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Facilitated Transport of Polychlorinated Biphenyls and Polybrominated Diphenyl Ethers by Dissolved Organic Matter

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The exchange rate of hydrophobic organic chemicals between the aqueous phase and a sorbent (e.g., soil, organism, passive sampler) is relevant for distribution processes between environmental compartments, including organisms. Dissolved phases such as humic acids, proteins, and surfactants can affect the transfer of such chemicals between the aqueous and sorbent phases by sorption and desorption processes. In this study, the desorption of polychlorinated biphenyls and polybrominated diphenyl ethers from a polymer phase to an aqueous medium was monitored at different humic acid concentrations. The rate of release of the chemical by the polymer phase demonstrates that the chemical sorbed to dissolved humic acid contributed significantly to the total mass transfer when the affinity for the humic acid was sufficiently high. This illustrates that environmentally relevant humic acid concentrations can facilitate transport of hydrophobic organic chemicals. The consequences of these facilitated transport mechanisms for uptake into passive samplers are discussed, in particular in situations where equilibration is very slow or when exposure varies in time or space.

Introduction

Uptake of hydrophobic chemicals into aqueous organisms can be very slow (*1*). This might lead to internal concentrations that are not equilibrated with the environment. Additionally, exposure concentrations of these chemicals can fluctuate in time and space due to sorption processes, natural transport of contaminated dissolved and particulate phases to pristine areas, flooding of contaminated land, or disasters (e.g., oil spill) (*2*−*5*). Similarly, bioaccumulation studies and toxicity tests (*6*) might be too short to reach steady-state concentrations in organisms, and exposure concentrations can vary due to losses from the test system, (bio)degradation, and (de)sorption processes. As a consequence, concentrations in organisms or sorbents are not always equilibrated with the environment. If environmental systems, or organisms within these systems, are not at chemical steady state, the dynamic aspects of the exchange processes become important. For example, the mass transfer between an aqueous phase and a sorbent determines the mobilization and immobilization of a chemical, and the mass transfer between an organism and its environment affects biodegradation and bioaccumulation rates (*7*). Similarly, these dynamic aspects are also of interest in (de)sorption processes in sediment and soil, gut uptake (*8*), and internal distribution of chemicals between different organs within organisms (*9*).

The mass transfer of hydrophobic organic chemicals between the aqueous phase and sorbents such as soils, organisms, or passive samplers is often limited by diffusion in an aqueous diffusion layer (*10*). In environmental systems, aqueous diffusion layers generally contain dissolved, colloidal, and solid organic and mineral materials. Various studies have shown that these materials can generate additional transport of chemicals between water and a sorbent, even though the sorbed chemicals themselves are not available for uptake (*11*−*15*). For example, Kopinke et al. observed that the uptake kinetics of fluoranthene by a solid-phase microextraction fiber increased in the presence of humic acid (*12*), and Mayer et al. illustrated that the transfer of various chemicals over an aqueous diffusion layer was enhanced by various dissolved organic phases (*14*). Additionally, Kramer et al. showed that the mass transfer of pyrene was enhanced by the presence of serum proteins (*15*). Furthermore, the addition of surfactants (*16*) or dissolved humic material (*17*) can enhance desorption from soil and subsequently the availability for bacterial degradation. A relevant question is to what extent a chemical sorbed to a dissolved or particulate phase can contribute to the mass transfer between an aqueous phase and a sorbent and how this additional mass transfer can be quantified.

In this study, the facilitation of the transport of hydrophobic chemicals over aqueous boundary layers by dissolved organic matter is investigated. Obviously, suspended particulate phases can also facilitate transport. However, this study is focused on the transport facilitation of dissolved phases. For this purpose, the depletion of 13 polychlorinated biphenyls (PCBs) and 4 polybrominated diphenyl ethers (PBDEs) from a hydrophobic polymeric phase was studied at various humic acid concentrations using a passive dosing and sampling setup as described by ter Laak et al. (*18*). The tested humic acid concentrations were similar to or slightly higher than found in the environment (*19*, *20*). The distribution of chemicals over the aqueous phase and passive sampling phase at equilibrium enabled the determination of the sorption coefficient to humic acid. The depletion kinetics of the chemicals from the passive sampler enabled the determination of the mass transfer of the test chemicals between the polymer and aqueous phase. The objective of this study was to interpret the mass transfer in relation to freely dissolved and humic acid-sorbed fractions of the chemicals in solution and to model and discuss facilitated transport mechanisms for the exchange of hydrophobic chemicals between passive samplers and the aqueous phase. Insight into the sampling dynamics is relevant for estimating the fate of chemicals in the environmental systems and the uptake of chemicals by passive samplers and organisms.

