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Quantifying the Effect of Medium Composition on the Diffusive Mass Transfer of Hydrophobic Organic Chemicals through Unstirred Boundary Layers

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Unstirred boundary layers (UBLs) often act as a bottleneck for the diffusive transport of hydrophobic organic compounds (HOCs) in the environment. Therefore, a microscale technique was developed for quantifying mass transfer through a 100-μm thin UBL, with the medium composition of the UBL as the controllable factor. The model compound fluoranthene had to (1) partition from a contaminated silicone disk (source) into the medium, (2) then diffuse through 100 μm of medium (UBL), and finally (3) partition into a clean silicone layer (sink). The diffusive mass transfer from source to sink was monitored over time by measuring the fluoranthene content of the source and sink disks. The diffusive flux of fluoranthene was slightly higher for air than for water. Cyclodextrin, humic acids, and micelles of sodium dodecyl sulfate (SDS) enhanced the diffusive flux of fluoranthene in water by more than 1 order of magnitude. These results demonstrate that medium constituents, which normally are believed to bind hydrophobic organic chemicals, actually can enhance the diffusive mass transfer of HOCs in the vicinity of a diffusion source (e.g., contaminated soil particles). The technique can be used to evaluate the effect of natural fluids on diffusive mass transfer, as it integrates the different processes, partitioning and diffusion, in one laboratory model.

Introduction

The main characteristic of hydrophobic organic chemicals (HOCs) is that they "dislike" being surrounded by water molecules. HOC is thus a generic term that covers a wide range of aliphatic and aromatic, substituted and unsubstituted, low- and high-molecular-weight substances. Concentrations of these HOCs are generally orders of magnitude lower in water than in, for instance, soil particles, sediment particles, or aquatic organisms. This has important implications for their diffusive exchange at many environmental interfaces, where a thin aqueous film can act as an efficient barrier for diffusive mass transfer (*1*). Molecular diffusion of HOCs through these "unstirred boundary layers (UBL)" often constitutes the rate-limiting step for their desorption from soil and sediment matrixes (*2*) as well as for their uptake into organisms (*3*−*6*) and into passive samplers (*7*, *8*).

Fick's First Law of Diffusion is directly applicable to describe diffusive mass transport through homogeneous UBLs. Often, it is also applied in models describing diffusive transport through heterogeneous media and diffusive exchange at interfaces. However, such models are generally based on assumptions (e.g., transport is limited to diffusion of freely dissolved molecules) that may be rather difficult to confirm for hydrophobic organic chemicals (*9*). This makes the direct determination of diffusive mass transfer through an UBL worthwhile.

Recent research has indicated that diffusive mass transfer of HOCs through UBLs can be enhanced by the presence of medium constituents that normally are considered to reduce diffusive uptake (*10*, *11*). The application of our new experimental apparatus was, therefore, directed at quantifying the effects of such medium constituents.

Working Principle

The experimental apparatus (Figure 1) employs two disks of poly(dimethylsiloxane) (PDMS) silicone, one being clean, and the other containing the model substance, fluoranthene. The diffusive mass transfer from the contaminated disk (source) to the clean disk (sink) is initiated when positioning them 100 μm from each other. The medium between the source and sink is the variable factor of this experimental apparatus.

The transfer of fluoranthene molecules from source to sink requires the following three steps as illustrated in Figure 2: [1] Fluoranthene molecules partition at the interface between the source disk and medium, which is governed by the partition coefficient $K_{PDMS,Medium}$. [2] Fluoranthene molecules diffuse (planar diffusion) through the medium, which is a function of the concentration gradient ($\Delta C/\Delta x$) and the effective diffusion coefficient (D) in the medium (assuming Fickian diffusion). [3] Fluoranthene molecules partition at the interface between the medium and sink disk, which again is governed by the partition coefficient $K_{PDMS,Medium}$. The diffusive mass transfer from source to sink is monitored over time by measuring the fluoranthene contents of source and sink disks. A rate constant k (s^{-1}) is fitted to the measured data.

The design of the system gives the following characteristics: [1] The fraction of fluoranthene present in the medium is negligible ($V_{PDMS} > V_{Medium}$ and $K_{PDMS,Medium} \gg 1$ (*12*)). [2] Fluoranthene is homogeneously distributed within the PDMS disks due to the uniquely high permeability of this polymer (*12*−*14*). [3] As a consequence, the two disks impose a linear gradient in chemical potential (activity or fugacity) on the UBL.

