

# **Influence of Dissolved Organic Matter on the Availability of Organic Compounds: Desorption and Mass Transfer Kinetics**

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## Bibliographic Description

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# **Influence of Dissolved Organic Matter on the Availability of Organic Compounds: Desorption and Mass Transfer Kinetics**

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### Abstract:

Dissolved humic substances (DHS) belong to the most widespread natural surface-active substances which exist in all terrestrial and aquatic environments. Because of the presence of both hydrophilic and hydrophobic moieties in their structure, they are able to reduce surface tension in aqueous solution and can form micelle-like aggregates. These properties of DHS can play an important role for the mobility and bioavailability of hydrophobic organic pollutants. However, much less information is available on effects of DHS in the surface microlayer at phase boundaries. The influence of DHS on diffusion-controlled mass transfer processes was studied in the first part of this thesis. In the first manuscript, mass transfer coefficients ( $k_L \times A$ ) for transport from water to the gas phase were determined for two compounds with low sorption tendency towards DHS (benzene and cyclohexane) at varied conditions (DHS concentration, agitation intensity, solution pH and ionic strength). The applied DHS include natural humic (SRHA) and fulvic acids (SRFA) from surface water (Suwannee River) as well as a commercial humic acid. Mass-transfer coefficients of the model compounds were significantly reduced even by low, environmentally relevant concentrations of DHS. The observed results were interpreted by hydrodynamic effects due to the formation of a surface film of DHS at the water-air interface.

Based on the previous findings about the possible shuttle effect of DHS in chemicals transfer between water and solid sink phases (e.g. silicone phases, organisms), sorption-induced effects on water-gas exchange appeared to be very likely and highly relevant. Therefore, in the study presented in the second manuscript

n-octane which has a significant sorption tendency towards DHS was applied in addition to benzene and the experimental setup was complemented by a passive dosing system. The experimental results show that DHS can affect water-gas exchange rates not only by the above described hydrodynamic effects but also by sorption-induced effects. Whether sorption accelerates or retards mass transfer was shown to depend on its effect on the thermodynamic activity of the solute in the aqueous phase. Mass transfer will be retarded if the activity of the solute is decreased due to sorption. If it remains unchanged (e.g. due to fast equilibration with a sediment acting as a large source phase), then DHS can act as an additional shuttle for the pollutants, enhancing the flux through the boundary layer.

Whether DHS can act as efficient pollutant shuttle for transport through diffusion boundary layers depends not least on the rate of sorption/desorption processes between pollutant and DHS molecules. The methods applied so far are able to trace sorption/desorption processes in the time-scale of minutes to hours. However, when looking at the microscale, processes occurring in the sub-second to second scale can become highly relevant. Therefore, in the third manuscript a new experimental technique for measuring rates of desorption of organic compounds from DHS is presented. The time-resolved in-tube solid-phase microextraction (TR-IT-SPME) was applied to two humic acids and a surfactant as sorbents together with pyrene, phenanthrene and 1,2-dimethylcyclohexane as solutes. Due to its simplicity, the new technique has a wide application potential and should be accessible for many environmental laboratories.

Bibliographische Darstellung

Ksenia Surudo (geb. Ramus)

## **Influence of Dissolved Organic Matter on the Availability of Organic Compounds: Desorption and Mass Transfer Kinetics**

Universität Leipzig, Dissertation

133 Seiten, 30 Abbildungen, 4 Tabellen, 82 Literaturangaben

Kurzreferat:

Gelöste Huminstoffe (Dissolved humic substances, DHS) gehören zu den am weitesten verbreiteten natürlichen oberflächenaktiven Stoffen, welche in Erdböden und Gewässern vorkommen. Aufgrund des Vorkommens von sowohl hydrophoben als auch hydrophilen funktionellen Gruppen in ihrer Struktur sind sie in der Lage, die Oberflächenspannung in wässrigen Lösungen zu reduzieren und mizellartige Aggregate zu bilden. Diese Eigenschaften von DHS können eine wichtige Rolle für die biologische Verfügbarkeit und die Mobilität von hydrophoben organischen Schadstoffen spielen. Weit weniger ist bekannt über den Effekt von DHS auf die Oberflächen-Mikroschicht an Phasengrenzen. Der Einfluss von DHS auf den diffusionskontrollierten Stofftransport von organischen Verbindungen zwischen Wasser und Gasphase wurde im ersten Teil dieser Arbeit untersucht. Im ersten Manuskript wurden Stofftransportkoeffizienten ( $k_L \times A$ ) für den Übergang aus Wasser in die Gasphase für zwei Verbindungen mit niedriger Sorptionstendenz gegenüber DHS (Benzen und Cyclohexan) bei unterschiedlichen Bedingungen (Durchmischungsintensität, pH-Wert und Ionenstärke) ermittelt. Die verwendeten DHS beinhalten natürliche Humin- (SRHA) und Fulvinsäuren (SRFA) aus Oberflächengewässern (Suwanee River) wie auch eine kommerzielle Huminsäure. Die Stofftransportkoeffizienten der Modellverbindungen wurden selbst durch niedrige, umweltrelevante Konzentrationen von DHS signifikant gemindert. Die erhaltenen Ergebnisse wurden auf hydrodynamische Effekte infolge der Bildung eines Oberflächenfilms aus DHS-Molekülen an der Wasser/Gas-Grenzfläche zurückgeführt.

Basierend auf den bisherigen Erkenntnissen über einen möglichen ‚Shuttle‘-Effekt von DHS beim Transport von Schadstoffen in der Diffusionsgrenzschicht zwischen Wasser und kondensierten Phasen (z.B. Silikon-Phasen, Organismen), erschienen sorptionsinduzierte Effekte auf den Wasser-Gas-Transfer wahrscheinlich und sehr relevant. Deshalb wurde in der im zweiten Manuskript dargestellten Studie neben Benzen zusätzlich n-Octan verwendet, welches eine signifikante Sorptionstendenz gegenüber DHS aufweist. Außerdem wurde der Versuchsaufbau um ein Experiment mit passiver Dosierung erweitert. Die Versuche haben ergeben, dass DHS den Wasser-Gas-Austausch von organischen Verbindungen nicht nur durch die oben beschriebenen hydrodynamischen Effekte, sondern auch durch sorptionsinduzierte Effekte beeinflussen können. Ob die Sorption der Verbindungen an DHS beschleunigend oder verlangsamt auf den Austrag aus der Wasser- in die Gasphase wirkt, hängt dabei vom Effekt der Sorption auf die thermodynamische Aktivität der organischen Verbindungen in der Wasserphase ab. Der Stofftransport wird verzögert, wenn die Aktivität des Schadstoffs (bzw. dessen frei gelöste Konzentration) in der Wasserphase durch die Sorption an DHS reduziert wird. Wenn sie unverändert bleibt (z.B. durch eine schnelle Nachlieferung aus einem Sediment, das als große Quellphase fungiert), können DHS als zusätzliches Transportmittel (‚Shuttle‘) für die Schadstoffe wirken und damit den Fluss durch die Diffusionsgrenzschicht verstärken.

Ob DHS als ein effektives Schadstoff-Transportmittel in Diffusionsgrenzschichten wirken können, ist nicht zuletzt von der Geschwindigkeit der Einstellung des Sorptions-Desorptions-Gleichgewichtes zwischen Analyt und DHS abhängig.

Mit den bisher angewendeten Methoden zum Studium von Sorptions- und Desorptionsprozessen an DHS konnte lediglich der Zeitbereich von Minuten bis zu Stunden erfasst werden. Betrachtet man jedoch den mikroskaligen Bereich, können Prozesse, die im sub-Sekunden- bis Sekunden-Bereich ablaufen, höchst relevant sein. Deshalb wurde im dritten Teil der Arbeit eine neue experimentelle Methode zur Messung von Desorptionsraten von organischen Verbindungen von DHS entwickelt. Die zeitaufgelöste, Kapillar-Festphasenmikroextraktion (time-resolved in-tube solid-phase microextraction, TR-IT-SPME) wurde auf Lösungen von zwei Huminsäuren und einem Tensid als Sorbens zusammen mit Pyren, Phenanthren und 1,2-Dimethylcyclohexan als Modellschadstoffe angewendet. Aufgrund ihrer Einfachheit besitzt diese Methode ein breites Anwendungsgebiet und sollte für viele Umweltlabors zugänglich sein.

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# 1. General Introduction

## 1.1. Humic substances (HS)

Humic substances (HS) are a major component of natural organic matter (NOM). They are widespread on the earth's surface and represent the largest fraction of NOM in aquatic as well as terrestrial environments. They can exist in both forms, as the solid fraction (particles) as well as dissolved humic substances (DHS) (Hayase and Tsubota, 1983).

HS are complex and heterogeneous mixtures of polydispersed materials formed in soils, sediments and natural waters by biochemical and chemical reactions during the decay and transformation of plant and microbial remains. This process is called humification. Plant lignin and its transformation products, as well as polysaccharides, melanin, cutin, proteins, lipids, nucleic acids etc. are important components taking part in this process.

Depending on the solubility of HS in alkaline or acidic solutions, HS in soil and sediments can be divided into fulvic acids (FA) (water soluble), humic acids (HA) (water soluble only at alkaline pH) and humin (insoluble in the whole range pH), all of which are structurally related. Aquatic DHS contain only HA and FA (Pignatello, 1998; Schwarzenbach et al., 2003).

Due to the fact that HS are very complex heterogeneous organic compounds; their overall chemical structure has not been clarified yet. The precise properties and structure of a given HS sample depends on the water or soil source and the specific conditions of extraction. Therefore it is not possible to specify the structure or the molecular weight of HS molecules exactly. Most of the knowledge about structure of HS is inferred from studies of HA and FA. Bearing in mind each humic macromolecule can be unique, the first hypothetical structure of HA has been offered by Schulten and Schnitzer (1993) (Figure 1).

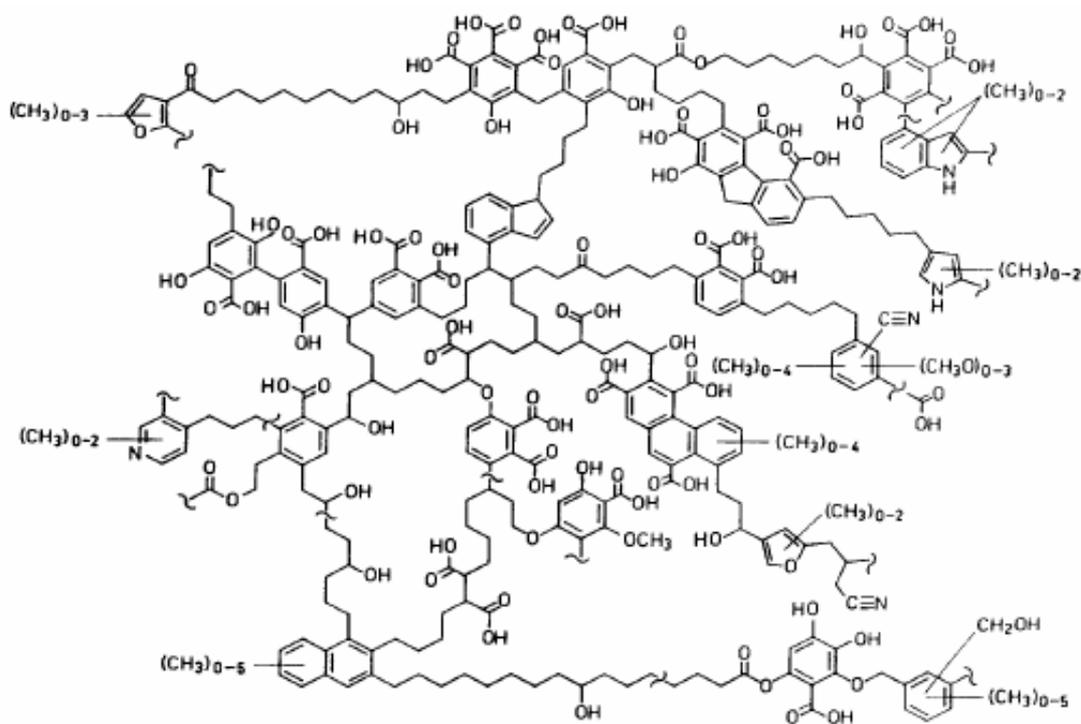


Figure 1. Schematic of a soil humic acid (HA) structure proposed by Schulten and Schnitzer (1993).

The HA structure shown in Figure 1 is the result of extensive pyrolysis-GC/MS and pyrolysis-FIMS,  $^{13}\text{C}$  NMR, chemical, oxidative and reductive degradation, colloid-chemical and electron microscope investigations done on HA over many years and exhaustive consultation on the voluminous literature in this subject (Schulten and Schnitzer, 1993).

However, due to the fact that HS are very complex heterogenous organic compounds, their overall chemical structure has not been clarified yet. Nevertheless, the HS structure can be visualized as a highly branched network of aliphatic and aromatic segments. HS have been shown to contain a wide variety of molecular components. Some typical components are: polysaccharides, fatty acids, polypeptides, lignins, esters, phenols, ethers, carbonyls, quinones, lipids, peroxides, various combinations of benzene, acetal, ketal and lactol, furan ringed compounds, and aliphatic (carbon chains) compounds.

## 1.2. Sorption and desorption processes on HS

Sorption is a phase distribution process that accumulates solutes at surfaces and interphases (i.e., adsorption) or from one phase to another (i.e., partitioning). This process is known both to affect the transport as well as to reduce chemical and biological reactivity of relatively hydrophobic organic chemicals (HOCs) such as PAHs and chlorinated aliphatic and aromatic compounds in surface aquatic and groundwater systems.

Sorption phenomena on HS have been extensively studied in recent decades and several models allowing a quantitative prediction of the extent of sorption depending on sorbate and HS properties have been proposed (Schwarzenbach et al., 2003).

Investigators in the late 1970s and early 1980s found that HOCs sorption is proportional to the amount of organic matter in soils and sediments and increases with the hydrophobicity of a compound (Chiou et al., 1983; Karickhoff, 1984). It was found that sorption by soils and sediments is driven by hydrophobic interactions including the entropic effects in the aqueous phase and non-specific interactions of the organic compounds with soil and sediment organic matter. A linear partitioning model was involved for mechanistically and quantitatively describing the sorption equilibria. In this model, sorption is envisioned as partitioning of organic compounds from an aqueous phase into a relatively homogeneous and amorphous, gel-like soil or sediment organic matter phase. The main driver for the transfer of organic compounds from the water phase to the organic matter is the raised entropy of the system. This comes from breaking of the strongly structured hydrate-shell during the passing of the molecules of HOCs from the aqueous to the organic phase. This produces a strong thermodynamic gradient (Pignatello, 1989). However, it became evident that many observations concerning sorption in soils and sediments cannot be explained with the partition model, which does not adequately address the sorption mechanisms of organic compounds to HS. The main contradictions to the partition model were e.g. non-linear isotherms (Huang and Weber, 1997), sorbate competition (White and Pignatello, 1999) and hysteresis (especially for PAHs) (Schwarzenbach et al., 2003) (Figure 2).

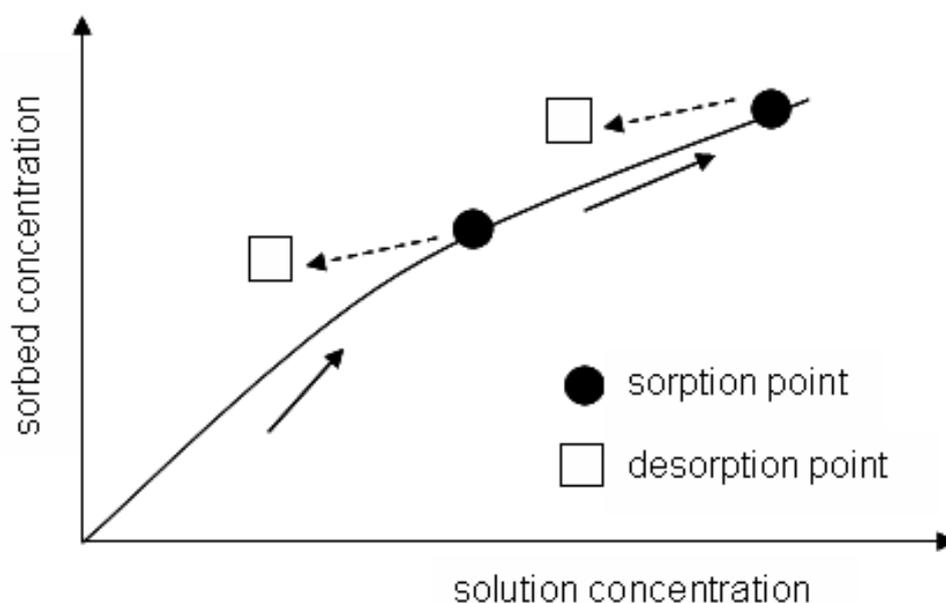


Figure 2 Sorption non-singularity (hysteresis).

Further studies on the interactions between organic compounds and the HS fraction led to the proposal that HS is analogous to synthetic polymers and its sorption behavior follows multimechanistic dual-mode sorption (DMSM) or dual-reactive domain (DRDM) models (Xing and Pignatello, 1997; LeBoeuf and Weber, 1997).

Nevertheless, all the disadvantages of the non-linear models make it worthwhile to investigate whether the partition model can hold for a clearly defined group of sorbents. This hypothesis was tested for e.g. DHS as sorbent with much more flexible conformation and not such a relatively rigid pore network (Kopinke et al., 2002). It was observed that partition model works quite well for DHS. (Georgi, 1998). Georgi, 1998 showed, that there were no significant differences in  $K_{DOC}$  values over a wide range of DHS concentrations (10-2000 mg L<sup>-1</sup>).

Sorption of organic chemicals on DHS is generally described as a partition process with a sorption coefficient  $K_{DOC}$ .

$$K_{DOC} = \left( \frac{n_{sorb}}{n_{free}} \right) \times \frac{1}{c_{DOC}} = \frac{c_{sorb}}{c_{free}} \quad \text{in mL g}^{-1} \quad (1)$$

where  $n_{sorb}$  and  $n_{free}$  are the amounts of sorbed and freely dissolved fractions in arbitrary units, respectively,  $c_{DOC}$  is the concentration of dissolved organic sorbent in the applied DHS solution (g DOC per mL water) and  $c_{sorb}$ ,  $c_{free}$  are the concentrations of the sorbed

and the freely dissolved solute fractions (g sorbed solute per g DOC and g freely dissolved solute per mL water, respectively).

Only a small number of observations has been made so far, which are not in conformity with the partition model for mechanism of interactions between DHS and HOCs. One of the most significant finding is the non-linear sorption of pentachlorobenzene (QCB) on a dissolved peat HA (Schlebaum et al., 1998). Schlebaum et al. (1998) results show the presence of a fast-desorbing, labile fraction and a slowly desorbing, non-labile fraction. The authors speculate that the non-labile fraction is a consequence of a change of conformation of the HA after the binding of QCB. This structural change leads to entrapment of the sorbate within the HA structure. The residual fraction of QCB was found to be about 1.3 to 3.7% of its initial concentration (0.1 to 0.8 mg g<sup>-1</sup> HA). This means that more than 95% of the bound QCB fraction could be assigned to the labile fraction, which obeys the partition mechanism. However, the authors could not find a model able to describe all their data.

### **1.3. Experimental methods for measuring interaction of solutes with dissolved humic substances (DHS)**

When sorption of HOCs from the aqueous phase to particulate sorbents is measured, simple phase-separation techniques, such as centrifugation have proved to be sufficient. For dissolved sorbents, such a phase separation is more complicated and may affect the sorption equilibrium. Therefore, when one is measuring interactions of solutes with dissolved sorbents, for example DHS, it is necessary to evaluate carefully the experimental methods to be applied (Kopinke et al., 1999; Mackenzie et al., 2002).

The predominant customary techniques have been discussed in (Kopinke et al., 1999; Mackenzie et al., 2002) and are listed below:

- the fluorescence quenching technique (FQT),
- the fast solid-phase extraction (SPE) or
- reversed phase (RP) method,
- flocculation,
- solubility enhancement,
- dialysis and the gas-purging or
- headspace-partitioning method.

However, all of the methods applied so far are able to trace sorption-desorption processes in the time-scale of minutes to hours or days.

The two most frequently used methods for studying sorption on DHS are solid-phase microextraction (SPME) and fluorescence quenching technique (FQT).

### 1.3.1. Fluorescence quenching technique (FQT)

Fluorescence quenching technique (FQT) is based on the quenching of the fluorescence of a fluorophore (e.g., polycyclic aromatic hydrocarbons (PAHs)) interacting with dissolved polymers such as DHS, while the freely dissolved fraction is not affected (Figure 3).

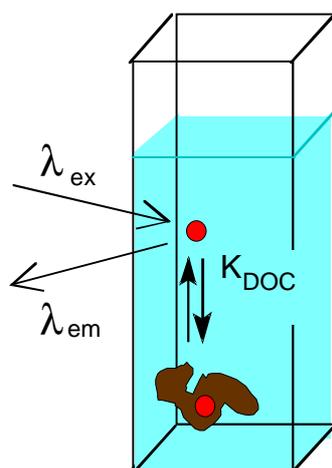


Figure 3. Application of fluorescence quenching technique (FQT) to study sorption phenomena on dissolved sorbents, where  $\lambda_{ex}$  and  $\lambda_{em}$  are emitted and excited wavelength, respectively. (Adapted from Kopinke et al., 2000).

The fluorescence intensity is considered to be measure of the concentration of the freely dissolved fluorophore. Therefore,  $K_{DOC}^{FQT}$  is a concentration-based coefficient (Kopinke et al., 1999; Kopinke et al., 2000; Mackenzie et al., 2002).

$$K_{DOC}^{FQT} = \left( \frac{F_0}{F} - 1 \right) \times \frac{1}{C_{DOC}} = \frac{C_{sorb}}{C_{free}} \quad (2)$$

where  $F_0$  and  $F$  are the fluorescence of reference sample without DHS and sample with DHS, respectively,  $c_{\text{DOC}}$  is the concentration of dissolved organic sorbent in the applied DHS solution and  $c_{\text{free}}$  are the concentrations of the sorbed and the freely dissolved solute fractions, respectively.

The interpretation of the results was found to be impaired by considerable experimental problems. One of the problem may result from the strong absorption of excitation and fluorescence light by the polymer (the inner filter effect), which has to be corrected for. Furthermore, the applicability of the method is limited to fluorescence-active compounds, it is a single-component method (i.e., mixtures of analytes in a sample cannot be measured), and the assumption of the formation of a “dark complex” between fluorophore and DHS is not undisputed. Moreover, the sorbed state is operationally defined by the FQT method (Figure 4): the sorbed fraction includes all solute molecules which are sufficiently close to the sorbent to be quenched. In order to explain the differences in KDOC values determined by means of FQT and SPME it has been hypothesized that different types of reversible interactions between pollutant and DHS can exist, i.e. inner sphere and outer sphere binding. FQT detects both interactions between DHS and fluorophore in the inner sphere of DHS, which is responsible for strong binding of solutes, as well as in outer sphere – responsible for weak binding (Kopinke et al., 2000; Mackenzie et al., 2002).

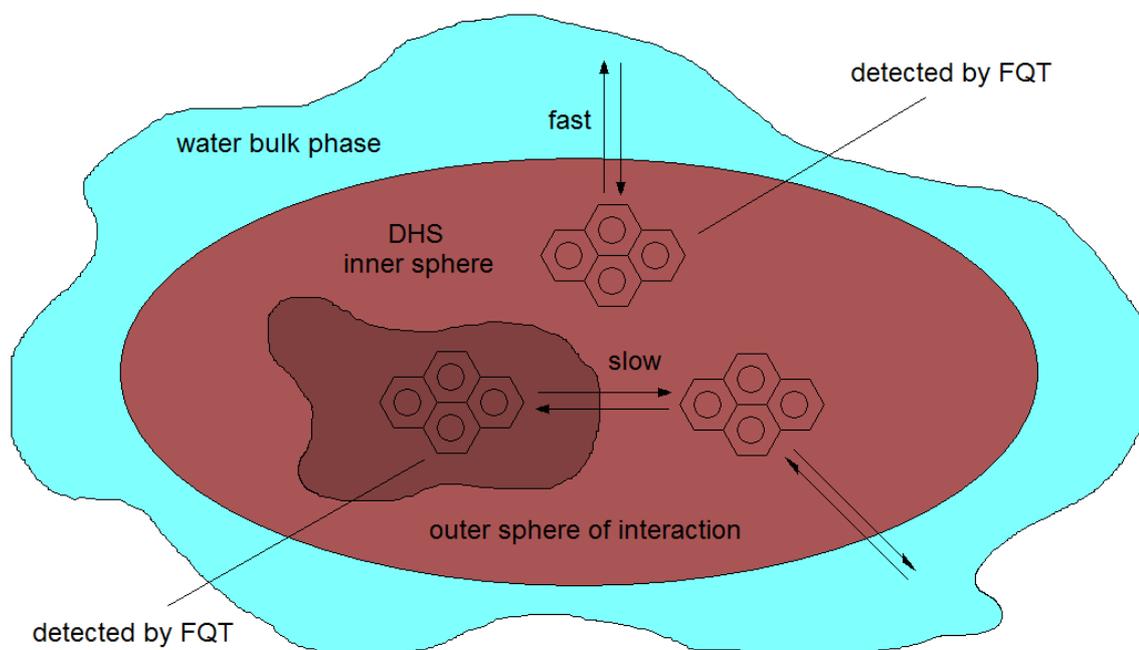


Figure 4. Schematic presentation of different sorbate states and their determination by fluorescence quenching technique (FQT). (Adapted from Kopinke et al., 2000).

