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Estimating the Effects of Dispersed Organic Polymers on the Sorption of Contaminants by Natural Solids. 2. Sorption in the Presence of Humic and Other Natural Macromolecules

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A triphase distribution model was used in conjunction with experimental observations to characterize the effects of humic polymers dispersed in an aqueous phase on the sorption of hydrophobic organic compounds from that phase by natural solids. The organic compound-humic substance binding constants employed in the model were estimated by using a partition equation that takes into account the solubility of the solute in both the aqueous and organic polymer phases as developed in the first paper of this two-part series. Experimental results and model predictions indicate that the sorption of moderately hydrophobic compounds by lacustrine sediments is relatively unaffected by the presence of humic polymers, but that the sorption of highly insoluble organic contaminants by the same sorbents is sensitive to small amounts of background organic polymers. The observations support earlier analyses by other investigators regarding the impact of the organic subphases on the fate and transport of pollutants in natural aquatic systems.

Introduction

The presence of dissolved or suspended organic macromolecules in natural waters has been observed to affect the sorptive behavior of many particle-reactive micropollutants. This phenomenon may have serious implications with respect to understanding and modeling the bioavailability, toxicity, fate, and transport of such contaminants. The first paper of this two-part series presented a conceptual thermodynamic model for the binding of sparingly soluble organic compounds to humic substances (1). In this paper an attempt is made to predict the effect of these natural organic polymers on solute sorption by using a simple triphase distribution model.

Triphase distribution models involving aqueous, solid, and dispersed polymer or colloid phases have been invoked in a number of instances (2-5) to explain the so-called "solids effect". These effects are frequently observed in experimental measurement of the sorption of target compounds by natural solids. Triphase distribution models are generally predicated upon three basic assumptions: (1) the total amount of target compound residual in the aqueous phase (i.e., not sorbed by the solid) comprises both free and polymer "bound" solute; (2) binding of the solute by the organic polymers in question and sorption of both solutes and polymers can be described in terms of partitioning relationships; and (3) equilibrium conditions exist

 Table I. Estimated and Observed Organic Carbon

 Normalized Binding Constants for Four Organic

 Compounds to Two Organic Substrates

	log	log	log	log
compd	K _p	K _{b,oc(obs)} *	K _{b,oc(pred)} ^b	K _{b,oc(pred)} ^c
1,4-DCB	2.19	2.92	2.91	2.43
1,2,4-TCB	2.77	3.11	3.32	2.62
2,2',5-PCB	3.36	4.57	4.85	4.15
a-chlordane	3.72	4.77	4.38	3.5

•Observed values reported in Chin and Weber (1). •For commercial Aldrich humic acid substrate with methyl salicylate ($\lambda =$ 7.8, $\tau =$ 7.16) as the model surrogate compound. •For organic polymers present in Huron River water with polymaleic acid properties ($\lambda =$ 8.09, $\tau =$ 10.9) as the model surrogate compound.



Figure 1. Observed and predicted effects of Aldrich humic acid on 1,4-DCB sorption by Lake Michigan sediments (LMS).



Figure 2. Observed and predicted effects of Aldrich humic acid on 1,2,4-TCB sorption by LMS.

in eq 2 were approximated by the hypothetical monomers methyl salicylate (for the commercial humic acid), and maleic anhydride (for the natural water organic matter). Details regarding selection of these two compounds are given in the first paper of this series (1). Agreement between measured and estimated commercial humic acid $K_{b,cc}$ values are generally good, with the exception of α chlordane. Measured natural water binding constants for these four probes were not available in the literature for comparison to the maleic anhydride estimated $K_{b,cc}$ values.

It is of interest to compare the $K_{b,cc}$ values given in Table I to values "backed out" of earlier attempts to explain the observed effects of solids concentration by retrofitting the triphase model to sorption data (3). Both the estimated and measured constants from the present work are orders of magnitude lower in numerical value, and the measured values are obviously more consistent with conceptual expectations.

