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Enhanced diffusion of polycyclic aromatic hydrocarbons (PAHs) in artificial and natural aqueous solutions

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Abstract

The biological uptake of hydrophobic organic compounds is often limited by the diffusive transport through a thin boundary layer. Therefore, a new micro-scale technique was applied to determine the diffusive mass transfer of 12 polycyclic aromatic hydrocarbons through water, air, surfactant solutions, humic acid solutions, aqueous soil and horse manure extracts, digestive fluid of a deposit-feeding worm and root exudates from willow plants. The diffusive mass transfer of PAHs was in most cases much higher in the tested media than in pure water, and the enhancement factors increased with increasing molecular size of the PAHs. The diffusive flux of benzo[a]pyrene was for instance enhanced 74 times through the gut fluid of a deposit-feeding worm when compared to water. These experimental results have significant implications for our perception of (bio)availability, for comparing different exposure routes, for the modelling of hydrophobic organics in dynamic systems and for the calibration of passive sampling techniques.

Briefs: The diffusive flux of polycyclic aromatic hydrocarbons is enhanced by surfactant micelles, humic acids and constituents of digestive fluids.

Introduction

A thin aqueous film often acts as an efficient barrier for the diffusive mass transfer of hydrophobic organic chemicals (HOCs) at many environmental interfaces (1). Molecular diffusion of HOCs through these "unstirred boundary layers (UBL)" can for instance be the rate-limiting step for their exchange between sediment and water (2), for their uptake into organisms (3-7) and for their uptake into passive samplers (8,9). 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).

A new experimental apparatus was therefore developed for quantifying the effects of such medium constituents on the diffusive conductivity of the UBL (11). This initial work demonstrated the enhancement of diffusive mass transfer of fluoranthene by humic acids, surfactant micelles and cyclodextrin, when present at high concentrations in the gram per liter range. The present study aims at extending this work to 12 polycyclic aromatic hydrocarbons (PAH), to different artificial and natural aqueous solutions and to lower concentrations of the medium constituent. The working hypothesis is that even low levels of medium constituents are sufficient to enhance the diffusive mass transfer of the most hydrophobic PAHs.

Working principle

The experimental apparatus (Figure 1) employs two disks of poly(dimethylsiloxane) (PDMS) silicone, one being clean, the other containing a mixture of 12 PAHs. 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 source and sink is the

variable factor of this experimental apparatus. The design of the system gives the following characteristics: [1] The fraction of PAHs present in the medium is negligible (V_{PDMS} > V_{Medium} and $K_{PDMS,Medium}$ >> 1 (12)). [2] The PAHs are 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 activity (or fugacity) on the UBL. For a more detailed description of the experimental apparatus we refer to reference (11).

Short description of the dynamic model of the system. The diffusive transfer of PAHs within the system can be described by

$$\frac{dm_{source}}{dt} = -am_{source} + am_{\text{sink}} \qquad \text{Equation 1}$$

where m is the mass (kg) of a PAH in source and sink disk, respectively, and a is a velocity constant (s^{-1}). Using the assumption of a closed mass balance yields a symmetry condition $m_{sink}=m_0 - m_{source}$, where m_{source} and m_{sink} are the mass of a PAH in the source and sink disk at time t and m_0 is the initial mass (in source disk). Substituting this into equation 1 gives

$$\frac{m_{\text{sink}}(t)}{m_0} = \frac{C_{\text{sink}}(t)}{C_0} = 50\% \cdot (1 - e^{-2at}) \qquad \text{Equation 2}$$

In analogy to Fick's 1st Law of diffusion, we may also express the differential equation as

$$\frac{dC_{sink}}{dt} = \frac{A}{V}\frac{K \times D}{\Delta x}\Delta C$$ Equation 3

where $DC = C_{source} - C_{sink}$, A is the surface area (m^2), V is the volume of the disc (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 now be identified as

$$a = \frac{A}{V \times \Delta x} \times \frac{D}{K_{PDMS,Medium}}$$ Equation 4

The velocity constant a 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 $t_{90\%} = \frac{\ln(10)}{2a}$, i.e., the time to transfer 45% of the initial PAH mass from the source to the sink. The velocity constant a 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 Dij in fugacity models (e.g. in $mol \cdot year^{-1} \cdot Pa^{-1}$) (15). 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_{source} and V_{sink}, are kept constant, as well as the surface area for exchange A and the thickness of the film Dx. Any difference in the exchange velocity a in two experiments i and j can therefore be contributed solely to the product of $K \times D$:

$$\frac{a_i}{a_j} = K_{ij} \times \frac{D_i}{D_j}$$ Equation 5

where *Kij* is the partition coefficient between medium i and j. The velocity ratio a_i/a_j describes a "relative conductivity for diffusive mass transfer" that for instance can be applied in the following way. The unknown flux of a PAH through medium i can be expressed as the flux of this PAH through medium j, multiplied with the measured velocity ratio a_i/a_j (11). For a more detailed mathematically model we refer to reference (11).