Dynamic Model of the System. Under the assumption that all chemical mass vanishing from disk 1 is recovered on disk 2, and that the mass present in the thin layer between is negligible, the mass balance of the system can be described by

$$\frac{dm_1}{dt} = -am_1 + am_2 \qquad (1)$$

where m is the mass (kg) in disk 1 and 2, respectively, and a is a velocity constant (s^{-1}). Using the assumption of a closed mass balance yields a symmetry condition $m_2 = m_0 - m_1$, where m_1 and m_2 are the mass in disk 1 and 2, respectively,

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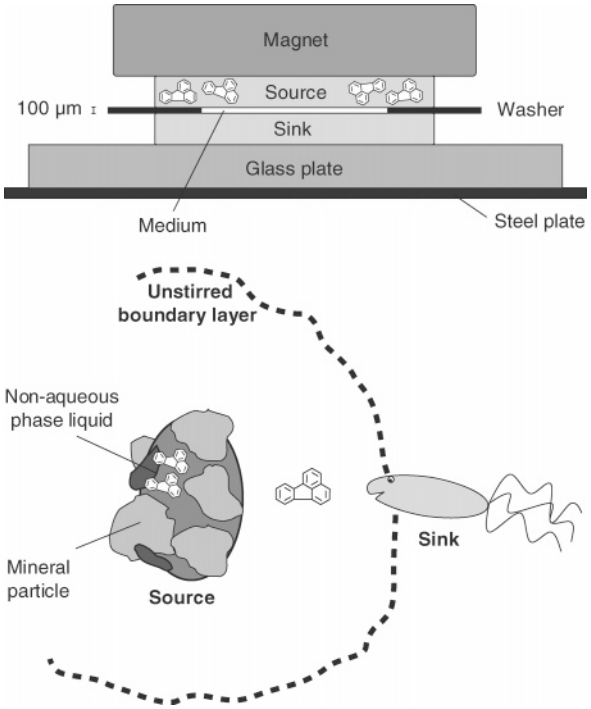

FIGURE 1. (a) Cross-section of the experimental apparatus. Poly(dimethylsiloxane) (PDMS) disks, serving as source and sink, are separated (100 μm) and sealed by a steel washer. The resulting microchamber is filled with test medium generating a model UBL. The assembly is pressed together by the mechanical force from a magnet. Replicate microchambers are mounted on the same glass plate at a distance of ~3 cm. (b) The microchamber mimics to some extent the conceptual relationship between an environmental source (e.g., a contaminated soil particle) and an environmental sink (e.g., a degrader organism).

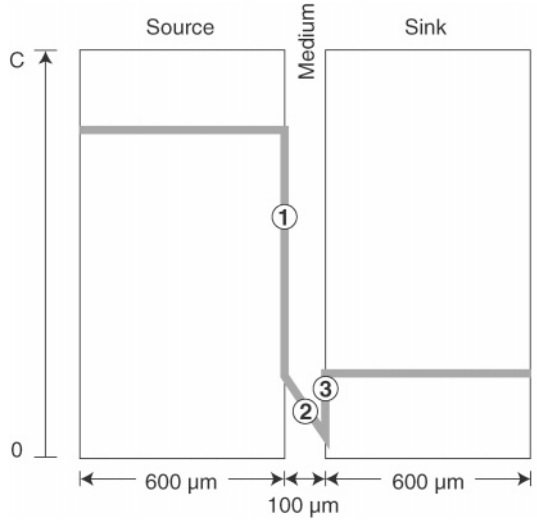

FIGURE 2. Concentration profile within the experimental apparatus including the three steps that are involved in the mass transfer from source to sink: (1) partitioning, $C_{Medium} = C_{Source}/K_{PDMS,Medium}$; (2) diffusion, flux $= -D \times \Delta C/\Delta x$; and (3) partitioning, $C_{Medium} = C_{Sink}/K_{PDMS,Medium}$.

at time t and m_0 is the initial mass (in disk 1). Substituting this into eq 1 gives

$$\frac{dm_1}{dt} = -am_1 + a(m_0 - m_1)$$

with the solution

$$m_1(t) = {}^1/_2 m_0 + {}^1/_2 m_0 \times e^{-2at} \quad (2a)$$

$$m_2(t) = {}^1/_2 m_0 - {}^1/_2 m_0 \times e^{-2at} \quad (2b)$$

or, with concentration C as mass m divided by volume V

$$C_1(t) = {}^1/_2 C_0 + {}^1/_2 C_0 \times e^{-2at} = {}^1/_2 C_0 \times (1 + e^{-2at}) \quad (3a)$$

$$C_2(t) = {}^1/_2 C_0 - {}^1/_2 C_0 \times e^{-2at} = {}^1/_2 C_0 \times (1 - e^{-2at}) \quad (3b)$$