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TABLE 1. Test Chemicals and Some of Their Properties

chemical	aqueous solubility at 25 °C[a] (μg L^{-1})	log K_{ow}[b]	aqueous diffusivity[c] (10^{-10} m^2 s^{-1})	log K_f[d] (L kg^{-1})	initial PDMS concn[e] (mg L^{-1})
PCB 14	225	5.28	5.43	4.86	221.6 (4.2)
PCB 18	413	5.24	5.15	5.05	123.6 (3.0)
PCB 28	164	5.67	5.15	5.27	47.82 (3.6)
PCB 35	52.0	5.82	5.15	5.23	699.9 (3.6)
PCB 52	29.6	5.84	4.91	5.58	31.21 (3.2)
PCB 72	23.5	6.26	4.91	5.78	354.7 (3.0)
PCB 77	9.36	6.36	4.91	5.61	78.22 (4.3)
PCB 101	10.5	6.38	4.70	6.07	57.64 (2.9)
PCB 118	2.09	6.74	4.70	6.10	48.36 (2.7)
PCB 126	1.05	6.89	4.70	6.09	39.61 (3.8)
PCB 153	0.922	6.92	4.51	6.48	87.96 (2.4)
PCB 180	0.638	7.36	4.34	6.67	24.02 (3.3)
PCB 203	0.069	7.65	4.19	6.85	28.20 (3.0)
PBDE 47	15	6.81	4.70	5.85	60.29 (4.4)
PBDE 99	9.4	7.31	4.49	6.22	66.75 (3.8)
PBDE 153	0.87	7.90	4.31	6.43	55.86 (3.7)
PBDE 183	1.5	8.27	4.14	6.52	83.53 (4.8)

[a] Aqueous solubilities of PCBs and PBDEs were obtained from refs *38* and *39*, respectively. [b] log octanol−water partition coefficients (log K_{ow}) of the PCBs and PBDEs were obtained from refs *40* and *41*, respectively. [c] The aqueous diffusivities were obtained from ref *21*. [d] log PDMS−water partition coefficients (log K_f) were obtained from ref *21*. [e] Standard deviations (%) are given in parentheses.

Experimental Section

Preparation of Fibers. Fused silica fibers with a core diameter of 110 μm and a 6.5 μm poly(dimethyslsiloxane) (PDMS) coating (Poly Micro Industries, Phoenix, AZ) were cut to 2.6 cm pieces (62 nL of PDMS) and cleaned and stored according to ref *21*. A total of 65 clean fibers were loaded with a mixture of 13 polychlorinated biphenyls (PCBs; Accustandard New Haven, CT) and 4 polybrominated diphenyl ethers (PBDEs; obtained from Ake Bergman Stockholm University, Sweden) in a single vial containing 10 mL of 1:1 methanol−water solution, spiked with these chemicals (*21*). The chemicals are listed in Table 1 together with some physical-chemical properties and their initial concentrations in the PDMS coating. All experiments were performed at 20 ± 1 °C.

Preparation of the Humic Acid Solution. A 300 mg L^{-1} concentration of humic acid sodium salt (Sigma Aldrich Chemie BV, Zwijndrecht, The Netherlands) was dissolved in Millipore water and the resulting solution gently shaken for 30 min and filtered at 0.45 μm (HV 0.45, Millipore Waters). Weighing dry filters before and after filtering in triplicate revealed that 17.7 ± 1.3% ($n = 3$) of the humic acid was retained on the filter. The filtered humic acid solution was buffered with a 5 mM phosphate buffer and sterilized with 0.77 mM sodium azide (both Merck, Amsterdam, The Netherlands). The dissolved organic carbon (DOC) content was 118 mg L^{-1} (determined by a Shimadzu TOC-5050A analyzer). This stock solution was diluted with buffered and sterilized Millipore water, and solutions with 0, 2.4, 11.8, 47.1, and 118 mg L^{-1} DOC were obtained.

