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On the Constancy of Sediment-Water Partition Coefficients of Hydrophobic Organic Pollutants

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■ If precautions are taken to eliminate or account for nonsettling (or nonfilterable) microparticles or organic macromolecules which remain in the aqueous phase during laboratory sorption tests, the observed partition coefficients (K_p or K_{oc}) for a group of model hydrophobic organic compounds (PCBs) are found to remain constant over a wide range of solid-to-solution ratios. Further, the partition coefficients for either sorptive uptake or desorptive release are indistinguishable and confirm the reversible nature of hydrophobic sorption. It is proposed that descriptions of the "speciation" of hydrophobic compounds in natural waters should include not only dissolved and sorbed-to-suspended-sediment fractions but also a component sorbed to nonsettling microparticles or organic macromolecules.

Introduction

One of the fundamental processes controlling the fate of hydrophobic organic compounds in aquatic environments is the exchange of these chemicals between dissolved and sorbed states. Many studies have shown that it is essential to distinguish dissolved from sorbed concentrations to describe either equilibrium conditions or kinetic rates. The tendency of hydrophobic organic compounds to associate with natural particles has been modeled by various workers (1-3) using an equilibrium expression for sorption: S (mass of compound/g of solid) = $K_p C$ (mass of compound/mL of solution). Further, the equilibrium constant in this relation generally can be predicted as a product, $K_p = f_{oc} K_{oc}$, where f_{oc} is the organic carbon weight percent in the solids of interest and K_{oc} quantifies the hydrophobic partitioning tendency of the compound of interest to "generic" natural organic matter. K_{oc} 's are

typically found to be constant within about a factor of 2 for sorption of a given hydrophobic compound to a variety of soils and sediments (e.g., ref 2). This simple partitioning model implies that sorption is reversible and that isotherms are linear. On the basis of our present "physical picture" of this process of sorption (4, 5) as a phase equilibration in which only weak attractive forces (no covalent bonds or ion exchange) between organic solutes and natural organic matter are involved, these qualities (i.e., linearity and reversibility) are expected.

However, two sets of observations have been made that challenge this view of sorption. The first involves the results of several studies showing that the equilibrium partition coefficient (K_p or K_{oc}) decreases as the ratio of solids-to-water increases (e.g., see ref 6, and references therein, and 7). The second set of results suggests that sorption is not a reversible process; that is, some organic molecules sorbed to natural particles are not free to be released when the exterior water concentrations decline (8-10). Both of these results conflict with the view described above of hydrophobic organic sorption as a partitioning process between two immiscible "solvents", and both suggest that using the associated linear isotherm approach for predicting the fate of organic pollutants will be inaccurate.

Since it is difficult to envision mechanistic explanations for these complex sorptive phenomena, we initiated this study to determine if they resulted from artifacts associated with the common phase separation techniques employed in batch equilibration sorption experiments. If the phase separations in these experiments were incomplete, noncentrifugable or nonfilterable microparticles or organic macromolecules released from the solids remained in the aqueous phase. Carter and Suffet (11) and Voice et al. (7)

have recently suggested the possibility that dissolved organic materials may cause the decline in partition constants with higher suspended solid loading, but they provided no direct evidence to support this assertion. In this report, we demonstrate that these nonsettling organic materials have a major impact on observed partition constants. Our results strongly suggest that this analytical consideration can fully explain the "solid concentration effect" and irreversible sorption phenomena observed in laboratory batch equilibration experiments. Moreover, we suggest that similar concepts must be employed in any discussion of truly dissolved hydrophobic pollutants in the "real world".

Materials and Methods

Materials. Several polychlorinated biphenyl isomers (Analabs Inc., North Haven, CT) were used as model nonpolar organic compounds for sorption studies. Isomers, containing two to seven chlorines (2Cl-PCB to 7Cl-PCB) to provide a range of hydrophobic tendencies ($\log K_{ow}$ of 5-7), were utilized as received. Lake Superior bottom sediment solids, obtained from Dr. Steven Eisenreich (box core S78-11 Bx, ref 12), had a 2.5% organic carbon content and were generally clayey in nature. The Missouri River sediments were supplied by Dr. Samuel Karickhoff (EPA-6, ref 2), exhibited an f_{oc} of 0.72%, and were of a silty-clay composition. Milli-Q water (Millipore, Bedford, MA) was used for aqueous preparations.