Materials and methods

Poly(dimethylsiloxane) (PDMS) sheets (SSP-M823) with a thickness of 600 µm (± 10 µm) were supplied by Specialty Silicone Products, Inc. (Ballston, USA). Analytical grade silicone was used in the present study in order to minimize analytical interferences, whereas a lower grade silicone was applied in the former study. The slight change of the silicone material might have lead to minor changes in absolute a-values, whereas the velocity ratios (a_i/a_j) should remain unaffected. Sodemann Industrifjedre A/S (Viby, Denmark) supplied 100-µm steel washers (ID 4 mm, OD 8 mm) to be used as spacers. The thickness of the specific batch varied too much and we thus selected those that were measured to be within 100 ± 5 µm. Nickel-plated neodymium iron boron magnets with a diameter of 10 mm and a thickness of 5 mm were supplied by Farnell (Herlev, Denmark).

Naphthalene (99%, Fluka), acenaphthene (99%, EGA), fluorene (98%, Aldrich), phenanthrene (98%, Aldrich), anthracene (98%, Sigma), fluoranthene (99%, Aldrich), pyrene (99%, EGA), benz[a]anthracene (Aldrich), chrysene (95%, Aldrich),

benzo[k]fluoranthene (98%, Aldrich), benzo[a]pyrene (98%, Aldrich) and dibenzo[ah]anthracene (97%, Aldrich) were supplied by Bie & Berntsen, Rødovre, DK. Their octanol water partition coefficients (log K_{OW}) were determined with the SPARC online calculator.

Humic acid sodium salt (38.28% carbon, Aldrich, product no. H1,675-2), sodium dodecyl sulfate (SDS) (≅ 99%, Sigma) and hydroxypropyl - β - cyclodextrin (Sigma, product no. CO926) were all obtained from Sigma-Aldrich (Vallensbæk Strand, Denmark). The non-ionic surfactant Tween 80 (polyoxyethylensorbetan monooleat) was obtained from Merck.

Ethanol (96%; De Danske Spritfabrikker, Aalborg, Denmark) was used as an extractant. HPLC grade methanol (99.9%) was provided by Merck (Darmstadt, Germany).

Preparation of natural solutions

The soil was a sandy loam from the Royal Veterinary and Agricultural University's experimental field station at Høje Taastrup, Denmark, and was identical to the soil used in a previous study (16). Top soil was collected after fall ploughing, sieved (2 mm) and stored at 4˚C until used. The organic matter content was determined by loss on ignition and measured at 4.8% (d.w.), the pH (water) was 6.5. The soil sample was water saturated by placing it for one hour on a sieve with a wet filter paper that was in direct contact with deionised water, thereby simulating a field condition with zero water potential. The wetted soil was then vacuum filtered (0.2 µm, – 0.5 bar) in order to obtain the solutions that were used in the diffusion experiments.

The horse manure was prepared from equal parts barley straw and horse feces. It was matured and composted outdoor for about 1 year and ready to be used as organic fertilizer. The water content of the manure was high, and it was thus sufficient to centrifuge it for 5 minutes at 6000 rpm in order to obtain the supernatant that was used for the diffusion experiment.

The root exudates were a kind gift of Danisco Seed (Holeby, Denmark). Seven sterile willow seedlings were each placed in 25 mL sterile water for 3 weeks and incubated under sterile conditions in a plant growth chamber. The solution was then harvested, filtered and freeze dried. We reconstituted the root exudate solution by adding 1/10 of the original water volume in order to obtain a ten times concentrated solution**.**

The gut fluid was collected from the deposit feeding polychaete *Nereis virens.*
The worms were supplied by Jan & Bo Lystfisker shop (Roskilde, Denmark) who obtained them from Topsy Baits (Wilhelminadorp, The Netherlands). The gut fluid was taken from the midgut, the most active section of the gut (17), by piercing the gut wall with a pipette and drawing out the fluid. The gut fluid was transferred to a plastic centrifuge tube and centrifuged with a 0.2 µm spin filter from Molecular Probes that was supplied by Invitrogen (Carlsbad, USA). About 250 µL was collected from each worm and gathered in one pool.

Experimental apparatus

More than 1000 disks with a diameter of 6 mm were cut out of the PDMS sheet and cleaned in three changes of > 200 mL methanol with a total contact time of at least 24 hours. Disks were contaminated according to Booij and coworkers (18) by placing them in a methanol:water solution containing all tested PAHs with a minimum contact time of 16

hours. For the first experiments we used a methanol:water solution (80:20, v/v) containing the PAHs at each 20-24 mg/L. Due to dosing problems of dibenzo[ah]anthracene we adjusted the procedure to a methanol:water solution (90:10, v/v) containing the PAHs at each 40-47 mg/L. At the day of the experiment contaminated disks were transferred to a small volume of water (@ 1 mL/disk) in order to remove methanol.

Microchambers (Figure 1) for measurement of mass transfer by partitioning-diffusion-partitioning 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 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 x 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. PAH molecules had now to partition from the source into the matrix, diffuse through the 100-µm model UBL and finally partition into the sink. Measurements were terminated (t = x) by removing the magnet and transferring each disk into 0.4 - 4 mL of methanol for extraction of the PAHs. Measurements were performed in triplicates and with termination times of 5 minutes to 48 hours.