Exposure and Extraction. The depletion of the chemicals from the loaded fibers was studied in these five DOC concentrations by sampling fibers after 0, 0.04, 0.10, 0.3, 1, 3, 9, 24, 120, 223, 367, 647, and 1468 h of exposure. Five loaded fibers were sampled directly at $t = 0$, and a single fiber exposed in a separate 7 mL amber vial (Supelco, Bellefonte, CA) containing 5.0 mL of medium was sampled per DOC concentration−exposure time combination ($n = 60$). During exposure, the vials were shaken by a Stuart roller mixer set at 10 rpm (SRT9D, Warrenville, IL). Exposed fibers were extracted with 200 μL of 2,2,4-trimethylpentane (pestiscan grade, Laboratory-Scan) containing 50 μg L^{-1} PCB 209 as an injection standard. The humic acid solutions of 0.04, 0.10, 0.3, 3, 24, 120, and 367 h exposure were used for pH determination. The pH ranged from 6.83 to 7.05. The total concentrations in the humic acid solutions of 1, 9, 223, and 647 h of exposure were determined by liquid−liquid extraction with *n*-hexane (pestiscan grade, Laboratory-Scan). The weighted retrievable humic acid solution (4.7 ± 0.1 mL) was extracted with 1 mL of *n*-hexane using a vortex for 30 s and the roller mixer for 6 h. After extraction the sample was frozen at −20 °C overnight, and the *n*-hexane was decanted. This extraction step was done four times in total. The collected *n*-hexane was evaporated in the fume hood, and 100 μL of trimethylpentane was added when approximately 100 μL of *n*-hexane was left. Subsequently, the residual *n*-hexane was evaporated, and 200 μL of trimethylpentane containing 50 μg L^{-1} PCB 209 was added as an injection standard. The extract (final volume ~250 μL) was stored until analysis. The extracts of the fibers and humic acid solutions showed that nearly all of the added chemical could be recovered from the test systems (the mass balance is 99 ± 9%).

Chemical Analysis. The concentrations in the aqueous and fiber extracts were determined by gas chromatography with electron capture detection (GC-ECD) as described in ref *21*.

Data Analysis. The data modeling approach was adopted from Kramer et al.'s eq 8 (*15*). In this approach it is assumed that the DOC-associated chemical contributes to the exchange of chemicals between the fiber and the bulk medium and that the exchange is not limited by the interfacial transfer reaction. The following mass balance equation was considered to describe fiber coating depletion:

$$\frac{dM_f}{dt} = -\frac{dM_m}{dt} = -S_f(m_u(C_{u(i)} - C_u) + m_b(C_{b(i)} - C_b)) \quad (1a)$$

where

$$C_{u(i)} = \frac{C_f}{K_f} \quad (1b)$$

and

$$\frac{C_b}{C_u} = \frac{C_{b(i)}}{C_{u(i)}} = K_{DOC}[DOC] \quad (1c)$$

In these equations, M_f and M_m denote the total masses (mg) of chemical in the fiber coating and bulk medium, C_u and C_b (mg L^{-1}) are the free and complexed chemical concentrations in the bulk medium, $C_{u(i)}$ and $C_{b(i)}$ (mg L^{-1}) denote the same concentrations at the medium−fiber interface, S_f (dm^2) is the surface area of the fiber, m_u and m_b (dm h^{-1}) are the mass-transfer coefficients of free and complexed chemical in the medium, K_f is the PDMS−water partition coefficient, C_f (mg L^{-1}) is the concentration of the chemical in the fiber coating, K_{DOC} (L kg^{-1}) is the DOC−water sorption coefficient of the chemical, and [DOC] (kg L^{-1}) is the concentration of DOC in the aqueous phase. The total concentration of the chemical in the bulk medium (C_m, mg L^{-1}) can be expressed as follows:

$$C_m = C_u + C_b = \frac{M_m}{V_m} \tag{2}$$

where V_m (L) is the medium volume.

Equation 1a was fitted to the elimination data of the fibers with ACSL Optimize 2.1 (The Aegis Technologies Group, Huntsville, AL), and K_{DOC} values and mass transfer coefficients were obtained. The fitting procedure consists of optimizing the log likelihood of the parameters. The log likelihood of the parameters involves the (weighted) sum of squares of deviations between the model and data and allows for a probability-based discrimination of models taking into account the number of parameters involved. For example, when an additional model parameter is introduced into a model, it can only be considered as a significant improvement when the log likelihood of the optimized set of parameters is increased by 1.92 (*22*). The mathematical code of the model is given in the Supporting Information, model S1.