In analogy to Fick's First Law of diffusion, we may also express the differential equation as

$$\frac{dC_2}{dt} = \frac{A}{V}\frac{K \times D}{\Delta x}\Delta C$$

where $\Delta C = C_1 - C_2$, A is the surface area (m^2), V is the volume of the disk (m^3), Δx is the thickness of the layer (m), K is the partition coefficient between the solution in the boundary layer and the polymer $K_{Medium,PDMS} = {}^1/K_{PDMS,Medium}$, and D is the diffusion coefficient ($m^2\ s^{-1}$), for composite media the effective diffusion coefficient. The velocity constant a (s^{-1}) from before can be identified as

$$a = \frac{A}{V}\frac{K \times D}{\Delta x} = \frac{A}{V \times \Delta x} \times \frac{D}{K_{PDMS,Medium}} \quad (4)$$

Determination of Unknown Boundary Layer Resistances. The equations show that the exchange rate and thus the diffusive flux can be affected by the medium composition in two different, sometimes opposite, ways. [1] The average velocity of the molecules is given by the diffusion coefficient D that is specific for any combination of medium and solute. Diffusion coefficients are, for instance, about 4 orders of magnitude higher in air than in water (*1*). Furthermore, diffusion coefficients decrease with increasing molecular volume (V) of the analyte. Complexed molecules will, because of their higher molecular volume, diffuse more slowly than freely dissolved molecules. Association and dissociation kinetics might also affect D, even though they are not explicitly accounted for (*10*). [2] The exchange rate is directly related to the partition coefficient between polymer and medium, $K_{PDMS,Medium}$, which again is specific for any combination of medium and solute. Hence, those medium constituents that improve the solubilization properties of the medium, for instance by complexation, can increase the diffusive mass transfer.

The experimental apparatus is designed to measure the diffusive flux through the medium, without distinguishing between these two effects. In this manner, it allows determination of "conductivity for diffusive mass transfer". This is in contrast to classical diffusion chambers, which aim at the determination of the diffusion coefficient (D).

The volumes of the two disks, V_1 and V_2, are kept constant, as well as the surface area for exchange A and the thickness of the film Δx. Any difference in the exchange velocity a in two experiments i and j can therefore be attributed solely to the product of $K \times$ D:

$$\frac{a_i}{a_j} = K_{ij}\frac{D_i}{D_j} \quad (5)$$

The velocity ratio a_i/a_j describes a "relative conductivity for diffusive mass transfer" that, for instance, can be applied in the following ways. [1] The unknown flux of fluoranthene through medium i can be expressed as the flux of fluoranthene through medium j, multiplied with the measured velocity ratio a_i/a_j. [2] The unknown flux of compound i across a given boundary layer can be expressed as the known flux of

compound j through this layer multiplied by the velocity ratio a_i/a_j determined in the experimental system.

Materials and Methods

Poly(dimethylsiloxane) (PDMS) sheets with a thickness of 600 μm (±20 μm) were supplied by Rubber BV (Hilversum, The Netherlands). Sodemann Industrifjedre A/S (Viby, Denmark) supplied 100-μm steel washers (i.d. 4 mm, o.d. 8 mm) to be used as spacers. Nickel-plated neodymium iron boron magnets with a diameter of 10 mm and a thickness of 5 mm were supplied by Farnell (Herlev, Denmark). Fluoranthene (>97%, Fluka), humic acid sodium salt (HASS) (38.28% carbon, Aldrich, product H1, 675-2), sodium dodecyl sulfate (SDS) (≅99%, Sigma), and hydroxypropyl-β-cyclodextrin (Sigma, product CO926) were all obtained from Sigma-Aldrich (Vallensbæk Strand, Denmark). Ethanol (96%; De Danske Spritfabrikker, Aalborg, Denmark) was used as an extractant. HPLC-grade methanol (99.9%) was provided by Merck (Darmstadt, Germany).