Analytical procedure. Methanol extract analysis of PAHs was carried out by HPLC with fluorescence detection (Agilent 1100 system with G1321A FLD (Ex. 260 nm; Em. 350, 420, 440 and 500 nm). The separation column “CP-Ecospher 4 PAH” was obtained from Varian Inc. (Palo Alto, CA) and it was operated at 0.5 mL/min (28 °C, 30 µL injection). Methanol (HPLC grade from Merck Darmstadt, Germany) and water (SUPER-Q treated, Millipore, MA) was used as mobile phase: 50% methanol at t=0-2 min, linear gradient from 50 -75% methanol at t=2-7 min, linear gradient from 75-100% at t=7–35 minutes and 100% methanol at t=35-48 min. Quantification of the PAH concentrations in the extracts was accomplished by a five-point external standard curve. Analysis was generally carried out within two weeks post sampling. Signal integration was performed with HP Chemstation software (A.06.03, Agilent Technologies, Palo Alto, CA) and corrected by hand as necessary.

Generally, a total of 90% to 110% of the initial PAHs were recovered in the final extracts of sink and source disks, indicating a complete mass balance. For naphthalene we had to accept recoveries down to 80% in order to obtain sufficient data sets. Finally, the percentage that was transferred to the sink disk (T_{sink}) was fitted for each PAH with the equation

$$T_{Sink} = 50\% \cdot (1 - e^{-2at}) \qquad \text{Equation 6}$$

in order to determine the velocity constant *a*, which then was normalized with the velocity constant determined for distilled water in order to calculate the relative conductivity for diffusive mass transfer (Equation 5). All non-linear regressions were done with GraphPad Prizm 4 (San Diego, California) by least squares. The last time points of each time series

were removed partly because of decreasing mass balances and partly because it appeared to be difficult to maintain a stable aqueous UBL for more than 15 to 25 hours.

Diffusion experiments. First, a validation experiment was carried out where 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 discs. Hereafter, diffusion experiments were carried out with the washers and with water, air and different artificial and natural aqueous solutions. All experiments were conducted at room temperature (23 ± 3 °C).

Results and Discussion

Direct contact and water. The mass transfer of all PAHs was high at direct contact between the two disks. The time to reach near equilibrium ($t_{90\%}$) ranged from 0.4 hours for naphthalene to 2.1 hours for dibenzo(ah)anthracene. This corresponds to 0.9 to 4.8 hours 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, which can be seen in Figure 2 that shows mass transfer curves for benzo[a]pyrene at direct contact and in the presence of an aqueous UBL. These observations confirmed that diffusion through the 100-μm water film was the rate-limiting step in the experimental setup.

The velocity rate constants of the PAHs in water are plotted against their octanol-water partition coefficients in Figure 3a. The effect of the aqueous boundary layer increases with

hydrophobicity (Figure 3b), which confirms that aqueous UBLs are efficient barriers for the diffusive mass transfer of particularly the most hydrophobic organics.

Air. The velocity rate constants in air are plotted against their octanol water partition coefficients in Figure 3c that also includes a-values for water. The lower molecular weight PAHs are better conducted through air, whereas the higher molecular weight PAHs are better conducted through water. This suggests that the drying of PAH contaminated soil should enhance the diffusive fluxes of the smaller molecular PAHs but reduce the diffusive fluxes of the higher molecular weight PAHs.

Sodium dodecyl sulfate (SDS). SDS is an anionic detergent with a critical micelle concentration (cmc) of about 1 g/L (19). The velocity rate constants in an SDS solution at 10 g/L are shown in Figure 3d. The diffusive mass transfer of naphthalene was only slightly enhanced. The effect on all other PAHs was much more pronounced and increased with increasing hydrophobicity of the PAH. The resulting mass transfer of the PAHs was independent of their hydrophobicity, which best can be explained by a mass transfer that is completely dominated by the diffusion of micelle bound PAHs.

Tween 80. This alkyl sorbitan ethoxylate is a hydrophilic nonionic surfactant (average M=1276 g/mole) with a critical micelle concentration of 0.024 mM (20). Tween 80 has been used for many pharmaceutical applications and within environmental biotechnology it has been used to enhance the solubility, the desorption and the biodegradation of PAHs in soil (21-23). The obtained diffusion data in a 0.24 mM Tween 80 solution show the same pattern as for the SDS and they were thus only included in the supporting data. The diffusive mass transfer of the lower molecular weight PAHs up to pyrene was only slightly enhanced. The enhancement increased with increasing hydrophobicity resulting in velocity

constants for the higher molecular weight PAHs that were independent of their hydrophobicity. The enhancement in diffusive mass transfer is much smaller than the enhancement of solubility, since Willumsen reported a factor 29 increase of apparent solubility of fluoranthene at the same Tween 80 concentration (20), which in the present study enhanced the diffusive conductivity by only 41%.

Hydroxypropyl - b - cyclodextrin. Cyclodextrins are cyclic oligosacharides with a hydrophobic inner cavity and a relatively hydrophilic exterior surface. The diffusive mass transfer of all PAHs was enhanced by the addition of 140 g cyclodextrin per liter as shown in Figure 3d. The enhancement factors ranged from 3.9 for naphthalene to 1135 for dibenzo[ah]anthracene and the velocity rate constants of all PAHs were within one order of magnitude. Aqueous solutions with high concentrations of cyclodextrin have been used to determine the bioaccessible PAH content in soils (24), and cyclodextrins have also been used to stimulate the bioremediation of PAHs in soil (25). Our results demonstrate that the addition of cyclodextrin not only enhances the capacity of the aqueous solution and thus its apparent solubility for PAHs, it also enhances the diffusive conductivity and thus the desorption kinetics in those situations where diffusion through stagnant water constitutes the rate limiting step.