This analysis contains four implicit assumptions (*21*). First, the rate-limiting step in the mass transfer from the fiber coating to the aqueous phase is in the aqueous phase (*15*) (eq 1b). Second, there is a diffusive aqueous boundary layer adjacent to the fiber−medium interface that limits this mass transfer of the chemicals (i.e., the layer where $C_{u(i)}$ and $C_{b(i)}$ are not equal to their bulk values C_u and C_b (eq 1a)). Third, the boundary layer thickness solely depends on the hydrodynamics of the water (i.e., stirring regime) and not on the diffusivities of the free and complexed chemical. Fourth, the complexes of the chemical and dissolved humic acids are labile (i.e., the sorption and desorption of the chemical from the humic material is instantaneous with respect to the time scale of the residence time of chemicals in the aqueous boundary layer). This means that there is equilibrium between free and DOC-sorbed chemical at any point in time and space in the medium (eq 1c).

The first assumption is probably correct. The mass transfer in the aqueous phase is limiting because the product of the PDMS−water partition coefficient and the diffusivity in the PDMS largely exceeds the diffusivity in the aqueous phase, while the lengths of the diffusion paths in the aqueous and PDMS phases are similar (*21*). This is consistent with the findings in ref *15*, where the diffusion of the chemical through PDMS and water was modeled. The described mass transfer limitation by the aqueous phase generates a concentration gradient near the interface of the sampler during equilibration. This gradient defines the *diffusive* aqueous boundary layer (assumption 2).

However, the third assumption, standard in the SPME literature (*23*), may not be applicable if the free and complexed chemicals have significantly different diffusivities. This can be explained by the diffusive boundary layer concept, as studied by Nernst (*24*) and quantified by Levich, chapter II.10 (*25*). This concept identifies a *diffusive* boundary layer (δ) within the *convective* boundary layer (δ_0). The convective boundary layer, as determined by Prandtl (*26*), is solely determined by the hydrodynamics of a fluid (water) near a surface, while the diffusive boundary layer is defined by a concentration gradient of a chemical near a surface. The diffusive boundary layer is therefore determined not only by hydrodynamics but also by the diffusivity of the chemical of interest (details can be found in ref *25*, Chapter I.3). The diffusive and convective boundary layers are related in the following way:

$$\delta = \left(\frac{D}{\nu}\right)^{1/3} \delta_0 \tag{3}$$

Here D is the diffusivity of the chemical species and ν the medium kinematic viscosity. The kinematic viscosity of water is 10^{-6} m^2 s^{-1} at 20 °C (*27*), while the diffusivities of organic chemicals in water are around 5×10^{-10} m^2 s^{-1}. Consequently, the diffusive boundary layer thickness is roughly 1 order of magnitude smaller than the convective boundary layer thickness. This diffusive boundary layer concept implies that the ratio of the boundary layer thicknesses of two chemicals (δ_u, δ_b) is related to their respective diffusivities (D_u, D_b):

$$\frac{\delta_u}{\delta_b} = \left(\frac{D_u}{D_b}\right)^{1/3} \tag{4}$$

In this study the transport of freely dissolved and complexed PCBs and PBDEs is investigated. The diffusivities of the freely dissolved PCBs and PBDEs are a factor 10−50 higher than the diffusivities of humic aggregates (*28, 29*). If we assume that the complexed PCBs and PBDEs have the same diffusivity as the humic aggregates, the diffusive boundary layer of the complexed chemicals is 2−3 times smaller than this layer of free chemicals (eq 4). However, this difference would only exist if the organic chemicals and humic aggregates do not interact. If complexes are labile (assumption 4) and humic acid is present in excess, the transport of the free and complexed chemical has an average diffusivity weighted for the complexed and free fractions in the diffusive boundary layer (*28*):

$$\bar{D} = \frac{D_u + K_{DOC}[DOC]D_b}{1 + K_{DOC}[DOC]} \tag{5a}$$

Consequently, the average diffusive boundary layer thickness will decrease from δ_u to δ_b with increasing DOC concentration (i.e., complexed fraction), which makes the overall mass transfer coefficients of free plus complexed chemicals dependent on the DOC concentration.

