DISTRIBUTION OF HYDROPHOBIC ORGANIC COMPOUNDS BETWEEN DISSOLVED AND PARTICULATE ORGANIC MATTER IN GREEN BAY WATERS

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ABSTRACT. Water samples freshly collected from southern Green Bay were innoculated with radiolabelled hydrophobic organic compounds (HOC) and, after equilibration, separated into particle bound, dissolved organic matter (DOM) bound and freely dissolved phases. Ambient suspended matter (2.7–28 ppm) and dissolved organic carbon (5.2–11.5 ppm) were high in concentration relative to the open Great Lakes, but HOC distribution coefficients were not significantly different between Green Bay and previously measured open Great Lakes values. HOC in the particle phase ranged from 3% for 4-MCB to 53% for BaP and DDT. HOC associated with DOM was generally higher than for open lake samples, and ranged from 2% for 2,2',5,5'-TCB to 26.5% for 4-MCB.
INDEX WORDS: Particulate matter, partitioning, Lake Michigan, organic compounds.

INTRODUCTION

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 lakes (Eadie and Robbins 1987). A number of laboratory and field studies have examined the role of partitioning and phase distribution in the behavior and fate of contaminants in aquatic ecosystems. Partitioning to particulate matter has been shown to be inversely proportional to log solubility of the HOC (Kenaga and Goring 1980) and to the log of total suspended matter (TSM) concentration (O'Connor and Connolly 1980) and proportional to the organic carbon content of the particulate matter (Karickhoff *et al.* 1979) and the octanol-water partition coefficient of the HOC. HOC also bind with the spectrum of materials operationally defined as dissolved (Carter and Suffet 1982, Landrum *et al.* 1985) 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 affects their bioavailability to various aquatic organisms (Leversee *et al.* 1983, McCarthy 1983, McCarthy *et al.* 1985, Landrum *et al.* 1987).

In this study, waters freshly collected from southern Green Bay were innoculated 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 phase equilibria of HOC with a wide range of solubilities in a system (Green Bay) that has relatively high ambient concentrations of DOM and TSM, and to test results

TABLE 1. Solubilities and innoculations of the HOC used in this study.

Compound	Code	μMol Innoculated	μMol Solubility	Log Kow
[14C] 4-Monochlorobiphenyl	MCB	0.005	4.3	4.5
[3H] Pyrene	Py	0.059	0.74	5.2
[14C] 2,2′,5,5′ Tetrachlorobiphenyl	TCB	0.031	0.055	5.7
[14C] DDT	DDT	0.0080	0.010	6.2
[3H] Benzo(a)pyrene	BaP	0.0008	0.0020	6.0

obtained in a study of open Great Lakes waters (Eadie *et al.* 1990) which showed that: 1) the major portion of the HOC was in the dissolved state, 2) the fraction of HOC associated with TSM is related to the organic content of the substrate and HOC solubility, and 3) the HOC associated with dissolved organic matter represents a small fraction of the total.

METHODS

Nine raw water samples were collected for this study on three cruises in southern Green Bay (5 May, 20 June, and 20 September 1988) from both near surface and near bottom. The water was placed in precleaned, sample water rinsed, plastic cubitainers and stored at 4°C prior to air shipment in insulated containers to our laboratory in Ann Arbor. Experiments were begun within 24 hours of receipt or 2 days of collection of the samples.

Three 250-mL aliquots were filtered through precombusted (4 h @ 400°C) 25 mm glass fiber filters (Gelman AE), and were analyzed for particulate organic carbon (POC) by the wet combustion method (Menzel and Vaccaro 1964). Coefficients of variation for POC were less than 7%. Dissolved organic carbon (DOC) was measured on 5-mL aliquots of the POC filtrate by the same procedure with similar precision. Three 2-L aliquots were filtered through prewashed, preweighed 47-mm diameter glass fiber filters (Gelman AE). The filters were dried at 90°C, equilibrated with room temperature and humidity, then reweighed along with controls. The difference in weights defined the total suspended matter (TSM). Coefficients of variation for TSM measurements were less than 5%.