On the other hand, the method is very sensitive and can be used for time-resolved measurements, which may be useful for studying sorption kinetics (Kopinke et al., 1999; Kopinke et al., 2000; Mackenzie et al., 2002). But mixing of solutions in order to initiate adsorption or desorption steps requires at least more than 10 s before the first measurements can be done. Thus, FQT is not suitable for tracing very fast sorption–desorption processes of organic compounds on and from DHS.

### 1.3.2. Solid-phase microextraction technique (SPME)

In contrast to FQT, which is limited to certain groups of compounds and/or is only applicable under specific experimental conditions to avoid problems inherent to the method used, the solid-phase microextraction (SPME) proved to be an attractive alternative for sorption measurements.

SPME is a very efficient analytical method for the extraction of organic compounds of environmental significance which was introduced and pioneered by Pawliszyn and co-workers in the early 1990s (Arthur and Pawliszyn, 1990). SPME uses a short piece of a fused silica fiber coated with a polymeric stationary phase. Analytes partition into the coating until equilibrium is reached between the coating and the fluid or air sample. Subsequently, the extracted analytes are thermally desorbed in the injector of a gas chromatograph (GC) for analytical separation and quantification. SPME can be applied to measure the distribution of chemicals in different speciation states. The standard SPME apparatus and procedures can be applied to measure free concentrations of a target compound spiked into pure water and spiked into water containing another pseudophase, such as DHS. Based on a comparison of results obtained for the two samples, the partitioning of the target analyte between water and the pseudophase is calculated (Poerschmann et al., 1997a). The application of SPME for measuring sorption coefficients on DHS was first described by Kopinke et al. in 1995 and later verified by Poerschmann et al. (1997a; b) and Georgi (1998). The SPME approach to determine sorption on DHS is based on the valid assumption that the SPME fiber samples only the freely dissolved analyte fraction ( $C_{\text{free}}$ ) rather than the fraction bound to the DHS matrix ( $C_{\text{bound}}$ ), thus allowing the determination of  $K_{\text{OM}}$  (or  $K_{\text{DOC}}$ ) data (Poerschmann and Kopinke, 2001).

However, the difference between FQT and SPME methods is fact, that they produce different types of sorption coefficients: concentration and activity-based

coefficients. The FQT measures a concentration proportional signal, the fluorescence intensity. Therefore,  $K_{DOC}^{FQT}$  is a concentration-based coefficient. On the other hand, SPME measures an activity proportional signal, the amount of extracted solute. Hence,  $K_{DOC}^{SPME}$  is an activity-based coefficient. Moreover, it was assumed that in contrast to FQT, SPME detects only interactions between DHS and fluorophore in the inner sphere of DHS (Figure 4) (Georgi, 1998; Kopinke et al., 1999; Kopinke et al., 2000; Kopinke et al., 2002).

The extraction of the analytes into the SPME fiber can be done from the gas phase using an analyte dissolver (headspace mode) as well as directly from the solution (direct mode) (Figure 5). (Georgi, 1998; Kopinke et al., 1999; Kopinke et al., 2000).

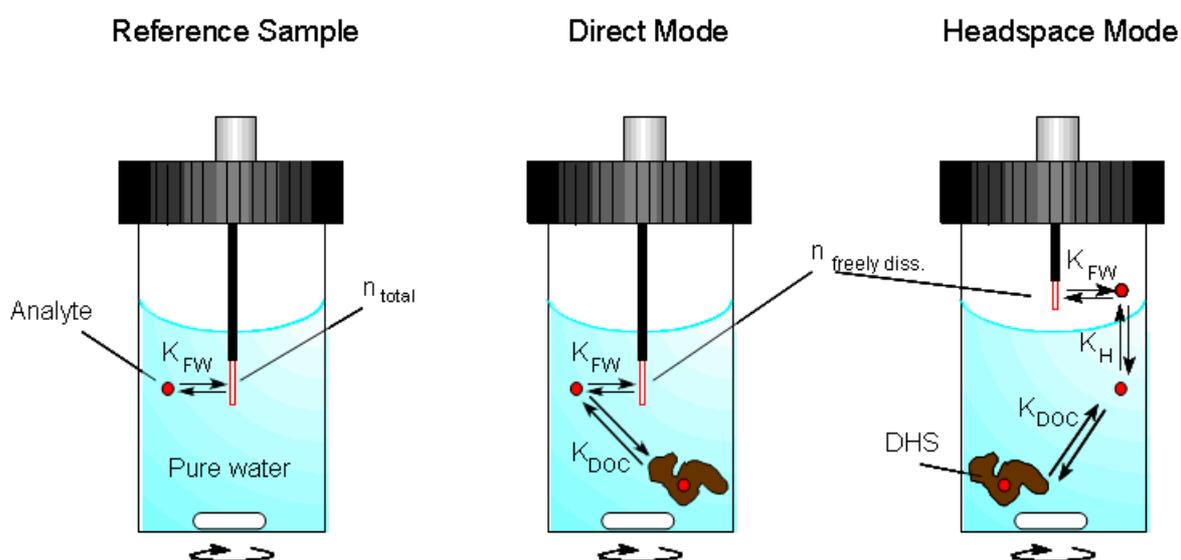


Figure 5. Solid-phase microextraction (SPME) modes and partition equilibria in the presence of dissolved humic substances (DHS). (Adapted from Kopinke et al., 2000).

The SPME method is applicable to a broad variety of different analytes and is not limited to a certain concentration range of DHS (Georgi, 1998). Moreover, in a mixture of xenobiotics sorption coefficients can be determined simultaneously in case of independent sorption processes. However, one of the limitations of the SPME method is its lack of speed due to the slow establishment of extraction equilibria. Sampling times up to 2 hours in the direct mode and up to 6 hours in the headspace mode were necessary in order to reach the extraction equilibrium with a 7  $\mu\text{m}$  polydimethylsiloxane (PDMS) fiber for pyrene. This makes the conventional equilibrium

SPME method inappropriate for measuring the kinetics of relatively fast processes. Quantitative measurements are possible under non-equilibrium conditions, however, this cannot be guaranteed with DHS since they can affect the uptake rate of the analyte into the fibre (Georgi, 1998; Poerschmann et al., 1997b). Poerschmann et al. (1997a) performed a fast SPME by using 100  $\mu\text{m}$  PDMS fiber and 10 s extraction time, combined with a fast GC analysis (10 s desorption time in the GC injector). In such way, it was possible to complete an SPME analysis in less than one minute. A fast direct SPME method was further used by Georgi (1998) for studying the kinetics of interactions between DHS and some PAH. They applied 30 s sampling time in combination with deuterated solutes. The time course of the isotope ratios of the extracted solute mixtures revealed the kinetics of the sorption process.

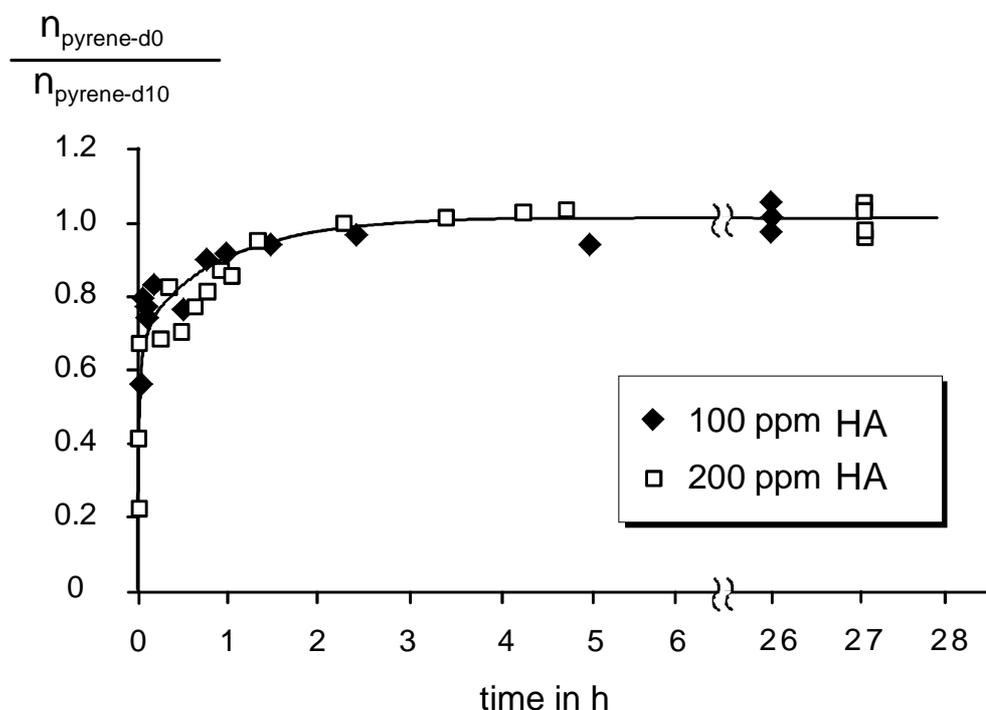


Figure 6. Kinetics of sorption of pyrene on humic acid (HA). (Adapted from Georgi, 1998).

The results show that about 70% of the pyrene sorption proceeded rapidly but than it takes up to 2 h until the process is complete (Figure 6). (Georgi, 1998). This fast process could not be monitored by the applied SPME technique due to its limited time resolution.

## 1.4. Impact of DHS on mass transfer of pollutants

DHS belong to the most widespread natural surface-active compounds which exist in all terrestrial and aquatic environments. Because of the presence of both hydrophilic (e.g. carboxylic and phenolic groups) and hydrophobic (e.g. aromatic rings and aliphatic chains) moieties in their structure, DHS are amphiphilic compounds. This amphiphilic character contributes to their significant affinity toward water phase boundaries such as those with the atmosphere, particles, bubbles and sediments (Hayase, 1992; Hayase and Tsubota, 1983; Lenhart and Saiers, 2004; Murphy et al., 1992; Spark et al., 1997). DHS are known to accumulate at the interface between surface water and atmosphere (surface microlayer) together with other classes of surface active compounds (e.g. proteins and lipids) (Figure 7). The formation of a thin film of surface active compounds on the water surface has been shown to retard gas exchange to the atmosphere for water soluble gases, i.e. CO<sub>2</sub> or O<sub>2</sub> (Frew, 1997). This effect is attributed to a change in the hydrodynamic characteristics of water motion at the interface (damping of eddies). Goldman et al. (1988) have shown that, under turbulent conditions, the addition of two synthetic surfactants (polyethylene oxide and oleyl alcohol) to distilled water and seawater led to reduction in oxygen evasion at the air-liquid interface. The oxygen exchange rate coefficient, relative to that of distilled water, asymptotically approached a lower limit of 50% as surfactant concentration was increased (Goldman et al., 1988).

It can be expected that the hydrodynamic retardation effect of surface films applies not only for gases but also for organic compounds. Thus, it is hypothesized that DHS can affect the surface by forming monomolecular barriers on surfaces that impede molecular diffusion across the interface. On the other hand, DHS can change the hydrodynamic characteristics of water motion at the interface and within the boundary layer below the surface giving rise to a smoothing of microwaves.

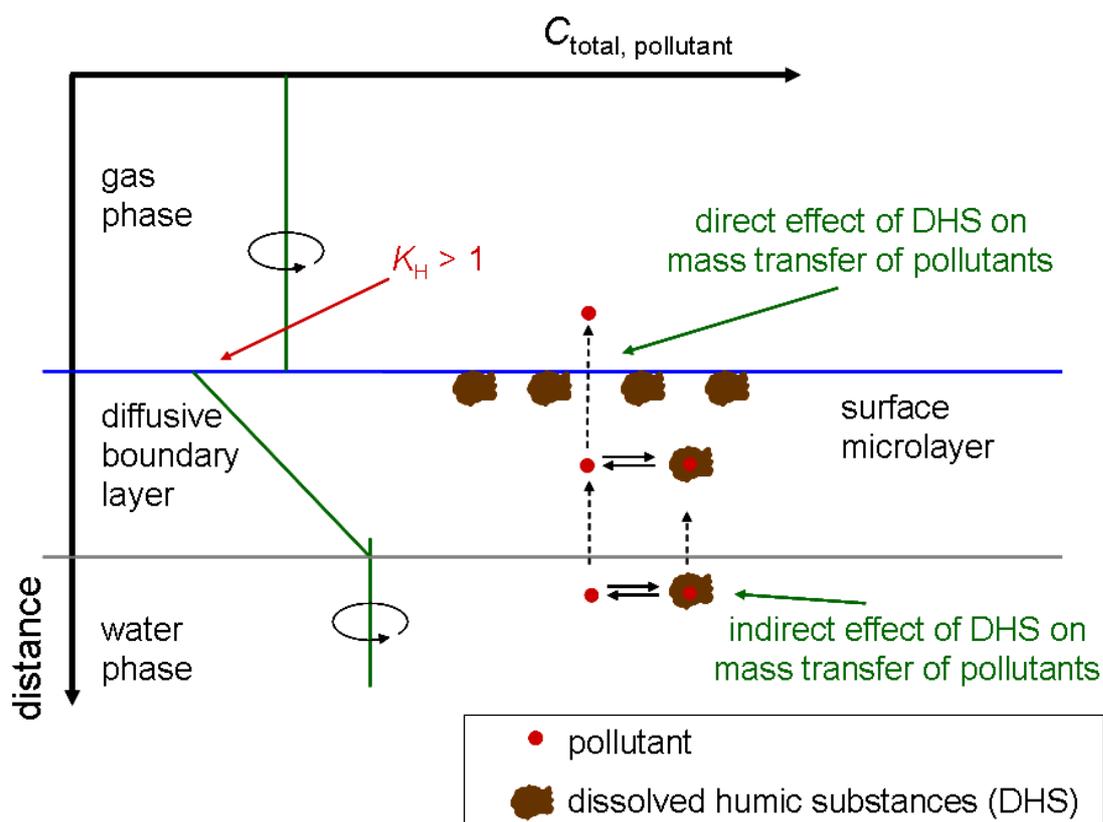


Figure 7. Possible effects of dissolved humic substances (DHS) on mass transfer of pollutants through the aqueous boundary layer.

With respect to the water-air phase transfer of persistent organic pollutants even more complicated mechanisms must be expected, including sorption to DHS (Figure 7), which has not been studied so far. Various studies have shown that sorption to DHS can affect the transport rate of hydrophobic organic compounds between water and solid sorbent phases. This includes acceleration of uptake and release of PAHs and polychlorinated biphenyls (PCBs) by solid phase microextraction fibers (Kopinke et al., 2000; Ter Laak et al., 2009). In addition, Mayer et al. (2007) in experiments with a source-sink system consisting of two PDMS plates separated by an unstirred water layer revealed an increased diffusive conductivity of water in the presence of various types of dissolved sorbents, including DHS (Mayer et al., 2005; Mayer et al., 2007). Furthermore, the rate of uptake or biodegradation of hydrophobic pollutants by aqueous organisms can also be accelerated in the presence of DHS and other dissolved sorbents (Smith et al., 2009; Ter Laak et al., 2009). Moreover, Smith et al. (2011) observed that DHS-enhanced mass transfer of PAHs between two liquid phases, i.e. from nonaqueous phase liquids (NAPLs) into the aqueous phase. In general, these

effects are ascribed to the occurrence of an additional diffusion flux due to the presence of a pollutant fraction which is reversibly bound by the dissolved sorbent (shuttle effect).

## **1.5. Aims and objective of the thesis**

For environmentally relevant processes such as adsorption or chemical and biotic degradation of pollutants, diffusion through boundary layers can be the rate-limiting step. It is well known that organic compounds with surface active properties are enriched at the phase boundary between water and atmosphere or between water and solid surfaces such as sediments and biota. DHS belong to the most widespread natural surface-active substances which exist in all terrestrial and aquatic environments. However, not much information is available on the effect of DHS in the surface microlayer (Figure 7). Therefore, the first aim of this thesis is to study the influence of DHS on the mass-transfer of volatile organic compounds at the air-water boundary layer by means of laboratory experiments under well-defined conditions.

Furthermore, DHS are able to sorb hydrophobic pollutants and indirectly affect the mass transfer of organic pollutants through the air/water interface (Figure 7). Therefore, the second principal aim of this thesis is to check possible additional sorption-induced effects of DHS at this phase boundary. Two scenarios will be distinguished: if I) pollutant activity in the aqueous phase is reduced due to sorption to DHS and II) sorption to DHS does not lead to a change in pollutant activity due to redelivery of the pollutant into the aqueous phase from a non-depleting source.

Nevertheless, sorption-induced effects of DHS on pollutant transport through stagnant water boundary layers depend strongly on the rate of uptake and release of the pollutant by the humic macromolecules. Only sufficiently labile complexes can contribute to mass transfer. However, all of the methods applied so far are able to trace sorption-desorption processes in the time-scale of minutes to hours. But, when looking at the microscale, processes occurring in the sub-second to second scale can become highly relevant. There is no experimental technique available or has been already applied for measuring the kinetics of sorption and desorption processes with a time resolution  $\leq 10$  s. In order to be able to study these processes in the required time resolution, a new experimental technique is needed. Therefore, the third aim of this thesis is to develop a technique in a way that enables us to measure the kinetics of

sorption-desorption processes between organic compounds and DHS in a wide range of time resolution, from the sub-second up to the minute or even hour range.

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## 2. Overview of the Following Manuscripts

The first manuscript presented in this thesis, which is entitled "Influence of dissolved humic substances on the mass transfer of organic compounds across the air-water interface" deals with an experimental approach which aims to describe direct effects of DHS on the diffusion-controlled mass transfer of volatile organic pollutants, such as benzene as well as cyclohexane, through the air/water interface. The effect arises from the fact that DHS are surface active compounds and thus accumulate in the surface microlayer adjacent to the interface. The applied DHS included natural humic (SRHA) and fulvic acids (SRFA) from surface water (Suwannee River) as well as a commercial humic acid (Roth) (CHA). Mass transfer coefficients of model compounds for transport from water into the gas phase were determined experimentally using two different approaches: a static and a dynamic system. The difference in the two experimental systems lies in the fact that the static system was closed while in the dynamic system the gas phase was continuously purged by a flow of helium. Mass transfer coefficients were determined from the rate of equilibration between water and gas phase (static system) and from the rate of depletion of target compounds from the system (dynamic system). The concentration of the model compounds in the gas phase was monitored by headspace analysis and detected using GCMS. The role of possible influencing factors such as degree of agitation, DHS concentration, pH and ionic strength of the water were studied.

The experimental results show that mass transfer resistance on the water side of the gas- or air-water interface can be significantly affected by environmentally relevant DHS concentrations and the retardation effect increased with increasing DHS concentration. In presence of DHS we observed slower equilibration between water and gas phase in the static system and a slower depletion of the compounds from the water in the dynamic system. The magnitude of the retardation effect on water-gas exchange was compared for Suwannee River fulvic and humic acid, a commercially available leonardite humic acid and two synthetic surfactants. The observed results are in accordance with the concept of hydrodynamic characteristics of water motion at the air-water interface and thus impede surface renewal.

The second manuscript entitled "Sorption-induced effects of humic substances on mass transfer of organic pollutants through aqueous diffusion boundary layers: the example of water/air exchange", continually addresses the problem of influence of DHS on the mass transfer process. It is known, that water-gas exchange is also relevant for

the fate of pollutants with higher hydrophobicity in the environment. Several authors have emphasized that the surface microlayer, which is formed due to accumulation of amphiphilic organic molecules at the water-air interface of all natural water bodies, might affect air-water exchange of HOCs due to sorptive interactions. However, mainly field studies have been conducted in this research area. Therefore in this paper the results of the lab-scale experiments on the sorption-based (indirect) effects of DHS on the mass transfer process of organic pollutants through the air/water interface are summarized. Two organic compounds with moderate hydrophobicity (benzene and n-octane) were applied in order to differentiate between hydrodynamic and sorption-induced effects of DHS on water-gas exchange. For comparison also a synthetic surfactant was used. Using homogeneous aqueous solutions with and without dissolved sorbents reflects the case where sorption decreases the chemical activity of organic compound in the aqueous phase (reduced-activity system). Passive dosing with loaded silicone sheets was applied in the constant-activity system. The experimental results show that DHS and surfactants can affect water-gas exchange rates by the superposition of two mechanisms: (1) hydrodynamic effects due to surface film formation ("surface smoothing"), and (2) sorption-induced effects. Whether sorption accelerates or retards mass transfer depends on its effect on the thermodynamic activity of the pollutant in the aqueous phase. Mass transfer will be retarded if the activity (or freely dissolved concentration) of the pollutant is decreased due to sorption. If it remains unchanged (e.g., due to fast equilibration with a sediment acting as a large source phase), then DHS and surfactant micelles can act as an additional shuttle for the pollutants, enhancing the flux through the boundary layer.

The third manuscript "Kinetics of desorption of organic compounds from dissolved organic matter", introduces the "Time-resolved in-tube solid phase micro-extraction (TR-IT-SPME)" as a new simple and easy to handle experimental technique for the measurement of the interaction kinetics between hydrophobic organic compounds and DHS or other dissolved sorbents (like surfactant micelles, proteins or other biological macromolecules). The method is based on a fast solid-phase extraction of the freely dissolved fraction of a solute when the solution is flushed through a polymer-coated capillary. The extraction interferes with the solute-DOM sorption equilibrium and drives the desorption process. Solutes which remain sorbed to DOM pass through the extraction capillary and can be analyzed afterwards. In this manuscript basic experiments for the verification of this new method are summarized and the theoretical background for the derivation of rate constants is discussed. Also the results of TR-IT-

SPME experiments on the rate of sorption/desorption processes on DHS are discussed in this paper. The TR-IT-SPME was applied to two humic acids and a surfactant as sorbents together with pyrene, phenanthrene and 1,2-dimethylcyclohexane as solutes. The results give evidence for a two-phase desorption kinetics: a fast desorption step with a half-life of less than 1 s and a slow desorption step with a half-life of more than 1 min. For aliphatic solutes, the fast-desorbing fraction largely dominates, whereas for polycyclic aromatic hydrocarbons such as pyrene, the slowly desorbing, stronger-bound fraction is also important. The difference in the behavior of PAHs and non-aromatic compounds (which do not show a slow desorption phase) can be interpreted in terms of the type of interactions between DHS and various compound classes.

There is no other experimental technique available or has been already applied for measuring the kinetics of sorption and desorption processes with a time resolution in the lower second range. The TR-IT-SPME method offers a broad application field since it allows to study sorption-desorption kinetics not only for DHS but also for other dissolved sorbents, like e.g. micelles or biological macromolecules.

### **3. Influence of Dissolved Humic Substances on the Mass Transfer of Organic Compounds across the Air-Water Interface**

Ksenia Ramus, Frank-Dieter Kopinke, Anett Georgi

Chemosphere 2012, 86, 138-143.

#### **Abstract**

The effect of dissolved humic substances (DHS) on the rate of water–gas exchange of two volatile organic compounds was studied under various conditions of agitation intensity, solution pH and ionic strength. Mass-transfer coefficients were determined from the rate of depletion of model compounds from an apparatus containing a stirred aqueous solution with continuous purging of the headspace above the solution (dynamic system). Under these conditions, the overall transfer rate is controlled by the mass-transfer resistance on the water side of the water–gas interface. The experimental results show that the presence of DHS hinders the transport of the organic molecules from the water into the gas phase under all investigated conditions. Mass-transfer coefficients were significantly reduced even by low, environmentally relevant concentrations of DHS. The retardation effect increased with increasing DHS concentration. The magnitude of the retardation effect on water–gas exchange was compared for Suwannee River fulvic and humic acids, a commercially available leonardite humic acid and two synthetic surfactants. The observed results are in accordance with the concept of hydrodynamic effects. Surface pressure forces due to surface film formation change the hydrodynamic characteristics of water motion at the water–air interface and thus impede surface renewal.