Experimental Apparatus. 500 disks with a diameter of 6 mm were cut out of the PDMS sheet and cleaned in three changes of >200 mL of methanol with a total contact time of 24 h. Disks were contaminated according to Booij and co-workers (*15*) by placing them in a methanol/water solution (80:20, v/v) containing the model substance fluoranthene (1 mmol/L), with a minimum contact time of 16 h. This spiking yielded disk concentrations of about 2 mmol/L PDMS based on partition coefficients from Booij et al. (*15*). The homogeneous distribution of fluoranthene within the PDMS was demonstrated earlier (*12*). At the day of the experiment contaminated disks were transferred to a small volume of water (≅1 mL/disk) to remove methanol.

Microchambers (Figure 1a) for measurement of mass transfer by partitioning−diffusion−partitioning (Figure 1b) were assembled by placing about 5 μL of the test matrix between a contaminated PDMS disk (the source) and a clean PDMS disk (the sink). The two disks were separated by inserting a steel washer with a thickness of 100 μm, which served as a circular spacer and as a gasket for keeping the test matrix in place. The actual distance between the disks might deviate slightly from 100 μm due to the flexibility of the PDMS polymer. The whole microchamber was conveniently assembled on a horizontal glass plate with steel backing and pressed together using a magnet. Typically, we mounted 30 microchambers on a 40 × 60 cm glass plate.

Measurements were started ($t = 0$) by placing a source disk and a washer on a magnet using a pair of tweezers and manually inverting them on top of a sink disk, after pipetting a droplet of matrix onto the sink disk. In this operation, excess test matrix was pressed past the washer, avoiding formation of air bubbles.

Assembly time was 20 s per microchamber. Three replicates each were immediately covered with a wet cotton pad to prevent the microchambers from drying. Fluoranthene molecules would partition from the source into the matrix, diffuse through the 100-μm model UBL, and partition into the sink. Measurements were terminated ($t = x$) by removing the magnet and transferring each disk into 3 mL of ethanol for fluoranthene extraction. The disassembly time was 1 min per microchamber. Measurements were performed in triplicates and with termination times of 5 min to 32 h.

The diffusive mass transfer of fluoranthene was determined by measuring fluorescence of the ethanol extracts using a Varian Cary Eclipse at an excitation wavelength of 358 nm (slit 5 nm) and an emission wavelength of 456 nm (slit 5 nm). Calibration curves were obtained by diluting extracts of unused source disks to give a five point calibration in the range of 0−100% ($r^2 > 0.995$). Generally, a total of 95−105% of the initial fluoranthene was recovered in the final extracts of sink and source disks, indicating a complete mass balance. Such recoveries of about 100% further indicated that fluorescence measurements remained unaffected by the tested media even at high humic acid concentrations. Finally, the percentage of fluoranthene that was transferred to the sink disk (T_{sink}) was fitted with the equation

$$T_{Sink} = 50\%(1 - e^{-kt}) \quad (6)$$

to determine the rate constant k, which was then normalized with the rate constant determined for distilled water to calculate the relative conductivity for diffusive mass transfer (eq 5). All nonlinear regressions were done with GraphPad Prizm 4 (San Diego, CA) by least squares. Five out of more than 250 individual measurements were excluded as being outliers, because all five deviated more than two standard deviations from the average of the other two replicates.

Measurement Endpoints. The rate constant k describes the kinetics of the system and may, for instance, be used to estimate the time required to reach 90% of the equilibrium concentration in the sink ($t_{90\%} = \ln(10)/k$), i.e., the time to transfer 45% of the mass of fluoranthene from the source to the sink. The rate constant k is proportionally related to the diffusive flux, and it is directly related to other established diffusion parameters: (*1*) the product K times D (m s^{-1}), also known as permeability P or conductivity g, and (*2*) the transfer coefficient for diffusive transport D (e.g., in mol·year^{-1}·atm^{-1}) (*16*).

From the mass balance of the system (eqs 1−4) follows

$$k = 2 \times a = 2 \times \frac{A}{V \times \Delta x} \times \frac{D}{K_{PDMS,Medium}} \quad (7)$$

for the relation between the experimentally fitted rate k and the velocity constant a.

Diffusion Experiments. First, a validation experiment was carried out in which the source disks were brought in direct contact with the sink disks, omitting the washers, to determine the mass transfer kinetics in the absence of the UBL. The two disks were pressed together in order to remove air, and the contact between the two disks was confirmed by an increased transparency of the two disks. Hereafter, diffusion experiments were carried out with the washers and with aqueous media, some of which contained complexing agents that are known to affect the partitioning of hydrophobic organic chemicals. All experiments were conducted at room temperature (23 ± 3 °C).