Radiolabelled HOC (Table 1) in methanol carrier, all greater than 97.9% pure as determined by

thin layer chromatography and liquid scintillation counting, were innoculated individually or in dual labelled pairs (in triplicate sets) into 50-mL Pyrex centrifuge tubes. The methanol was evaporated under a stream of nitrogen. Raw lake water (50mL) was added, and the tubes capped (with an aluminum foil liner) and rotated (8 rpm) for 3 days at approximately 25°C. Time to apparent partitioning steady state (Kds not significantly different from 20-day exposure) had been previously measured to be less than 48 hours for Pyrene and BaP and the amount innoculated to be within the linear portion of the sorption isotherm for all of these compounds (Morehead *et al.* 1986). Three days was a compromise between approaching partitioning steady-state and concern for decomposition of the DOM and POM. For the higher solubility compounds used, the experiments may not have reached steady-state.

Five fractions were collected from each replicate to calculate phase separation (for details see Eadie *et al.* 1990). Briefly, the mixture was vacuum filtered (25-mm filter, stainless steel screen support) through a pair of glass fiber filters. The top filter was counted for particle associated plus filter sorbed HOC. The bottom filter adsorbs an equal amount of dissolved HOC as the top one and was counted to correct both the particulate and dissolved fractions. Two mL of water were removed from the filtrate and placed in a scintillation vial to count the freely dissolved plus dissolved organic matter associated HOC. Six mL of filtrate were pushed through a Waters reverse phase Sep Pak as a rinse, then 2 mL, representing the DOM bound HOC, were passed through the Sep Pak into a scintillation vial. Finally, 12 mL of scintillation cocktail (Research Products International 3a70b) was used to wash the filtering apparatus and collected for counting. The five fractions represent:

1) Particle associated HOC + HOC sorbed to filter
2) HOC sorbed to filter
3) HOC freely dissolved + HOC associated with DOM
4) DOM bound HOC
5) 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 89 to 107% of the innoculation for the 69 experiments. These recoveries include the HOC sorbed to the centrifuge tube which was extracted by adding 12 mL of scintillation cocktail to the tube and rotating for the 10-15 minutes required to complete the other phase separations. The sorbed amount varied from an average of 9.2% for BaP to 4.3% for MCB.

The phase partitioning by reverse phase chromatography using a Sep Pak are flow rate dependent (Landrum *et al* 1984, Morehead *et al.* 1986). Separation of the freely dissolved and bound HOC requires the rate of adsorption of the freely dissolved HOC to the resin be larger than the breakdown rate of the HOC-DOM complex or the adsorption rate of the complex to the resin. The flow rate dependence was analyzed in Morehead *et al.* (1986) and shown to contribute less than 10% error to the estimate of Kb. Column breakthrough for various HOC has been less completely examined and could artificially elevate the calculated values of Kb.

Concentrations in the three defined phases were calculated as:

C_f = freely dissolved HOC concentration (g/mL)
   = (fraction 3 - fraction 4) + 2 * fraction 2 + fraction 5

C_p = particle associated HOC concentration (g/g TSM)
   = (fraction 1 - fraction 2)/TSM

C_b = DOC associated HOC concentration (g/g DOC)
   = fraction 4/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 relations were used:

C_t = total contaminant concentration (g/mL)
K_d = C_p/C_f (mL/g)
K_{oc} = $100*K_d/$(% Organic C of TSM)
Kb = C_b/C_f (mL/g)

Fraction free: Ff = Cf/C_t = $[1 + K_d*TSM + Kb*DOC]^{-1}$
Fraction DOC bound: Fb = DOC * Kb * Ff
Fraction particle bound: F_p = TSM * K_d * Ff

RESULTS

The data collected in our experiments allowed us to separate the inoculated HOC among three operationally defined phases in near ambient environmental conditions. The characteristics of these water samples, listed in Table 2, generally exhibit higher DOC and TSM than open Great Lake samples (Eadie *et al.* 1990). From each of the nine water samples we calculated equilibrium distribution coefficients and HOC phase distributions; an example is plotted against HOC solubility in Figure 1. The Koc for the five HOC are strongly related to solubility. A visual comparison with the data collected in the open Great Lakes (Figure 1, solid line) shows that Green Bay waters, although generally higher in TSM concentrations, yield similar equilibrium HOC distribution coefficients when normalized for substrate organic carbon. The log Kb shows a minimum value for TCB, but the values are in the same general range as observed in open lake waters (solid line). When the results of the nine experiments were combined, the average of the log transformed distribution coefficients (Table 3) were not significantly different from those that were measured, using the same approach, in the open Great Lakes (Eadie *et al.* 1990).