General Batch Equilibration Protocol. Several microliters of our stock PCB solution (at 2-90 ng of individual PCB isomers/ μ L of acetone) were spiked into 40 mL of water in 45-mL glass graduated centrifuge tubes with Teflon-lined screw caps. A preweighed portion of solids was then added to each tube to yield various, but known, solids-to-water ratios (ρ_s). The tightly capped tubes were then agitated with a wrist-action shaker for 48 h to allow sorption equilibration. Subsequently, the tubes were centrifuged at either 760g for 20 min or 1700g for 60 min (corresponding to complete settling of particles having a density of 1.2 g/cm³ and a 1.0- or 0.4- μ m diameter, respectively, based on Stokes' settling velocities) to separate the solid and aqueous phases. If desorption experiments followed, the supernatant was carefully withdrawn, replaced with clean water, agitated again, and finally re-centrifuged. After centrifugation, the supernatant was transferred with a Pasteur pipet to a clean centrifuge tube; the pellet was resuspended in a minimum of Milli-Q water and transferred by pipet to a second centrifuge tube. The original cap and tube used for equilibration, the tube containing the water, and the tube with the sediments were each spiked with an internal standard (4-Cl PCB) and then were individually extracted overnight by shaking with 2 mL of 1:1 pentane-acetonitrile. The organic phase was collected from each sample, and the three fractions were each shaken briefly 2 additional times with 1 mL of pentane which was combined with the appropriate first extracts. The resultant organic extracts were spiked with a second internal standard (6-Cl PCB) and reduced to approximately 0.2 mL by evaporating under a N₂ gas stream.

The PCB contents of these extracts were ultimately determined by glass capillary gas chromatography with electron capture detection. This GC approach allows quantitation of several isomers simultaneously and provides direct evidence that biodegradation of sorbates had not occurred even over prolonged equilibrations. The instrument was a Carlo Erba Fractovap, Model 2100, equipped with a ⁶³Ni electron capture detector. The 15 m long by 0.32 mm i.d. fused silica capillary column coated

with SE-54 (Analabs, Inc., North Haven, CT) was operated with H₂ carrier at 0.5 m/s linear velocity and was held isothermally at 70 °C for 2 min and then programmed from 70 to 250 °C at 6 °C/min; splitless injections were made. The detector was operated at 300 °C with 5% CH₄-Ar in the constant current mode with 0.5- μ s pulse intervals, a differential electrode potential of 50 V, and a standing current of about 250 nA.

PCB peak heights were used for quantitation, and results were not corrected for losses as both standards were consistently recovered with about 95% efficiency. Some losses of 2-Cl and 3-Cl compounds were commonly observed (80% and 85% average recoveries, respectively, while more highly chlorinated PCB's were always recovered at >90%), and these were traced to losses during evaporation under N₂. Losses of PCB's to the glass walls of the equilibration tubes plus Teflon liners of the screw caps proved to be less than 4% of the dissolved PCB load in all cases. Analytical reproducibility for concentration determinations in each phase from replicate equilibration experiments was $\pm 10\%$, which indicates a precision on our K_p determinations of better than $\pm 15\%$ due to propagation of errors. Since f_{oc} could be measured to within $\pm 5\%$, calculated K_{oc} errors were $\pm 15\%$.

In some cases, the sediments used for equilibrations were "prewashed" to remove nonsettling microparticles and macromolecules. This washing was done by suspending the sediments in 40 mL of water in the 45-mL graduated centrifuge tubes, shaking for 48 h, centrifuging at 760g for 20 min, and discarding the supernatant. After several (approximately five) washes, the solids were used in the batch experiments.

In order to assess the impact of prewashing sediments, the quantities of solids lost with the discarded supernatants were determined in three ways. Small aliquots of the supernatant were carefully evaporated on small preweighed aluminum pans, and the dry weight was determined with a Cahn microbalance. Additionally, turbidity of the supernatant was monitored by measuring the absorbance of the solution in a 10-cm cell at 500 nm in a spectrophotometer. Finally, dissolved organic carbon (DOC) measurements were made on the supernatants by persulfate wet oxidation of acidified CO₂-free aliquots (13) and subsequent CO₂ determination with a Shimadzu GC 8A (Columbia, MD) equipped with a thermal conductivity detector. The organic carbon content of the noncentrifugable microparticles and macromolecules is the ratio of the "DOC" to the dry weights.