Humic acid solution. Diffusion experiments were carried out at 40, 200 and 1000 mg humic acid sodium salt/L which corresponds to 15.3, 76.6 and 382.8 mg C/L. The velocity constants of 10 PAHs as a function of carbon concentration were plotted in figure 4 (benzo[k]fluoranthene and dibenzo[ah]anthracene were excluded due to poor regression fitting). No enhancement was observed for the least hydrophobic PAHs, high carbon concentrations were required in order to enhance the diffusive mass transfer of the

intermediate PAHs and relatively low carbon concentrations were already sufficient to enhance the mass transfer of the most hydrophobic PAHs. Figure 4 might be used for a rough estimation of diffusion enhancement of a given PAH at a certain DOC concentration. However, more research is required in order to assess how generally applicable Figure 4 is to different kinds of DOC.

Root exudates solution. The diffusive conductivity in the root exudate solutions was only slightly higher than in water (Table 1). The present results do not indicate that the produced root exudates will have a significant impact on the diffusive mass transfer of PAHs within the interstitial soil water near a willow root. However, it can not be excluded that higher levels of root exudates within an aqueous film on the root surface might affect the diffusive mass transfer.

Soil solution. The tested soil solution was obtained from a relatively poor agricultural soil and it was included in order to investigate whether the enhanced diffusion also plays a role in such soil. The diffusive conductivity was enhanced by factors ranging from 1.14 to 1.89 when compared to water, and this enhancement can be characterized as slight to moderate (Table 1). However, higher enhancement can be expected in other soils with a higher content of humic acids, after the addition of organic fertilizers and possibly also within the water filled pores that might have higher DOC levels than the tested interstitial water.

Horse manure solution. Horse manure can be applied as soil fertilizer and the diffusion measurements on horse manure solution complement thus those on the poor agricultural soil. The diffusive conductivity of the intermediate PAHs was enhanced by factor 2 to 6,

whereas the diffusive conductivity of the most hydrophobic PAHs was enhanced by 1-2 orders of magnitude (Table 1). This demonstrates that amendments of manure and other organic waste can enhance the diffusive exchange within contaminated soil. Several studies have demonstrated that such amendments can speed up the bioremediation of PAHs (26,27), and one overlooked explanation might be the enhanced diffusive mobility of the PAHs.

Gut fluid from sediment worm. The diffusive conductivity in the gut fluid was enhanced by factors ranging from 1.3 for naphthalene to 74 for benzo[a]pyrene when compared to water. The diffusive mass transfer within the gut is thus enhanced compared to the transfer at the outer skin of the worm. This suggests an enhanced uptake in the gut due to an enhanced diffusive conductivity of the gut fluid. However, the diffusive flux will still be directed from high to low chemical activity and equilibrium will still be reached at equal chemical activity of the PAHs in soil and worm (28). The enhanced diffusion will thus speed up the uptake kinetics within the gut, without being in conflict with the equilibrium partitioning theory (29).

Implications for the exposure to hydrophobic organics.

Recently, we proposed that accessibility and chemical activity are two complementary sides of bioavailability (28). The present study demonstrates that the exposure to PAHs not only depends on accessibility and chemical activity both characterizing the pollution, it also depends on the diffusive conductivity that characterizes the exposure medium.

Several studies have shown that binding of hydrophobic organic chemicals to different types of DOC can lead to a reduction of the freely dissolved water concentration

and to a reduction of the diffusive uptake into for instance fish (30-33). The reason for this is that the total concentration of the HOC is given and that the main effect of the DOC is a reduction of the freely dissolved concentration or chemical activity. The present study shows that different types of DOC also can enhance the diffusive conductivity and that this can lead to an increase in the velocity of diffusive uptake into for instance a sediment worm in situations where the chemical activity is controlled from a diffusion source. Whether a medium constituent reduces or enhances the diffusive uptake of PAHs depends thus on the given exposure scenario.

The diffusion enhancement can shorten the time to reach equilibrium and it can also lead to higher steady state concentrations in case of metabolic degradation. However, the enhancement of the diffusion velocity does not affect the equilibrium partitioning concentrations in the organisms, and the obtained results are thus not in conflict with the applicability and validity of the equilibrium partitioning theory.

The experimental approach can be used to study the importance of the exposure media for the different routes of exposure. The diffusive mass transfer was much higher in the gut fluid of a sediment worm than in water. However, an even more efficient mass transfer was observed at the direct contact between the two disks. These observations suggest that direct contact exposure might be an important route of uptake for the most hydrophobic organics and that water constitutes a diffusion barrier for highly hydrophobic organics rather than being an efficient conductor.

Implications for dynamic fate models

The results of the present study might be used to assess whether diffusion through aqueous media can be approximated with coefficients that were derived in pure water. Additionally, the obtained velocity rate ratios (a_{media}/a_{water}) might be applied in dynamic fate

models to calculate diffusive processes in composed media more realistically. This should preferably be done with velocity rate ratios that were determined on the specific media and it will thus require additional measurements. Empirical relations may be established, that can predict the diffusive conductivity of composite media based on environment-specific and compound-specific input data.