The equilibrium HOC phase distributions for the nine separate water samples are plotted (Figure 2) against the total particulate organic carbon (TPOC = TSM*POC). For the nine samples analyzed, the TPOC covers a range from 0.27 to 1.83 mgC.l[-1] (Table 2). The maximum TPOC was in a sample collected near the mouth of the Fox River in June, 1988 and appears furthest on the right in Figure 2. This sample generally has the greatest fraction of particulate bound HOC, although the next lower TPOC sample has similar (high proportions of particle bound) distributions for TCB and

TABLE 2. Water sample characteristics (in the same order as Figure 2).

Sta	Z(m)	Collection Date	DOC mgC.L^{-1}	TSM mg.L^{-1}	POC mgC.(mgTSM)$^{-1}$	TPOC mgC.L^{-1}
1	10 bs	20 June	9.7	3.6	0.08	0.27
1	2 ab	20 June	8.2	4.6	0.07	0.33
2	2 bs	20 Sept	6.5	2.7	0.19	0.50
1	2 bs	20 Sept	7.6	3.4	0.21	0.71
1	2 ab	20 Sept	6.1	4.9	0.15	0.72
2	2 bs	20 Sept	5.2	4.6	0.19	0.86
1	2 bs	20 June	9.7	3.0	0.29	0.87
1	2 bs	5 May	5.5	5.4	0.23	1.26
R	2 bs	20 June	11.5	28.0	0.07	1.83
Open G.L.*			3.6	1.5	0.16	0.23

*Average of 71 open Great Lake water samples (Eadie *et al.* 1990)
Station 1 (44 55.7, 87 34.2) 22 m total depth
Station 2 (44 51, 87 40) 16 m total depth
Station R (44 43, 87 50) 7 m total depth
Sample depths are in meters bs (below surface) and ab (above bottom)

DDT. The remaining seven water samples, although considerably different in composition (Table 2), have very similar distribution patterns for the five HOC. With the exception of MCB, the fraction of HOC associated with DOM is small.

DISCUSSION

It is well recognized that HOC are distributed among a spectrum of substrates that differ in particle size and chemical characteristics, as well as in a truly dissolved state. Recent efforts have shown that only the dissolved compounds are readily bioavailable (Leversee *et al.* 1983, McCarthy 1983, McCarthy *et al* 1985, Landrum *et al.* 1987), thus the factors influencing associations with indigenous substrates need to be understood in order to develop comprehensive contaminant cycling models.

ROLE OF TSM, POC, AND DOC

Previous laboratory (O'Connor and Connolly 1980) and field (Baker *et al.* 1986) 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 (Gschwend and Wu 1985) and by increases in particle collision frequency as concentration increases (DiToro 1985, Mackay and Powers 1987). Least squares regressions between

the log of the distribution coefficients (Kd and Koc) and both the substrate concentration (TSM) and the total particulate carbon (TPOC) as well as their log transformations were examined for each compound. The distribution coefficient for dissolved organic matter (log Kb) was similarly treated with respect to the concentration of DOC. All correlations were non-significant (P < 0.2) except for the log Kd of pyrene and BaP vs total particulate organic carbon. This result is similar to the low (although in several cases significant at P < 0.01 because of the large number of cases) regression coefficients obtained for open lake water samples and HOC (Eadie *et al.* 1990). Note that for most of the HOC, the phase distribution (Fig. 2) is relatively constant over an order of magnitude range of TSM.