The effects of Aldrich humic acid (AHA) on the sorption of 1,4-DCB, and 1,2,4-TCB by Lake Michigan sediments are illustrated in Figures 1 and 2. The solid lines and closed circles represent model predictions and observed results, respectively, for sorption in the presence of 12.5



Figure 3. Observed and predicted effects of Huron River water on 1,4-DCB sorption by LMS.







Figure 5. $K_{\rm p,obs}$ predictions for 1,2,4-TCB in the presence of varying amounts of Aldrich humic acid.

mg/L commercial AHA, expressed in terms of total organic carbon (TOC). The open squares denote sorption data measured only with distilled deionized water and serve as a zero background reference. The triphase model predicts essentially no effect at this concentration of polymeric organic matter on sorption by these two substances, and this is verified by the data. Similarly, the sorption of the probes by Lake Michigan sediments is predicted and observed to be insignificantly affected by the presence of Huron River water (background organic matter TOC = 11mg/L) as illustrated in Figures 3 and 4. These findings agree with the observations made by Caron and co-workers (9) for sorption of lindane, a compound of similar hydrophobicity. Chiou et al. (13) also observed insignificant lindane solubility enhancement by low concentrations of dissolved humic materials, which further supports these findings.

The relatively low binding capacity of the organic polymer phase for the two halogenated benzene compounds explains the observations and model predictions presented in Figures 1-4. A sensitivity analysis was per-

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among all phases of the system.

Three-phase models can provide plausible explanations for observed solids effects. Moreover, they have been successfully fitted to experimental data known to be influenced by such effects (3). This "after the fact" fitting has, however, been less than totally satisfying in terms of thermodynamic rigor. Quantitative verification of this type of model in a manner consistent with conceptual expectations of system behavior is still lacking. This present work attempts to address this deficiency.

To simplify the mathematical form of the model, the data-gathering phase of this work involved completely mixed batch reactor (CMBR) experiments in which the solids to water ratio was kept constant for all batch experiments, and varying amounts of humic acid solution or river water were introduced into each system. Under such conditions the triphase distribution model simplifies to the following expression:

$$K_{\rm p,obs} = \frac{K_{\rm p}}{(1 + K_{\rm b,oc}X(10^{-6}))}$$
(1)

where $K_{b,\infty}$ is the solute-polymer binding constant (L/kg), X is the amount of polymer present expressed as organic carbon (mg/L), and $K_{p,obs}$ and K_p are the solute/sorbent partition coefficient in the presence and absence of a third phase, respectively (L/kg). The constant 10^{-6} corrects for the proper units of mass. Equation 1, while simple in concept and structure, should provide reasonable first estimates of $K_{p,obs}$, provided that K_p , $K_{b,oc}$, and X can be accurately estimated or measured for the system of interest. For purposes of this work, the parameters K_p and X were determined from CMBR experiments while $K_{b,oc}$ values were predicted by using a semiempirical equilibrium model. Previous efforts at "fitting" the triphase model to observed partitioning data had yielded values for this binding constant that were admittedly "unexpected and difficult to interpret" (3). It was a major objective of this work to provide more physically significant numerical values for this constant. The model used to aid this effort incorporated a modified form of the Flory-Huggins equation (1, 6, 7):

$$\log K_{\rm b,oc} = \log \gamma_{\rm i}^{\rm w} - \log \rm oc - \log \rho + \log V_{\rm w} / V_{\rm i} - (1 + \chi) / 2.303$$
(2)

where $\gamma_i^{\mathbf{w}}$ is the solute aqueous phase activity coefficient (dimensionless), oc is the organic carbon content of the humic substrate, χ is the Flory parameter, ρ is the density of the polymer phase (g/mL), and V_w/V_i is the water to solute molar volume ratio (6, 7). The value χ comprises both entropy and enthalpy components, the former determined empirically while the latter is estimated from polymer and solute properties by use of an expanded Regular Solution equation. Derivation of eq 2 is similar to the one presented by Chiou and co-workers (6) for soil/water systems and is presented in detail in the first paper of this series (1). This paper compares model estimations of $K_{p,obs}$ from eq 1 to results from CMBR sorption experiments for four hydrophobic organic compounds (probes) and Lake Michigan sediment in the presence of two types of aquatic organic matter, a commercial humic acid and filtered river water. The environmental implications of the triphase model are discussed with regard to fate and transport processes.