The last assumption states that the complexes are labile. If this assumption is incorrect, the diffusion kinetics of free and complexed chemicals is coupled with the sorption and desorption kinetics of the complex in time. To account for this, a lability factor ξ can be introduced to correct for incomplete association and dissociation of the chemicals and DOC in the diffusion boundary layer (*28*):

$$\bar{D} = \frac{D_u + \xi K_{DOC}[DOC]D_b}{1 + \xi K_{DOC}[DOC]} \tag{5b}$$

Theoretically this lability parameter can range from 1 (completely labile) to 0 (completely inert).

Within the strict interpretation of this concept, i.e., eq 5a or 5b, the mass transfer of free and complexed chemicals cannot be distinguished. This concept can only be implemented in a mass balance equation such as eq 1a if total medium concentrations (C_m, $C_{m(i)}$) and an average mass transfer coefficient $\bar{m}$ for the free and complexed chemical are used instead of free and complexed concentrations and their individual mass transfer coefficients:

$$\begin{gathered}\frac{dM_f}{dt} = -\frac{dM_m}{dt} = -S_f(\bar{m}(C_{m(i)} - C_m))\\ \bar{m} = \frac{\bar{D}}{R_f \ln(1 + \bar{\delta}/R_f)}\\ \bar{\delta} = \frac{\bar{D}}{\nu}\delta_0\end{gathered} \tag{6}$$

TABLE 2. Organic Carbon Normalized Aldrich Humic Acid−Water Distribution Coefficients (L kg^{-1}), Mass Transfer Coefficients (dm h^{-1}) of Free Chemical When No DOC Is Present (m_u), and Apparent Mass Transfer Coefficients of the Chemical Complexed with Humic Acid (m_b)[a]

chemical	log K_{DOC}	m_u	m_b
PCB 14	4.63 (4.60−4.68)	5.50 (5.39−5.64)	0.144 (0.085−0.203)
PCB 18	4.54 (4.52−4.60)	4.60 (4.48−4.79)	
PCB 28	4.95 (4.92−5.00)	4.62 (4.35−4.82)	
PCB 35	5.20 (5.15−5.26)	3.01 (2.85−3.18)	0.041 (0.030−0.061)
PCB 52	5.12 (5.10−5.15)	4.14 (3.84−4.81)	
PCB 72	5.37 (5.35−5.40)	4.62 (4.18−5.44)	
PCB 77	5.77 (5.68−5.90)	2.72 (2.65−2.81)	0.040 (0.028−0.041)
PCB 101	5.60 (5.58−5.62)	4.77 (4.68−4.93)	
PCB 118	5.85 (5.81−5.89)	4.27 (3.63−4.60)	
PCB 126	6.39 (6.26−6.53)	3.57 (3.48−3.73)	0.015 (0.010−0.021)
PCB 153	6.10 (6.10−6.11)	1.16 (0.883−1.82)	0.027 (0.0077−0.0097)
PCB 180	6.39 (6.37−6.40)	0.31 (0.25−0.37)	0.012 (0.010−0.013)
PCB 203	6.33 (6.28−6.37)	0.12 (0.0001−0.15)	0.0075 (0.0055−0.0098)
PBDE 47	5.96 (5.91−6.03)	2.17 (2.05−2.28)	0.023 (0.016−0.025)
PBDE 99	6.35 (6.31−6.43)	1.42 (1.19−1.50)	0.0092 (0.0067−0.0098)
PBDE 153	6.71 (6.66−6.80)	0.50 (0.46−0.56)	0.0043 (0.0033−0.0052)
PBDE 183	6.63 (6.59−6.68)	0.23 (0.18−0.30)	0.0021 (0.0015−0.0026)

[a] log DOC−water sorption coefficients (log K_{DOC}) and mass transfer coefficients were obtained by fitting all depletion curves of the fibers parallel with eq 1a using ACSL. The ranges given in parentheses are the maximum and minimum values observed when one of the DOC treatments is left out of the analysis. m_b is not shown when the range (calculated as mentioned above) covers zero.

Here the expression for the mass transfer coefficient has been corrected for the cylindrical geometry of the fiber and adjacent boundary layer. If δ is much smaller than R_f, the usual planar expression $m = D/\delta$ is retained.