#### **1. Introduction**

Dissolved humic substances (DHS) are the most widespread natural polyelectrolytes in all terrestrial and aquatic environments, since they occur in surface and groundwater as well as in soil pore water. They are a heterogeneous mixture of components with a wide range of molecular weights and different chemical moieties. Due to the presence of both hydrophilic (e.g. carboxylic and phenolic groups) and

hydrophobic (e.g. aromatic rings and aliphatic chains) structural units in DHS macromolecules, they are amphiphilic compounds. This amphiphilic character contributes to their significant affinity toward water phase boundaries such as those with the atmosphere, particles, bubbles and sediments (Hayase and Tsubota, 1983; Hayase, 1992; Lenhart and Saiers, 2004; Murphy et al., 1992; Spark et al., 1997). DHS are known to reduce the surface tension in an aqueous solution (Anderson et al., 1995; Hayase and Tsubota, 1983; Hayase, 1992; Kopinke et al., 2002). Furthermore, DHS are able to interact with hydrophobic pollutants. In contrast to synthetic surfactants, micelle formation is not a pre-requisite for sorption of hydrophobic pollutants by DHS. For very hydrophobic compounds, a significant sorption effect is already observed at DHS concentrations as low as  $10 \text{ mg L}^{-1}$  (Kopinke et al., 2001; Ter Laak et al., 2005; Durjava et al., 2007). It is a generally accepted view that DHS play an important role for transport, bioavailability and biodegradability of xenobiotics in the environment. Adsorption of DHS at the solid surfaces of sediments not only changes the solid surface properties and reactivity, but also strongly influences the fate of contaminants in the aquatic environment. Thus, the process of sorption of DHS and their associated contaminants at the solid-water interface has received much attention. Comparatively little effort has been devoted to the behaviour of DHS macromolecules themselves at air-water interfaces. However, these interfacial reactions of DHS can have important implications for the fate of xenobiotics in natural environments with extensive air-water interfaces. In addition, they can also play a role in engineered systems, e.g. in water treatment by air stripping.

It is known that organic films of surface-active compounds on the water surface can retard gas exchange to the atmosphere for water-soluble gases, e.g.  $\text{CO}_2$  or  $\text{O}_2$  (Frew, 1997). For instance, Goldman et al. (1988) have shown in a series of laboratory gas exchange studies that, under turbulent conditions, the addition of two synthetic surfactants (polyethylene oxide and oleyl alcohol) to distilled water and seawater led to reduction in oxygen evasion at the air-liquid interface. The oxygen exchange rate coefficient relative to that of distilled water asymptotically approached a lower limit of 50% as surfactant concentration was increased.

Two basic mechanisms have been discussed in order to explain the retardation of gas exchange by surface films: (i) direct surface effects from closely packed, rigid monolayers which create an additional mass-transfer resistance for molecular diffusion across the interface (Jarvis, 1967), and (ii) hydrodynamic effects. According to Davies (1966), the presence of surface films can change the hydrodynamic characteristics of

water motion at the interface and within the boundary layer below the surface. In effect, the thickness of the viscous and diffusive sub-layers increase, the rate of surface renewal is reduced and gas exchange is retarded (Davies, 1966; Davies, 1972). In Schwarzenbach et al. (2003), this effect is described as hydrodynamic damping or surface-calming.

Under turbulent conditions, such as are typical for the sea surface, the barrier effect (mechanism (i)) is not considered to be important since it requires the existence of condensed, solid-type surfactant films, which would be dispersed under such conditions. Films of well-soluble surfactants are too permeable to offer significant liquid-phase resistance (Frew, 1997).

In practice, Davies' model of a hydrodynamic effect has been widely accepted and used to explain the drastic reduction in gas exchange observed in the presence of various synthetic surfactants and natural surface-active compounds (e.g. exudates of phytoplankton and algae) in a number of laboratory studies (for a review see Frew, 1997).

It can be expected that the hydrodynamic retardation effect of surface films applies not only for gases but also for organic compounds. However, this hypothesis has not yet been experimentally proven and there is still a need for experimental data in order to elucidate and quantify the underlying mechanisms. A review of the currently available methods for estimating overall mass-transfer coefficients for air/water exchange from surface water as a function of wind speed is given in (Loux, 2008). Wurl et al. (2006) conducted a field study with simultaneous measurements of organochlorine compounds such as hexachlorocyclohexane in seawater, the sea-surface microlayer (SML) and the atmosphere in order to study the flux of these compounds between ocean and atmosphere. The authors pointed out that hydrodynamic effects caused by surface film formation and sorption-induced effects due to the enrichment of dissolved organic matter in the SML should be considered for the air-sea exchange of the hydrophobic organochlorine compounds studied. They emphasized the need for further experimental and modelling studies in order to allow a parameterization of these processes (Wurl et al., 2006).

Within the present study, the influence of DHS on the mass-transfer of organic compounds at the air-water boundary layer is investigated by means of laboratory experiments under well-defined conditions. The DHS under study include a commercially available humic acid (CHA) which was extracted from leonardite, and two natural aquatic humic substances. In addition, two synthetic surfactants and a

water-soluble polymer were used for comparison. Sorption of the model compounds to the DHS was experimentally determined by means of a headspace analysis method which is based on the proportionality between the equilibrium gas phase concentration and the concentration of the freely dissolved analyte in the water phase.

## **2. Material and methods**

### **2.1. Chemicals**

Benzene, cyclohexane, sodium chloride and sodium dodecyl sulphate (SDS) were obtained from Merck (Germany), poly(acrylic acid) (PAA) (average molecular weight  $2000 \text{ g mol}^{-1}$ ) from Sigma-Aldrich (Germany) and 4-octyl phenol polyethoxylate (Triton X 100) from J.T. Baker (Germany). All the chemicals and organic solvents were obtained in the highest available grade and used as received.

### **2.2. Humic Substances**

The CHA was purchased from Carl Roth GmbH, Karlsruhe, Germany. Suwannee river humic acid (SRHA) and fulvic acid (SRFA) were purchased from the International Humic Substance Society (IHSS), St. Paul, USA. Aqueous solutions of the humic acids (HAs) were prepared by dissolving the solid HAs without previous purification in dilute NaOH. After further dilution with deionized water, the pH of the solutions was adjusted by adding dilute HCl. SRFA was dissolved in deionized water and the pH was adjusted by adding dilute NaOH.

### **2.3. Experimental procedure**

#### **2.3.1. Determination of partition coefficients**

Partition coefficients of the organic compounds between water and DHS were determined by means of headspace analysis. The solution containing the sorbent and an aqueous reference solution of the analyte without sorbent were analysed under identical conditions, then the corresponding GC peak areas were compared. Erlenmeyer flasks with a total volume of about 300 mL were filled with an appropriate

volume of the aqueous solutions (about 290 mL), so that the volume of the gas phase was 10 mL. After closing the flasks with Mininert™ valves, the solutions were spiked with 100 mg L<sup>-1</sup> and 30 mg L<sup>-1</sup> of benzene and cyclohexane, respectively, using a methanolic stock solution. After overnight equilibration, the concentration of the model compounds in the gas phase was determined by means of manual headspace sampling using gas-tight microlitre syringes (25 µL) and GC-MS analysis (GCMS-QP 2010, Shimadzu, Germany) in the selected ion monitoring mode (SIM). The conditions were as follows: split ratio 1:60, 0.8 mL min<sup>-1</sup> He flow, column: DB-1 (30 m, 0.25 mm, 25 µm, J&W Scientific), injector, oven and ion source temperatures were 100 °C, 70 °C and 200 °C, respectively. The standard deviation of the single values for the headspace GC-MS analysis method was in the range of 3-5%.

Partition coefficients ( $K_{\text{DOC}}$ ) were calculated according to Eq. (1) (for derivation cf. Suppl. Mat., Section B):

$$K_{\text{DOC}} = \left( \frac{A^{\text{ref}}}{A^{\text{DHS}}} - 1 \right) \times \frac{1}{c_{\text{DOC}}} \times \left( \frac{K_{\text{H}} \times V_{\text{g}}}{V_{\text{l}}} + 1 \right) \quad (1)$$

where  $A^{\text{ref}}$  and  $A^{\text{DHS}}$  are the peak areas for the analyte obtained by means of headspace GC analysis of the reference solution without DHS and the DHS solution, respectively,  $c_{\text{DOC}}$  (kg L<sup>-1</sup>) is the concentration of dissolved organic carbon in the applied DHS solution,  $K_{\text{H}}$  is the dimensionless Henry's law coefficient,  $V_{\text{g}}$  (L) is the gas phase volume and  $V_{\text{l}}$  (L) is the volume of the aqueous phase.

The dissolved organic carbon (DOC) content was determined by means of a custom-made carbon analyser based on a high-temperature combustion (800 °C) of the aqueous samples and NDIR detection of CO<sub>2</sub>. Inorganic carbon was removed prior to analysis by acidification and purging of the solution with nitrogen. Throughout the manuscript the concentration of DHS in solution is given as mass concentration  $c_{\text{DHS}}$  (weight of air-dry sample of humic material added into a certain volume of water). This mass concentration is related to the DOC concentration of the DHS solution by the factor  $f_{\text{OC}} = \text{DOC}/c_{\text{DHS}}$ . This factor has a value of 0.50 for CHA, 0.48 for SRFA and 0.45 for SRHA.

### 2.3.2. Surface tension measurements

Surface tension measurements were performed by means of a micro-stalagmometric method, based on weighing drops of a solution flowing out of the flat needle of a microsyringe (500  $\mu\text{L}$ ). 20 droplets of the sample were captured in a small vial and weighed afterwards on a microbalance. The weight of a droplet is inversely proportional to its surface tension.

### 2.3.3. Experiments on water-gas exchange using the dynamic system

Erlenmeyer flasks with screw caps and PTFE-lined septa were used, which were equipped with needles for continuous purging of the gas phase. 300 mL of the model solution were filled into the Erlenmeyer flasks and spiked with benzene (100  $\text{mg L}^{-1}$ ) and cyclohexane (30  $\text{mg L}^{-1}$ ). The following model solutions were applied: deionized water with and without addition of salts such as NaCl or  $\text{CaCl}_2$ , as well as solutions of DHS, surfactants or PAA. After overnight equilibration, 50 mL of the solution was removed, resulting in final liquid and gas phase volumes of 250 mL and 50 mL, respectively. The flask was then closed again with a screw cap and a PTFE-lined septum, through which two needles were inserted. The needles were positioned at different heights in order to avoid any short-circuiting of the gas flow. The needle in the upper position was connected to He supply via a gas flow controller (GFC, Bronckhorst Ruurlo, The Netherlands). At the start of each experiment, the gas phase of the flask was purged for 5 min with He ( $\dot{V}_g = 200 \text{ mL min}^{-1}$ ), avoiding any disturbance of the water surface. Mixing of the aqueous phase by magnetic stirring was then started, whereby purging of the gas phase was continued. The concentration of the model compounds in the gas phase was monitored by means of manual headspace sampling (100  $\mu\text{L}$ ) through the longer needle and GC-MS analysis. The first measurements were performed ( $t_0$ ) after 30 s mixing of the aqueous phase, and sampling was continued over a time period of 90 min. The mass-transfer coefficients were determined from the rate of depletion of benzene and cyclohexane from the system (see below). The experiments were conducted at ambient temperature ( $21 \pm 1.5 \text{ }^\circ\text{C}$ ).

### 3. Results and discussion

#### 3.1. Comparison of the methods

Experiments on the kinetics of water-gas exchange of benzene were conducted using two different model systems: a static and a dynamic system. The difference between these two model systems lies in the fact that the static system is closed, whereas in the dynamic system the headspace phase is continuously purged. Information on the mass-transfer rates of the model compounds can be derived either from the rate of equilibration between water and gas phase in the static system or from the rate of depletion of the model compounds from the dynamic system. Due to the fast equilibration of the target compounds between water and gas phase, only a limited number of useful data points (those in the non-equilibrium period) for each experiment could be obtained (for experimental details see Suppl. Mat.).

In contrast, the dynamic system allows the water-gas exchange to be followed over much longer time periods. Therefore, in combination with headspace sampling and GC-MS analysis, this setup is more appropriate for the precise determination of effective mass-transfer coefficients ( $k_L \times A$ ); these values will be discussed in detail in the following sections ( $k_L$  ( $\text{m s}^{-1}$ ) is the mass-transfer coefficient;  $A$  ( $\text{m}^2$ ) is the water-gas interface area). Nevertheless, the two experimental setups gave similar results: the presence of DHS hinders the transport of the organic molecules from the water to the gas phase, i.e. it leads to slower equilibration between water and gas phase in the static system (Fig. A1 in Suppl. Mat.) and slower depletion of the target compounds in the dynamic system (Fig. 1). In the dynamic experiments, we followed the depletion of the model compounds from the system by measuring the effluent concentration over time. This process can be described by a first-order kinetics:  $\ln (c/c_0)_{\text{gas}} = -k \times t$ , as shown for benzene in Fig. 1.

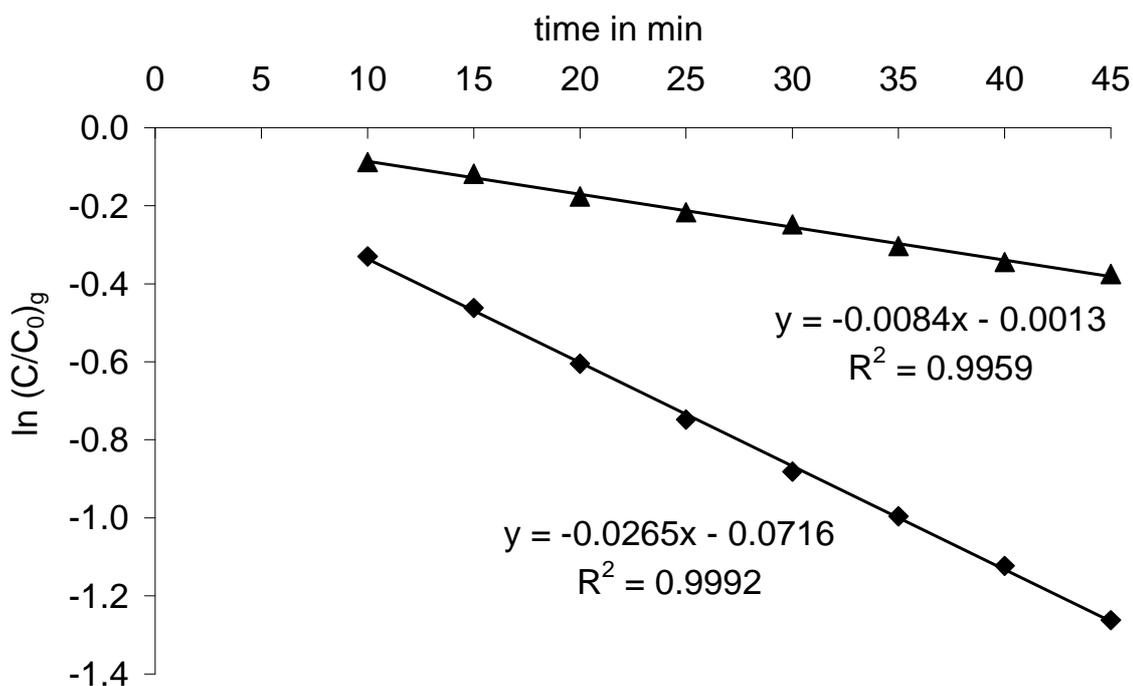


Fig. 1. Depletion of benzene from aqueous solution in the dynamic purge system in the absence (◆) and presence of CHA(▲)(conditions:  $c_{\text{CHA}} = 1 \text{ g L}^{-1}$ ,  $\text{pH} = 7$ ,  $c_{0,\text{benzene}} = 100 \text{ mg L}^{-1}$ , stirring speed  $700 \text{ min}^{-1}$ ).

Mass-transfer resistance in the dynamic system can be expected to be predominantly caused by the transport processes in the aqueous boundary layer. Due to the high gas flow rate and the resulting turbulence in the gas phase, the contribution of the gas boundary layer to the overall mass-transfer resistance should be negligible. This assumption is confirmed by the observation that benzene and cyclohexane, two compounds which differ largely in their Henry's law coefficients, show similar depletion rates in the dynamic experiments (for a more detailed discussion see Suppl. Mat., Section C).

In order to derive quantitative data about the mass-transfer rates, we applied the stagnant boundary layer model:

$$\dot{n} = k_L \times A \times (C_{\text{bulk}} - C_{\text{surface}}) \quad (2)$$

where  $\dot{n}$  is the flux of analyte ( $\text{mol s}^{-1}$ ),  $A$  the interface area ( $\text{m}^2$ ),  $k_L$  the mass-transfer coefficient ( $\text{m s}^{-1}$ ) and  $c_{\text{bulk}}$ ,  $c_{\text{surface}}$  are the analyte concentrations ( $\text{mol L}^{-1}$ ) in the liquid bulk phase and at the water surface respectively.  $k_L = D/\delta$  is usually defined as the ratio

of the analyte's diffusion coefficient  $D$  ( $\text{m}^2 \text{s}^{-1}$ ) in water and the thickness  $\delta$  (m) of the hydrodynamic (stagnant) boundary layer. Because  $k_L$  and  $A$  are hardly determinable independently, we use the product  $k_L \times A$  ( $\text{m}^3 \text{s}^{-1}$ ) as effective mass-transfer coefficient. This was determined from the slope ( $m$ ) of the linear regression for  $\ln(c/c_0)_g$  versus time ( $t$ ) according to Eq. (3).  $c$  and  $c_0$  are the analyte's concentrations in the purge gas flow at the times  $t$  and  $t = 0$ . Eq. (3) can be easily derived from Eq. (2) using Henry's law and mass balances, as is explained in detail in the Suppl. Mat.

$$\ln\left(\frac{c}{c_0}\right)_g = -\frac{1}{V_{\text{water}} \times \left(\frac{1}{\dot{V}_g \times K_H} + \frac{1}{k_L \times A}\right)} \times t = -m \times t \quad (3)$$

### 3.2. Effect of DHS type and concentration on mass-transfer kinetics

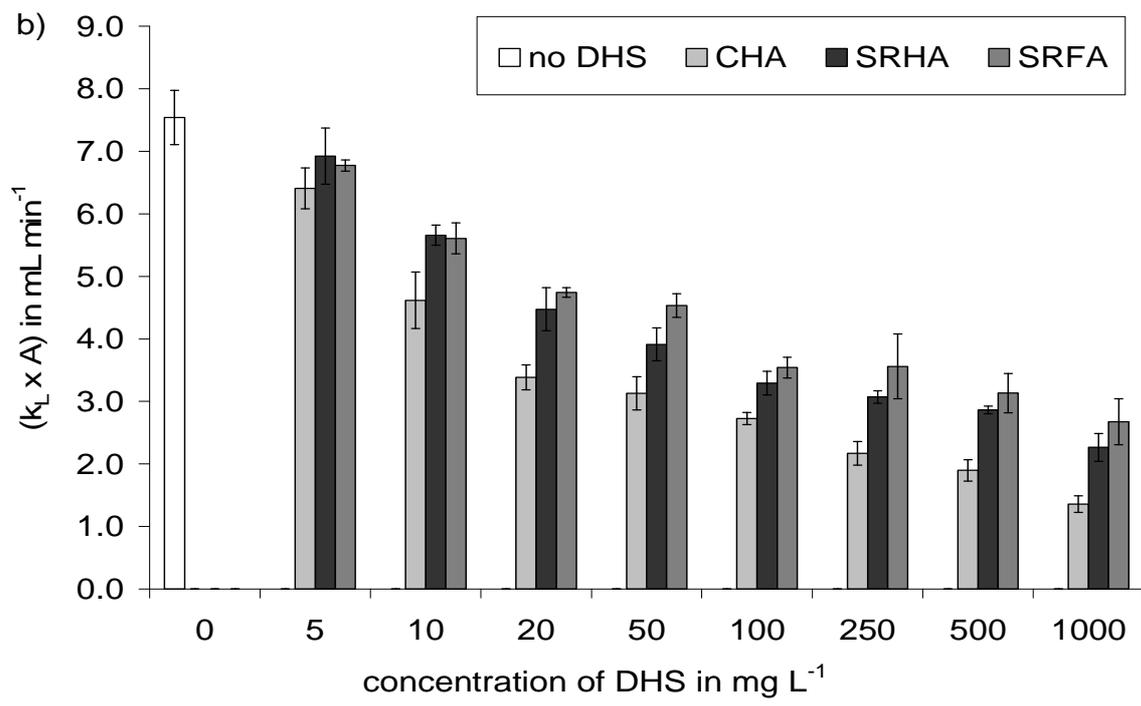
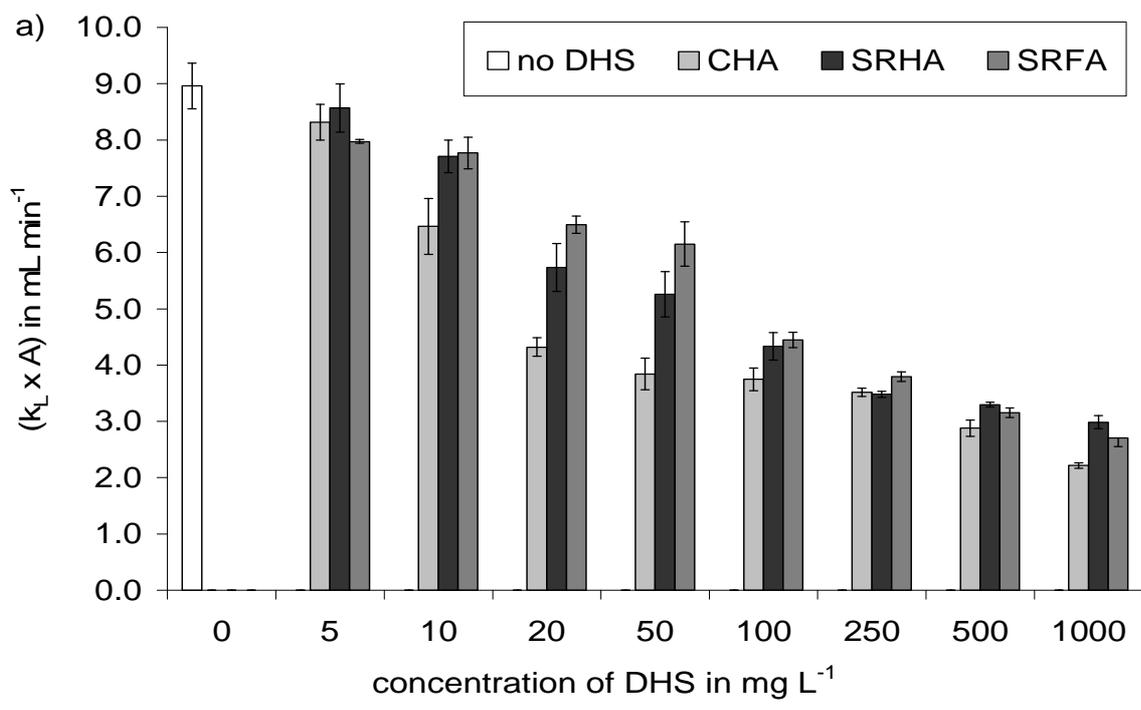
Water-gas exchange rates were studied at various concentrations of DHS having different properties with respect to molecular size and hydrophobicity. Natural humic substances extracted from water, such as SRHA and SRFA, generally have a lower molecular weight, are less polydisperse and more hydrophilic than the commercially available HAs such as those from Aldrich or Carl Roth GmbH, which are extracted from leonardite (Baalousha et al., 2006; Chin et al., 1997; Kopinke et al., 2001).