Results and Discussion

Direct Contact and Water. The mass transfer of fluoranthene was high in the absence of a UBL, i.e., in direct contact of the two disks, leading to 90% equilibrium between the two disks within 1.0 h (Figure 3a, Table 1). This corresponds to 2.3 h at the effective surface area of the other experiments, which all were conducted with the washers. Introducing a 100-μm thin water film reduced the mass transfer by several orders of magnitude (Figure 3b, Table 1), leading to an estimated $t_{90\%}$ of 444 h ($k = 0.00519\text{h}^{-1}$, $r^2 = 0.90$). These observations confirmed that diffusion through the 100-μm water film was the rate-limiting step in the experimental setup, and they confirmed that aqueous UBLs are efficient barriers for the diffusive mass transfer of hydrophobic organics.

It should also be mentioned that water remained the matrix that gave rise to the most technical difficulties. Water provided the slowest mass transfer, which in turn required long experimental runs, and it was also more difficult to "wet" the PDMS surface with pure water than with other aqueous solutions. Water was, in addition to the initial experiment, also tested twice together with the different

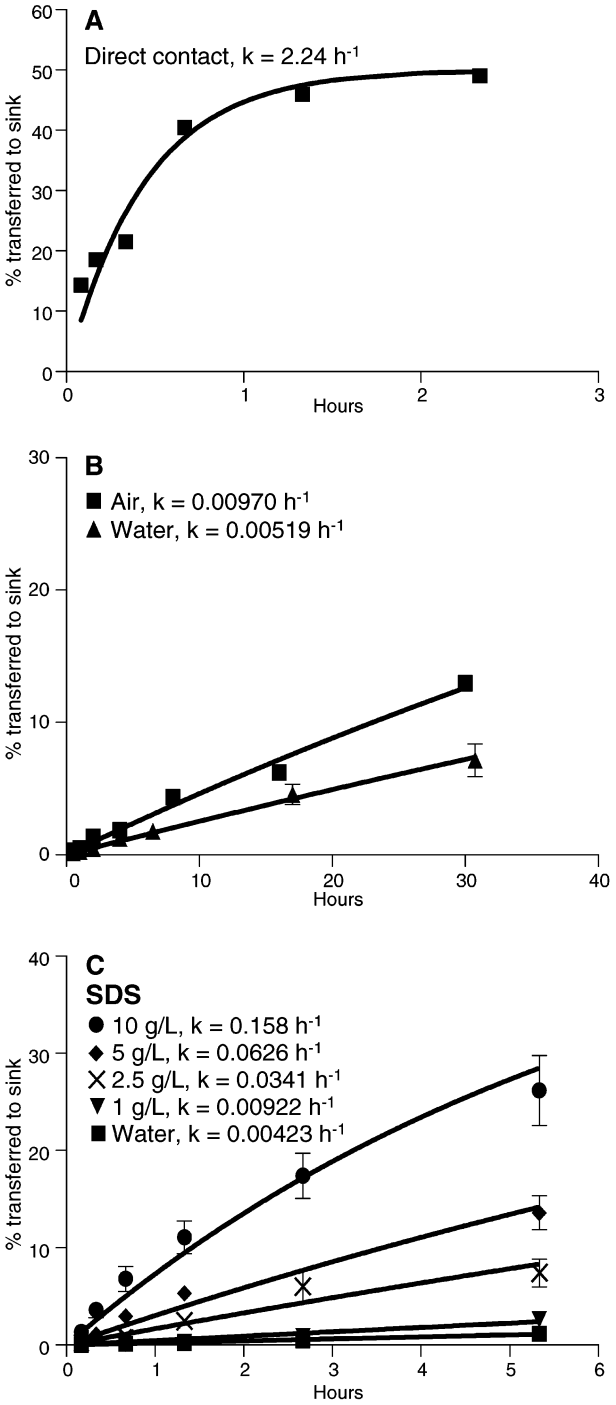

FIGURE 3. (a) Within about 1 h fluoranthene was evenly distributed between source and sink (direct contact), (b) whereas the presence of an aqueous or gaseous UBL prolonged equilibration times by orders of magnitude. (c) The diffusive flux increased at increasing concentrations of the surfactant SDS. Standard deviations between replicates are included as error bars, which in some cases are smaller than the symbols. Least-squares fits to eq 6 are included as solid lines.

aqueous solutions leading to estimated k values of 0.0042 ($t_{90\%} = 544$ h; $r^2 = 0.96$) and 0.0036 h^{-1} ($t_{90\%} = 640$ h; $r^2 = 0.96$). We consider these values to be more precise and more accurate compared to the estimate from the initial experiment.