Results and Discussion

DOC−Water Distribution Coefficients. The system consists of a glass fiber with a hydrophobic coating, water, and dissolved organic carbon (humic acid). The change in the concentrations of PCBs and PBDEs in the fiber coating was monitored as a function of time elapsed after the loaded fiber was placed in the aqueous phase. Table 2 shows the obtained K_{DOC} values to Aldrich humic acid. The model assumes that the sorption coefficient of the chemicals to DOC is independent of the (free) concentration of the chemicals. Sorption of hydrophobic organic chemicals to humic acids is generally considered an absorption process and is therefore expected to be linear (i.e., concentration independent) (*30*). Although deviations from linearity are reported in the literature (*31*), the assumption of a constant K_{DOC} is likely valid because the range of the free concentrations of the PCBs and PBDEs did not exceed 1 order of magnitude. Even though the chemicals probably are absorbed by the humic aggregates, the more general term "sorption" is used throughout this paper.

The observed K_{DOC} values of some PCBs are similar to observations in the literature (*30*), but lower than reported values using a similar setup (*32*). The differences between the current study and earlier experiments are likely due to the buffering and filtering treatment of the humic acid solution in the current study. A more detailed study on the effect of the treatment of the DOC solution on the DOC sorption can be found in the Supporting Information (Table S1 and related discussion).

Three isomers with three, four, and five chlorine atoms have been tested to compare the DOC sorption of planar and nonplanar PCBs. PCB 18, 28, and 35 are isomers with three chlorine atoms, PCB 52, 72, and 77 have four chlorine atoms, and PCB 101, 118, and 126 have five chlorine atoms. PCB 18, 52, and 101 have two ortho-substituted chlorine atoms, PCB 28, 72, and 118 have only one ortho-substituted chlorine atom, and PCB 35, 77, and 126 do not have ortho-substituted chlorine atoms. Ortho substitutions reduce the ability of the phenyl rings to rotate independently and to form a planar configuration, which might affect the sorption affinity (*33*). Table 2 shows that K_{DOC} varies with planarity. The sorption coefficients of the PCBs with two ortho substitutions are 0.25−0.41 log unit lower than those with one ortho-substituted chlorine atom, and the sorption coefficients of the mono-ortho-substituted PCBs are 0.25−0.54 log unit lower than those with no ortho substitutions. Apparently the planarity affects the sorption affinity to humic acid. The same trend on the sorption coefficients for the planar and nonplanar isomers is observed for octanol−water partition coefficients (Table 1).

Mass Transfer Coefficients. Figure 1 shows the depletion profiles of PCB 14, PCB 101, and PBDE 183 as an example. The full curves represent the fits of eq 1a. The depletion profiles of the other chemicals can be found in the Supporting Information (Figure S1). The mass transfer coefficients of the free and complexed chemicals obtained from this analysis are listed in Table 2. For some of the less hydrophobic chemicals the complexed fraction was too low to give rise to significant additional mass transfer. The fitting of the data by eq 1a using ACSL did not always allow for a reliable determination of the estimated parameter variances. Alternatively, the variability of the fits was assessed qualitatively by a jackknife method where each of the DOC treatments was left out of the analysis once. The maximum and minimum observed values of these analyses are given in parentheses in Table 2.

The mass transfer coefficients and sorption coefficients given in Table 2 can be used to calculate the relative increase of total mass transport of a chemical at a specific DOC concentration. Figure 2 shows the relative increase in mass transport at 25 mg L^{-1} DOC plotted against K_{DOC}. If the PCBs and PBDEs are considered separately, it can be observed that the increase in transport is more pronounced for the chemicals with the highest affinities for DOC. Furthermore, the additional transport of the PCBs except for PCB 126 appears to be greater than the additional transport of the PBDEs. This difference might be due to lower lability of PBDE−humic complexes compared to PCB−humic complexes. This might be a result of different interactions with the humic acids due to different physical-chemical properties of the chemicals.