The experimental results show that effective mass-transfer coefficients of benzene and cyclohexane decrease with increasing concentrations of DHS (Fig. 2a and b). The maximum effect is a factor of three to four at the highest DHS concentration ( $1 \text{ g L}^{-1}$ ). Even at low, i.e. environmentally relevant, concentrations of DHS ( $10\text{-}20 \text{ mg L}^{-1}$ ), a significant retardation of the water-gas exchange of the model compounds benzene and cyclohexane was observed. An explanation of this effect is based on DHS accumulation at the air-water interface. The ability of DHS to decrease the surface tension of water, similar to that of surfactants, is well known (Anderson et al., 1995; Hayase and Tsubota, 1983; Hayase, 1992; Kopinke et al., 2002). In general, the surface tension of water decreases as the DHS concentration increases. However, the slope of the surface tension versus. concentration curve decreases at high concentrations (typically in the range of several  $\text{g L}^{-1}$  DHS), which has been interpreted in terms of aggregation phenomena (Guetzloff and Rice, 1994; Hayase and Tsubota, 1983). Reviewing the existing literature, Lenhart and Saiers (2004) came to the conclusion that, although

exceptions exist, the affinity for gas-water interfaces is generally higher for larger, more hydrophobic components of DHS than for smaller, more hydrophilic components. Surface tension measurements conducted in the present study are in agreement with this general conclusion. At DHS concentrations  $\leq 500 \text{ mg L}^{-1}$ , a measurable decrease in surface tension ( $\sigma$ ) was observed only for solutions of CHA, not for SRFA and SRHA ( $\Delta\sigma \leq 1\%$  compared to clean water (Vargaftik et al., 1983)). At a concentration of  $1 \text{ g L}^{-1}$  DHS, the surface tension was decreased by 2.0%, 2.6%, and 8.7% in case of SRFA, SRHA and CHA solutions, respectively. Obviously, DHS are less effective as tensides than typical synthetic surfactants.

The hindrance effect on mass-transfer follows the same trend, i.e. it is larger for CHA than for SRFA and SRHA (Fig. 2a and b). Among the two aquatic DHS, there is a slight trend towards a stronger effect in the case of SRHA. It is remarkable that SRHA and SRFA effect a significant reduction of water-gas exchange rates at concentrations  $\leq 500 \text{ mg L}^{-1}$ , where the effect on surface tension was insignificant. Goldman et al. (1988) described a similar behaviour for the rate of oxygen evasion from seawater samples compared to distilled water, where strong effects occurred even for samples with very small surface pressures ( $\leq 0.5 \text{ mN m}^{-1}$ , corresponding to  $\Delta\sigma \leq 0.7\%$ ).

Fig. 2c shows the ratio of the effective mass-transfer coefficients for cyclohexane and benzene at the highest DHS concentration of  $1 \text{ g L}^{-1}$ . The two compounds differ by more than one order of magnitude in their hydrophobicities, expressed as octanol-water partition coefficient  $K_{OW}$  ( $\log K_{OW,benzene} = 2.13$  and  $\log K_{OW,cyclohexane} = 3.44$  (Schwarzenbach et. al., 2003)). Partition coefficients of the compounds for CHA were determined using headspace analysis. Since the measurable sorption effect at a concentration of  $1 \text{ g L}^{-1}$  CHA was rather small, resulting in a large error in  $K_{DOC}$ , measurements were repeated with  $5 \text{ g L}^{-1}$  CHA. By this means, the following partition coefficients were determined for dissolved CHA at  $\text{pH} = 7$ :  $\log K_{DOC,benzene} = 1.5 \pm 0.2$  and  $\log K_{DOC,cyclohexane} = 2.5 \pm 0.1$ . Based on these values, we can conclude for the bulk phase of the solution that benzene is not significantly sorbed and cyclohexane only to a low extent (about 13%) at the highest concentration of CHA applied ( $1 \text{ g L}^{-1}$ ). SRHA and SRFA can be expected to have even lower sorption affinities.



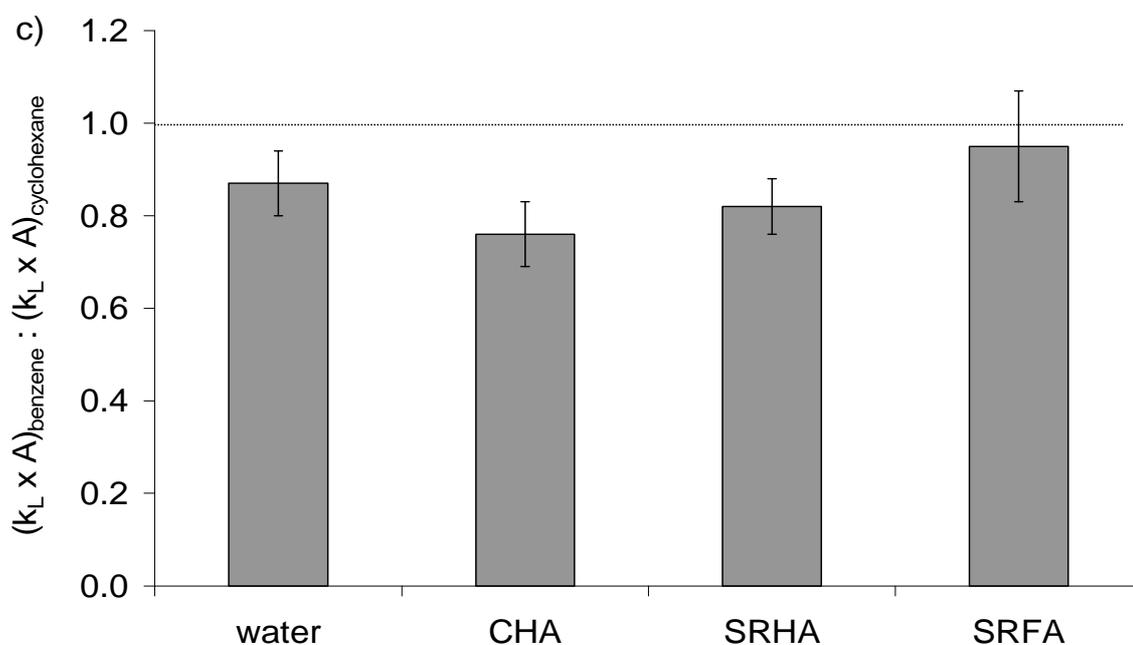


Fig. 2. Effective mass-transfer coefficients of benzene (a), cyclohexane (b) and their ratio (c) at various concentrations of DHS at pH 7 (dynamic purge system, stirring speed  $700 \text{ min}^{-1}$ ).

From Fig. 2a and b it can be seen that the two model compounds show the same trend of decreasing mass-transfer coefficients with increasing DHS concentration. The ratio of the mass-transfer coefficients of cyclohexane and benzene for solutions with  $1 \text{ g L}^{-1}$  of DHS is not significantly different from the value which was determined for clean water without DHS ( $(k_L \times A)_{\text{benzene}} : (k_L \times A)_{\text{cyclohexane}} = 0.87 \pm 0.07$ ), as can be seen in Fig. 2c. The error intervals given in the figures correspond to two standard deviations of the average values from three to five parallel measurements. Based on a mass-transfer kinetics which is purely controlled by diffusion in the water phase, a value of  $D_{\text{benzene}} : D_{\text{cyclohexane}} = 1.21$  (Lide, 1994) has to be expected. The measured values are slightly lower, indicating some additional mass-transfer resistance on the gas side of the interface. The value for CHA solution ( $0.75 \pm 0.07$ ) is slightly lower than the value for clean water ( $0.87 \pm 0.07$ ), which might point to a small sorption-based effect for cyclohexane. However, this difference is not significant. Apparently, interactions between solutes and DHS do not affect mass-transfer rates of VOCs as long as bulk-phase sorption effects are small, i.e. as long as the freely dissolved fraction dominates. In a forthcoming paper, sorption-based effects on mass-transfer will be studied in more detail using n-octane as a model compound with higher hydrophobicity.

### 3.3. Influence of inorganic salts and solution pH on the mass transfer of VOCs

The presence of inorganic ions can have direct and indirect effects on the processes at the gas-water interphase. Indirect effects can arise from changes in the conformation of DHS molecules in the presence of cations (especially multivalent cations) which could also affect their enrichment in the surface layer. Direct effects could be deduced from recent findings of experimental and theoretical studies reviewed in Garret (2004), which suggest that atomic ions such as halides can be enriched at the gas-water interface.

In order to test whether the low concentrations of NaCl produced during the preparation of the DHS solutions have an effect on the mass-transfer through the gas-water interface, dynamic experiments were performed with various concentrations of NaCl in the absence and presence of 0.1 g L<sup>-1</sup> CHA. In addition, Ca<sup>2+</sup> as a divalent cation was tested. Fig. 3 shows that low concentrations of NaCl (0.1 M) and CaCl<sub>2</sub> (0.01 M) did not change the  $k_L \times A$  values for benzene in pure water, i.e. direct effects can be excluded. In the presence of CHA, effective mass-transfer coefficients were also not significantly affected by NaCl and CaCl<sub>2</sub>, although multivalent cations can have an even stronger effect on DHS conformation (Baalousha et al., 2006; Engebretson and Von Wandruszka, 1994).

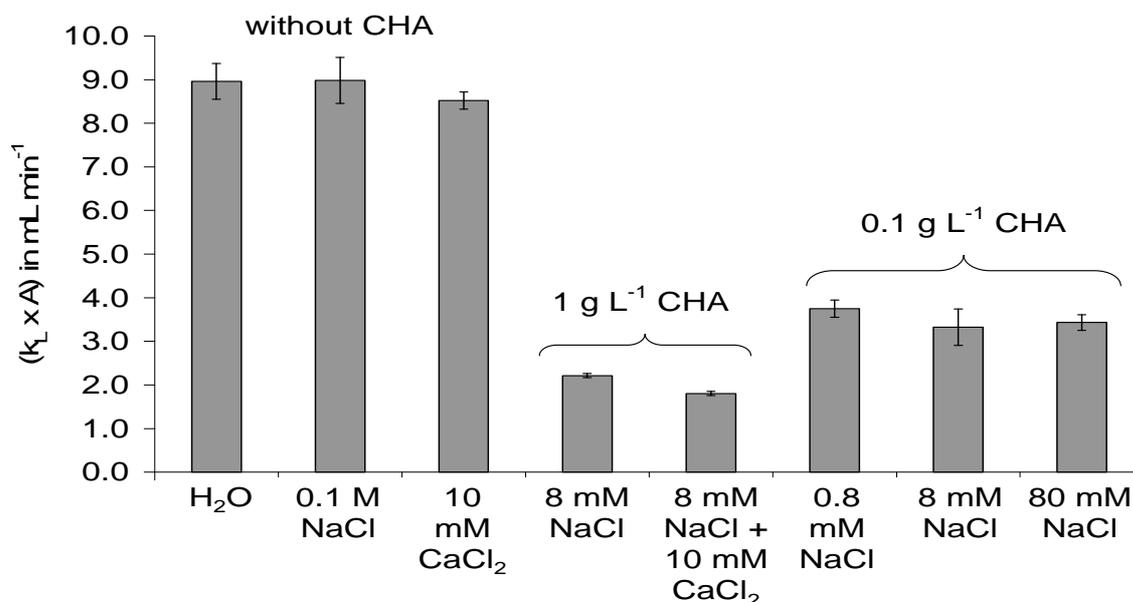


Fig. 3. Effective mass-transfer coefficients of benzene in water and CHA solutions containing various concentrations of NaCl and CaCl<sub>2</sub> (dynamic purge system, pH 7, stirring speed 700 min<sup>-1</sup>).

DHS conformational behaviour and aggregation characteristics are also affected by the pH value (Baalousha et al., 2006; Engebretson and Von Wandruszka, 1994; Terashima et al., 2004). However, we did not observe significant pH effects: effective mass-transfer coefficients of benzene were 2.14, 2.21 and 2.16 mL min<sup>-1</sup> at pH 4, 7 and 9, respectively, in solutions containing 1 g L<sup>-1</sup> CHA. Overall, the solution conditions showed little effect on the mass-transfer kinetics in clean water and CHA solutions.

### **3.4. Comparison of DHS with other compound classes**

In order to rank DHS among other surface-active compounds with respect to their effects on water-gas exchange, experiments with SDS and Triton as surfactants of low molecular weight (MW) and PAA as a synthetic polymer (average molecular weight 2000 g mol<sup>-1</sup>) were conducted under identical conditions (stirring speed 700 min<sup>-1</sup>). Addition of PAA up to a concentration of 1 g L<sup>-1</sup> did not significantly alter the mass-transfer rates of benzene (data not shown). Apparently, PAA is not hydrophobic enough to accumulate at the air-water interface. From this finding, we can conclude that retardation of mass-transfer kinetics through boundary layers is not a general property of organic polyelectrolytes.

In contrast, for solutions which contained an anionic (SDS) or nonionic (Triton) surfactant at concentrations below their critical micelle concentration (CMC), a strong reduction of the gas-exchange rates of benzene was observed (up to a factor of 5, Fig. 4).

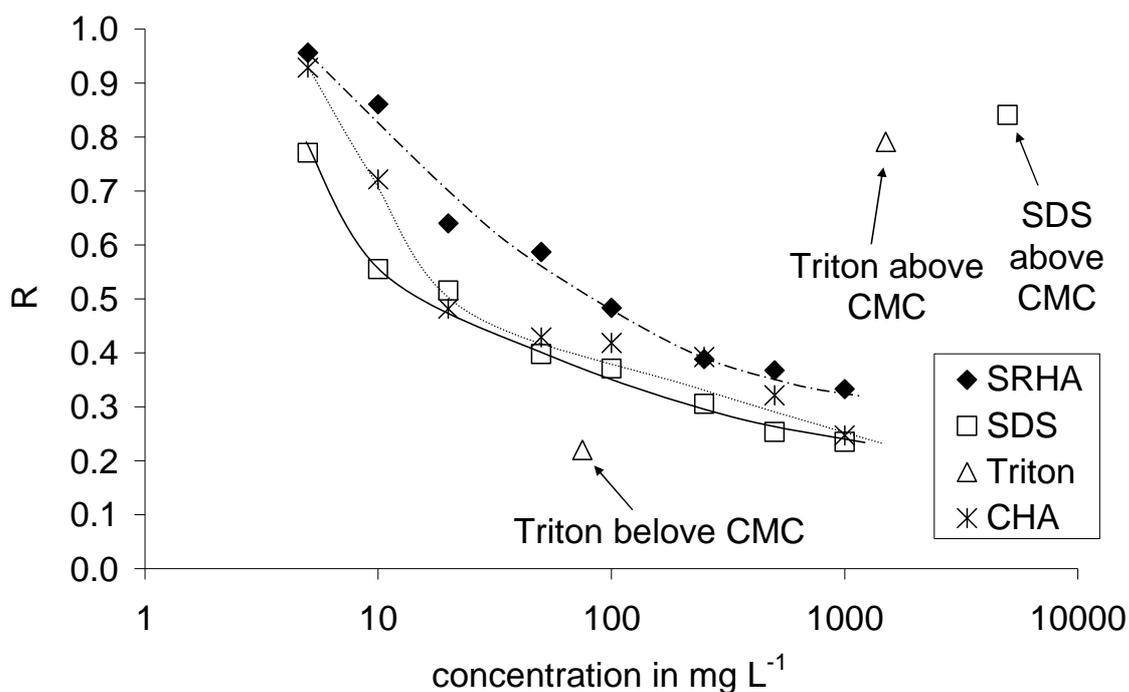


Fig. 4. Ratio ( $R$ ) of benzene mass-transfer coefficients determined in the presence of various surface-active compounds related to the value for deionized water (dynamic purge system, stirring speed  $700 \text{ min}^{-1}$ , pH 7). Synthetic surfactants were applied below and above their CMCs ( $\text{CMC}_{\text{Triton}} = 150 \text{ mg L}^{-1}$ ,  $\text{CMC}_{\text{SDS}} = 2300 \text{ mg L}^{-1}$ ).

The synthetic surfactants are much more effective than DHS in decreasing the surface tension of water, whereby the highest surface pressure (difference in surface tension compared to pure water) is reached for Triton. Surface tensions for solutions with  $1 \text{ g L}^{-1}$  surfactant are  $56 \text{ mN m}^{-1}$  in the case of SDS and  $30 \text{ mN m}^{-1}$  for Triton, compared to  $66 \text{ mN m}^{-1}$  in the case of CHA. The trend in surface activity of the studied compounds does largely reflect the trend in their effect on mass-transfer rates for water-gas exchange of benzene. Frew (1997) noted in his review that, for a given surfactant, the reduction of mass-transfer coefficients of gases (e.g.  $\text{CO}_2$  and  $\text{O}_2$ ) is a smooth function of the surfactant's surface concentration and pressure. This correlation does not hold, however, when different surfactants are compared (Frew, 1997). Lee et al. (1980) observed that macromolecular protein surfactants are more effective in reducing mass-transfer coefficients of  $\text{O}_2$  than SDS. It has been suggested that, in addition to the extent of surface enrichment of surfactants, the rate of reestablishment of the surface film after disruption by turbulence might be an important factor for the hydrodynamic effect. This film recovery rate can depend on factors such as molecular weight, water solubility and adsorption rate, as well as bulk and surface diffusivities (Frew, 1997).

An interesting phenomenon appeared when SDS and Triton were applied at a concentration above their CMC. In this case, the effective mass-transfer coefficient of benzene increased by a factor of about four compared to solutions containing subcritical surfactant concentrations. It reached a value of about 80% of that in pure water (Fig. 4). The authors were unable to find other papers in the literature which describe similar experiments. For natural systems (e.g. marine environments), such high surfactant concentrations are not likely to occur. However, in engineered systems, e.g. for mobilization and removal of hardly water soluble contaminants, such conditions are quite realistic. As the CMC is reached, the surface layer becomes saturated by surfactant molecules. Therefore, there is no further increase in surface pressure, i.e. in the forces directed against surface renewal by eddies. In contrast, one can speculate that pre-arranged surfactant micelles approaching the interface are favourable for surface renewal, so that the overall mass-transfer rate is increased.

### **3.5. Influence of agitation intensity**

Fig. 5 demonstrates the influence of the intensity of agitation in the water phase on the retardation of benzene water-gas exchange caused by CHA and SDS. It is obvious that there is a certain range of agitation intensity where the retardation effect is maximal. The conceptual model of Davies (1966) predicts that the hydrodynamic effect of surface-active compounds is restricted to a certain degree of turbulence. Surface renewal at low near-surface turbulences is limited by bulk fluid constraints, and eddies do not reach the surface; hence neither DHS or surfactants cause changes in the viscous boundary layer. On the other hand, retardation effects are suppressed when eddies approach the surface rapidly and with sufficient force at higher turbulence to overcome any opposing forces due to surface films (Davies, 1966). Our results on the effect of the stirring speed on relative gas-exchange rates are in accordance with the hypothesis that the reduction in mass-transfer rates caused by DHS is hydrodynamic in nature.

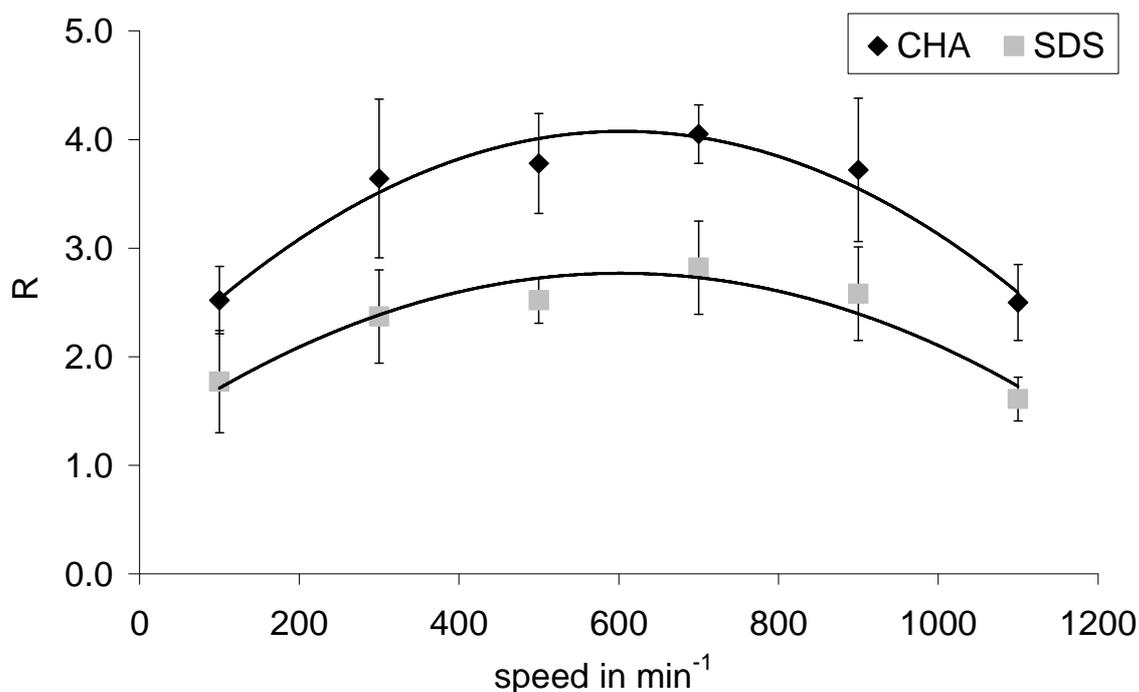


Fig. 5. Ratio ( $R$ ) of benzene mass-transfer coefficients in solutions of  $1 \text{ g L}^{-1}$  CHA (pH 7) ( $\blacklozenge$ ) or  $0.1 \text{ g L}^{-1}$  SDS ( $\blacksquare$ ) related to the value for deionized water as a function of stirring speed applied in the dynamic purge system.

#### 4. Conclusion

In a system where the exchange rate is controlled by the transfer resistance on the water side of the water-gas interface, we observed a significant hindrance effect of DHS on water-gas exchange of benzene and cyclohexane. This hindrance effect was observable over a broad range of agitation conditions with a maximum at moderate agitation. Mass-transfer coefficients for benzene and cyclohexane were affected to the same extent by DHS additions up to  $1 \text{ g L}^{-1}$ , despite the fact that the two compounds differ in their sorption tendency towards DHS. These results are in conformity with the hypothesis that the effect of DHS is mainly due to changes in the hydrodynamic characteristics of water motion at the interface and within the boundary layer below the surface. Sorption-induced effects of DHS on the water-gas exchange rate can be neglected under most environmental conditions for compounds with low to moderate hydrophobicity ( $\log K_{OW} \leq 3.5$ ). The hydrodynamic effect of DHS is comparable to that of synthetic surfactants at concentrations below their CMC. However, it is remarkable that the inhibiting effect of surfactants on mass transfer is greatly diminished if the surfactant concentration exceeds the CMC.

In summary, mass-transfer resistance on the water side of the gas-water interface can be significantly affected by environmentally relevant DHS concentrations. It should clearly be taken into account in models for air-sea or air-surface water fluxes of organic compounds, which might be even more important considering the current global trend towards increasing DOM concentrations in freshwaters.

## **Supplementary Material**

Supplementary Material contains in section A: results on water-gas exchange obtained with the static system; in section B: the derivation of Eq. (1); in section C: a consideration about the rate-determining step of water-gas exchange in the dynamic purge system, and in section D: the derivation of Eq. (3).

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## **Supplementary Material**

### **A. Experiments on water-gas exchange using the static system**

Experiments on the mass-transfer of benzene from the aqueous phase to the gas phase in the static system were conducted as follows: 250 mL of the model solution (deionized water and DHS solutions, which were prepared as described above) were filled into a glass flask with a nominal volume of 250 mL and capped with a Mininert™ valve. The solution was spiked with a methanolic stock solution of benzene and cyclohexane in order to obtain final concentrations of 100 mg L<sup>-1</sup> and 30 mg L<sup>-1</sup> for benzene and cyclohexane, respectively. After overnight equilibration, 50 mL of the solution was removed in order to have final volumes of 200 mL and 50 mL for solution and gas phase, respectively. The gas phase was then purged for 5 minutes with helium (200 mL min<sup>-1</sup>) through an input needle, whereby any disturbance of the aqueous phase was avoided. During this time the Mininert™ screw cap was loosened. Here and in all other experiments a gas flow controller (GFC, Bronckhorst Ruurlo, The Netherlands) was used in order to adjust the flow rate. PTFE tubing was used for connections. After removing the input needle and closing the system, mixing of the aqueous phase by means of magnetic stirring was immediately started ( $t = 0$ ).