Experimental Protocol

The sorbent was obtained from Lake Michigan offshore of South Haven, MI. It was wet sieved to less than 60 μ m,

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freeze-dried, and stored in a sealed container at -20 °C. The organic carbon content was determined to be 1.42%, by use of a persulfate oxidation technique. Aqueous total organic carbon (TOC) analyses were performed on a wet-oxidation UV/persulfate analyzer (Dohrmann Co.)

Aldrich humic acid, a commercially available natural organic polymer commonly used as a convenient surrogate in chemical reactivity studies, was employed as one source for organic macromolecules. Stock solutions were made by adding specific amounts of Aldrich humic acid (400–500 mg) to 1 L of distilled water and raising the pH to 11 with 1.0 N NaOH. The solution was agitated for 1 h, titrated with 1.0 N HCl to a pH of 7.0, and filtered through two type A/E prewashed glass fiber filters (Gelman Science). Working concentrations (12.5 mg/L organic carbon) of humic acid were made by diluting the stock solutions with 10 mM sodium bicarbonate buffered water (pH 7.5). Sodium azide (1.5 mM) was added to inhibit microbial growth.

Surface water from the Huron River, sampled at Barton Park in Ann Arbor, MI, during the spring runoff period, was chosen as a source of natural aquatic organic matter. This sample was filtered through two prewashed type A/Eglass fiber filters, poisoned with sodium azide (1.5 mM), and stored in amber bottles at 4 °C. TOC results yielded a concentration of 11 mg/L organic carbon.

Four chlorinated hydrocarbons, 1,4-dichlorobenzene (DCB), 1,2,4-trichlorobenzene (TCB), 2,2',5-polychlorinated biphenyl (PCB), and α -chlordane were selected as probes or target compounds. These compounds, all considered as "EPA priority pollutants", exhibit a wide range of physical-chemical properties and are relatively stable and easy to assay.

CMBR sorption experiments were carried out using 150-mL Hypovials (C. P. Pierce). A 100-mL aliquot of either Huron River water or Aldrich humic acid solution was added to each vial, and the target compound was introduced by direct injection in an acetone carrier to give a range of different solute concentrations. Lacustrine sediment (100 mg) was then added to each reactor, sonicated to break up large aggregates, and sealed with aluminum crimp seals lined with Tuff-Bond Teflon-lined disks (C. P. Pierce). The sealed reactors were placed on a rotary tumbler and the systems allowed to equilibrate for 120 h. A previous study (8) determined this to be sufficient time to attain an apparent equilibrium condition. Sorption experiments for two of the probes (DCB and TCB) were conducted in reactors with no headspaces to minimize losses due to volatilization.

A similar set of experiments was conducted using distilled water poisoned with sodium azide to determine the ideal two-phase thermodynamic partition coefficient. Control experiments (i.e., no sorbents added) revealed that solute losses to the walls were 5% or less.

Following equilibration, the reactors were centrifuged to separate the solids from the aqueous phase. A portion of the supernatant was pipetted out and extracted with pesticide-free hexane for 30 min. The phases were allowed to separate, and the hexane was assayed for the probe on a Hewlett-Packard 5890 gas chromatograph equipped with a 63 Ni electron capture detector and a glass column containing an appropriate stationary phase.

