing slopes observed indicate that POC and DOC association range from complete independence at very low solubility to near equality as solubility increases.

#### Natural DOC vs Aldrich Humic Acid Binding

In previous reports (6,11) we have used cleaned Aldrich humic acid (AHA) as a standard substrate and have shown that natural DOC has a substantially lower binding capacity. In this study we used low concentrations (ca. 2 mgC/L) of AHA as a control in many of the experiments. The results (Figure 6), confirm our earlier findings, as well as those of others (table IV). In nearly all of these examples, DOC from natural waters displays a wide range of binding capacity for HOC, but is rarely as efficient a binding substrate as Aldrich Humic Acid. It is probable that only a small fraction of natural DOC has any significant binding capacity. Our results (figure 6), would look the same if only a few to 10% of the DOC had the binding capacity of AHA and the remainder of the DOC was not involved. It is also apparent that AHA is a less efficient HOC binding substrate than POC. Organic matter associated with particles

may be spatially oriented in a favorable way for HOC association due to a charge on the particle or the hydrophilic nature of the compounds' functional groups. Whatever the explanation, it is apparent that ambient aqueous suspensions of organic matter, as DOC or POC, have a wide range of binding capacities for any individual HOC and that attempting to reduce the range of distribution coefficients by normalizing with substrate organic carbon is not successful, as it appears to be for suspensions of sediments (4).

Table IV. Comparison of binding capacity of AHA and Natural DOC

Compound	Log Kb		Reference
	AHA	Natural DOC	
DDT	5.56	4.39 - 5.06	27, 28
DDT	5.61-5.74	4.84	5
DDT	5.44	4.28-4.46	6, 31
DDT	5.40	4.26 +/- 0.44	This work
TCB	4.86	--	25, 32
TCB	4.40	3.57-5.68	6, 31
TCB	--	4.9 - 5.6	21
TCB	5.00	3.88 +/- 0.53	This Work
PYR	5.01	4.46 - 5.5	30
PYR	5.20	3.76 +/- 0.39	This Work

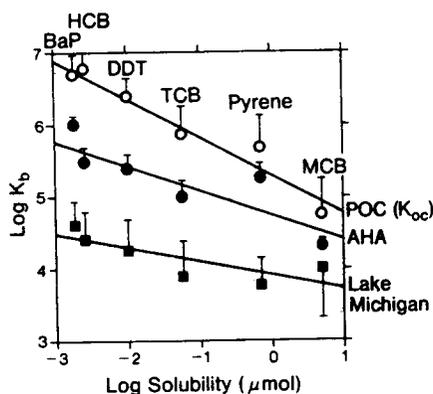


Figure 6. A comparison of log Kb vs solubility for Aldrich Humic Acid and the natural DOC examined in this study. It is evident that the high molecular weight AHA is a more efficient substrate for binding than natural DOC, however the higher values for  $K_{OC}$  show that the AHA is not as effective a sorption substrate as ambient POC.

### Conclusions

For the HOC examined in natural waters of low TSM and DOC, we found:

1. that although substrate composition changed significantly, there were no apparent seasonal trends in the distribution coefficients or in the mass distribution among the three defined phases,
2. as observed by others, HOC distribution coefficients were inversely related to compound solubility,
3. a weak inverse relationship between the log  $K_d$  and ambient particle concentration; normalizing  $K_d$  by organic carbon ( $K_{oc}$ ) dramatically reduced this relationship,
4. binding of HOC to DOC in these waters was small; the amount associated with this phase averaged less than 5% and did not exceed 10% of the total, and
5. the solubility and substrate relationships for  $K_b$  are different from those for  $K_{oc}$ , indicating a separate phase is a valid assumption, but this does not account for all of the substrate concentration effect on partitioning to particles.

### Acknowledgements

The authors are grateful for the assistance of the crew members of the RV Shenehon and to Doug Berner and Brian Lake for help with sample collection and processing. We also appreciate the comments of Wayne Gardner and two anonymous reviewers. GLERL contribution number 618.

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(Received in Germany 30 October 1989; accepted 9 November 1989)