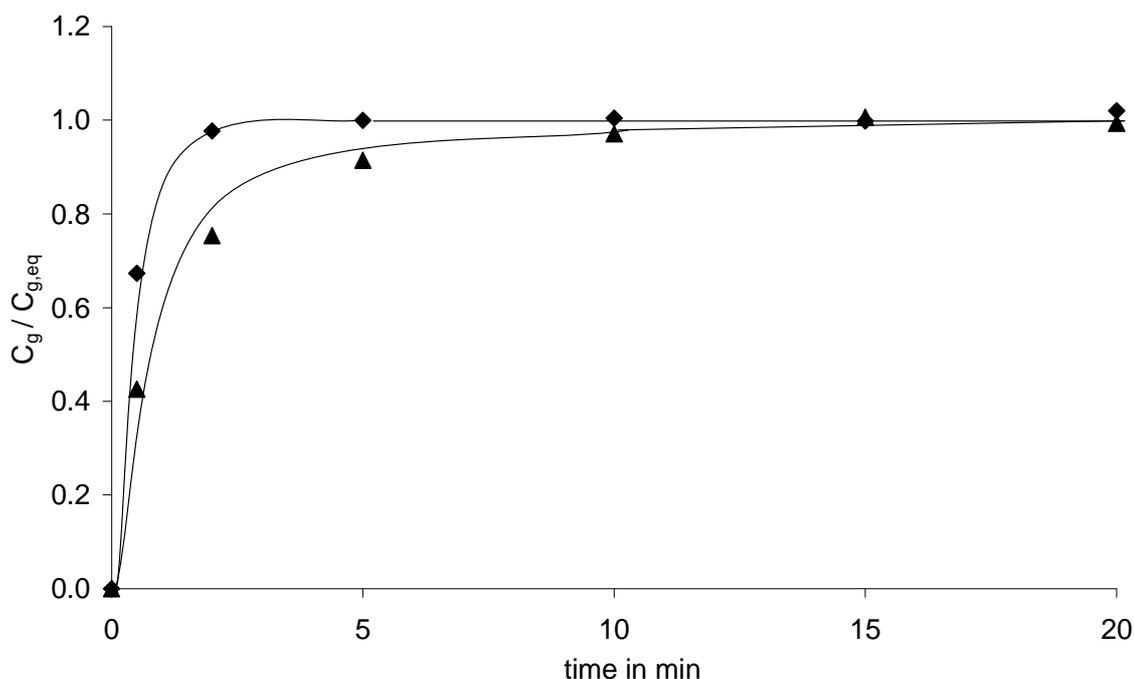


Fig. A1. Mass-transfer kinetics of benzene in a static system at a stirring speed of  $700 \text{ min}^{-1}$ , represented as gas-phase concentrations ( $c_g$ ) normalized to the equilibrium concentration ( $c_{g,eq}$ ) for a solution of benzene ( $c_0 = 100 \text{ mg L}^{-1}$ ) in deionized water ( $\blacklozenge$ ) and in CHA-containing solution ( $1 \text{ g L}^{-1}$ , pH 7) ( $\blacktriangle$ ).

The concentration of the model compounds in the gas phase was monitored by manual headspace sampling using gas-tight microlitre syringes ( $100 \mu\text{L}$ ) and GC-MS analysis (conditions as described above). The first measurements were performed after 30 sec, and sampling was continued over a time period of 1 h. The experiments were conducted at ambient temperature ( $21 \pm 1.5 \text{ }^\circ\text{C}$ ). The temperature rise during the experiment due to stirring heat was minimized by placing a sheet of polystyrene between the sample and the stirring plate.

Qualitatively, the mass-transfer of benzene proceeds faster in clean water than in the presence of DHS. However, due to the very fast transfer kinetics and the limited number of meaningful data points, a quantitative treatment is not reasonable.

## B. Determination of $K_{\text{DOC}}$ by means of headspace GC/MS analysis

The partition coefficient  $K_{\text{DOC}}$  is defined as the concentration ratio of the sorbed and freely dissolved fractions of the sorbate

$$K_{\text{DOC}} = \frac{q_{\text{sorb}}}{c_w} = \frac{c_{\text{sorb}}}{c_w} \frac{1}{c_{\text{DOC}}} \quad (\text{B.1})$$

where  $q_{\text{sorb}}$  is the mass of sorbed analyte per mass of dissolved organic carbon (DOC) of the sorbent ( $q_{\text{sorb}} = m_{\text{sorb}}/m_{\text{DOC}}$ ),  $c_w$  is the concentration of the freely dissolved analyte,  $c_{\text{sorb}}$  is the concentration of the sorbed analyte related to the water volume ( $c_{\text{sorb}} = m_{\text{sorb}}/V_w$ ) and  $c_{\text{DOC}}$  is the concentration of DOC ( $c_{\text{DOC}} = m_{\text{DOC}}/V_w$ ).

$K_{\text{DOC}}$  values were determined by measuring the headspace concentration of the analyte above a reference solution (without addition of DHS) and a DHS-containing solution. The reference and DHS-containing solution contained identical total concentrations of the analyte. All measurement conditions (liquid volume and total volume of the flasks, manual sampling with gas-tight 100  $\mu\text{L}$  syringes and GC-MS conditions) were identical.

The mass balance of the analyte in the reference solution is given by

$$m_{\text{total}} = (m_w)^{\text{ref}} + (m_g)^{\text{ref}} \quad (\text{B.2})$$

where  $m_{\text{total}}$  is the total amount of analyte added to the system and  $m_w$ ,  $m_g$  are the amounts which are present in the water and gas phases, respectively.

For the DHS-containing system, the mass balance is described by

$$m_{\text{total}} = (m_w)^{\text{DHS}} + (m_{\text{sorb}})^{\text{DHS}} + (m_g)^{\text{DHS}} \quad (\text{B.3})$$

In this case, the amount of analyte present in the liquid phase is differentiated into a fraction which is indeed freely dissolved in water ( $m_w$ ) and a fraction which is sorbed by DHS ( $m_{\text{sorb}}$ ).

Using Eq. (B.1) and the dimensionless Henry's law coefficient which relates the gas phase ( $c_g$ ) and the aqueous phase concentrations ( $c_w$ ) of the analyte according to

$$K_H = \frac{c_g}{c_w} \quad (\text{B.4})$$

we can transform Eqs. (B.2) and (B.3) into (B.5) and (B.6).

$$m_{\text{total}} = (m_{\text{g}})^{\text{DHS}} \times \left( 1 + \frac{K_{\text{DOC}} \times m_{\text{DOC}}}{K_{\text{H}} \times V_{\text{g}}} + \frac{V_{\text{w}}}{K_{\text{H}} \times V_{\text{g}}} \right) \quad (\text{B.5})$$

$$m_{\text{total}} = (m_{\text{g}})^{\text{ref}} \times \left( 1 + \frac{V_{\text{w}}}{K_{\text{H}} \times V_{\text{g}}} \right) \quad (\text{B.6})$$

Thus, for the ratio of the gas phase concentrations of the analyte in the DHS-containing system and the reference system one can write

$$\frac{(c_{\text{g}})^{\text{DHS}}}{(c_{\text{g}})^{\text{ref}}} = \frac{(m_{\text{g}})^{\text{DHS}}}{(m_{\text{g}})^{\text{ref}}} = \frac{K_{\text{H}} \times V_{\text{g}} + V_{\text{w}}}{K_{\text{H}} \times V_{\text{g}} + K_{\text{DOC}} \times m_{\text{DOC}} + V_{\text{w}}} \quad (\text{B.7})$$

Eq. (B.7) can be rearranged in order to obtain the partition coefficient  $K_{\text{DOC}}$

$$K_{\text{DOC}} = \left( \frac{(c_{\text{g}})^{\text{ref}}}{(c_{\text{g}})^{\text{DHS}}} - 1 \right) \times \frac{1}{c_{\text{DOC}}} \times \left( \frac{K_{\text{H}} \times V_{\text{g}}}{V_{\text{w}}} + 1 \right) \quad (\text{B.8})$$

For analytes with low Henry's law coefficients or at a high water to gas phase volume ratio, the following relation holds

$$\frac{K_{\text{H}} \times V_{\text{g}}}{V_{\text{w}}} \ll 1 \quad (\text{B.9})$$

In this case, Eq. (B.8) can be simplified to

$$K_{\text{DOC}} = \left( \frac{(c_{\text{g}})^{\text{ref}}}{(c_{\text{g}})^{\text{DHS}}} - 1 \right) \times \frac{1}{c_{\text{DOC}}} \quad (\text{B.10})$$

Note that an identical value for  $K_{\text{H}}$  is applied for the analyte in the reference solution and the solution containing DHS.  $K_{\text{H}}$  is proportional to the activity coefficient of the compound in the aqueous solution. The  $K_{\text{DOC}}$  value determined by the headspace analysis method is, therefore, an activity-based partition coefficient similar to the solid phase microextraction method or the method of solubility enhancement. For a detailed discussion of this problem, see (Mckenzie et al., 2002; Kopinke et al., 2002).

In addition, the fractions of the freely dissolved and sorbed analyte in the aqueous phase can be calculated based on Eq. (B.1)

$$X_{\text{free}} = \frac{C_w}{C_w + C_{\text{sorb}}} = \frac{1}{K_{\text{DOC}} \times C_{\text{DOC}} + 1} \quad (\text{B.11})$$

$$X_{\text{sorb}} = \frac{C_{\text{sorb}}}{C_w + C_{\text{sorb}}} = \frac{1}{1 + \frac{1}{K_{\text{DOC}} \times C_{\text{DOC}}}} \quad (\text{B.12})$$

### C. Evaluation of the rate-determining step of gas-water exchange in the dynamic purge system

The rate of transfer of compounds from water to the gas phase (and vice versa) is determined by the combined resistances of two boundary layers ( $1/k_{\text{total}}$ ), which is the sum of the resistances of the water and the gaseous boundary layers (Schwarzenbach et al., 2003)

$$\frac{1}{k_{\text{total}}} = \frac{1}{k_L} + \frac{1}{k_G \times K_H} \quad (\text{C.1})$$

where  $k_L$  and  $k_G$  are the interface-area-normalized, effective mass-transfer coefficients for the liquid and gaseous boundary layers, respectively;  $K_H$  is the dimensionless Henry's law coefficient;  $k_L$  and  $k_G$  depend on the diffusion coefficients of the compound in the two phases and the degree of turbulence in the system. In the *stagnant two-film model*, the degree of turbulence in the system is reflected by the thickness of the diffusion layer, and in the *surface renewal model* it is reflected by the surface renewal rate (Schwarzenbach et al., 2003). These parameters are system parameters and do not depend on the type of molecule for which the phase transfer is considered. Thus, the only compound-specific parameters are the diffusion coefficients  $D_w$  and  $D_g$  as well as  $K_H$ .

One can now consider two scenarios: (i) the transfer resistance in the liquid boundary layer is rate-determining, i.e.  $\frac{1}{k_L} \gg \frac{1}{k_G \times K_H}$ . In this case,  $k_{\text{total}}$  is dominated by  $k_L$  and the rate of gas-water exchange of various compounds does not depend on  $K_H$ . In

another scenario, (ii) the transfer resistance in the gaseous boundary layer is rate-determining, i.e.  $\frac{1}{k_L} \ll \frac{1}{k_G \times K_H}$ . In this case,  $k_{\text{total}}$  is proportional to  $K_H$ , i.e. the more volatile the compound is, the faster is its mass-transfer through the interface. In our experiments, we applied benzene and cyclohexane, which differ insignificantly in their diffusion coefficients but strongly in their Henry's law coefficients ( $K_{H,\text{benzene}} = 0.2$  at 25 °C,  $K_{H,\text{cyclohexane}} = 7.4$  at 25 °C (NIST chemistry webbook)). If scenario (ii) were to be valid under the applied experimental conditions, we would expect the half-life for depletion of benzene in the dynamic system to be about 40 times higher than the half-life of cyclohexane. However, the experimentally determined half-lives for the two compounds are almost identical. This consideration strongly supports the hypothesis that there is no significant transfer resistance in the gas boundary layer under the conditions applied in the dynamic purge system.

#### **D. Derivation of Eq. (3) for calculation of mass-transfer coefficients from analyte depletion profiles obtained in the dynamic purge system**

In order to derive quantitative data about the mass-transfer rates in the aqueous boundary layer, we applied the stagnant film model as described already in the main text. The flux of molecules through the boundary layer is described by Eq. (2). Under the precondition that the mass-transfer resistance in the gas phase is negligible, the concentration of the model compound at the surface of the water phase ( $c_{\text{surface}}$ ) is in equilibrium with the gas phase concentration  $c_g$ , so that Henry's law can be applied. The concentration of the model compound in the bulk phase ( $c_{\text{bulk}}$ ) is related to the gas phase concentration which would be reached under equilibrium conditions ( $c_g^\infty$ ).

Thus, using Henry's law, we can substitute the liquid phase concentrations in Eq. (2) by gas phase concentrations

$$\dot{n} = \frac{k_L \times A}{K_H} \times (c_g^\infty - c_g) \quad (\text{D.1})$$

In addition, the flux of the model compound in the effluent can be described by

$$\dot{n} = \dot{V}_g \times c_g \quad (\text{D.2})$$

where  $\dot{V}_g$  is the volumetric gas flow rate ( $\text{mL min}^{-1}$ ).

Combining Eqs. (D.1) and (D.2) results in Eq. (D.3), which describes the deviation of the gas phase concentration of the model compound under dynamic conditions from the equilibrium concentration:

$$\left( \frac{c_g^\infty}{c_g} \right) = \frac{\dot{V}_g \times K_H}{k_L \times A} + 1 \quad (\text{D.3})$$

In principle  $k_L \times A$  can be determined by means of Eq. (D.3) by measuring  $c_g$  under conditions where the purging still did not cause a significant depletion of the model compound, or by extrapolation to such conditions ( $t \rightarrow 0$ ).  $c_g^\infty$  can be determined after interruption of the gas flow or can be calculated from the bulk phase concentration  $c_{\text{bulk}}$  using Henry's law.

However, more precise results for  $k_L \times A$  can be obtained from a larger data set measured under dynamic conditions, i.e. during purging of the gas phase. The depletion of the model compound in the system due to the purging can be described by Eq. (D.4):

$$c_w = c_{w,0} - \frac{\dot{V}_g}{V_w} \times \int_0^t c_g dt \quad (\text{D.4})$$

with  $c_w$ ,  $c_{w,0}$  as aqueous concentrations of the analyte at  $t$  and  $t = 0$ , respectively. Applying Henry's law, the aqueous phase concentrations can be replaced by gas phase concentrations

$$c_g^\infty = c_{g,0} - \frac{\dot{V}_g}{V_w} \times K_H \times \int_0^t c_g dt \quad (\text{D.5})$$

Eq. (D.3) can be used to replace  $c_g^\infty$  by  $c_g$ . Thus, after combination of Eqs. (D.3) and (D.5) and subsequent derivation by  $dt$ , it is possible to describe the change of the gas phase concentration as a function of time:

$$\frac{dc_g}{dt} = -\frac{1}{V_w \times \left( \frac{1}{\dot{V}_g \times K_H} + \frac{1}{k_L \times A} \right)} \times c_g \quad (\text{D.6})$$

Integration of Eq. (D.6) yields Eq. (D.7) which is identical with Eq. 3 in the original part of this paper

$$\ln\left(\frac{c}{c_0}\right)_g = -\frac{1}{V_w \times \left( \frac{1}{\dot{V}_g \times K_H} + \frac{1}{k_L \times A} \right)} \times t = -m \times t \quad (\text{D.7})$$

Thus, a graph of  $\ln\left(\frac{c}{c_0}\right)_g$  versus time should be linear. The effective mass-transfer coefficient  $k_L \times A$  is calculated from the slope  $m$  using Eq. (D.8). For this purpose, any time period of the purging experiment can be considered. The initial concentration  $c_0$  is the gas phase concentration of the model compound at the start of the observation period and  $t$  is the time elapsed after start of purging.

$$k_L \times A = \frac{1}{\frac{1}{m \times V_w} - \frac{1}{\dot{V}_g \times K_H}} \quad (\text{D.8})$$

If  $\frac{c_g}{c_g^\infty} \ll 1$ , i.e. if the gas phase concentration under dynamic conditions is far away from its equilibrium value, then according to Eq. (D.3) it holds that  $\frac{k_L \times A}{\dot{V}_g \times K_H} \ll 1$ .

Under these conditions, Eq. (D.8) can be simplified, yielding

$$\ln\left(\frac{c}{c_0}\right)_g = -\frac{k_L \times A}{V_w} \times t \quad (\text{D.9})$$

where  $-\frac{k_L \times A}{V_w}$  is the slope of the linear regression, from which  $k_L \times A$  can be calculated. The preconditions necessary for the validity of Eq. (D.9) were fulfilled for

most of the applied experimental conditions. Therefore, this equation was applied for determination of effective mass-transfer coefficients.

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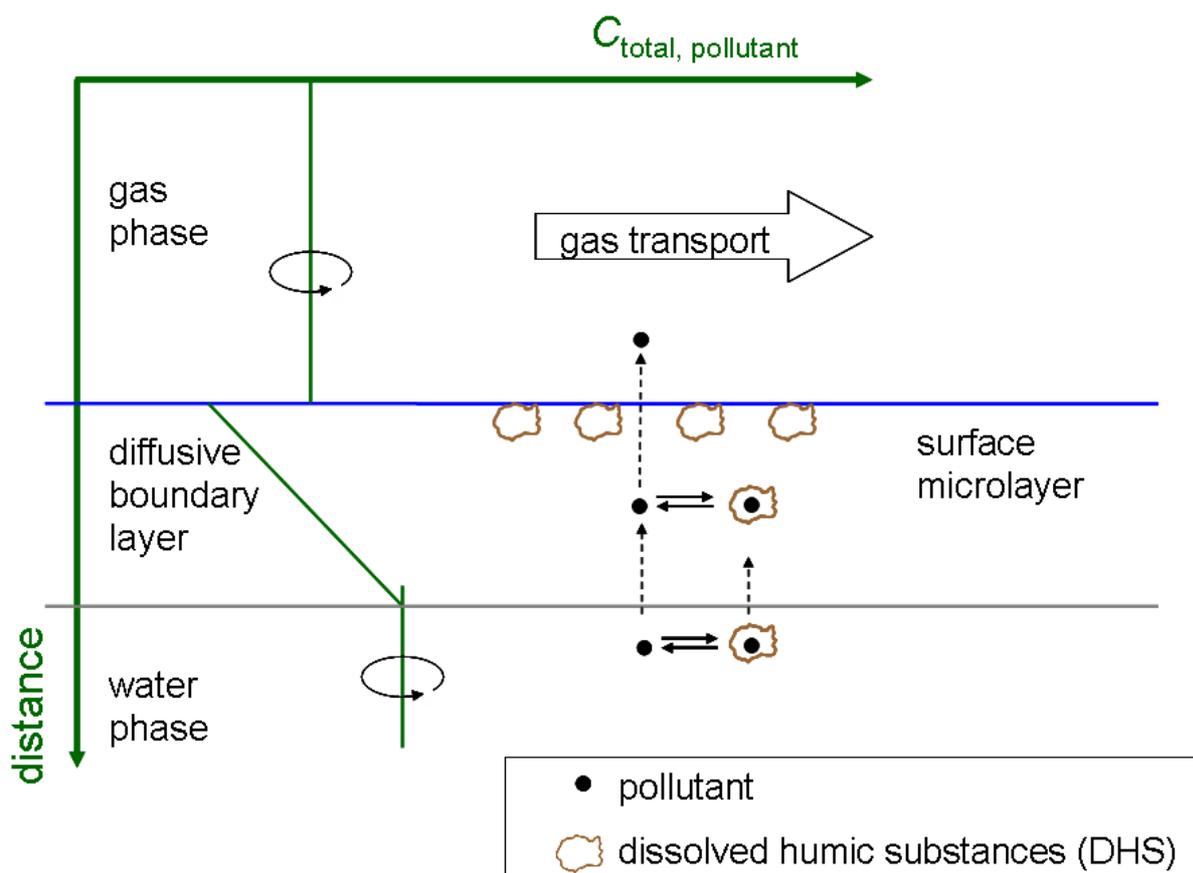
#### **4. Sorption-Induced Effects of Humic Substances on Mass Transfer of Organic Pollutants through Aqueous Diffusion Boundary Layers: Example of Water/Air Exchange**

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##### **Abstract**

This study examines the effect of dissolved humic substances (DHS) on the rate of water-gas exchange of organic compounds under conditions where diffusion through the aqueous boundary layer is rate-determining. A synthetic surfactant was applied for comparison. Mass-transfer coefficients were determined from the rate of depletion of the model compounds by means of an apparatus containing a stirred aqueous solution with continuous purging of the headspace above the solution. In addition, experiments with continuous passive dosing of analytes into the water phase were conducted, in order to simulate a system where thermodynamic activity of the chemical in the aqueous phase is identical in the presence and absence of DHS. The experimental results show that DHS and surfactants can affect water-gas exchange rates by the superposition of two mechanisms: I) hydrodynamic effects due to surface film formation ('surface smoothing'), and II) sorption-induced effects. Whether sorption accelerates or retards mass transfer depends on its effect on the thermodynamic activity of the pollutant in the aqueous phase. Mass transfer will be retarded if the activity (or freely dissolved concentration) of the pollutant is decreased due to sorption. If it remains unchanged (e.g. due to fast equilibration with a sediment acting as a large source phase), then DHS and surfactant micelles can act as an additional shuttle for the pollutants, enhancing the flux through the boundary layer.



## Introduction

Dissolved humic substances (DHS) form a major part of dissolved organic matter (DOM) in natural waters. Due to their amphiphilic nature they are able to sorb hydrophobic organic xenobiotics and thereby affect their fate in the environment. Sorption to DOM is generally described as a partition process with a sorption coefficient ( $K_{\text{DOM}}$  or  $K_{\text{DOC}}$ ). The effect of sorption to DHS on partitioning equilibria of organic compounds between various compartments (aqueous phase, DOM, biota, air etc.) is quite well understood and predictions of  $K_{\text{DOC}}$  values are possible based on multiparameter LFER concepts (e.g. 1-2).

However, under dynamic conditions, i.e. in case of significant fluctuation of concentrations in time and space, the rate of exchange processes can become important for the effect of pollutants in ecosystems and their overall fate in the environment. Several studies have shown that sorption to DHS can affect the transport rate of pollutants between water and solid sorbent phases. This includes acceleration of uptake and release of PAHs and PCBs by solid phase microextraction fibers (3-5). In addition, experiments with a source-sink system consisting of two PDMS plates

separated by an unstirred water layer revealed an increased diffusive conductivity of water in the presence of various types of dissolved sorbents, including DHS (6-7). Furthermore, the rate of uptake or biodegradation of hydrophobic pollutants by organisms can be also accelerated in the presence of DHS and other dissolved sorbents (8-9). Just recently, DHS-enhanced mass transfer of PAHs between two liquid phases, i.e. from nonaqueous phase liquids (NAPLs) into the aqueous phase, has been reported (10). In general, these effects are ascribed to the occurrence of an additional diffusion flux due to the presence of a pollutant fraction which is reversibly bound by the dissolved sorbent (shuttle effect). Ter Laak et al. (9) summarized that dissolved material will only contribute to the transport of chemicals between the aqueous environment and an organism, if (i) the aqueous diffusion layer limits the transport process, (ii) a substantial part of the chemical is associated with the dissolved material and (iii) the complexes are labile to a certain extent. For completely labile complexes sorption/desorption kinetics is instantaneous compared to their residence time in the diffusion boundary layer, whereas non-labile or inert complexes are not able to release the chemical within this residence time and thus cannot contribute to the overall transport (11).

In our previous paper we have studied the influence of DHS on mass transfer of two organic compounds with moderate hydrophobicity (benzene and cyclohexane) across the air-water interface (12). Under conditions where mass-transfer resistance on the water side of this interface determines the overall transport rate, the presence of low, environmentally relevant concentrations of DHS hindered water-gas exchange of benzene and cyclohexane. This behavior was explained by the concept of hydrodynamic effects (13-14): amphiphilic molecules such as DHS are enriched at the water-gas interface and create a film pressure. Surface renewal by turbulent eddies approaching a film-influenced surface is opposed by an additional tangential stress due to this film pressure. As a result, the thickness of the viscous and diffusive sublayers increases, thus reducing the rate of mass transfer (14).

In our experiments, the two test compounds benzene and cyclohexane showed a very similar behavior despite their different hydrophobicities and sorption tendencies towards DHS (12). Obviously, sorption to DHS does not influence water-gas exchange rates under conditions where bulk-phase sorption effects are insignificant, as is the case for the moderately hydrophobic test compounds ( $\log K_{OW} \leq 3.5$ ) in a range of DHS concentrations from  $10^1$  to  $10^3$  mg L<sup>-1</sup>.