Air. The mass transfer of fluoranthene was slightly faster through air ($t_{90\%} = 237$ h) than through water (Figure 3b). This is in good agreement with eq 5, since the diffusion coefficient D is about 4 orders of magnitude higher in air than in water (*1*), whereas the partition coefficient $K_{Air,Water}$ is 0.00043 (*1*).

TABLE 1. Experimental Rate Constants Determined in Different Media

matrix	k (h^{-1})	95% confidence interval	R^2
direct contact	2.239	1.916−2.561	0.94
water (initial exp.)	0.0052	0.0045−0.0058	0.90
air (initial exp.)	0.0097	0.0091−0.0103	0.98
water (final exp. 1)	0.0042	0.0039−0.0046	0.96
water (final exp. 2)	0.0036	0.0033−0.0040	0.96
0.1 g HASS/L[a]	0.0048	0.0044−0.0053	0.95
0.3 g HASS/L[a]	0.0054	0.0052−0.0056	0.99
1 g HASS/L[a]	0.0074	0.0070−0.0079	0.98
3 g HASS/L[a]	0.0161	0.0155−0.0168	0.99
10 g HASS/L[a]	0.0350	0.0311−0.0388	0.93
1 g SDS/L	0.0092	0.0072−0.0112	0.81
2.5 g SDS/L	0.0341	0.0261−0.0421	0.73
5 g SDS/L	0.0626	0.0530−0.0721	0.91
10 g SDS/L	0.1579	0.1347−0.1812	0.90
9 g cyclodextrin/L	0.0177	0.0161−0.0193	0.96
18 g cyclodextrin/L	0.0447	0.0374−0.0520	0.92
36.25 g cyclodextrin/L	0.0623	0.0569−0.0678	0.98
72.5 g cyclodextrin/L	0.0977	0.0898−0.1057	0.99
145 g cyclodextrin/L	0.1443	0.1272−0.1614	0.99

[a] HASS = humic acid sodium salt.

Comparison to Calculated Permeability for Air and Water. Equation 7 was applied to calculate theoretical values for k and $t_{90\%}$ in air and water using the following input data. The layer thickness Δx was set to 100 μm (0.0001 m), the disk volume V was set to 1.7×10^{-8} m^3, the exchange area A was set to 1.26×10^{-5} m^2, and the partition coefficient $K_{PDMS,Water}$ was set to 12 302 (from ref *12*). Diffusion coefficients for fluoranthene ($M = 202.2$ g mol^{-1}) were estimated to 6.23×10^{-10} m^2 s^{-1} in water and 4.91×10^{-6} m^2 s^{-1} in air using the regressions $D_{water} = 2.7 \times 10^{-8}$ m^2 $s^{-1}/M^{0.71}$ and $D_{air} = 1.55 \times 10^{-4}$ m^2 $s^{-1}/M^{0.65}$ from (*1*).

Putting these data into eq 7 gave $k = 0.0027$ $hours^{-1}$, and $t_{90\%} = 852$ h for water, which is in fair agreement with the experimental results. For air we obtained $k = 0.0092$ $hours^{-1}$, and $t_{90\%} = 252$ h, which is in good agreement with the experimental results.

Humic Acids. The diffusive mass transfer of fluoranthene was enhanced by the presence of humic acids, since the rate constant increased proportionally with the concentration of humic acids, as shown in Figure 4A. The relative conductivity increased about 8 times at a humic acid sodium salt concentration of 10 g/L that corresponds to about 4 g carbon/L. Based on the linear regression, it requires 460 mg carbon/L to double the conductivity for diffusion. These are rather high concentrations at which the majority of the fluoranthene molecules will be present in the bound form (*17*−*19*). While such humic acid concentrations are also above typical bulk concentrations in river, lake, and sea waters, it is less clear whether such concentrations can be reached on the microscale, for instance, within the micropores of soils and sediments. High concentrations of humic acids and other dissolved organic matter (DOM) have been measured in the interstitial water of activated sludge, compost, and liquid manure (*20*). The diffusive conductivity for higher-molecular-weight PAHs can be expected to be enhanced already at much lower humic acid concentrations due to their higher humic acid to water partition coefficients (see eq 5).