The observed diffusion enhancement was generally most pronounced for the most hydrophobic PAHs, and the data for benzo[a]pyrene across all tested media are thus summarized in Table 2. These data clearly show that different types of dissolved organic carbon at environmental relevant concentrations can enhance the diffusive mass transfer of highly hydrophobic organics. The enhancement of convective mass transfer by DOC will generally be even more pronounced. Enhancement of the diffusive mass transfer requires generally that most of the HOC is bound to the DOC, because diffusion coefficients are much lower for bound compared to free molecules. Enhancement of the convective transport due to solubility enhancement requires in contrast only that a significant fraction of the HOC is bound to the DOC (34).

Implications for calibration of passive sampling

Passive sampling that is operated in the kinetic regime and that is calibrated in pure water, will not lead to well defined measurements of “freely dissolved concentrations” in media with an enhanced diffusive conductivity. Such methods will instead measure some kind of labile concentration. The equilibration time of equilibrium sampling devices will also be affected by the diffusive conductivity of the exposure medium, however, the eventual equilibrium measurement will not.

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Table 1. Velocity rates of 12 PAHs in water together with their velocity rate ratios (a_x/a_{water}) in willow root exudate solution, soil solution, horse manure solution and the gut fluid from the sediment worm *Nereis virens.* The relative standard error of velocity rate constants was on average 5.3% for water, 5.3% for root exudates, 4.5% for soil solution, 5.1% for horse manure solution and 8.5% for gut fluid. Differences of more than 20% can thus be considered to be statistically significant, which corresponds to a ratio of 1.2.

PAH	a_{water} (h^{-1})	$a_{exudates}/a_{water}$	$a_{soilsolution.}/a_{water}$	a_{manure}/a_{water}	$a_{gut\ fluid}/a_{water}$
Naphthalene	$8.57 \cdot 10^{-2}$	1.10	1.14	0.96	1.34
Acenaphtene	$1.56 \cdot 10^{-2}$	1.12	1.20	0.95	1.73
Fluorene	$1.15 \cdot 10^{-2}$	1.08	1.22	1.21	1.82
Phenanthrene	$6.59 \cdot 10^{-3}$	1.00	1.18	1.72	2.24
Anthracene	$5.87 \cdot 10^{-3}$	0.93	1.15	1.44	2.42
Fluoranthene	$1.87 \cdot 10^{-3}$	1.19	1.32	4.48	5.21
Pyrene	$1.64 \cdot 10^{-3}$	1.22	1.42	5.73	6.27
Benz[a]anthracene	$4.50 \cdot 10^{-4}$	1.25	1.39	17.2	18.6
Chrysene	$5.25 \cdot 10^{-4}$	1.24	1.22	16.7	17.7
Benzo[k]fluoranthene	$1.81 \cdot 10^{-4}$	1.30	1.89	33.1	51.5
Benzo[a]pyrene	$1.52 \cdot 10^{-4}$	1.34	1.59	54.9	73.7
Dibenzo[ah]anthracene	$5.95 \cdot 10^{-5}$	no data	no data	77.4	no data

Table 2. Velocity rates of benzo[a]pyrene measured in different media.

Matrix	a (h^{-1}) 10^{-3}	95% interval (h^{-1}) 10^{-3}	R^2	a_x/a_{water}
Direct contact	648	487 – 808	0.86	4263
Water	0.152	0.142 - 0.162	0.97	1
Air	0.068	0.022 - 0.114	0.48	0.45
Humic acid, 15.3 mg C/L	0.203	0.186 – 0.220	0.96	1.3
Humic acid, 76.6 mg C/L	0.770	0.694 – 0.847	0.94	5.1
Humic acid, 382.8 mg C/L	5.46	5.00 - 5.92	0.97	36
10 g SDS/L	42.6	34.0 - 51.2	0.81	280
0.24 mM Tween 80	1.48	1.06 – 1.90	0.52	9.7
145 g cyclodextrin/L	51.4	45.5 – 57.2	0.94	338
Soil solution	0.242	0.220 – 0.263	0.97	1.6
Phytoexudates	0.204	0.174 - 0.233	0.83	1.3
Gut fluid	11.2	9.6 - 12.8	0.90	74
Horse manure solution	8.4	7.3 – 9.4	0.90	55

Figure 1. Cross-section of the experimental apparatus. Poly(dimethyl-siloxane) (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.

Figure 2. Mass transfer of benzo(a)pyrene from source to sink disk at direct contact (a) and in the presence of 100 µm aqueous UBL (b). The diffusive flux of benzo[a]pyrene was orders of magnitude reduced by the aqueous UBL. Standard deviations between replicates are included as error bars, which in some cases are smaller than the symbols. Least square fits to Equation 6 were included as solid lines. Mean of 3 replicates.

Figure 3: Velocity constants in different media plotted against the octanol water partition coefficient of the PAHs. The figures show diffusive mass transfer (a) through water, (b) at direct contact, (c) through air, (d) through a 10 g SDS/L solution and (e) through a 140 g cyclodextrin/L solution.

Figure 4: Velocity rate constants of PAHs at different humic acid concentrations. The addition of humic acids did not enhance the diffusive mass transfer of the least hydrophobic PAHs such as naphthalene and fluorene, and it required rather high humic acid concentrations in order to enhance the mass transfer of intermediate PAHs such as fluoranthene and pyrene. The mass transfer of the most hydrophobic PAHs such as benzo[a]pyrene was enhanced already at rather low concentrations.