Results and Discussion

Nonsettling Microparticles or Macroparticles in the Supernatant. All three measures of "dissolved" sorbing phase (weight of dissolved solids, turbidity, and dissolved organic carbon) demonstrated the increased loading of nonsettling microparticles or macromolecules (NSPs) in the supernatants of batch equilibrium experiments as the solids-to-water (ρ_s) ratio increased (Figure 1). The NSPs were seen to increase in a fixed proportion to the total solids. For the Missouri River sediment this fraction (weight of NSP/weight of solids) was 5.6%, while the Lake Superior solids maintained a 4.9% NSP fraction under the conditions of our phase separations. At suspended solids concentrations less than 500 mg/L, we were unable to measure NSPs by dissolved organic carbon methods due to blank problems. Voice et al. (7) also attempted to assess NSPs by turbidity and DOC measurements of supernatants recovered from equilibrations with 10-200 mg of solids/L and had poor success, concluding that the methods were insufficient. Nonetheless, it is clear

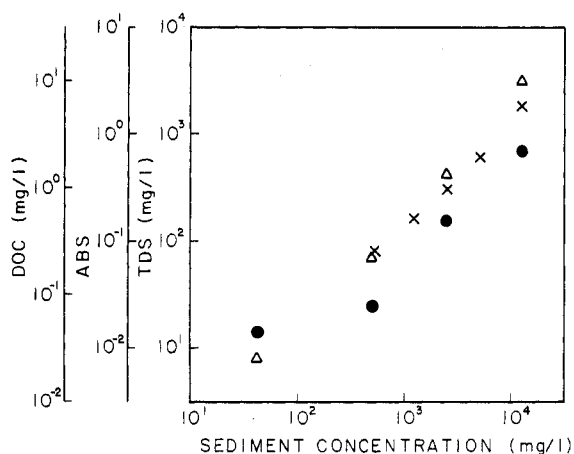


Figure 1. Nonsettling particles in the first wash supernatants vs. varying Missouri River solid concentrations as determined by DOC (crosses), light absorption (triangles), and total dissolved solids (solid circles).

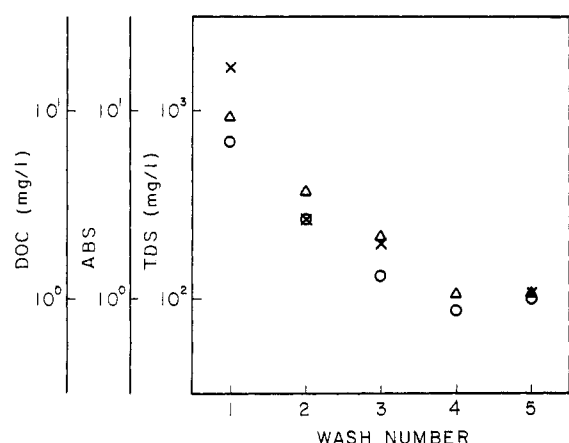


Figure 2. Nonsettling particles in successive washes of Lake Superior sediment (12 000 mg/L) as determined by DOC (crosses), light absorption (triangles), and total dissolved solids (circles).

from our data that NSPs vary regularly with suspended solid concentration.

That this occurs should not be particularly surprising. First, particle size distributions of natural sediments and soils are undoubtedly continuous and do not drop to zero abundance in the region of typical centrifugation or filtration separation capabilities. Additionally, there is some evidence to indicate that the DOC and POC (particulate organic carbon) in natural waters are in dynamic equilibrium, causing new particles or new dissolved molecules to be formed when others are removed (14, 15). Finally, experiments with soil columns have shown that natural soils can release large quantities of DOC into percolating fluids (16). Consequently, since there are NSPs remaining in the aqueous phase, we should take their effects into account.

One approach to diminish the NSPs effect is to try to reduce their abundance, for example, by washing the sediments. Figure 2 shows the decrease in NSP content of supernatants after successive washes of 12 000 mg/L Lake Superior sediment. The NSP content dropped by about an order of magnitude, yet remained at an amazingly high level of 100 mg/L even after five washes. As a result, if K_p for readily settled particles is desired, we recommend the strategy of centrifuging washes relatively weakly (e.g., 760g for 20 min) and discarding the supernatant containing microparticles and macromolecules that may be incompletely settled during subsequent phase separation oper-

ations (e.g., 1700g for 60 min).