Sodium Dodecyl Sulfate (SDS). SDS is an anionic detergent with a critical micelle concentration (cmc) of about 1 g/L (*21*), and the number of micelles increases linearly with concentrations above this cmc. The fluoranthene transfer at different SDS concentrations is shown in Figure

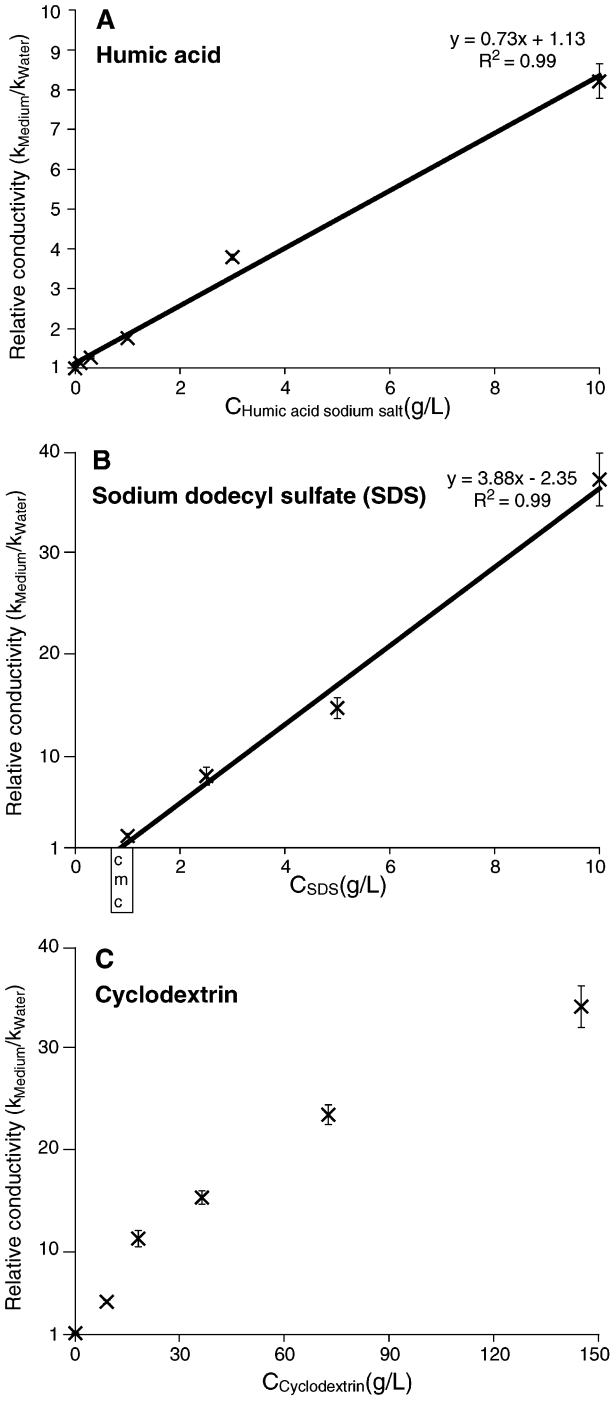

FIGURE 4. Diffusive flux increased at increasing concentrations of (A) humic acids, (B) sodium dodecyl sulfate (SDS), and (C) cyclodextrin; cmc refers to the critical micelle concentration. Linear regression is included in Figure A and B.

3c, and the effect of SDS on the conductivity is shown in Figure 4b. Little or no effect on diffusive mass transfer was observed at the cmc, which indicates that free SDS molecules do not have a significant effect on the diffusion process. Above the cmc, the rate constant increased linearly with the micelle concentration, being enhanced by a factor of 39 at the highest concentration of 10 g/L.

Hydroxypropyl-β-cyclodextrin. The diffusive mass transfer of fluoranthene was also enhanced by the addition of cyclodextrin as shown in Figure 4c. The conductivity for diffusion was 34 times higher through a solution of 140 g cyclodextrin per liter than through water. A recent analytical technique uses aqueous solutions of this cyclodextrin in the high g/L range to determine the bioaccessible polycyclic aromatic hydrocarbon (PAH) content in soils (*22*). Our results strongly suggest that high concentrations of cyclodextrin indeed will enhance the desorption process in situations where PAH release is controlled by an aqueous boundary layer resistance. The quantity of bound PAHs that can be released from the soil matrix might, in such situations, be estimated based on short-term extractions with cyclodextrin. We suggest the presented technique to be a valuable investigative tool in this context.