However, water-gas exchange is also relevant for the fate of pollutants with higher

hydrophobicity in the environment. An important example is the air-sea exchange of PAHs and organochlorine compounds, such as hexachlorocyclohexanes (HCH) and PCBs (15-17). Several authors have emphasized that the surface microlayer, which is formed due to accumulation of amphiphilic organic molecules at the water/air interface of all natural water bodies, might affect air-water exchange of hydrophobic organic pollutants due to sorptive interactions. However, mainly field studies have been conducted in this research area. To elucidate and quantify the underlying mechanisms is considered as important (15-16), but might require laboratory experiments under more defined, i.e. simplified, conditions.

Based on the previously discussed findings about the role of the shuttle effect of DHS in pollutant transfer between water and solid sink phases (e.g. silicone phases, organisms), sorption-induced effects on water-gas exchange appeared to us very likely and highly relevant. In addition, the hydrodynamic effect as a consequence of the surface-activity of DHS (12) is expected to superimpose upon any sorption-induced effects of DHS on water-gas exchange. In the present study we applied two model compounds, benzene and n-octane, which differ strongly in their hydrophobicity ( $\log K_{OW,benzene} = 2.13$ ,  $\log K_{OW,n-octane} = 5.18$  (18)) in order to differentiate between hydrodynamic and sorption-induced effects of DHS on water-gas exchange. Using homogeneous aqueous solutions with and without dissolved sorbents reflects the case where sorption decreases the chemical activity of the organic compound in the aqueous phase (reduced-activity system). Passive dosing with loaded silicone sheets was applied in the constant-activity system. This is, to the best of our knowledge, the first experimental study that investigates and demonstrates the superposition of hydrodynamic and sorption-induced effects of DHS on water-gas exchange.

## **Material and Methods**

### **Chemicals**

All chemicals and solvents were purchased in the highest grade available from Merck (Germany) and used as received. 500  $\mu\text{m}$  thick AlteSil™ silicone sheets were obtained from Altec (United Kingdom).

## Humic Substances

The commercial humic acid (CHA) was obtained from Carl Roth GmbH, Karlsruhe, Germany. Suwannee river humic acid (SRHA) and fulvic acid (SRFA) were purchased from the International Humic Substance Society (IHSS), St. Paul, USA. Aqueous solutions of the humic acids were prepared by dissolving the powder without previous purification in dilute NaOH. After further dilution with deionized water, the pH of the solutions was adjusted by adding dilute HCl. SRFA was dissolved in deionized water and the pH was adjusted by adding dilute NaOH.

### Determination of partition coefficients

In order to determine the partition coefficients of the model compounds between the aqueous phase and the dissolved sorbents (surfactant micelles or humic substances), a simple headspace analysis method (12) was applied. This method is based on the fact that the concentration of the freely dissolved fraction of the analyte in the water phase is proportional to its headspace concentration (Henry's law). Briefly, the solution containing the sorbent and an aqueous standard solution of the analyte without any sorbent were analyzed under identical conditions and the results were compared. Erlenmeyer flasks with a total volume of 1120 mL were used for analyses with CHA and SDS. The flasks were filled with an appropriate volume of the aqueous solutions (1110 mL), so that the volume of the gas phase was 10 mL in each case. After closing the flasks with Mininert™ valves, the solutions were spiked with a methanolic stock solution in order to obtain final concentrations of 25 mg L<sup>-1</sup> and 0.5 mg L<sup>-1</sup> for benzene and n-octane, respectively. The final methanol concentration did not exceed 0.1 vol%. After overnight equilibration, the concentration of the model compounds in the gas phase was determined by manual headspace sampling using gas-tight microliter syringes (25 µL). GC-MS analyses (Shimadzu GCMS-QP 2010) were carried out isothermally (373 K) in the SIM mode.

### Determination of mass-transfer rates using homogeneous solutions (*reduced-activity system*)

Mass transfer of benzene and n-octane from homogeneous aqueous solutions to the gas phase was studied by measuring their depletion from an apparatus containing a

stirred aqueous solution with continuous purging of the headspace, which is described as the dynamic system in our previous paper (12). Briefly, 300 mL of the model solution was filled into Erlenmeyer flasks with a nominal volume of 300 mL and spiked with a methanolic stock solution, resulting in final concentrations of 25 mg L<sup>-1</sup> and 0.5 mg L<sup>-1</sup> for benzene and n-octane, respectively. The flasks were closed with screw caps and PTFE-lined septa. After overnight equilibration, 50 mL of the solution was removed. The flask was then closed again. In order to start the purging experiment, two needles were inserted through the septum and placed in the flask as described in (12). At the start of each experiment, the gas phase of the flask was purged for 5 min with helium (100 mL min<sup>-1</sup>), avoiding any disturbance of the aqueous phase (no mixing). The gas flow was controlled by an electronic gas flow controller (GFC, Bronckhorst Ruurlo, The Netherlands). Mixing of the aqueous phase by magnetic stirring was then started, whereby purging of the gas phase was continued. The concentration of the model compounds in the gas phase was monitored by manual headspace sampling through the longer needle using gas-tight microliter syringes (100 µL). GC-MS analyses (Shimadzu GCMS-QP 2010) were carried out isothermally at a column temperature of 373 K in the SIM mode. The first measurements were performed ( $t_0$ ) after 120 s mixing of the aqueous phase; sampling was continued over a time period of 2 h. The mass-transfer coefficients were determined from the rate of depletion of benzene and n-octane from the system. The experiments were conducted at ambient temperature (21 ± 1.5 °C).

### **Determination of mass-transfer rates using passive dosing (*constant-activity system*)**

Twenty silicone sheets (1.0 x 1.0 cm, total weight 2 g) were fastened on a thin wire and washed twice with methanol and deionized water. They were then loaded with n-octane by exposing them for 7 days in a solution of 5 g n-octane in 250 mL methanol. Loaded sheets were briefly washed by dipping into ethanol and immediately placed into Erlenmeyer flasks containing 250 mL model solution. These flasks were capped with screw caps and PTFE-lined septa, whereby the wire with the silicone sheets was fixed by piercing its two ends through the septum. The solutions were then spiked with the appropriate stock solution of benzene to obtain a final concentration of 100 mg L<sup>-1</sup> and equilibrated overnight. After that, the concentrations of the model compounds in the gas phase at equilibrium were determined by manual headspace sampling using gas-tight

microliter syringes (10  $\mu\text{L}$ ). In order to start the purging experiment, the two needles were inserted through the septum as described above. At the start of each experiment, the gas phase of the flask was purged for 30 min with helium ( $100 \text{ mL min}^{-1}$ ) avoiding any disturbance of the aqueous phase (no mixing). Mixing of the aqueous phase by magnetic stirring was then started, whereby purging of the gas phase was continued. Concentrations of benzene and n-octane in the gas phase were determined as described above. Mass-transfer coefficients of benzene were determined from the rate of depletion of this compound from the system. The concentration of n-octane in the gas phase was constant during the duration of the purging experiment (about 2 h). From the mean value of gas-phase concentration data determined over 2 h, the flux of n-octane from water to the gas phase was calculated.

## Data Analysis

### Determination of partition coefficients

Partition coefficients  $K_{\text{DOC}}$  ( $\text{L kg}^{-1}$ ) of benzene and n-octane between water and DHS were determined using eq 1 (12), where  $A^{\text{ref}}$  and  $A^{\text{DHS}}$  are the peak areas for the analyte obtained by headspace GC-MS analysis of the reference solution without DHS and the DHS solution, respectively.  $K_{\text{H}}$  is the dimensionless Henry's law coefficient ( $K_{\text{H,benzene}} = 0.22$  and  $K_{\text{H,n-octane}} = 134$  at  $25 \text{ }^{\circ}\text{C}$  (19)),  $c_{\text{DOC}}$  is the concentration of dissolved organic carbon ( $\text{kg L}^{-1}$ ),  $V_{\text{g}}$  (L) the headspace volume,  $V_{\text{W}}$  (L) the aqueous phase volume and  $x_{\text{free}}$  the freely dissolved fraction of the sorbate ( $x_{\text{free}} = c_{\text{free}}/c_{\text{total}}$ ):

$$K_{\text{DOC}} = \left( \frac{A^{\text{ref}}}{A^{\text{DHS}}} - 1 \right) \times \frac{1}{c_{\text{DOC}}} \times \left( \frac{K_{\text{H}} \times V_{\text{g}}}{V_{\text{W}}} + 1 \right) = \left( \frac{1}{x_{\text{free}}} - 1 \right) \times \frac{1}{c_{\text{DOC}}} \quad (1)$$

The partition coefficient between water and SDS micelles  $K_{\text{mc}}$  ( $\text{L kg}^{-1}$ ) was calculated analogously, but substituting  $c_{\text{DOC}}$  by the micelle concentration ( $c_{\text{SDS}} - \text{CMC}_{\text{SDS}}$ ) with  $c_{\text{SDS}}$  being the total surfactant concentration in the solution and  $\text{CMC}_{\text{SDS}}$  the critical micelle concentration.

## Data interpretation for purging experiments

The gas-phase concentration of the analyte  $c_g$  ( $\text{mol L}^{-1}$ ) is determined by the ratio of the flux of the analyte from water to the gas phase  $j$  ( $\text{mol s}^{-1}$ ) and the volumetric gas flow  $Q$  ( $\text{m}^3 \text{h}^{-1}$ ):

$$c_g = j/Q \quad (2)$$

Mass-transfer resistance in the dynamic system can be expected to be predominantly caused by diffusion through the aqueous boundary layer. Due to the high gas-flow rate and the resulting turbulence in the gas phase, the contribution of the gas boundary layer to the overall mass-transfer resistance should be negligible. This assumption was confirmed by the observation that benzene and cyclohexane, two compounds which differ widely in their Henry's law coefficients, showed similar depletion rates in experiments with the same setup (12).

In order to derive quantitative data about the mass-transfer rates, we applied the stagnant boundary layer model:

$$j = k_L \times A \times (c_{\text{bulk}} - c_{\text{surface}}) \quad (3)$$

where  $A$  is the interface area ( $\text{m}^2$ ),  $k_L$  the mass-transfer coefficient ( $\text{m s}^{-1}$ ) and  $c_{\text{bulk}}$  and  $c_{\text{surface}}$  are the analyte concentrations ( $\text{mol L}^{-1}$ ) in the liquid bulk phase and at the water surface, respectively. The mass-transfer coefficient  $k_L$  is usually defined as the ratio of the analyte's diffusion coefficient  $D$  ( $\text{m}^2 \text{s}^{-1}$ ) in water and the thickness  $\delta$  (m) of a diffusion (sometimes called hydrodynamic or stagnant) boundary layer  $k_L = D/\delta$ . Because  $k_L$  and  $A$  are hardly determinable independently, we use the product  $k_L \times A$  ( $\text{m}^3 \text{s}^{-1}$ ) as effective mass-transfer coefficient.

Due to the continuous purging of the headspace, the gas-phase concentration of the analytes was much lower than the concentration which would be reached under equilibrium conditions. This means that the concentration at the surface ( $c_{\text{surface}}$ ) was close to zero, i.e.  $j = k_L \times A \times c_{\text{bulk}}$ .

If the system contains only a homogeneous water phase, the purging results in a continuous and measurable depletion of the analytes from the system, which follows a first-order kinetics (exemplarily shown in Figure S1 in Supporting Information (SI, part A)). Thus, the effective mass-transfer coefficient ( $k_L \times A$ ) can be calculated from the

slope of a half-logarithmic plot of the gas-phase concentration over time:

$$\ln\left(\frac{c}{c_0}\right)_g = -\frac{k_L \times A}{V_w} \times t \quad (4)$$

Derivation of eq 4 and consequences of the presence of the PDMS sheets are explained in SI (parts B and E).

In the constant activity system, PDMS sheets were used as quasi non-depleting source for n-octane. In this case, the flux of n-octane from water to the gas phase was determined, based on n-octane concentrations measured in the gas phase and the volumetric flow rate of the purge gas (according to eq 2:  $j_{n\text{-octane}} = c_{g,n\text{-octane}} \times Q$ ).

In order to identify the sorption-induced effect of DHS and SDS micelles and to compensate for any changes in the hydrodynamic conditions among the various experimental setups, we always consider the *ratio* of mass-transfer rates of n-octane and benzene which were determined in one and the same system. In order to do so, the ratio of  $(k_L \times A)_{n\text{-octane}} / (k_L \times A)_{\text{benzene}}$  is considered for the reduced activity system, whereas the ratio of n-octane flux and effective mass-transfer coefficient of benzene is used for the constant-activity system (i.e. with PDMS sheets):

$$c_{N,n\text{-octane}} = j_{n\text{-octane}} / (k_L \times A)_{\text{benzene}} \quad (5)$$

The resulting term  $c_{N,n\text{-octane}}$  has the dimension of a concentration ( $\text{mol L}^{-1}$ ) and can be considered as an n-octane gas-phase concentration normalized to constant hydrodynamic conditions.

### **Prediction of sorption-induced effects on mass transfer based on existing models**

In order to take into account sorption-induced effects on mass transfer in the diffusive boundary layer, Ter Laak et al. (5) suggested using an average mass-transfer coefficient for the complexed and free fractions together with total dissolved concentrations of the chemicals. This requires considering an averaged diffusivity  $\bar{D}$  weighted for the complexed and free fractions ( $x_{\text{free}}$  and  $x_{\text{sorb}}$ ):

$$\bar{D} = x_{\text{free}} \times D_u + x_{\text{sorb}} \times D_b = \frac{D_u + K_{\text{DOC}} \times c_{\text{DOC}} \times D_b}{1 + K_{\text{DOC}} \times c_{\text{DOC}}} \quad (6)$$

with  $D_u$  and  $D_b$  being the diffusion coefficients of the freely dissolved chemical and its complexes with the sorbent and  $K_{\text{DOC}}$  the partition coefficient of the chemical with the sorbent. The use of a single  $K_{\text{DOC}}$  value implies a linear sorption isotherm, which is an admissible approximation for the majority of hydrophobic organic compounds (e.g. PAHs, alkanes, PCBs) and DHS studied so far (20).

In addition, a lability factor  $\xi$  can be introduced in order to correct for incomplete dissociation of the complexes in the boundary layer (eq 7).  $\xi = 1$  is valid for labile complexes, i.e. if sorption and desorption processes are instantaneous with respect to the timescale of residence of the sorbate in the boundary layer, and  $\xi = 0$  is valid for non-labile complexes.

$$\bar{D} = x_{\text{free}} \times D_u + \xi \times x_{\text{sorb}} \times D_b = \frac{D_u + \xi \times K_{\text{DOC}} \times c_{\text{DOC}} \times D_b}{1 + K_{\text{DOC}} \times c_{\text{DOC}}} \quad (7)$$

The mass-transfer coefficient  $k_L$  is determined by the average diffusion coefficient and diffusion layer thickness. For a simple planar geometry it holds that  $k_L = \bar{D}/\bar{\delta}$ , where  $\bar{\delta}$  is the average diffusion layer thickness. Ter Laak et al. (9) discussed that, according to the theoretical model of Levich (21), the diffusion layer thickness depends on the diffusivity of the considered compound, and thus the average diffusion layer thickness should be defined as

$$\bar{\delta} = \left( \frac{\bar{D}}{\nu} \right)^{1/3} \delta_0 \quad (8)$$

where  $\nu$  is the kinematic viscosity of water and  $\delta_0$  is the thickness of the convective boundary layer, which is solely determined by the hydrodynamic conditions.

Consequently, the flux of a chemical in the presence of sorptive interactions should be described by:

$$j = \bar{D}^{2/3} \times \nu^{1/3} \times \delta_0^{-1} \times A \times (c_{\text{bulk}} - c_{\text{surface}}) = k_L \times A \times (c_{\text{bulk}} - c_{\text{surface}}) \quad (9)$$

Thus, the sorption-induced change in the effective mass-transfer coefficient for a chemical due to the presence of DHS can be described by:

$$\frac{(k_L \times A)^{\text{sorp}}}{(k_L \times A)^{\text{no sorp}}} = \left( \frac{1 + K_{\text{DOC}} \times c_{\text{DOC}} \times \xi \times D_b / D_u}{1 + K_{\text{DOC}} \times c_{\text{DOC}}} \right)^{2/3} \quad (10)$$

## Results and Discussion

### Partition coefficients of applied compounds

Table 1 shows the freely dissolved fractions of the analytes at  $c_{\text{CHA}} = 1 \text{ g L}^{-1}$  and  $c_{\text{SDS}} = 5 \text{ g L}^{-1}$  together with their partition coefficients. Benzene was not significantly sorbed at a concentration of  $1 \text{ g L}^{-1}$  CHA, whereas the fraction of sorbed n-octane was  $(85 \pm 1)\%$ . SDS has a CMC of  $2.3 \text{ g L}^{-1}$  (22). In the presence of  $5 \text{ g L}^{-1}$  SDS, the sorbed fraction of benzene was  $(29.5 \pm 4)\%$  and almost all n-octane was sorbed  $((97.6 \pm 0.3)\%)$ . Because of the very high volatility of dissolved n-octane ( $K_{\text{H}} = 134$ ) determination of its  $K_{\text{DOC}}$  value requires an experimental setup with a high water to gas-phase ratio: a large volume of DHS solution with a relatively high DOC concentration must be available. Otherwise, there is either no significant sorption effect or the uncertainty for the obtained  $K_{\text{DOC}}$  value is too high. SRHA and SRFA were not available in quantities sufficient for conducting such experiments. However, based on previous studies which compared the sorption potential of DHS of various origins, it can be deduced that  $K_{\text{DOC}}$  values decrease in the order  $\text{CHA} \gg \text{SRHA} > \text{SRFA}$  and that the difference in the  $K_{\text{DOC}}$  values of n-octane with the less hydrophobic aquatic SRHA and SRFA compared with leonardite HA (CHA) is about one order of magnitude (23-25).

Table 1. Freely dissolved fractions ( $x_{\text{free}}$ ) determined at  $c_{\text{CHA}} = 1 \text{ g L}^{-1}$  or  $c_{\text{SDS}} = 5 \text{ g L}^{-1}$  and partition coefficients of the model compounds with the applied dissolved sorbents.

	<b>Benzene</b>	<b>n-Octane</b>
<b>CHA</b>		
$\log K_{\text{DOC}}^{\text{a)}}$	$\leq 1.8$	$4.05 \pm 0.03^{\text{b)}}$
$x_{\text{free}}$ at $1 \text{ g L}^{-1}$ CHA	$\geq 0.95$	$0.15 \pm 0.01$
<b>SDS</b>		
$\log K_{\text{mc}}^{\text{a)}}$	$2.20 \pm 0.1$	$4.18 \pm 0.06$
$x_{\text{free}}$ at $5 \text{ g L}^{-1}$ SDS	$0.71 \pm 0.04$	$0.025 \pm 0.003$

<sup>a)</sup> unit of  $K_{\text{DOC}}$  and  $K_{\text{mc}}$  is  $\text{L kg}^{-1}$ ,  $c_{\text{DOC}} = 0.50 \times c_{\text{CHA}}$  for CHA solution (12)

<sup>b)</sup> the scattering interval corresponds to  $2 \sigma$  from three replicates

### **Mass-transfer rates determined for homogeneous solutions without additional sources or sinks (*reduced-activity system*)**

Figure 1 shows the effective mass-transfer coefficients for water-gas exchange of n-octane in solutions containing various concentrations of DHS and the synthetic surfactant SDS. All types of DHS caused a decrease in the water-gas exchange rates even at low, i.e. environmentally relevant, DHS concentrations. In general, mass-transfer coefficients decreased with increasing concentration of DHS and SDS at concentrations below its CMC (Figure 1).

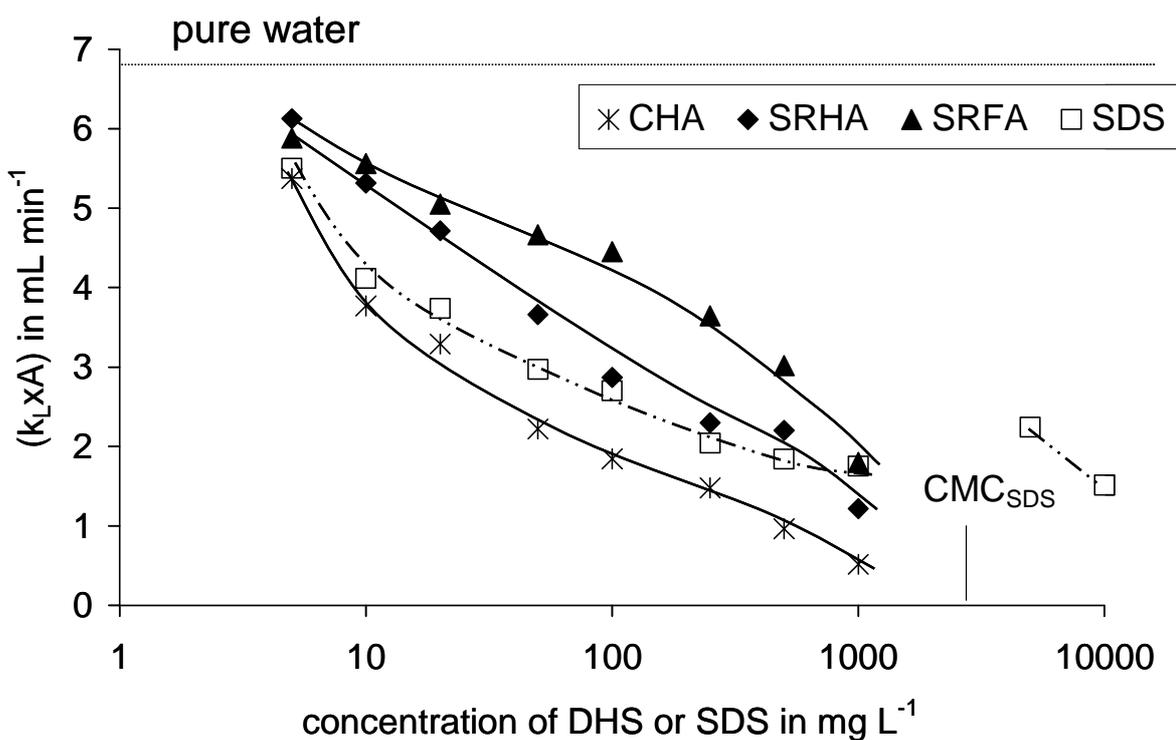


Figure 1. Effective mass-transfer coefficients of n-octane at various concentrations of DHS and SDS (below and above  $CMC_{SDS}$ ) in the reduced-activity system. Relative error of  $(k_L \times A)$  expressed as  $2\sigma$  is in general lower than 15%. Lines were drawn as guide to the eye. For pure water:  $k_L \times A = 6.8 \pm 0.8$ .

Similar results were described already in our earlier study for the less hydrophobic compounds benzene and cyclohexane (12). For these compounds, the changes in the water-gas exchange rates are mainly due to the hydrodynamic effect caused by the enrichment of DHS or SDS at the water surface (12). Effective mass-transfer coefficients for benzene which were determined in the present study are shown in Figure S2 in SI (part C).

In case of the synthetic surfactant SDS, the absolute values for the effective mass-transfer coefficients of n-octane and benzene are not steadily declining with increasing surfactant concentration. In contrast, there is an increase in  $k_L \times A$  when the CMC is reached (see Figure 1 and Figure S2 in SI). This behavior is probably due to a reduction in the hydrodynamic effect (12) and not related to sorption by surfactant micelles, since it is much more pronounced for the less sorbing compound benzene ( $x_{free,benzene} = 0.71$  vs.  $x_{free,n-octane} = 0.025$  at  $5 \text{ g L}^{-1}$  SDS).

In order to emphasize any sorption-induced effect, we calculated the ratio of the effective mass-transfer coefficients for n-octane and benzene, which were determined

simultaneously in each experiment. The hydrodynamic effect of DHS on mass transfer should be similar for the two compounds, so that a normalization of this effect is achieved. In pure aqueous solutions of the compounds, the ratio of their effective mass-transfer coefficients  $(k_L \times A)_{\text{n-octane}} / (k_L \times A)_{\text{benzene}}$  was  $0.82 \pm 0.05$ . A value close to unity is in line with the hypothesis that mass-transfer resistance in the liquid boundary layer determines the rate of water-gas exchange. The actual value of 0.82 corresponds well with an estimation of their diffusivity ratio (18), i.e.  $D_{\text{n-octane}}/D_{\text{benzene}} = (V_{\text{m,benzene}}/V_{\text{m,n-octane}})^{0.862} = 0.81$ . In case of a significant contribution of the gaseous boundary layer to the overall mass-transfer resistance, the compound with the higher Henry's law coefficient (i.e. n-octane) would be strongly favored with respect to water-gas exchange rates (12, 18). Obviously, this is not the case in our experiments.