Results and Discussion

Effects of Background Organic Matter on the Sorption of Hydrophobic Organic Compounds by Lake Michigan Sediments. The measured and estimated binding constants for the four target compounds are listed in Table I. Humic polymer properties required



Figure 11. $K_{p,obs}$ predictions for α -chlordane as a function of $K_{b,oc}$

A sensitivity analysis to determine the effect of the amount of polymer present (X as TOC) on the sorption of 2,2',5-PCB is illustrated in Figure 10. The triphase model is clearly more sensitive to small increases in the dispersed polymer concentration for target compounds with large organic polymer partition coefficients than it is for relativley more water soluble substances such as DCB and TCB. For the 2,2',5-PCB probe a realistic surface water background humic acid concentration of only 5 mg/L results in a 26.1% change in K_p . This is supported by the partition-interaction model of Chiou and co-workers (13) in explaining the effect of organic substrates on the apparent water solubility of different hydrophobic probes, and by the findings of Brownawell (11, 12), who consistently observed a decrease in partition coefficients with increasing pore water TOC levels in sediment cores for various PCB congeners.

Several investigators (2, 18) have suggested that $K_{b,cc}$ is approximately equal to the organic-carbon-normalized solute/sediment partition coefficient, while others show that $K_{b,cc}$ is generally smaller than K_{cc} (1, 8, 13, 14). The sensitivity of model predictions to the magnitude of the solute binding constants at a constant value for X = 10mg/L TOC is examined in Figure 11 for α -chlordane, which exhibited the widest variations in $K_{b,cc}$ based on estimations made by eq 2. An 18-fold increase in $K_{b,cc}$ (from $10^{3.5}$ estimated with PMA as the surrogate polymer to $10^{4.77}$ for Aldrich humic acid) resulted in a 35% change in K_p . Such wide variations again suggest the need for an expanded and more accurate data base regarding solute and polymer properties if a thermodynamic modeling approaches such as that presented in this two-part series of papers is to be fully exploited.

Environmental Implications. Several investigators (2-4) have presented evidence implicating the binding of organic solutes to a dispersed organic polymer phase as a plausible explanation for the "solids effect" commonly observed in measurements of organic solute sorption by soils and sediments. The work presented here supports this implication by showing that organic polymers in the aqueous phase can effect significant changes in the sorption characteristics of nonpolar organic contaminants. The magnitude of these effects are dependent upon the nature and amount of dispersed polymer present in the aqueous phase, and the relative hydrophobicity of the probe. The extent to which the solids effect is observed in partitioning experiments is additionally dependent on the desorbability of such polymers from the solids and the effectiveness of the particular solids/liquid separation process employed prior to measurement of "residual" solute concentration in the aqueous phase (4).

It is highly unlikely that the amount of organic matter desorbed from the solid phase in most batch experiments

would have a major impact on the sorption of relatively soluble low molecular weight organic compounds ($K_{ow} <$ 10⁵). As observed in this work, the presence of Aldrich humic acid at very high concentrations had a relatively minor effect on K_p for trichlorobenzene. Gschwend and Wu (2) reported that the amount of TOC desorbed from up to 10 g/L solids concentration was significantly less than 10 mg/L. Thus, one would not expect to see a large change, if any, in the partition coefficient as a function of the solids concentration for weakly hydrophobic substances. Even in subsurface water systems, where these types of contaminants are most prevalent and the ratios of solids to water are high, the solute partition coefficients for these substances should generally remain constant given the low aqueous TOC levels of such systems. Exceptions to this may occur near hazardous waste sites. where cosolvents (e.g., acetone, methanol, etc.) or large amounts of heterogeneous polymers in leachates might impact sorption (15, 16). The existence of inorganic colloids may also facilitate transport under such near-site conditions (17).

Conversely, the amount of polymeric organic matter commonly found in natural aqueous systems is apparently enough to effect the partitioning of very hydrophobic and recalcitrant organic contaminants such as PCBs, PAHs, and pesticides, making the K_p values for such compounds highly dependent upon the solids to water ratios. These observations are substantiated by the findings of Baker and co-workers (18), who observed a high dependency of K_p values on solids concentration for sorption of PCBs from the Lake Superior water column. Under such circumstances, the organic geochemistry, fate, and transport of micropollutants becomes closely dependent upon the amount and nature of dispersed organic polymers present in the aqueous phase.