THE ROLE OF SOLUBILITY

The log of all three distribution coefficients was highly correlated (P < 0.01) with the log of HOC solubility over the four orders of magnitude of compound solubility examined (Table 1). The equations for all of the data are:
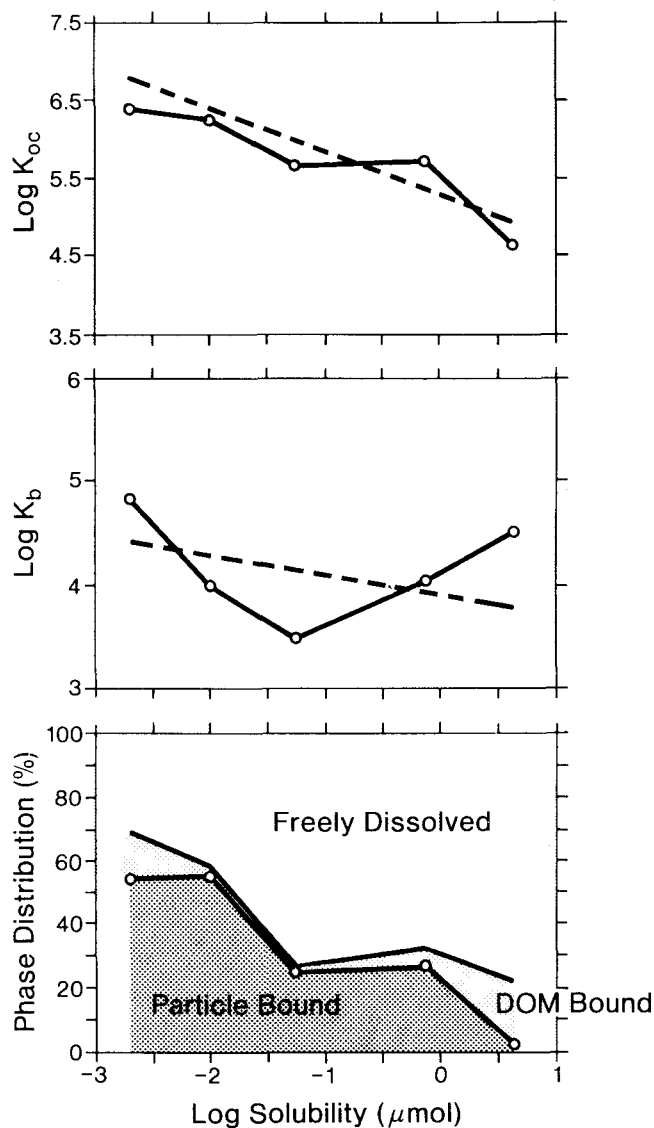
log Kd = 4.5 – 0.44 log S r = 0.91
log Koc = 5.3 – 0.44 log S r = 0.91
log Kb = 4.2 + 0.01 log S r = 0.72

where the solubility has units of uM.
The Koc slope is not significantly different from

FIG. 1. Experimental results for a near surface water sample collected west of Sturgeon Bay in Green Bay on 20 September 1986. The total suspended matter (TSM) was 3.4 mg.L⁻¹ and contained 21% organic carbon. The DOC was 7.6 mg.L⁻¹. Data are plotted against the log of the innoculated HOC solubility. In the upper panel, the symbols are the means of the triplicates for the log transformed Koc in this water sample; the dashed line is the regression derived from 219 samples for the open Great Lakes (Eadie et al. 1990). The central panel is a parallel treatment for the Kb. The bottom panel represents the HOC phase distribution for this water sample. The percentage of HOC that is freely dissolved is shown as the region above the upper line. The region between the two lines represents the HOC bound to the DOC and the region below the lower line represents the particle bound HOC.

TABLE 3. Statistics on distribution coefficients.

		BaP	DDT	TCB	PY	MCB
Log Kd	(x)	5.60	5.46	4.96	5.01	3.92
	(s)	0.10	0.18	0.27	0.15	0.28
Log Koc	(x)	6.38	6.24	5.74	5.79	4.70
	(s)	0.15	0.12	0.19	0.19	0.29
Log Kb	(x)	4.77	3.97	3.66	4.14	4.61
	(s)	0.14	0.30	0.25	0.38	0.37

x = mean of log transformed data
s = 1 standard deviation
n = 23

others that have been reported (Kenaga and Goring 1980, Karickhoff et al. 1979, Eadie et al. 1990). 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.