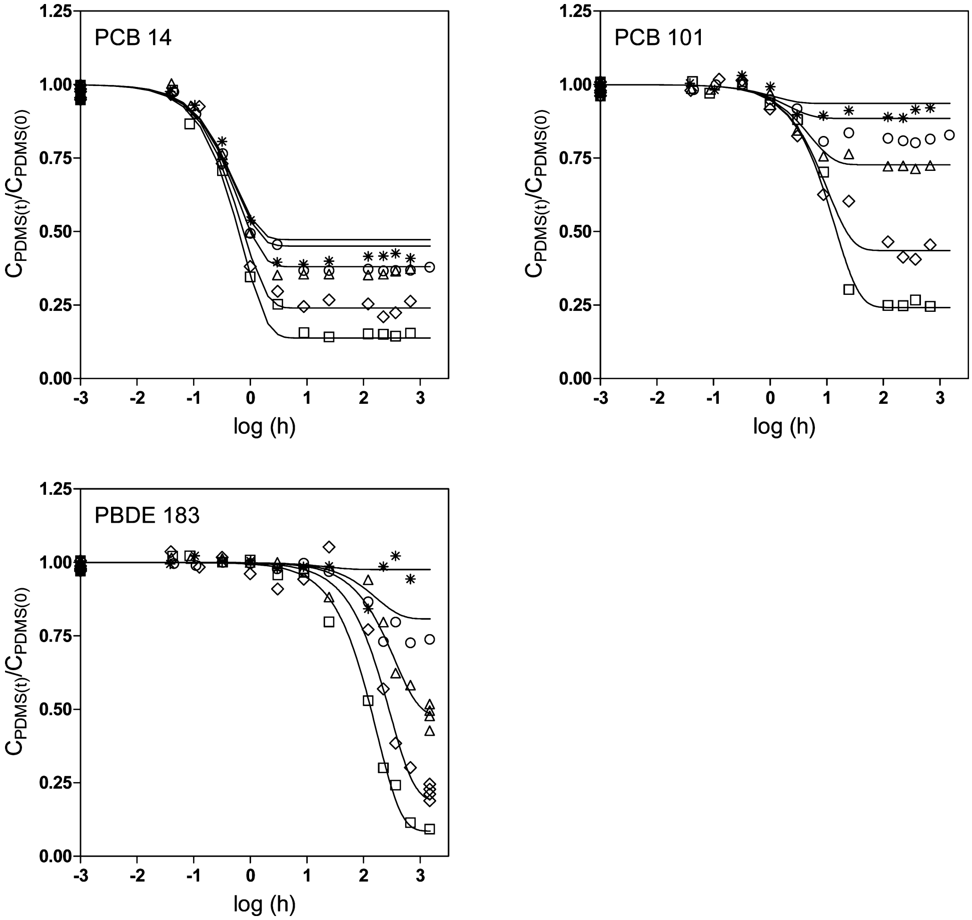

FIGURE 1. Depletion of PCB 14 and 101 and PBDE 183 from the PDMS fiber at 0 mg L^{-1} (asterisks), 2.4 mg L^{-1} (circles), 11.8 mg L^{-1} (triangles), 47.1 mg L^{-1} (tilted squares), and 118 mg L^{-1} (squares) dissolved organic carbon vs time. $t = 0$ is set at 10^{-3} h for visual purposes. The lines represent the fits of eq 1a.

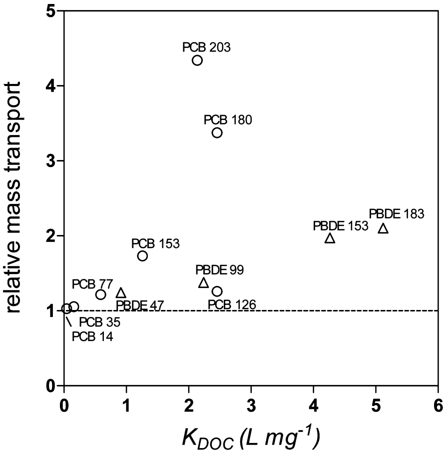

FIGURE 2. Ratio of the total mass transport and the mass transport generated when no humic acid is present (i.e., $(m_uC_u + m_bC_b)/m_uC_u$) plotted against K_{DOC} (expressed in L mg^{-1} instead of L kg^{-1}) at 25 mg L^{-1} DOC. The circles represent the PCB data and the triangles the PBDE data. The broken line illustrates the situation when DOC does not affect mass transport.

The analysis of the elimination−time profiles of the fibers with the model based on eq 1a shows that the humic acid in solution facilitates transport of the PCBs and PBDEs. However, as discussed in the Data Analysis, the diffusive boundary layers of the free chemical and complex are not the same, underscoring the approximation involved in assumption 3. Consequently, the mass transfer coefficients of the free and complexed chemical can describe the apparent increase in mass transfer with the addition of DOC, but cannot be used to compute transport coefficients on the basis of algebraic addition of fluxes of free and complexed chemical as done in eq 1a.