Using the quotient of the observed DOC and NSP weight results, we calculated the f_{oc} values for the NSPs in our experiments. Lake Superior NSPs contained 2.5% organic carbon, and Missouri River NSPs had 0.83% organic carbon. Both results are indistinguishable from the f_{oc} values of the parent solids, and as a result we did not find that washing significantly affected the sediment f_{oc} . Thus, at least for these laboratory-derived microparticles and macromolecules, it may be reasonable to assign to them a similar affinity for hydrophobic compounds as that exhibited by the larger mass of solids (i.e., $K_{NSP} = K_p$ or $K_{oc-NSP} = K_{oc}$). This assumption is reasonable if the organic matter of the NSPs is of similar composition as that in the settling solids and if sorption is truly a partitioning process.

Other recent studies have provided mixed insights to this last assumption. Means and Wijayarathne (17) found that atrazine and linuron sorbed 10–35 times more strongly on natural colloids than on soils and sediments, suggesting that small particles or macromolecules should be treated with enhanced K_{oc} 's. If sorption entails an adsorption process to the "surface" exposed by organic macromolecules, then K_{oc} 's associated with colloids could reasonably be expected to be greater than those for soil and sediment organic matter since colloidal organic matter has a greater surface area per mass of organic carbon. However, it is known that nitrogen-containing organic compounds may "sorb" by ion exchange (18, 19) or by condensation reactions (18, 20–22) in addition to hydrophobic interactions. Since the sorption constants observed for atrazine and linuron varied with pH (17), these nonhydrophobic sorption mechanisms were likely operating. Thus, these enhanced K_{oc} 's may simply reflect the greater reactive nature of colloidal organic matter than that in sediments and soils. In contrast, Carter and Suffet (11) have focused on DDT (nonionizable and unable to participate in condensation reactions) sorption to natural humic acids and found carbon normalized partition constants ($\log K_{oc} = 4.8$ – 5.7) which were similar to values previously reported for soils [$\log K_{oc} = 5.3$ (23)]. Finally, at least for some components of the DOC, one could reasonably expect the phase equilibrium partition coefficients to be less than those of the organic matter on particles since macromolecules in solution must be relatively hydrophilic in nature to maintain favorable aqueous interactions. This view is supported by the reports describing heteroatom compositional differences between fulvic and humic acids recovered from natural waters. The smaller, more water-soluble fulvic acids have higher oxygen-to-carbon ratios compared to the larger humic compounds (24). Presumably the sequence of "defunctionalization" continues into condensed phases (25). Thus, smaller, more water-soluble macromolecules may be expected to be more polar sorbents (i.e., exhibit relatively lower K_{oc} 's) than related larger macromolecules and particulate organic matter. Clearly more work is needed to understand these possibilities.

Effect of Suspended Solids on Observed Partition Coefficients. The observed sorption partition coefficients (determined with no precautions against NSP effects) were found to diminish with suspended solid loadings as reported previously by many workers (Figure 3). This effect was strongest for the sediment with the greatest organic carbon content (i.e., Lake Superior) and for hydrophobic compounds with the strongest tendencies to sorb (i.e., 7-Cl > 5-Cl). This result is precisely as predicted if the observed ratio is viewed:

$$K_p^{obsd} = \frac{P/\text{mass particles}}{(D + N)/\text{volume of water}} \quad (1)$$

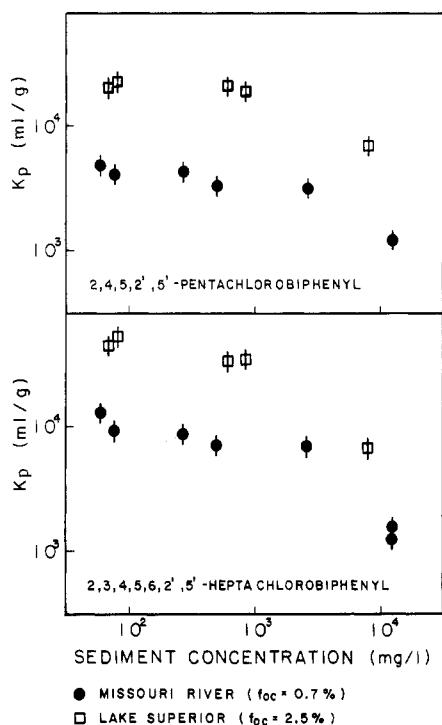


Figure 3. K_p for two PCB isomers vs. initial sediment concentration when no precautions are taken for NSPs. Missouri River (solid circles) and Lake Superior (squares).