Suggestion for a Simplified Way to Consider Enhanced Diffusion. It was not the primary aim of this study to unravel the processes that lead to the observed enhanced diffusion in mixtures. It seems possible to explain the enhanced fluxes across the UBL by substantial increases in the concentration gradients, due to increased partitioning into the medium, combined with minor decreases in the diffusion coefficients. Rather, we want to provide a new experimental tool to quantify the medium effect on the diffusive mass transfer through an UBL. A strong point of the proposed method is that it actually measures diffusive mass transfer instead of the diffusion coefficient, and that the results can be used directly to predict mass transfer phenomena. The unit flux J (kg m^2 s^{-1}) of fluoranthene or another chemical across a layer of pure water may be easily estimated (see above) and is

$$J_{\text{Water}} = -\frac{D_{\text{Water}}}{\Delta x}\Delta C \tag{8}$$

According to eq 5, the unit flux J_{DOM} across an aqueous layer of same thickness, but with dissolved organic matter DOM (or in a similar manner with SDS or cyclodextrin) can be determined as

$$J_{\text{DOM}} = -\frac{k_{\text{DOM}}}{k_{\text{Water}}}J_{\text{Water}} = -\frac{k_{\text{DOM}}}{k_{\text{Water}}}\frac{D_{\text{Water}}}{\Delta x}\Delta C \tag{9}$$

This approach does not require a determination of the partition coefficient $K_{\text{DOM,water}}$ nor of the effective diffusion coefficient $D_{\text{DOM.}}$ Instead, the exchange rates (a or k) may be determined by repeated experiments in the proposed apparatus, first with fluoranthene and water, then with fluoranthene and the DOM−water mix (see, e.g., Figure 4A). From this, the flux of fluoranthene across any boundary layer of DOM−water mix can be directly calculated. Exchange area and thickness of the boundary layer, which do not depend on the chemical and medium properties, can vary freely, and the expression can be used in any model where the diffusive flux of fluoranthene in the presence of DOM is required.

Diffusion from Bulk Solution versus Microscale Partitioning. The medium constituents tested (SDS, humic acids, and cyclodextrin) can affect diffusive mass transfer in two distinctly different ways. [1] Within an aqueous solution they will reduce the chemical potential (activity, fugacity, or freely dissolved concentration) of the chemical, which in turn will reduce its diffusive uptake into aquatic organisms (*18*, *23*−*25*). The presence of the medium constituents will, under these conditions, lead to a decrease in exposure of an aquatic organism, which has been reported in a number of studies (*17*, *26*−*29*). [2] The present study demonstrates that in the vicinity of a diffusion source, complexing medium constituents can actually enhance diffusive mass transfer and, hence, increase exposure of soil organisms. Under these conditions, the gradient in chemical potential (activity, fugacity, or freely dissolved concentration) is given, and the medium constituents can increase the concentration gradient, which in turn can enhance diffusive mass transfer.

Diffusive Mass Transfer in Dynamic Systems versus Equilibrium Partitioning. Finally, it is important to distinguish between dynamic systems and systems that have attained their thermodynamic equilibrium. Enhanced diffusive mass transfer will increase the diffusive uptake into, for instance, a sediment organism (dynamic system). This can then shorten the time to reach a thermodynamic equilibrium and it can heighten the eventual steady-state concentration in the organism. However, it will not affect the equilibrium partitioning levels of the system. The presented method is a new investigative tool to study diffusion and partitioning processes in dynamic systems, whereas equilibrium methods should be applied to investigate equilibrium partitioning phenomena (e.g., refs *7*, *30*).

Perspectives. This study was conducted with only one model substance at a relatively high concentration, which was required for the simple fluorescence measurements. The application of HPLC or GC analyses will allow for testing with mixtures of hydrophobic organic substances and at a range of concentrations. The new experimental setup was applied to determine the diffusive flux through different well-defined media. Present research aims at the application of the new technique to biological fluids such as digestive fluids of animals, biosurfactants from bacteria, and root exudates from plants. The observed enhancement of diffusive mass transfer from a source into a sink will apply to a wide range of dynamic systems, such as the uptake into xenobiotic-degrading microorganisms near contaminated soil particles (see Figure 1), and the enhanced release of plasticizers from synthetic materials in the presence of detergents.

We expect the technique to be a strong investigative tool to study, understand, and quantify the diffusive flux of HOCs at the microscale. Furthermore, we expect it to be useful for the screening of detergents, solvents, and other auxiliary agents with regard to their ability to enhance contaminant release from soil, sediment, and sludge. Another area of application might be the direct determination of mass transfer coefficients to be used in toxicokinetic models and environmental fate models.

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