The analysis of the data with eq 1a contains questionable assumptions. Therefore, we can only conclude that the significance of the mass transfer coefficients is semiempirical and more refined experiments are necessary to investigate the exchange of chemicals and facilitated transport phenomena in detail. This needs a better defined dissolved or colloidal sorbent, because humic acid solutions are heterogeneous and the size of the aggregates is circumstantial (*29, 34*). Additionally, measurements should be done more frequently in time. Shorter initial time windows would yield complementary data that allow for a more detailed type of analysis (as indicated above) of the sorption/desorption kinetics and the coupled mass transfer of complexed and free chemicals (*35*).

Implications and Relevance in the Environment. Complexed chemicals can only contribute to exchange processes when an aqueous diffusion layer is the rate-limiting step in the exchange process, a substantial part of a chemical is associated with a certain dissolved or particulate phase, and the associates are labile to a certain extent. Very hydrophobic chemicals are of special interest, because they have a high affinity for dissolved organic matrixes and the exchange of these chemicals between water and a sorbent such as a passive sampler (*21*) or an organism (*1*) is often slow. Additional transport through the aqueous diffusion layer will not affect equilibrium concentrations in samplers and organisms if exposure conditions are constant (*36*). However,

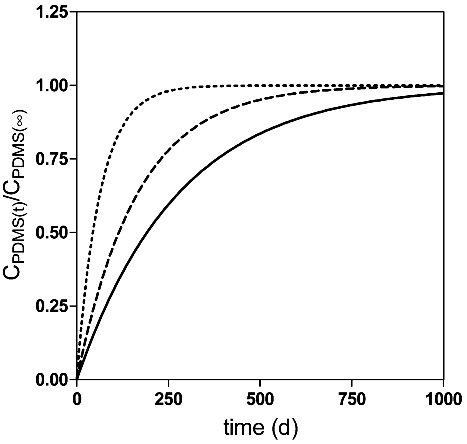

FIGURE 3. Simulation of the uptake of PCB 203 in time by the PDMS fiber exposed in 0 (solid line), 5 (dashed line), and 25 (dotted line) mg L^{-1} DOC.

if we consider that equilibration times of samplers and organisms (due to migration or life span) can be longer than exposure times and that environmental concentrations can vary in time and space (*4*), additional transport of complexed chemicals can significantly affect concentrations reached in samplers and organisms.

Figure 3 illustrates the potential effect of additional transport on the concentration in a passive sampler in time. In this scenario a sampler is exposed to a chemical at 0, 5, and 25 mg L^{-1} DOC. For this simulation, the K_{DOC} values and (apparent) m_u and m_b values of PCB 203 were selected as an example (Table 2). It was assumed that the free concentration was identical at the different DOC concentrations. This is a realistic assumption if a large contaminated matrix, such as sediment, is able to buffer the aqueous concentration including the dissolved organic phase present in this aqueous phase. The respective uptake rates of the fibers exposed to 25 and 5 mg L^{-1} DOC are 4.3 and 1.7 times larger than the uptake rates of the fibers exposed to 0 mg L^{-1} DOC. This means that the equilibrium concentration is reached 4.3 and 1.7 times faster and that pre-equilibrium concentrations in the sampler exposed in 25 and 5 mg L^{-1} DOC solution can be up to 4.3 and 1.7 times higher than at 0 mg L^{-1}. This example illustrates how concentrations in the sampler are affected by DOC concentrations if the sampler is not equilibrated with its environment. Therefore, facilitated transport phenomena should be taken into account when passive samplers are calibrated for laboratory or field studies.

These transport phenomena can also affect internal concentrations in organisms when the duration of the exposure is too short to reach the steady state due to migration or a limited lifespan of an organism in the environment or due to short exposure times in bioassays (*37*). Additionally, internal concentrations can be affected when organisms have a limited capacity to metabolize certain chemicals. Consequently, kinetic phenomena and additional transport by chemicals associated with dissolved (or particulate) phases in the aqueous phase can affect internal concentrations and thereby toxicological effects and environmental risks.

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Supporting Information Available

Absorption coefficients to buffered filtered and untreated humic acid, depletion profiles of the fibers, the model used to fit the depletion data, and the results of the fits of eq 1a. This material is available free of charge via the Internet at http://pubs.acs.org.

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