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Several complicating factors for natural systems and for attempts to estimate partitioning parameters for natural systems in ex situ experiments should be noted. First, the degree of association (e.g. sorption) of an organic polymer with a solid in a natural system is controlled by a specific set of thermodynamic conditions, equilibrium or otherwise. That set of conditions is perturbed by exposing the solid to different experimental circumstances. Organic polymers may desorb, resorb, or merely stay on the solid, depending upon these new circumstances. The situation is further complicated when another background organic substance (e.g., humic acid) or other natural or surrogate dissolved organic matter (DOM) is added. While the results from this work do not suggest this to be an important process for the systems studied, it is possible that the sorptive properties of the solid, with respect to target compounds, can be affected by the sorption of the added DOM under certain conditions. As a final caution, it must be recognized that "natural organic polymers" generally comprise complex mixtures of specific compounds. These polymers will vary in their tendency to bind target compounds, as demonstrated in the first paper of this series, and in their tendency to sorb on natural solids; different fractions of the polymers and DOM will act selectively and differently with respect to binding and sorption. The specific chemical makeup of a natural organic polymer is in turn influenced by the conditions a particular "starting" chemical mixture has been exposed to over its relevant history. These facts have been demonstrated dramatically for sorption of humic substances by activated carbon (19-21) and should be anticipated for natural solids. Sorption and binding processes thus influence, and in turn are influenced by the historical profile of a particular system.



Figure 6. Observed and predicted effects of Aldrich humic acid on 2,2',5-PCB sorption by LMS.



Figure 7. Observed and predicted effects of Aldrich humic acid on α -chlordane sorption by LMS.

formed by using a fixed log $K_{b,cc}$ value of 3.32 (predicted by using eq 2 for TCB and an Aldrich humic acid substrate) and varying the polymer concentration X in eq 1. The model outputs are illustrated in Figure 5. It is appears evident from the predictions that K_p is relatively insensitive to the amount of organic polymers present in the aqueous phase, even at TOC levels that are unrealistic for most natural waters. A humic acid concentration of 40 mg/L affects the partition coefficient by only 7.8%, while a 200 mg/L humic acid solution decreases K_p by only 30.2%. Thus, the effects of normal levels of dispersed polymers in natural aquatic systems on the sorption of relatively water soluble low molecular weight moderately hydrophobic organic contaminants by natural solids are relatively small.

The presence of humic polymers in the aqueous phase has a much more pronounced effect on the two larger and more hydrophobic probes. This is illustrated in Figures 6 and 7 for sorption of 2,2',5-PCB and α -chlordane, respectively, in the presence of Aldrich humic acid at a concentration of 12.5 mg/L TOC. Agreement between model (eq 1) predictions and observed values for the effect of Aldrich humic acid on the sorption of 2,2',5-PCB is once again good. In the case of α -chlordane (solid line), however, $K_{p,obs}$ is underpredicted. The $K_{b,oc}$ estimated from eq 2 is approximately a factor of 2.5 lower than the experimental value measured by the dialysis method (1). By adjusting for this the triphase model fits the experimental sorption data quite well (dashed line). It is rather evident that, for these types of compounds, accurate values of $K_{\rm hor}$ are necessary to provide reliable predictions by using eq 1.

The effects of the organic substrates in Huron River water on sorption processes is anticipated to be lower than those observed with Aldrich humic acid due to their binding efficiency as discussed by Chiou et al. (14) and in the first paper of this series (1). The effects of Huron River water organics on the sorption of 2,2',5-PCB and α chlordane by Lake Michigan sediments is depicted in



Figure 8. Observed and predicted effects of Huron River water on 2,2',5-PCB sorption by LMS.