Figure 1

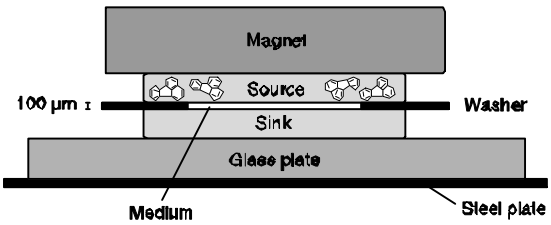
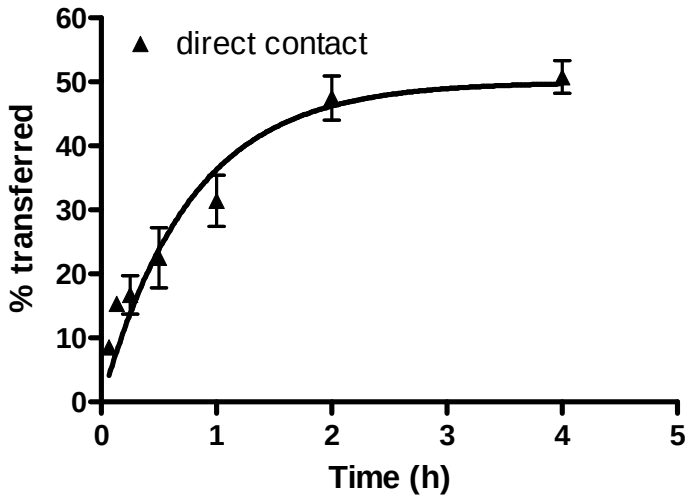

Magnet
Source
100 µm
Washer
Sink
Glass plate
Medium
Steel plate

Figure 2


direct contact
% transferred
Time (h)
0
10
20
30
40
50
60
0
1
2
3
4
5

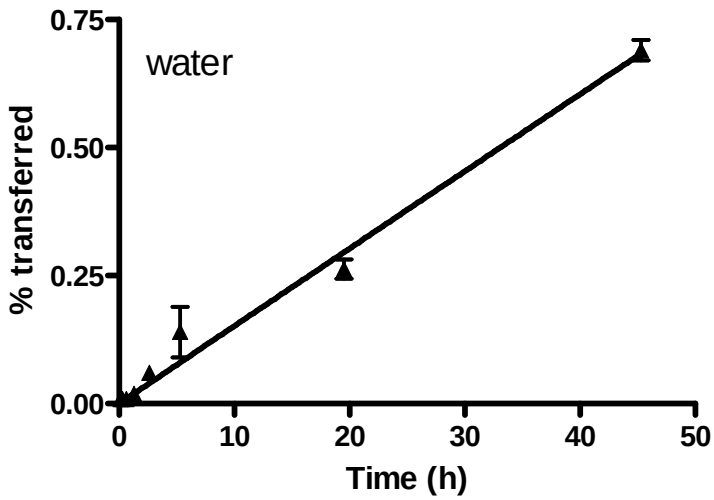
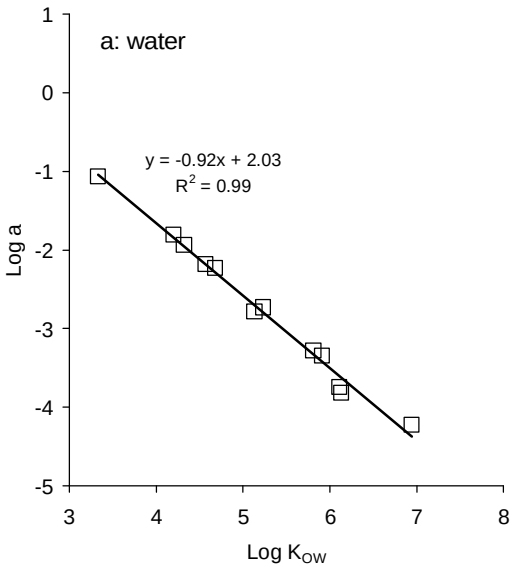
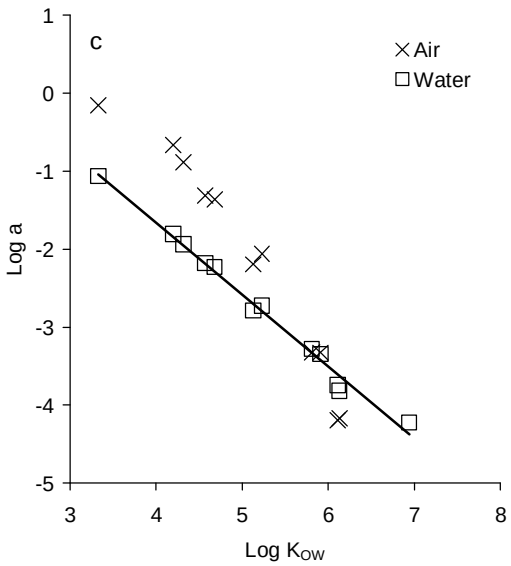
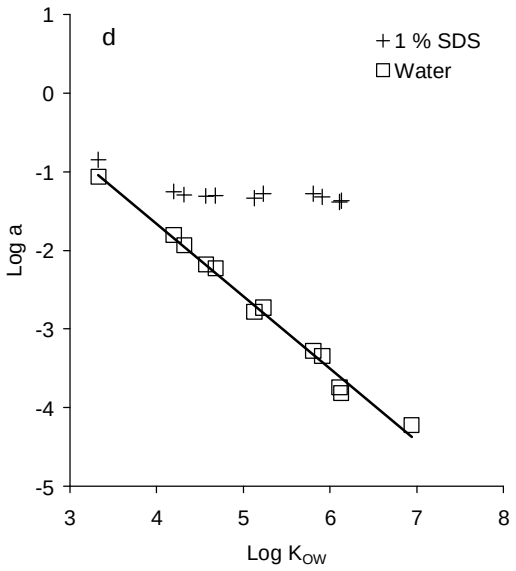