where P is the mass of compound sorbed to settleable particles, D is the mass of compound dissolved, and N is the mass of compound sorbed to NSPs. At sufficiently low suspended solid loadings, the volume of water to weight of NSPs is great enough that the $D \gg N$; under these conditions the K_p^{obsd} could be considered the "true" value for the compound of interest. This is the value which should be used to quantify sorption to settling particles irrespective of the suspended solid concentration. However, as the suspended solid loadings are increased and the NSPs increase concomitantly and/or as the hydrophobicity of the compounds of interest increases, then D will no longer greatly exceed N and the K_p^{obsd} will decline accordingly. This observed partitioning constant has no real phase equilibration meaning.

By utilization of the simple approach of centrifuging with greater settling forces for longer periods to reduce the abundance of NSPs, it can be readily seen that the K_p^{obsd} remains unchanged at low ρ_s and increases somewhat in equilibrations with high ρ_s especially with the more hydrophobic 7-Cl PCB (Figure 4). Nonetheless, as indicated by these results and those of other workers (7), more stringent centrifugal conditions still do not eliminate NSPs completely, and the observed partition constants are inaccurate.

In order to greatly reduce the effect of the NSPs, a succession of prewashing treatments is necessary. This is particularly true for Lake Superior and Missouri River solids since they contained a significant proportion of fine clay grains, and the vigorous mixing provided by our wrist-action shaker undoubtedly continuously released these particles from larger aggregates. When prewashed sediments were used for batch equilibration experiments, the observed K_p remained virtually constant over the range of suspended solids tested (Figure 5). This is most dramatically shown for the partitioning of the most hydrophobic compound, 7-Cl PCB, and the difference in K_p^{obsd} with and without prewashing clearly reflects the great sensitivity of very strongly sorbed compounds to small

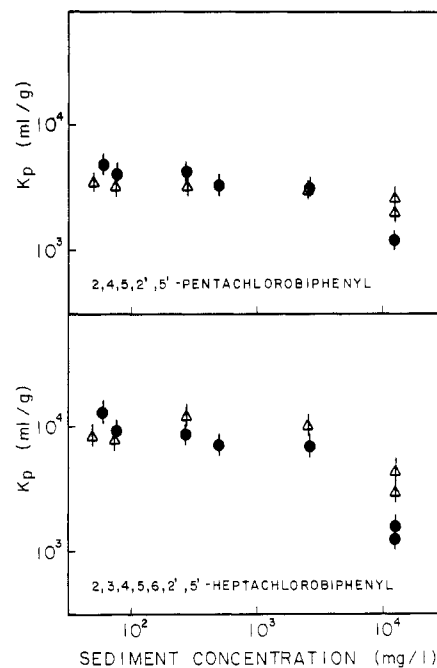


Figure 4. K_p for two PCB isomers vs. initial sediment (Missouri River) concentration when different centrifugation conditions are used: 760g for 20 min (solid circles) and 1700g for 60 min (triangles).

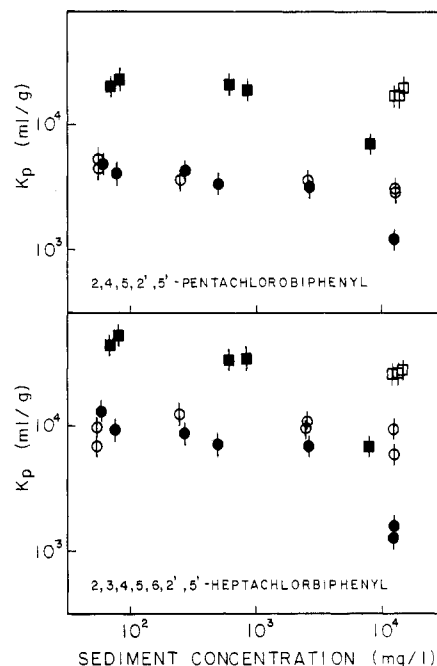


Figure 5. K_p for two PCB isomers vs. initial sediment concentration with (open symbols) and without (closed symbols) prewashing to remove NSPs. Missouri River (circles) and Lake Superior (squares).

NSP loadings in the aqueous phase.