The relationships of the binding of these compounds to DOM and POC were also compared to their reported Kow:

$$\text{Log Koc} = 0.90 \text{ Log Kow} + 0.81 \quad r = 0.94 \quad P < 0.01$$
This work
$$\text{Log Kb} = -0.21 \text{ Log Kow} + 5.37 \quad r = 0.32 \quad P < 0.2$$
This work

In results separately reported for open Great Lakes waters (Eadie et al. 1990), these relationships were:

$$\text{Log Koc} = 0.90 \text{ Log Kow} + 0.82 \quad r = 0.94 \quad P < 0.01$$
$$\text{Log Kb} = 0.24 \text{ Log Kow} + 2.78 \quad r = 0.61 \quad P < 0.01$$

The relationships for Koc in open Great Lake and Green Bay waters are virtually the same while the Kb relationships are markedly different. The significance of the Green Bay Kb data is weak and the negative coefficient may be an artifact of the data. This is more clearly seen in Figure 1, where the Kb vs solubility has a pronounced minimum for TCB. This is also true for the entire data set (Table 3). From these results it is also apparent that ambient Great Lakes POC is similar to octanol as a substrate for binding, while the DOM is much less effective and more variable. In these and other published examples, DOM from natural waters displays a wide range of binding capacity for HOC (summarized in Eadie et al. 1990) but is rarely as efficient a binding substrate as commercially available humic acids (Landrum et al. 1984). It is probable that only a small fraction of natural DOC in
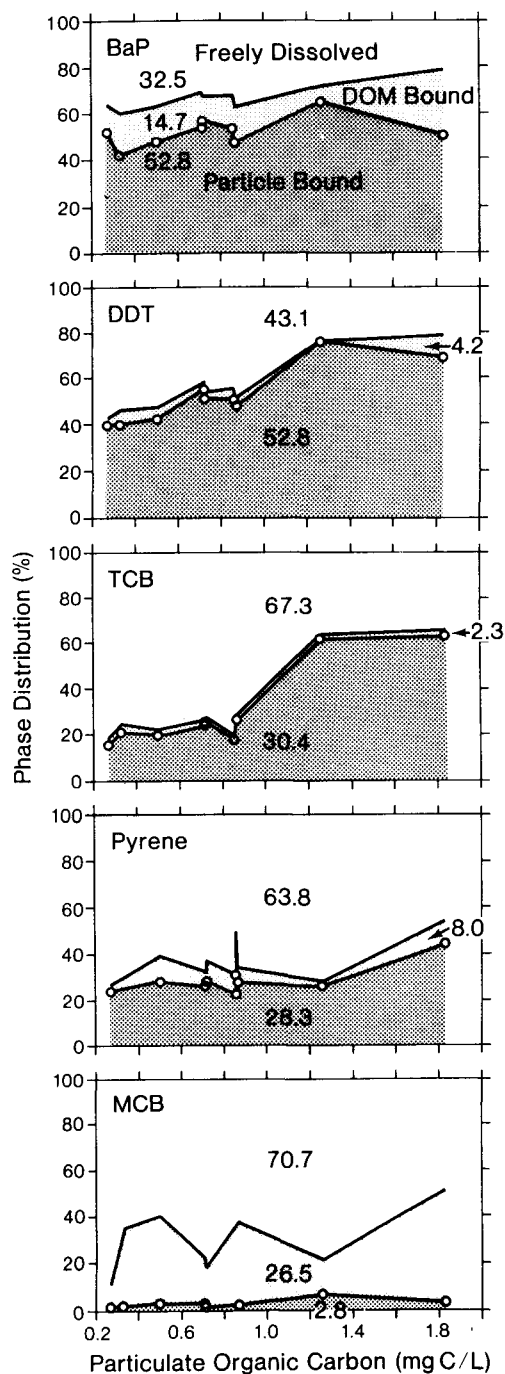
FIG. 2. *Equilibrium phase distributions of the five innoculated HOC in the nine Green Bay water samples described in Table 2. The region below the bottom line represents particle bound HOC. The region above the top line represents freely dissolved HOC. The DOC associated HOC is represented by the region between the two lines. The numerical values associated with each fraction are the average values for the nine water samples.*

Great Lakes waters has any significant binding capacity.

CONCLUSIONS

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

1. the HOC distribution coefficients measured in Green Bay waters were not significantly different from those measured in open Great Lakes waters,
2. as observed by others, HOC distribution coefficients were inversely related to compound solubility,
3. although binding of HOC to DOC in these waters was small (the amount associated with this phase averaged less than 10% and did not exceed 20% of the total), it was approximately 2-3 times the average for open Great Lakes waters, and
4. the solubility and substrate relationships for Kb are different from those for Koc, indicating a separate phase is a valid assumption.

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