Figure 2 shows the ratio of the effective mass-transfer coefficients of n-octane and benzene as a function of the concentration of DHS or SDS in the solution. Considering the two Figures 1 and 2 together, they illustrate that the water-gas exchange rate of n-octane is more affected than that of benzene. For example,  $(k_L \times A)_{\text{n-octane}}$  is roughly three times more strongly reduced compared to  $(k_L \times A)_{\text{benzene}}$  in the presence of  $1 \text{ g L}^{-1}$  CHA. For benzene, the reduction in  $k_L \times A$  at  $1 \text{ g L}^{-1}$  CHA compared to DHS-free water is by a factor of 4.6 (Figure S2) whereas for n-octane it is by a factor of 13 (Figure 1). Consequently, 35% of the reduction in  $(k_L \times A)_{\text{n-octane}}$  at  $1 \text{ g L}^{-1}$  CHA can be explained by the hydrodynamic effect (since it is also observed for benzene, which is not significantly sorbed under these conditions), whereas 65% of the overall effect would be due to sorption effects.

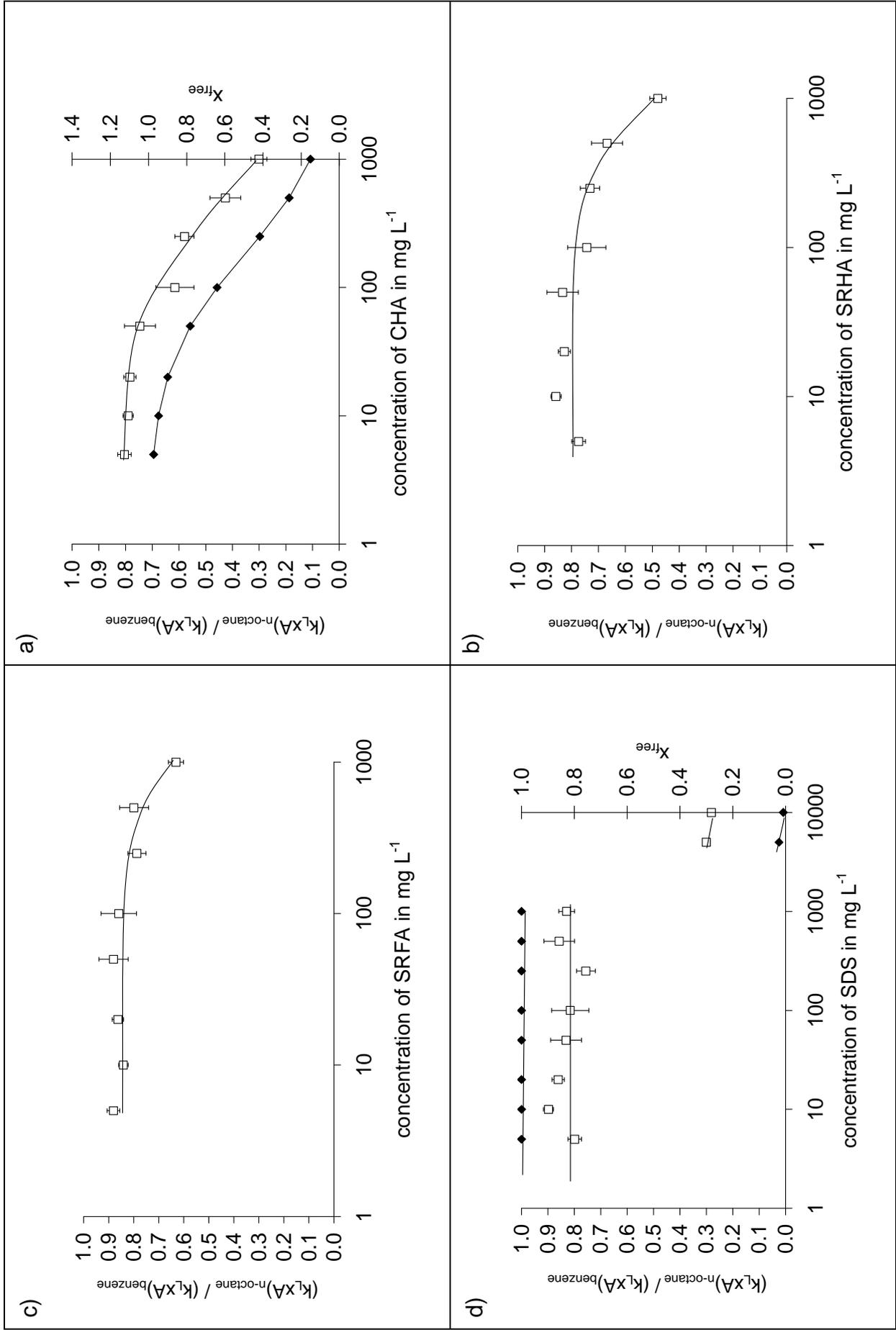


Figure 2. Ratio of the effective mass transfer coefficients of n-octane and benzene ( $\square$ , lines drawn as guide to the eye) and freely dissolved fraction of n-octane ( $\blacklozenge$ , calculated according to eq 1) for solutions containing various concentrations of a) CHA, b) SRHA, c) SRFA and d) SDS (below and above  $CMC_{SDS}$ ) in the reduced activity system. Error bars represent  $2\sigma$ .

In addition, the freely dissolved fractions of n-octane and benzene were calculated for CHA and SDS solutions, based on their  $K_{DOC}$  and  $K_{mc}$  values given in Table 1, and plotted for n-octane in Figures 2 a and d, respectively. Underlying assumptions are: (i)  $K_{DOC} = \text{const.}$  over the CHA-concentration range studied, which is justified by the findings described in (25), and (ii) sorption of n-octane to SDS is dominated by partitioning into SDS micelles, whereas the contribution of SDS monomers is negligible.

The trend in the ratio of the effective mass-transfer coefficients of n-octane and benzene is clearly reflected by the trend in the ratio of the freely dissolved fractions of the two compounds. Both ratios are steadily decreasing in the case of CHA, whereas in the case of the synthetic surfactant SDS there is no effect at concentrations below its CMC, but a strong effect on  $x_{\text{free}}$  and mass-transfer ratios at concentrations exceeding its CMC. Among the various DHS, the specific hindrance effect on n-octane mass transfer increased in the order SRFA < SRHA < CHA, which is in accordance with the expected trend in their sorption potential towards hydrophobic organic compounds (23-25). These results clearly indicate a sorption-induced effect of DHS and surfactant micelles on water-gas exchange of hydrophobic compounds.

Figure 3 shows the measured ratio of  $k_L \times A$  for n-octane and benzene as a function of CHA concentration together with three model curves calculated on the basis of eq 10 (for details see eq S8 in part D of SI). The model calculation was done for non-labile complexes ( $\xi = 0$ ) and for fully labile complexes ( $\xi = 1$ ). The diffusion coefficient of the freely dissolved n-octane was assumed to be 5 or 50 times higher than for the complexes with CHA. This reflects the range of diffusivities reported for humic acids of various origins in the literature (26-27).

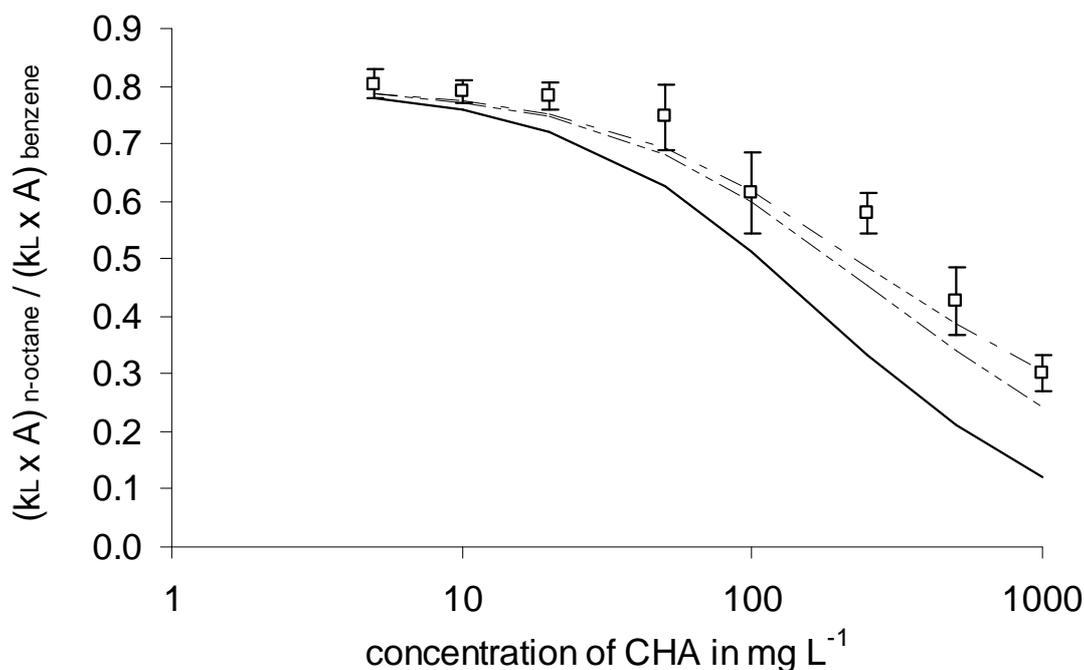


Figure 3. Ratio of effective mass-transfer coefficients for n-octane and benzene at various concentrations of CHA in the reduced-activity system, illustrating the sorption-induced effect on water/gas exchange rates: experimentally determined values and model predictions (based on eq 10) for non-labile complexes ( $\xi = 0$ , solid line) as well as for fully labile complexes ( $\xi = 1$ ) with ratios of the diffusion coefficients of free and complexed n-octane ( $D_f/D_b$ ) of 5 (upper dashed line) and 50 (lower dashed line). Error bars represent  $2\sigma$ .

Figure 3 shows that the measured values for  $(k_L \times A)_{n\text{-octane}} / (k_L \times A)_{\text{benzene}}$  are very close to the model prediction for fully labile complexes with a relatively high diffusivity at low CHA concentration. However, at the highest CHA concentration ( $1 \text{ g L}^{-1}$ ) they are closer to the low-diffusivity curve, which might be due to the formation of larger CHA agglomerates at this high concentration.

As expected, water/air exchange of hydrophobic compounds is not only affected by the hydrodynamic retardation effect of DHS, which was recently reported by our group (12), but additionally by sorption to DHS. Our experiments clearly show that sorption effects leading to a reduction in the freely dissolved concentration of the chemical have a negative effect on the diffusional mass-transfer rate. This is due to the fact that a proportion of the chemical is strongly hindered in diffusion due to complexation by the more bulky sorbent.

## Mass-transfer rates determined using passive dosing (*constant-activity system*)

Passive dosing experiments were conducted in order to simulate a system where sorption of a chemical by dissolved sorbents does not affect its thermodynamic activity (or freely dissolved concentration) in the aqueous phase due to re-delivery from a large source, as for instance in the presence of a contaminated sediment. Benzene and n-octane were again applied simultaneously in order to differentiate between hydrodynamic and sorption-induced effects on mass transfer.

The silicone sheets, which were preloaded with n-octane, provided a constant concentration of n-octane in the aqueous phase during the purging experiment, showing that the redelivery of n-octane from the sheets was faster than its depletion from the aqueous phase by purging (see Figure S3, part E of SI). Consequently, the flux of n-octane from the water to the gas phase was constant over the time of the experiment (2 h). Benzene, due to its lower hydrophobicity, was less buffered by the silicone sheets. Therefore, its concentration in the system was continuously decreasing during the purging experiment, similar to the reduced-activity system.

Absolute values for  $(k_L \times A)_{\text{benzene}}$  varied by less than a factor of 1.3 in the presence of the various DHS and also SDS in the constant-activity system (data not shown). In comparison, a factor of 4-5 reduction in  $(k_L \times A)_{\text{benzene}}$  was observed in the reduced activity system, i.e. under nearly identical conditions but in absence of the silicone sheets for 1 g L<sup>-1</sup> of CHA or SDS (Figure S2, part C of SI). Based on these results, we conclude that the hydrodynamic effect is much less pronounced in the constant-activity system. The magnitude of the hydrodynamic effect of surface-active compounds on water/gas exchange rates clearly depends on the agitation conditions, with a maximum at moderate agitation intensity (14). While the stirring rate was identical for the reduced- and constant-activity systems, the intensity of agitation in the water phase was drastically lower in the latter case due to the damping effect of the sheets. This was observed visually, but it also follows from the lower absolute values for  $k_L \times A$  of the two compounds in pure water compared to the system without dosing sheets (see also discussion in SI, part E). Thus, it is not surprising that the hydrodynamic effect is strongly reduced in this system.

In order to identify the sorption-induced effect we analyzed the ratio of the n-octane gas-phase concentrations normalized to constant hydrodynamic conditions ( $c_{N,n\text{-octane}}$ ) in the presence and absence of dissolved sorbents:

$$R_{n\text{-octane}}^{\text{sorp}} = \frac{(C_{N,n\text{-octane}})^{\text{sorp}}}{(C_{N,n\text{-octane}})^{\text{water}}} \quad (11)$$

Figure 4 shows that this ratio is  $> 1$  in the presence of  $1 \text{ g L}^{-1}$  of the various DHS and  $5 \text{ g L}^{-1}$  of SDS, indicating a positive effect of sorption on mass-transfer rates. At identical concentrations of these sorbents, sorption had a negative effect on  $k_L \times A$  values and thus the flux of n-octane from water to gas phase in the reduced-activity system. In both systems, the average diffusion coefficient of the chemical is reduced due to the lower diffusion coefficient of the complexed fraction. However, in the constant-activity system this can be overcompensated by the higher total concentration of the chemical in the aqueous phase, leading to a steeper concentration gradient in the diffusion boundary layer.

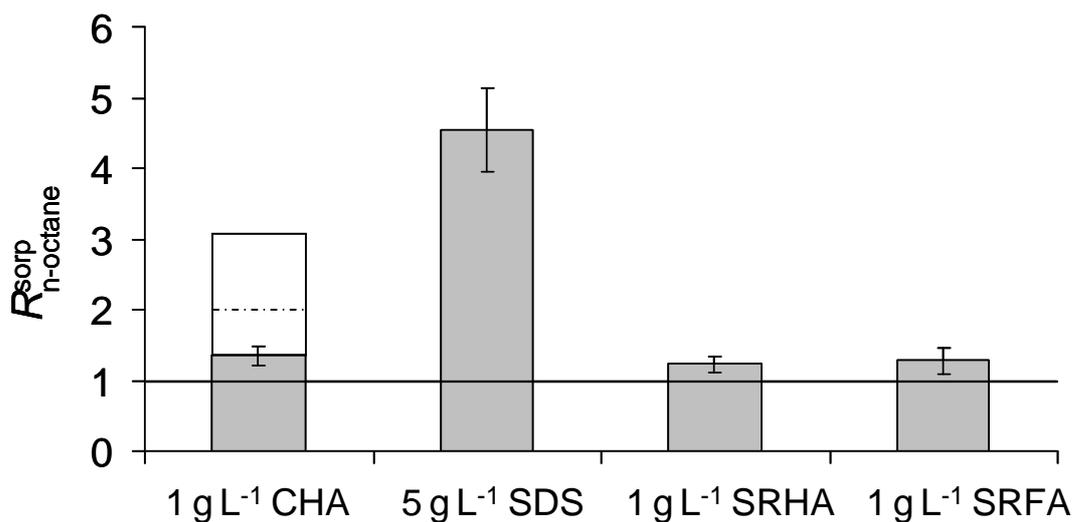


Figure 4. Sorption-induced increase in n-octane flux from water to the gas phase ( $R_{n\text{-octane}}^{\text{sorp}}$ ) for solutions containing various types of DHS and SDS in the constant-activity system (with silicone sheets for passive dosing of n-octane): experimentally determined values (grey bars) and predicted values for  $1 \text{ g L}^{-1}$  CHA solution in the case of fully labile complexes ( $D_u/D_b = 5$  (white bar),  $D_u/D_b = 50$  (dashed line)).

A value of  $R_{n\text{-octane}}^{\text{sorp}} = 1.35$  at  $1 \text{ g L}^{-1}$  CHA means that the presence of sorbed n-octane ( $x_{\text{sorb},n\text{-octane}} = 0.85$ ) leads to a factor of 1.35 increase in n-octane flux from water to the gas phase compared to pure water. In Figure 4, the experimental result for CHA is again compared with predicted values, which were calculated on the basis of

eq 12. Eq 12 can be easily derived based on eq 10 in the case of a maximal concentration gradient ( $c_{\text{surface}} \approx 0$ ) (see SI, part F).

$$R_{\text{n-octane}}^{\text{sorp,calc}} = \frac{(C_{\text{N,n-octane}})^{\text{CHA}}}{(C_{\text{N,n-octane}})^{\text{water}}} = \left( 1 + K_{\text{DOC}} \times c_{\text{DOC}} \times \xi \times \frac{D_b}{D_u} \right)^{2/3} \times (1 + K_{\text{DOC}} \times c_{\text{DOC}})^{1/3} \quad (12)$$

Model calculations were performed for the cases of fully labile complexes ( $\xi = 1$ ) with  $D_u/D_b$  ratios of 5 and 50. The maximum increases in flux due to sorption by CHA are expected to be a factor of 3.1 and 2.0 with  $D_u/D_b = 5$  and 50, respectively. In the case of non-labile complexes ( $\xi = 0$ ), the normalized flux ratio for n-octane should be 1, i.e. mass-transfer rates are not affected by sorption. The experimental result for CHA ( $R_{\text{n-octane}}^{\text{sorp}} = 1.35 \pm 0.13$ ) falls within the predicted range and shows a positive effect of sorption on n-octane mass transfer (Figure 4). However, the effect is lower than predicted for fully labile complexes, even with  $D_u/D_b = 50$ . This is different from the result obtained for the reduced-activity system (Figure 3). A possible explanation of this finding might be a higher tendency of CHA to form larger agglomerates at the lower agitation intensity, leading to a decrease in diffusivity and/or a slower desorption rate of n-octane from its complexes with CHA ( $\xi < 1$ ). Examples for decreasing complex lability with increasing agglomerate size were reported e.g. in (28-29).

It should be emphasized that the sorption-induced effect on contaminant flux from water to the gas phase depends on (i) the decrease in the averaged mass-transfer coefficient and (ii) the change in the concentration gradient in the diffusion boundary layer. The latter is increased in the presence of a sorbed fraction in the constant-activity system. With increasing tendency of sorption (i.e.  $x_{\text{free}} \rightarrow 0$ ) the averaged mass-transfer coefficient approaches a limiting value, i.e. that of the sorbed fraction. In contrast, the solubility-enhancing effect of DOM towards the sorbate is (theoretically) not limited. Thus, the concentration gradient in the boundary layer can be increased proportionally to the DOM concentration.

The stronger increase of n-octane flux in the presence of 5 g L<sup>-1</sup> SDS compared to the solutions with 1 g L<sup>-1</sup> DHS is probably caused to a large extent by the higher total n-octane concentration in the aqueous phase (i.e. a factor of 6 higher for 5 g L<sup>-1</sup> SDS than for 1 g L<sup>-1</sup> CHA) leading to a steeper concentration gradient in the boundary layer. A small positive sorption-induced effect on mass-transfer rates was also observed for the aquatic DHS samples.

## Interplay of effects

In contrast to the reduced-activity system, where sorption to DHS and SDS micelles decreased the rate of mass transfer of n-octane from the water to the gas phase, the effect of sorption in the constant-activity system is positive. This behavior is similar to the shuttle effect of DHS and other dissolved sorbents on the mass transfer of hydrophobic chemicals from water to particle surfaces, as described in the references cited above. In this respect, water/gas interfaces have common features with water/particle interfaces. The hydrodynamic effect, however, seems to be more specific for water/gas interfaces.

The magnitude of sorption-induced effects further depends on the mobility of the sorbent (diffusion coefficient) and the lability of the complexes in terms of their residence time in the diffusion layer. Using a time-resolved in-tube SPME method, Kopinke et al. (28) showed that the dominant fraction of the sorbate (e.g. pyrene and dimethyl cyclohexane) desorbs from CHA and SRHA with a half-life of less than 3 s. However, a certain fraction desorbs much more slowly, i.e. with a half-life in the order of minutes. The thickness of the aqueous diffusion layer at air-water interfaces in the environment is typically in the range of 20 - 200  $\mu\text{m}$  (18). Based on the Einstein-Smoluchowsky correlation, a corresponding residence time range of 2 to 200 s for DHS molecules can be estimated (assuming  $D_{\text{DHS}} = 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ). Thus, significant but possibly incomplete lability of pollutant-DHS complexes is to be expected for transport through aqueous diffusion boundary layers at air-water interfaces in the environment.

The results obtained with our simplified model system clearly demonstrate that DHS are able to exert hydrodynamic and sorption-induced effects on the kinetics of water/gas exchange. Two aspects, i.e. the change of the chemical activity and overall diffusivity of organic compounds due to their interaction with DHS, have to be considered. Improved mechanistic understanding of sorption-induced effects on water/air exchange is highly relevant for the refinement of estimation models which describe pollutant transport between the atmosphere and oceans (15-17).

For typical DHS concentrations in the environment, in the range of 10 to 50  $\text{mg L}^{-1}$ , sorption-induced effects on water/air exchange rates are only to be expected for very hydrophobic compounds with  $\log K_{\text{DOC}} \geq 5$ , such as highly chlorinated PCBs or PAHs. In technical processes, where DHS or surfactant concentrations can be much higher (e.g. stripping of soil-washing solutions), a broader relevance can be expected.

## Acknowledgements

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## Supporting Information Available

Full versions of derivation of equations, additional figures showing experimental data of this study and discussion of boundary conditions in the passive dosing experiment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Supporting Information

### A) Figure S1

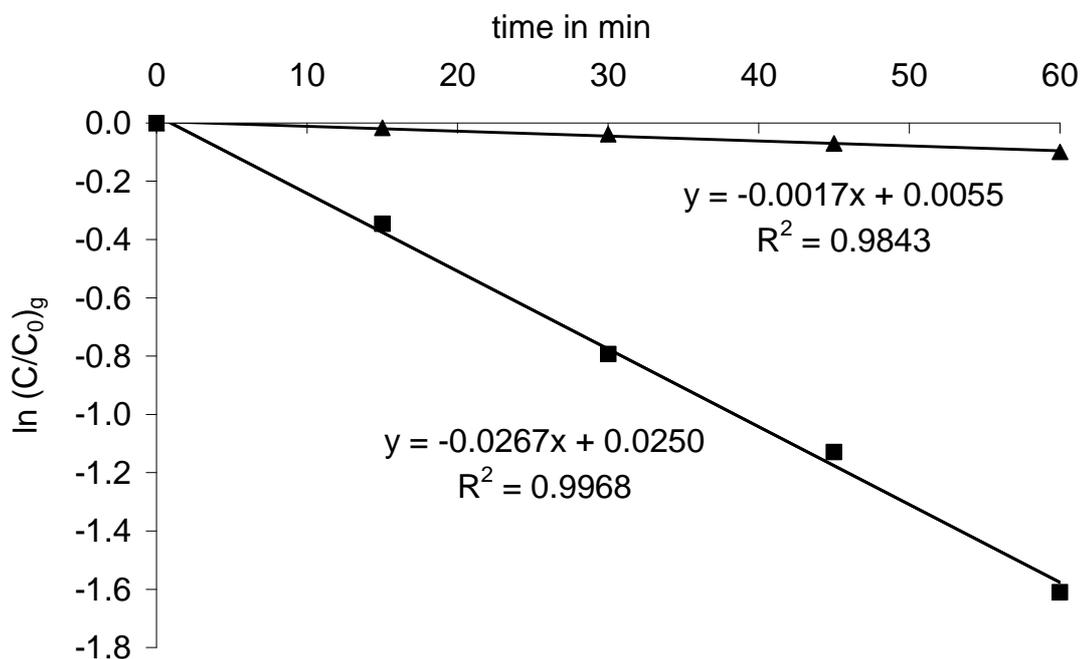


Figure S1. First-order plot of normalized gas-phase concentration of n-octane, showing the depletion of n-octane during dynamic purging experiments with aqueous solutions in the absence (■) and presence(▲) of CHA (reduced-activity system).