Utilizing the measured NSP loadings in batch equilibrations with no prewashings, we can predict the K_p^{obsd} (or K_{oc}^{obsd}) vs. ρ_s . By definition

$$K_p^{true} = \frac{P/\text{mass settleable particles}}{D/\text{volume of water}} \quad (2)$$

By incorporating the hypothesis that some sorption to NSPs occurs in the supernatant [as suggested by this work and previous studies (7, 11)], we have

$$K_p^{obsd} = \frac{P/\text{mass settleable particles}}{(D + N)/\text{volume of water}} \quad (3)$$

Combining (2) and (3)

$$K_p^{\text{obsd}} = K_p^{\text{true}} \left(1 + \frac{N}{D} \right)^{-1} \quad (4)$$

Now defining

$$K_{\text{NSP}}^{\text{true}} = \frac{N/\text{mass of NSPs}}{D/\text{volume of water}} \quad (5)$$

then

$$K_p^{\text{obsd}} = K_p^{\text{true}} \left(1 + K_{\text{NSP}}^{\text{true}} \frac{\text{mass of NSPs}}{\text{volume of water}} \right)^{-1} \quad (6)$$

Recalling $K_p = f_{\text{oc}} K_{\text{oc}}$ (and correspondingly $K_{\text{NSP}} = f_{\text{oc-NSP}} K_{\text{oc-NSP}}$), then we may write

$$K_{\text{oc-p}}^{\text{obsd}} = K_{\text{oc-p}}^{\text{true}} \left[1 + K_{\text{oc-NSP}}^{\text{true}} \frac{f_{\text{oc-NSP}}(\text{mass of NSPs})}{\text{volume of water}} \right]^{-1} \quad (7)$$

Finally, since the $f_{\text{oc-NSP}}$ was determined in our experiments by utilizing DOC measurements, then

$$\text{DOC} = \frac{f_{\text{oc-NSP}}(\text{mass of NSPs})}{\text{volume of water}} \quad (8)$$

and

$$K_{\text{oc-p}}^{\text{obsd}} = K_{\text{oc-p}}^{\text{true}} (1 + K_{\text{oc-NSP}}^{\text{true}} \text{DOC})^{-1} \quad (9)$$

Expressions 6 and 9 allow us to predict the observed change in partition coefficients due to varying suspended solid concentrations, if the values of K_{NSP} or $K_{\text{oc-NSP}}$ can be estimated. For example, using our measured fixed proportions of NSP mass to suspended solids (for Lake Superior, 4.9%, and for Missouri River, 5.6%), recalling that the organic carbon contents of the settleable and nonsettleable particles were identical, allowing K_p^{true} to be just high enough to fit the data at the lowest solids loads, and assuming $K_p^{\text{true}} = K_{\text{NSP}}^{\text{true}}$, we have predicted the observed K_p for the batch equilibrations with untreated suspended solids (Figure 6). The fit for the Missouri River solids for the entire range of sediment concentrations tested is excellent. Although the model shows the correct trend for experiments using Lake Superior solids, it overpredicts the decline in K_p^{obsd} by about a factor of 2 at the highest ρ_s . This may indicate that the $K_{\text{oc-NSP}}$ is lower than the $K_{\text{oc-p}}$ for these solids from Lake Superior. Despite this minor misfit, we conclude that the NSPs were the primary cause of declining observed K_p 's and therefore that K_{oc} remains constant irrespective of the proportion of solids-to-solution. Interestingly, this result predicts that at high NSP masses the K_p 's for all the PCBs collapse to the same values which are simply the volume of water/mass of NSPs.

Effect of Suspended Solids on Observed Sorption Reversibility. It has been suggested (8) that hydrophobic organic compound sorption to natural sediment particles may be irreversible to some degree. Unless either some unusual chemical bond between these nonreactive compounds (e.g., PCB's or PAH) and natural organic matter or mineral surfaces is forming or some deformation of the natural organic matter around the sorbates to form a "cagelike" structure is occurring, we do not understand how such an apparently irreversible uptake could take place (especially on the time scale of hours to days). Consequently, we hypothesized that irreversible sorption behavior could also be due to washing out the NSPs during sequential sorption and desorption experiments.