Figure 9. Observed and predicted effects of Huron River water on α -chlordane sorption by LMS.



Figure 10. $K_{p,obs}$ predictions for 2,2',5-PCB in the presence of varying amounts of Aldrich humic acid.

Figures 8 and 9. Agreement between observed data and model predictions for sorption of 2,2',5-PCB in the presence of Huron River water is good using an estimated K_{hoc} value, based upon the structure of polymaleic acid, which is similar in properties to the more polar constituents found in natural waters. Predictions for α -chlordane sorption are, however, much less successful when a hypothetical binding constant based upon PMAs solubility parameters (solid line) is used. This implies that the association of α -chlordane with organic matter found in the natural water sample is much greater than model predictions based upon the surrogate, PMA. As noted previously, estimations of Aldrich humic acid $K_{b,\infty}$ values were also lower than those determined experimentally. It is plausible that the organic matter present in the Huron River during spring runoff may have polymeric constituents that could bind certain hydrophobic substances more efficiently. Such processes are not unreasonable, given the dynamic nature of humic materials and other heterogeneous organic substances found in aquatic systems. Rather, such results underscore the need to acquire a reliable data base of related physicochemical properties for both target compounds and different types of aquatic organic polymers.

While such processes are complex and are not readily predictable or quantifiable, an appropriate account of them should be made in related parameter estimates and in the use of these parameters for systems other than those for which they are estimated.

Summary and Conclusions. The results of this research provide additional insights to the complex and dynamic interactions that can occur between organic micropollutants, solid phases, and dispersed polymer subphases present in natural waters. The observations of the study can be summarized as follows: (1) the sorption of hydrophobic organic compounds with octanol/water partition coefficients less than 10⁵ is relatively insensitive to the type and environmentally observed concentration of organic polymers dispersed in the aqueous phase; (2) the sorption of very hydrophobic organic substances (K_{ow} $> 10^{5}$) is highly sensitive to both the nature and concentration of such dispersed organic polymers; (3) reliable estimates or measurements of K_{hoc} are essential for accurate prediction of the impact of organic polymers on K_p ; and (4) the dependence of experimentally measured partition coefficients for organic contaminants on natural solids, the so-called solids effect, appears to relate, among other things, to the hydrophobicity of the compound in question, with K_p values for relatively soluble compounds exhibiting little effect and those for highly hydrophobic substances exhibiting significant sensitivity to solids concentrations.

Acknowledgments

We thank Ingrid Padilla and Kathy Smee for their assistance in the experimental aspects of this work, Phil Gschwend and Cary Chiou for their many hours of valuable discourse, and two anonymous reviewers for their constructive comments.

Glossary

K _{b.oc}	organic carbon normalized binding constant, L/kg
K	two-phase sorbent/water partition coefficient, L/kg
K _{p,obs}	three-phase sorbent/water partition coefficient in
.	the presence of colloids, L/kg
Vi	solute molar volume, mL/mol
V.	water molar volume, mL/mol
X	colloid concentration expressed as organic carbon, mg/L
γi ^w	solute aqueous-phase activity coefficient, dimen- sionless
ρ	organic colloid density, g/mL
x	Flory parameter, dimensionless

Registry No. DCB, 106-46-7; TCB, 120-82-1; PCB, 37680-65-2; α-chlordane, 5103-71-9.

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Received for review August 4, 1989. Revised manuscript received January 2, 1990. Accepted January 16, 1990. This publication is a result of work sponsored by the Michigan Sea Grant College Program, Project R/TS-29 under Grant NA86AA-0-SG043 from the Office of Sea Grant, National Oceanic and Atmospheric Administration (NOAA), U.S. Department of Commerce, and funds from the State of Michigan. Additional aspects of this research were carried out as part of National Science Foundation project ECE-8503903, Environmental Engineering Program, Dr. Edward H. Bryan, program director. The U.S. government is authorized to produce and distribute reprints for governmental purposes not withstanding any copyright notation appearing hereon.