water
% transferred
Time (h)
0.00
0.25
0.50
0.75
0
10
20
30
40
50

Figure 3


a: water
y = -0.92x + 2.03
R2 = 0.99
Log a
Log KOW
1
0
-1
-2
-3
-4
-5
3
4
5
6
7
8


c
Air
Water
Log a
Log KOW
1
0
-1
-2
-3
-4
-5
3
4
5
6
7
8


d
+ 1 % SDS
Water
Log a
Log K_{OW}
1
0
-1
-2
-3
-4
-5
3
4
5
6
7
8

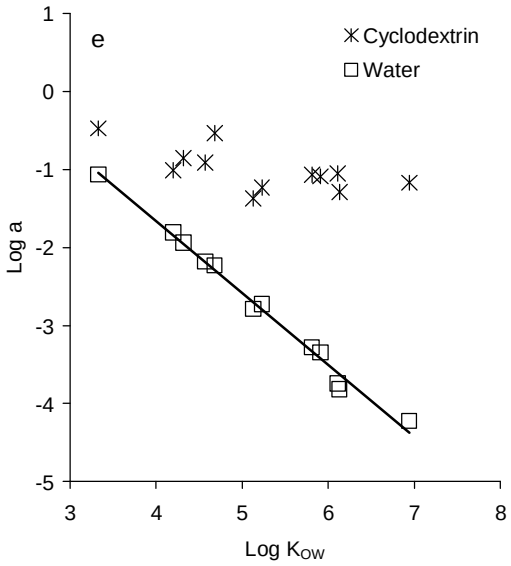
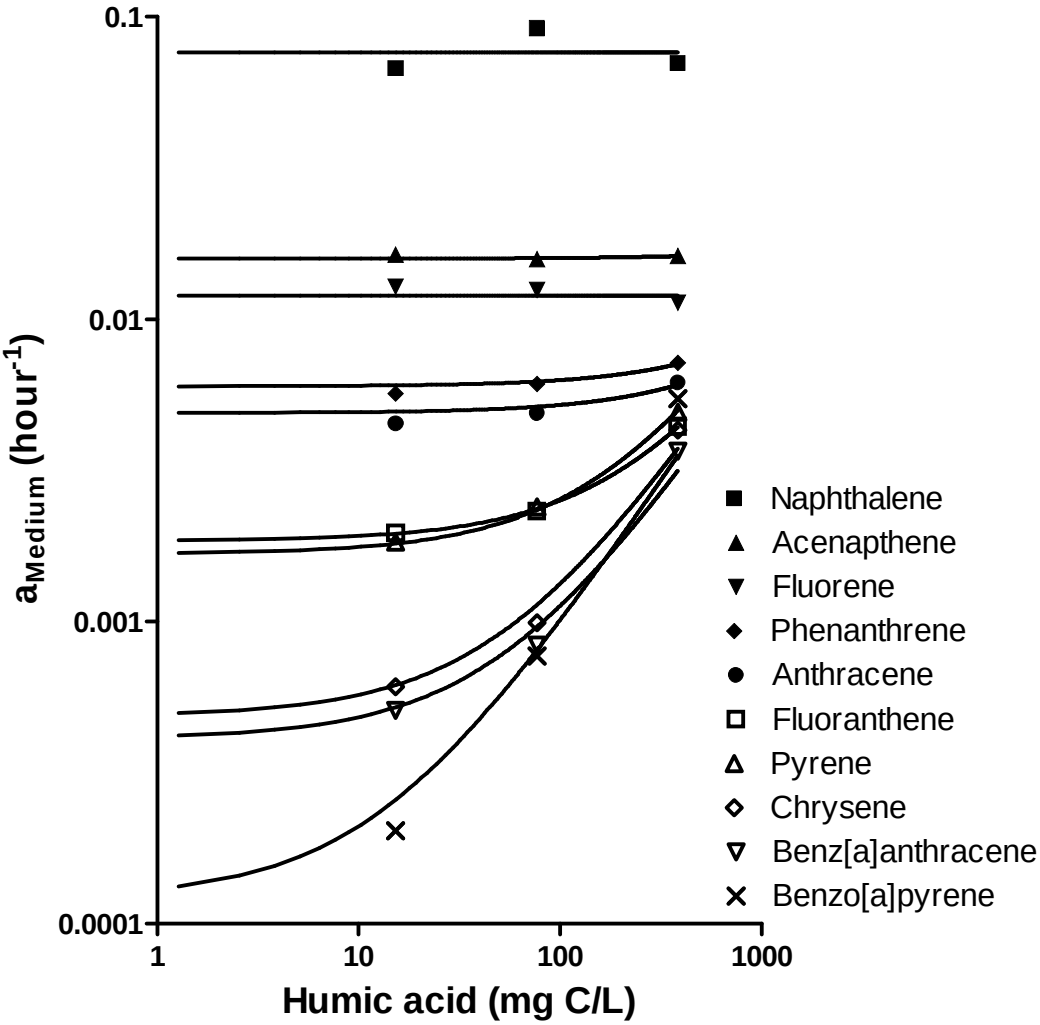

e
Cyclodextrin
Water
Log a
Log K_{OW}
1
0
-1
-2
-3
-4
-5
3
4
5
6
7
8

Figure 4


0.1
0.01
0.001
0.0001
1
10
100
1000
a_{Medium} (hour^{-1})
Humic acid (mg C/L)
Naphthalene
Acenapthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Chrysene
Benz[a]anthracene
Benzo[a]pyrene