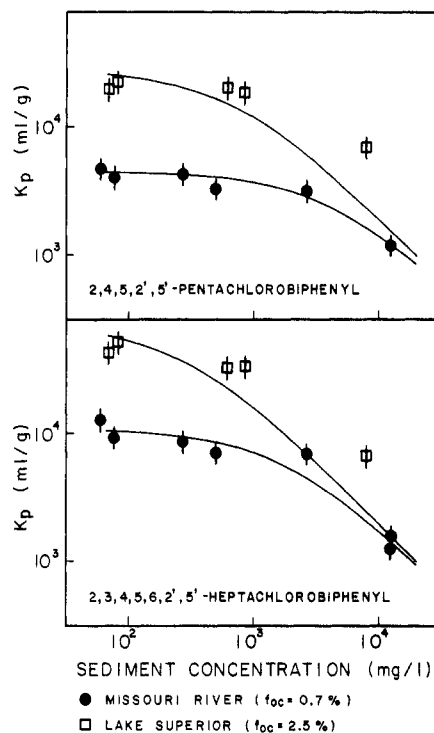


Figure 6. Model predictions of K_p vs. initial sediment concentrations assuming weight of NSPs/weight of solids is 5% and $K_{\text{NSP}} = K_p$.

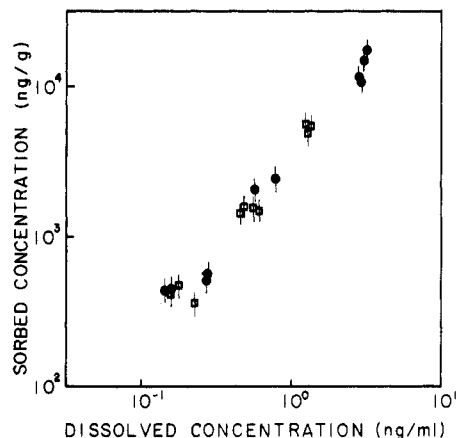


Figure 7. Dissolved vs. sorbed concentrations for pentachlorobiphenyl in sorption (solid circles) and desorption (squares) tests using pre-washed Lake Superior solids.

In typical desorption protocols, a sorptive batch equilibration is performed by first establishing a sorption equilibrium between the solid and aqueous phases. In preparing to establish desorption equilibrium, the initial aqueous layer is discarded and with it the first wash load of NSPs, and clean water is added to take its place. After shaking and allowing hydrophobic compounds in the solids to exchange back into the aqueous phase, the solid and aqueous phases are separated again and concentrations determined in each. However, unlike the initial sorptive uptake experiment, the NSPs in this inadvertently pre-washed condition are reduced in quantity, and the resultant aqueous load contains proportionately less NSP-sorbed material. Hence the $observed K_{\text{oc}}^{\text{desorption}}$ is greater than the previous $K_{\text{oc}}^{\text{sorption}}$. Further successive desorption tests will continue to be effected by NSPs less and less.

When we performed sorption and desorption experiments with prewashed sediments, our uptake and release isotherms were indistinguishable (Figure 7). This result was more easily obtained with less hydrophobic com-

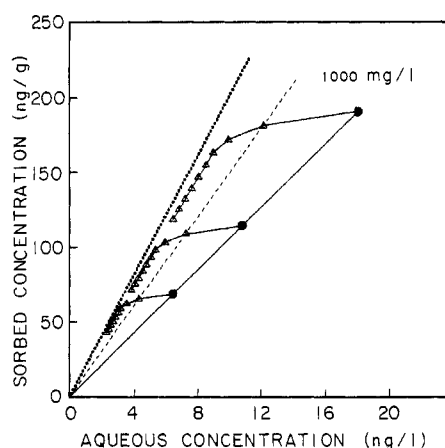


Figure 8. Model predictions for successive desorption equilibrations (triangles) after initial uptake experiments using 1000 mg of solids/L of solution (solid circles). Solid line through uptake data indicates observed uptake isotherm, while dashed line through first desorption points demonstrates associated desorption isotherm. Dotted line reflects uptake isotherm when NSPs have been eliminated or are negligible.

pounds, with solids containing lower organic contents, and with lower initial solid-to-water ratios as in these cases the resulting NSP-sorbed contents in equilibrations were more readily diminished relative to the dissolved concentrations.

Given our data on the NSP abundance in successive wash solutions of Lake Superior and Missouri River solids (NSPs sequentially declined to the following percentages of the solids: 5%, 2%, 1%, and $\approx 0.6\%$ each wash thereafter), we can estimate the impact of these nonsettling sorbents in a typical succession of sorption-then-desorption equilibrations with $\rho_s = 1000$ mg/L. For example, DiToro and Horzempa (8) have studied the desorptive behavior of a hexachlorobiphenyl from Saginaw Bay sediments ($f_{oc} \approx 2.3\%$). Using eq 7 and their observed K_p and assuming an NSP loading of 5% in the first equilibration, we can calculate a "true" $K_p = 2.0 \times 10^4$ mL/g. By combining this result and our observed decline in NSPs with successive washes and by maintaining a mass balance for the hexachlorobiphenyl (i.e., system load of equilibration n equals system load of equilibration $n - 1$ minus the amount discarded with the aqueous phase), we can predict the desorptive isotherm points shown in Figure 8. These results are remarkably similar to those observed experimentally by DiToro and Horzempa, as well as in other studies (9, 10) particularly when large solid-to-solution ratios were used. The isotherms predicted by using the first desorption equilibration data indicates a higher $K_{oc, desorption}$ than $K_{oc, sorption}$. These results would lead to the erroneous conclusions that irreversible binding was occurring and that there was a hysteric effect in the extent of irreversibly bound material as a function of the initial dissolved concentrations to which the solids were exposed. Notably, previous studies showed successive desorption data eventually to trend toward the origin. We believe these data asymptotically coincided with the true isotherms as shown in Figure 8 for our model calculations using a relatively low ρ_s (and hence low NSPs concentration). Clearly the effects of nonsettling microparticles and macromolecules can account for these apparent nonideal sorption observations.

Implications. It is clear that precautions must be taken to avoid laboratory artifacts derived from incomplete phase separations. These precautions may consist of either elimination of the nonsettling (or nonfilterable) sorbents by prewashing the solids or by actually measuring the

abundance of the NSPs in the otherwise presumed "purely" aqueous phase. Simply centrifuging at greater forces will be helpful but will not necessarily remove all the sorbents from suspension (especially neutrally buoyant organic macromolecules).

More importantly, our results support the idea that modeling sorption in the "real world" must include binding to two types of materials, one with and one without appreciable settling velocities. This second sorbing material includes a poorly characterized mixture of "microparticles" and dissolved macromolecules. This view of three exchanging environmental compartments is necessary not only to predict the actual transport properties of hydrophobic pollutants (i.e., their tendency to be removed from solution by settling to bottom sediments) but also to assess their water column chemical activities. It is likely that nonpolar compounds sorbed to nonsettling particles (be they humic or fulvic acids, colloidal aggregates, or other neutrally buoyant phases) behave much differently in various environmental processes such as bioconcentration and photo- or biodegradation than do the truly dissolved molecules. Since much of the DOC in natural waters is polymeric humic substances, measurements of DOC may allow us to roughly quantify nonsettling organic sorbents. Using this information in addition to knowledge of the suspended sediment load, we may more accurately estimate the hydrophobic compound partitioning between the three water column compartments. That is, we may evaluate the "speciation" of hydrophobic organic compounds with the following:

$$\text{dissolved fraction} = \frac{1}{1 + \text{DOC } K_{oc-NSP} + \text{POC } K_{oc-p}}$$

$$\text{NSP-sorbed fraction} = \frac{\text{DOC } K_{oc-NSP}}{1 + \text{DOC } K_{oc-NSP} + \text{POC } K_{oc-p}}$$

$$\text{fraction sorbed to settling particles} = \frac{\text{POC } K_{oc-p}}{1 + \text{DOC } K_{oc-NSP} + \text{POC } K_{oc-p}}$$

Summary

Our results support the view of Chiou and others that sorption of hydrophobic organic compounds to natural sediments and soils can be viewed as a phase partitioning process, quantifiable with a single K_{oc} equilibrium constant. This constant is the same for uptake or desorption and does not vary as the "volumes" of the solid and aqueous phases change with respect to one another. Previous experiments suggesting "complex" sorptive behaviors were probably subject to analytical artifacts caused by incomplete phase separations. Our work, taken in the context of recent studies showing sorption to natural microparticles or organic macromolecules, suggests that equilibrium environmental speciation of hydrophobic organic compounds should include three "phases": dissolved, sorbed to nonsettling particles or macromolecules, and sorbed to settling solids. With further work on partition constants appropriate for natural nonsettling particles or macromolecules, this three-phase equilibration process, possibly using site-specific DOC and POC measurements, can be used to greatly improve our predictive capabilities concerning the fate of hydrophobic organic pollutants.

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