Supporting information: Enhanced diffusion of polycyclic aromatic hydrocarbons (PAHs) in artificial and natural aqueous solutions

Reference media	**a (h^{-1}) * 10^{-3}, including 95% confidence interval**		
PAH	**direct contact**	**water**	**air**
Naphtalene	3041 (2141-3941)	85.7 (65.4-106.0)	695 (576-815)
Acenaphtene	1661 (1306-2017	15.6 (12.5-18.7)	217 (193-242)
Fluorene	1886 (1528-2244)	11.5 (9.8-13.3)	129 (115-143)
Phenanthrene	1508 (1205-1810)	6.59 (5.83-7.35)	48.6 (44.5-52.8)
Anthracene	1442 (1108-1775)	5.87 (5.09-6.66)	43.1 (39.3-46.8)
Fluoranthene	845 (653-1037)	1.87 (1.67-2.07)	8.66 (7.81-9.51)
Pyrene	939 (720-1159)	1.64 (1.49-1.79)	6.36 (5.74-6.98)
Benz(a)anthracene	727(538-917)	0.450 (0.429-0.471)	0.472 (4.64-0.479)
Chrysene	734(536-931)	0.525 (0.498-0.553)	0.477 (0.433-0.521)
Benzo(k)fluoranthene	601(454-747)	0.181 (0.170-0.192)	0.0639 (0.0576-0.0702)
Benzo(a)pyrene	648(487-808)	0.152 (0.142-0.162)	0.0681 (0.0222-0.1139)
Dibenzo(ah)anthracene	542(414-669)	0.0595 (0.0520-0.0670)	no data

Composed media	**a (h^{-1}) * 10^{-3}, including 95% confidence interval**					
PAH	**145g Cyclodex./L**	**10 g SDS/L**	**0.24 mM Tween 80**	**HA, 15.3 mg C/L**	**HA, 76.6 mg C/L**	**HA, 382.8 mg C/L**
Naphtalene	335 (292-379)	141 (116-166)	87.7 (77.7-97.8)	67.6 (47.8-87.4)	91.7 (69.5-114)	70.3 (55.8-84.8)
Acenaphtene	98.3(91.3-105)	55.8 (45.3-66.4)	19.2 (15.3-23.1)	16.3 (12.5-20.2)	15.8 (13.6-18.0)	16.2 (13.5-18.9)
Fluorene	140 (125-155)	50.9 (41.2-60.6)	13.2 (10.8-15.7)	12.8 (10.2-15.5)	12.5 (11.1-13.9)	11.3 (9.6-13.0)
Phenanthrene	122 (108-136)	49.0 (39.5-58.5)	6.98 (6.09-7.86)	5.68 (5.24-6.12)	6.09 (5.67-6.52)	7.17 (6.37-7.96)
Anthracene	290 (250-331)	49.7 (40.2-59.2)	4.90 (4.24-5.56)	4.52 (4.10-4.93)	4.90 (4.51-5.29)	6.17 (5.42-6.92)
Fluoranthene	58.0 (52.8-63.3)	52.6 (42.5-62.7)	2.64 (2.31-2.97)	1.96 (1.85-2.07)	2.32 (2.23-2.40)	4.42 (4.00-4.84)
Pyrene	42.8 (37.2-48.4)	46.3 (36.3-56.3)	2.60 (2.25-2.96)	1.82 (1.74-1.93)	2.40 (2.25-2.54)	4.93 (4.50-5.37)
Benz(a)anthracene	81.6 (73.7-89.4)	47.6 (37.9-57.2)	1.57 (1.25-1.90)	0.508 (0.489-0.526)	0.835 (0.792-0.878)	3.66 (3.34-3.99)
Chrysene	84.8 (76.1-93.5)	52.3 (41.6-63.0)	1.75 (1.38-2.12)	0.609 (0.582-0.636)	0.991 (0.931-1.05)	4.30 (3.89-4.70)
Benzo(k)fluoranthene	88.2 (79.9-96.5)	29.9 (33.5-48.3)	1.39 (1.02-1.76)	0.156 (0.141-0.170)	0.523 (0.471-0.576)	4.10 (3.73-4.46)
Benzo(a)pyrene	51.4 (45.5-57.2)	42.6 (34.0-51.2)	1.48 (1.06-1.90)	0.203 (0.186-0.220)	0.770 (0.694-0.847)	5.46 (5.00-5.92)
Dibenzo(ah)anthracene	67.5 (60.6-74.4)	no data	1.64 (1.13-2.16)	0.0742(0.0485-0.0998)	0.409 (0.337-0.482)	2.76 (2.47-3.05)