### B) Derivation of eq. 4

In order to derive quantitative data about the mass-transfer rates across the aqueous boundary layer, we applied the boundary layer model as described already in the main text. The mass flux of any compound through the boundary layer is described by eq. 3 of the main text ( $j = k_L \times A \times (c_{\text{bulk}} - c_{\text{surface}})$ ), which in case of  $c_{\text{surface}} \approx 0$  can be simplified to eq. S1.

$$j = k_L \times A \times c_{\text{bulk}} \quad (\text{S1})$$

In addition, the flux of the model compound in the effluent can be described by

$$j = Q \times c_g \quad (\text{S2})$$

where  $Q$  is the volumetric gas flow rate.

Combining eqs. S1, and S2 results in eq. S3:

$$c_{\text{bulk}} = \frac{Q}{k_L \times A} \times c_g \quad (\text{S3})$$

The depletion of the model compound in the system due to the purging can be described by eq. S4:

$$c_{\text{tot}} = c_{\text{tot},0} - \frac{Q}{V_w} \times \int_0^t c_g dt \quad (\text{S4})$$

with  $c_{\text{tot}}$  and  $c_{\text{tot},0}$  as total concentrations of the analyte in the liquid phase at  $t$  and  $t = 0$ , respectively. If the system consists only of headspace volume and a homogeneous aqueous phase than it holds  $c_{\text{tot}} = c_{\text{bulk}}$  and  $c_{\text{tot},0} = c_{\text{bulk},0}$  so that eq. S3 can be used to introduce gas phase concentrations into eq. S4 in order to give eq. S5:

$$c_g = c_{g,0} - \frac{k_L \times A}{V_w} \times \int_0^t c_g dt \quad (\text{S5})$$

By means of derivation by  $dt$ , it is possible to describe the change of the gas phase concentration as a function of time:

$$\frac{dc_g}{dt} = -\frac{k_L \times A}{V_w} \times c_g \quad (\text{S6})$$

Integration of eq. S6 yields eq. S7 which is identical with eq. 4 in the main text:

$$\ln\left(\frac{c}{c_0}\right)_g = -\frac{k_L \times A}{V_w} \times t = -m \times t \quad (\text{S7})$$

Thus, a plot of  $\ln\left(\frac{c}{c_0}\right)_g$  versus time should be linear. The effective mass-transfer coefficient  $k_L \times A$  is calculated from the slope  $m$ . For this purpose, any time period of a running purging experiment can be considered. The initial concentration  $c_0$  is the gas phase concentration of the model compound at the start of the observation period and  $t$

is the time elapsed after this start time.

The derivation of an equation for interpretation of contaminant depletion in terms of effective mass-transfer coefficients for the case of  $c_{\text{surface}} \neq 0$  is described in the Supplementary material of (Ramus et al. 2011). There we also showed that the approximation  $c_{\text{surface}} \approx 0$  is justified if the gas phase concentration of the compound measured during purging ( $c_g$ ) is much smaller than the value measured at equilibrium ( $c_{g,\text{eq}}$ , after closing the system), i.e. if it holds that  $c_g/c_{g,\text{eq}} \ll 1$ .

C) Figure S2

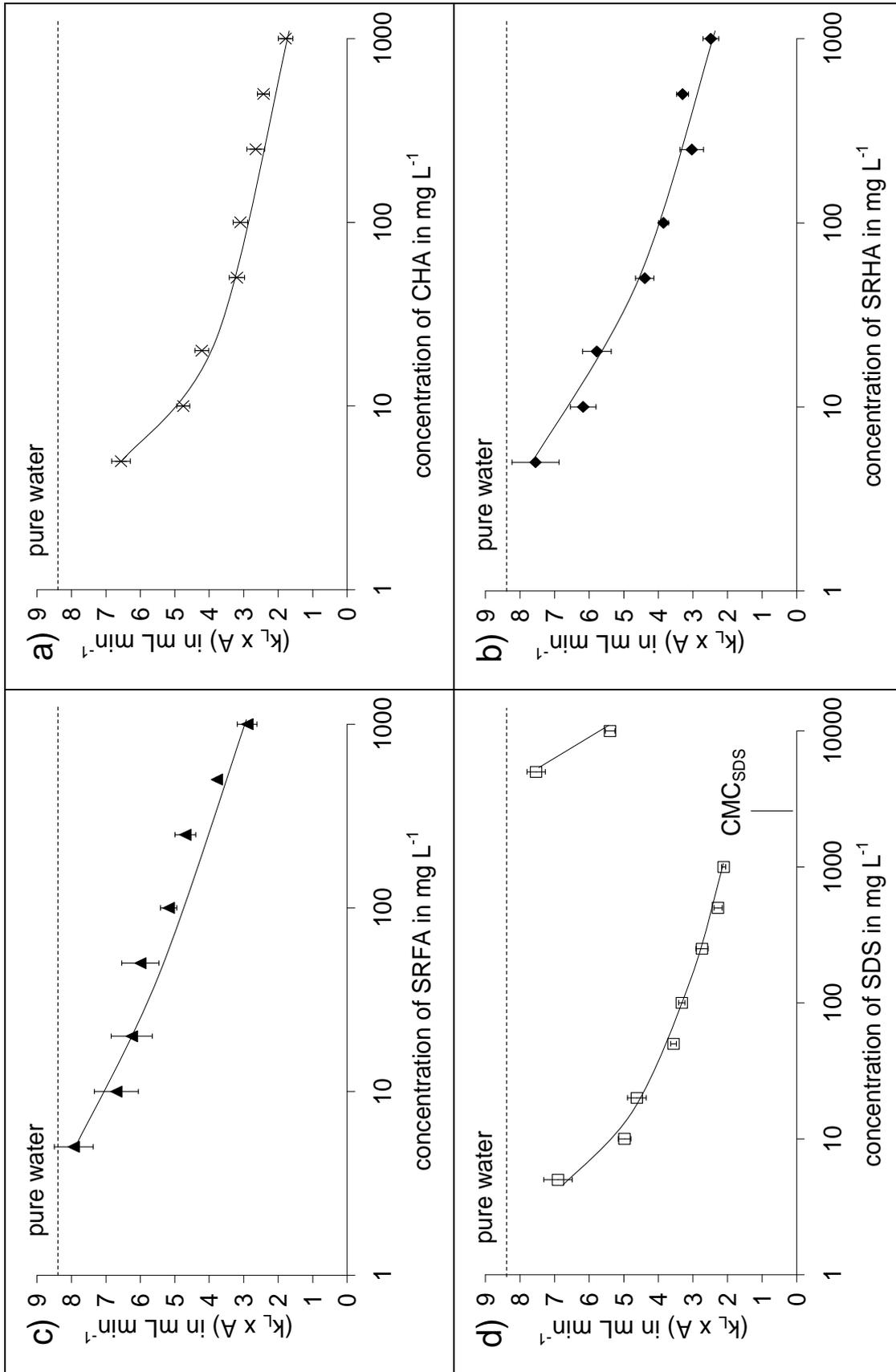


Figure S2. Effective mass-transfer coefficients of benzene at various concentrations of a) CHA, b) SRHA, c) SRFA and d) SDS (below and above  $CMC_{SDS} = 2300 \text{ mg L}^{-1}$ ) determined for the reduced-activity system. Solid lines were drawn as guides to the eye. Error bars represent  $2 \sigma$ .

**D) Equation S8 for calculation of predicted values for the ratio of effective mass-transfer coefficients in the presence of CHA (Figure 3 in the main text)**

$$\left( \frac{(k_L \times A)_{n\text{-octane}}}{(k_L \times A)_{\text{benzene}}} \right)^{\text{CHA}} = \left( \frac{(k_L \times A)_{n\text{-octane}}}{(k_L \times A)_{\text{benzene}}} \right)^{\text{water}} \times \frac{(k_L \times A)_{n\text{-octane}}^{\text{sorp}}}{(k_L \times A)_{n\text{-octane}}^{\text{no sorp}}} \quad (\text{S8})$$

The effective mass-transfer coefficient of benzene was assumed not to be affected by sorption-induced effects, due to its insignificant sorbed fraction for CHA concentrations  $\leq 1 \text{ g L}^{-1}$ . Therefore, this term does not need to appear in eq. S8.

$\frac{(k_L \times A)_{n\text{-octane}}^{\text{sorp}}}{(k_L \times A)_{n\text{-octane}}^{\text{no sorp}}}$  was calculated according to eq. 10, using  $\log K_{\text{DOC}} = 4.05$ ,  $\xi = 1$  and  $D_u/D_b = 50$  and  $5$ , respectively.

### E) Figure S3 and discussion of conditions in the constant-activity system

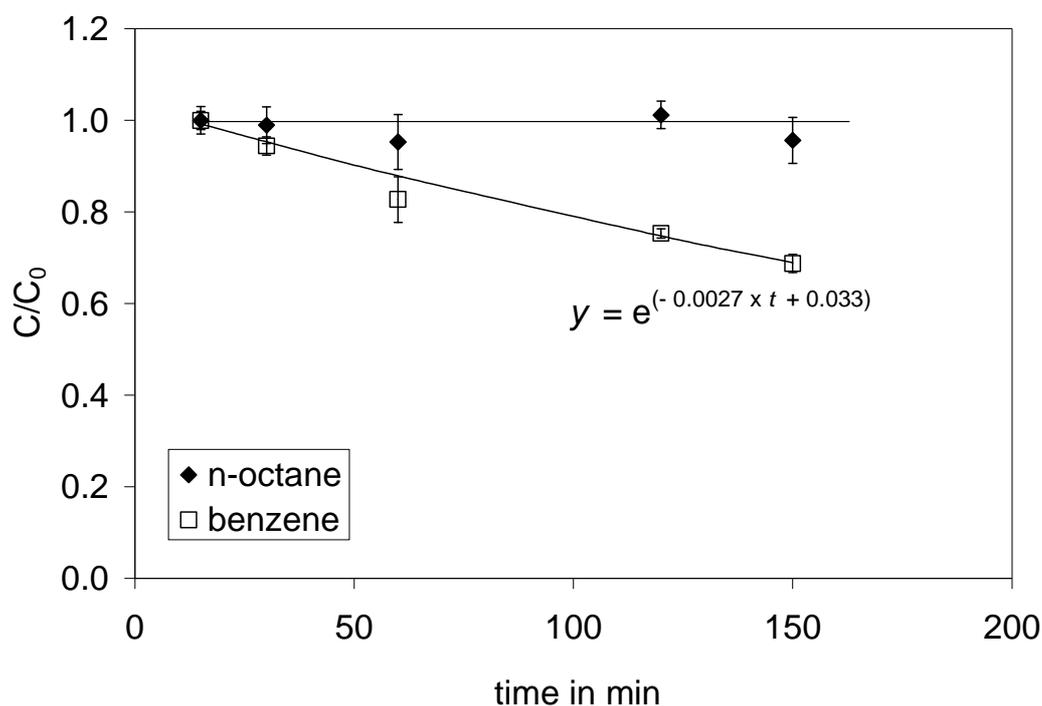


Figure S3. Normalized concentrations of n-octane and benzene in the gas phase during the purging experiment with passive dosing (constant-activity system). Concentrations measured at the first sampling point (15 min after starting purging + mixing of the aqueous phase) were used for normalization ( $c_0$ ). Line for benzene was obtained by fitting to first-order kinetics, line for n-octane illustrates hypothetical case of  $c/c_0 = 1$ . Error bars represent  $2\sigma$ .

#### *Partitioning of the model compounds between PDMS and water phase*

The partition coefficients of the PDMS sheets  $K_{\text{PDMS}}$  for benzene and n-octane can be approximately predicted from the PDMS/water partition coefficients reported in the literature for the PDMS phase of SPME fibers. For n-octane  $\log K_{\text{PDMS-fiber,n-octane}} = 4.42$  (Kopinke et al. 1999) was determined and for benzene values between  $\log K_{\text{PDMS-fiber,benzene}} = 1.94$  (Paschke and Popp 1999) and 2.10 (Nardi et al. 2003) were reported.

Based on  $\log K_{\text{PDMS,n-octane}} = 4.42$  for system containing water and  $2 \text{ g L}^{-1}$  of the PDMS sheets the ratio between the PDMS-sorbed amount ( $n_{\text{PDMS,n-octane}}$ ) and the freely dissolved amount of n-octane ( $n_{\text{free,n-octane}}$ ) is predicted as  $n_{\text{PDMS,n-octane}}/n_{\text{free,n-octane}} = K_{\text{PDMS,n-octane}} \times c_{\text{PDMS}} = 53$ . Due to this high ratio, it is reasonable to expect that the PDMS sheets act as a non-depleting source for n-octane during the considered time

scales ( $t \leq 150$  min). This assumption was confirmed experimentally by the results shown in Fig. S3, where constant n-octane concentrations were observed over about 150 min of purging in the passive dosing system.

For benzene, enrichment in PDMS is not high enough in order to provide a significant source effect. Adding  $2 \text{ g L}^{-1}$  PDMS sheets into an aqueous solution of benzene results in a benzene depletion by a factor of  $f_{\text{PDMS}} = c_{\text{bulk}}/c_{\text{total}} = 0.44 \pm 0.03$ . The partition coefficient  $\log K_{\text{PDMS,benzene}} = 2.20$  which is calculated from the experimentally determined  $f_{\text{PDMS}}$  value is in accordance with the above mentioned values for  $K_{\text{PDMS-fiber,benzene}}$ .

The sorption effect caused by the PDMS sheets reduces the rate constant for removal of benzene by purging by a factor of  $f_{\text{PDMS}}$  according to

$$\ln\left(\frac{c}{c_0}\right)_g = -\frac{k_L \times A}{V_w} \times f_{\text{PDMS}} \times t \quad (\text{S9})$$

Eq. S9 which is different from eq. S7 only by the factor  $f_{\text{PDMS}}$ , can be derived analogously to the procedure described in part B of this Supporting information, with the exception that the bulk water phase concentration is related to the total concentration of benzene in the system by  $c_{\text{bulk}} = f_{\text{PDMS}} \times c_{\text{tot}}$ .

The presence of the various DHS in a concentration of  $1 \text{ g L}^{-1}$  did not significantly affect  $f_{\text{PDMS}}$ , which is reasonable taking into account the insignificant sorption of benzene by DHS at this concentration (Table 1). Only in the presence of  $5 \text{ g L}^{-1}$  SDS,  $f_{\text{PDMS}}$  was increased to  $0.56 \pm 0.02$ , which is due to the solubility enhancement effect of the micelles for benzene ( $\chi_{\text{sorb,benzene}} = 0.29$  at  $5 \text{ g L}^{-1}$  SDS, Table 1).

Even after taking into account the buffering effect of the sheets (by applying eq. S9) there is still a difference in the  $k_L \times A$  values determined for benzene in the constant activity system in comparison to the system without PDMS sheets (a factor of about 4). This is clearly due to the reduced agitation intensity of the water phase in the presence of the PDMS sheets (at the same stirring rate) which was also observed visually.

#### *Rate of compound redelivery from the PDMS sheets*

In order to interpret the passive dosing experiments with respect to mass transfer in the aqueous boundary layer at the water/gas interface, it is necessary to assure that

compound delivery by the PDMS sheets into the water phase is instantaneous compared to depletion from the water by purging. Fig. S3 illustrates that this assumption is indeed justified. From the start of measurement of n-octane headspace concentrations (15 min after starting purging + mixing of the water phase) this concentration was constant within the experimental error range. This observation disproves the objection that delivery of n-octane from the sheets has any influence on mass transfer of n-octane into the gas phase. Otherwise, the approach to a steady state concentration (determined by both, water/gas and PDMS/water mass transfer) different from the start concentration should have been observable during the experiment shown in Fig. S3.

In order to explain this in more detail: the aqueous phase is initially in equilibrium with the PDMS sheets. After starting the mixing in addition to purging, n-octane is continuously removed from the aqueous phase. If the re-delivery from the PDMS sheets was too slow in order to compensate this loss, then there should be a decline in the measured headspace concentration until a steady state concentration is reached. This steady state concentration cannot be reached in less than 15 min, considering the low rate of water/gas mass transfer (as illustrated by the slow decline of  $c/c_0$  for benzene in Figure S3).

#### F) Derivation of eq. 12 for calculation of predicted values in Fig. 4

In order to predict the sorption-induced effect on the n-octane flux, we make again use of eqs. 3 and 10 of the main text, which are presented as eqs. S10 and S11 here again:

$$j = k_L \times A \times (c_{\text{bulk}} - c_{\text{surface}}) \quad (\text{S10})$$

$$\frac{(k_L \times A)^{\text{sorp}}}{(k_L \times A)^{\text{no sorp}}} = \left( \frac{1 + K_{\text{DOC}} \times c_{\text{DOC}} \times \xi \times D_b / D_u}{1 + K_{\text{DOC}} \times c_{\text{DOC}}} \right)^{2/3} \quad (\text{S11})$$

In case of the constant activity system, the concentration of the freely dissolved sorbate fraction is expected to be identical in the presence and absence of dissolved sorbents, whereas the bulk water phase concentration is increased by the sorbed fraction:

$$(C_{\text{bulk}})^{\text{no sorp}} = C_{\text{free}} \quad (\text{S12})$$

$$(C_{\text{bulk}})^{\text{sorp}} = C_{\text{free}} + K_{\text{DOC}} \times C_{\text{DOC}} \times C_{\text{free}} = C_{\text{free}} \times (1 + K_{\text{DOC}} \times C_{\text{DOC}}) \quad (\text{S13})$$

The ratio of compound flux in the presence and absence of partitioning to a sorbent depends thus on the ratio of the mass-transfer coefficients and the different bulk-phase concentrations of the compound (provided that the boundary conditions of  $c_{\text{surface}} = 0$  holds, which is given in our experiments):

$$\frac{j^{\text{sorp}}}{j^{\text{no sorp}}} = \frac{(k_L \times A)^{\text{sorp}}}{(k_L \times A)^{\text{no sorp}}} \times \frac{(C_{\text{bulk}})^{\text{sorp}}}{(C_{\text{bulk}})^{\text{no sorp}}} \quad (\text{S14})$$

Introducing eqs. S11 - S13 into eq. S14 results in eq. S15:

$$\frac{j^{\text{sorp}}}{j^{\text{no sorp}}} = (1 + K_{\text{DOC}} \times C_{\text{DOC}} \times \xi \times D_b / D_u)^{2/3} \times (1 + K_{\text{DOC}} \times C_{\text{DOC}})^{1/3} \quad (\text{S15})$$

We can now calculate the expected ratio of the normalized gas phase concentrations of n-octane in the presence and absence of CHA according to eq. S16:

$$R_{\text{n-octane}}^{\text{sorp,calc}} = \frac{(C_{\text{N,n-octane}})^{\text{CHA}}}{(C_{\text{N,n-octane}})^{\text{water}}} = \frac{(j_{\text{n-octane}})^{\text{sorp}}}{(j_{\text{n-octane}})^{\text{water}}} \quad (\text{S16})$$

The effective mass-transfer coefficient of benzene was assumed not to be affected by sorption-induced effects, due to its insignificant sorbed fraction for CHA concentrations  $\leq 1 \text{ g L}^{-1}$ . Therefore, the terms  $(k_L \times A)_{\text{benzene}}$  from eq. 5 (main text) do not need to appear in eq. S16.

Substituting the flux ratio in eq. S15 by eq. S16 results in eq. S17, which is identical with eq. 12 in the main text.

$$R_{\text{n-octane}}^{\text{sorp,calc}} = \frac{(j_{\text{n-octane}})^{\text{sorp}}}{(j_{\text{n-octane}})^{\text{no sorp}}} = \left(1 + K_{\text{DOC}} \times C_{\text{DOC}} \times \xi \times \frac{D_b}{D_u}\right)^{2/3} \times (1 + K_{\text{DOC}} \times C_{\text{DOC}})^{1/3} \quad (\text{S17})$$

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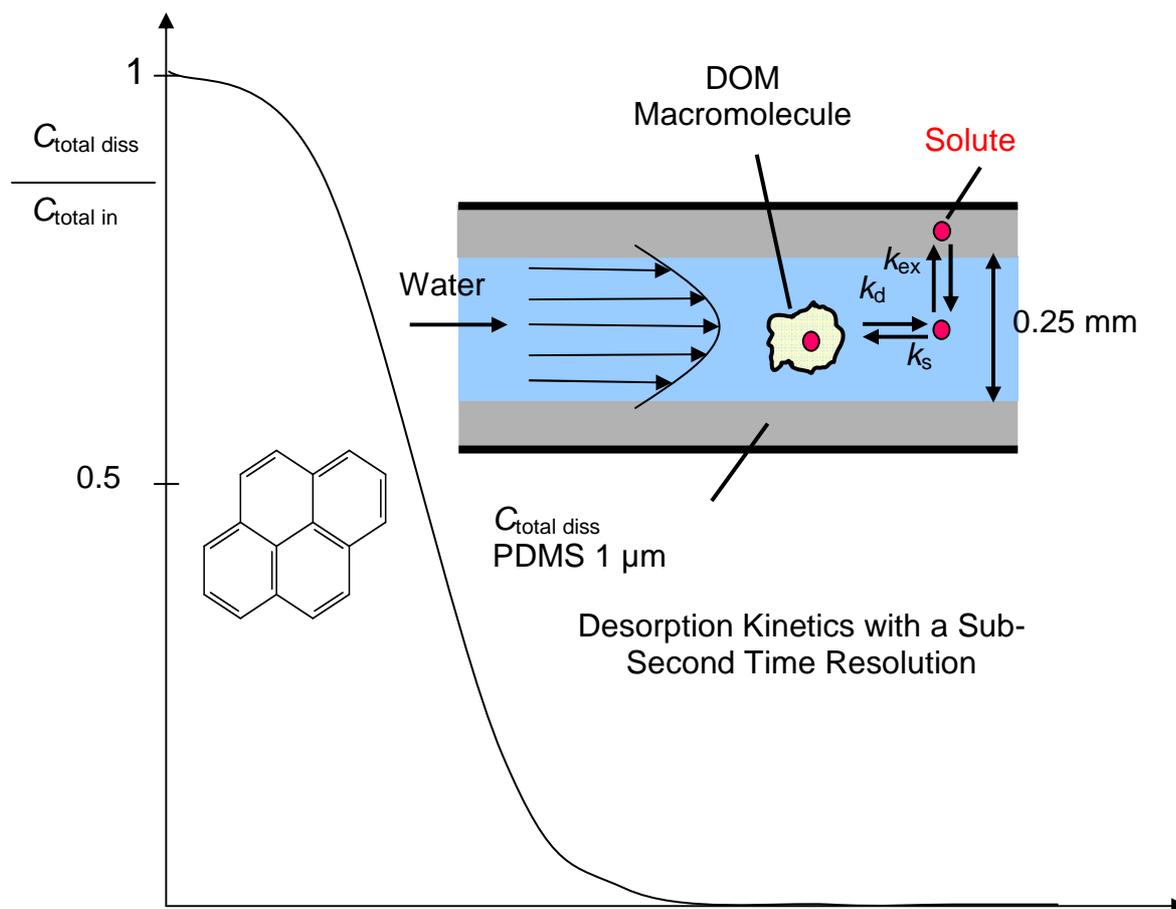
## 5. Kinetics of Desorption of Organic Compounds from Dissolved Organic Matter

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Environmental Science & Technology 2011, 45, 10013-10019.

### Abstract

This study presents a new experimental technique for measuring rates of desorption of organic compounds from dissolved organic matter (DOM) such as humic substances. The method is based on a fast solid-phase extraction of the freely dissolved fraction of a solute when the solution is flushed through a polymer-coated capillary. The extraction interferes with the solute-DOM sorption equilibrium and drives the desorption process. Solutes which remain sorbed to DOM pass through the extraction capillary and can be analyzed afterwards. This technique allows a time resolution for the desorption kinetics from sub-seconds up to minutes. It is applicable to the study of interaction kinetics between a wide variety of hydrophobic solutes and polyelectrolytes. Due to its simplicity it is accessible for many environmental laboratories.

The time-resolved in-tube solid-phase microextraction (TR-IT-SPME) was applied to two humic acids and a surfactant as sorbents together with pyrene, phenanthrene and 1,2-dimethylcyclohexane as solutes. The results give evidence for a two-phase desorption kinetics: a fast desorption step with a half-life of less than 1 s and a slow desorption step with a half-life of more than 1 min. For aliphatic solutes, the fast-desorbing fraction largely dominates, whereas for polycyclic aromatic hydrocarbons such as pyrene, the slowly desorbing, stronger-bound fraction is also important.



Desorption Kinetics with a Sub-Second Time Resolution

## Introduction

The fate of many organic chemicals in the environment depends on their bioavailability. This includes their bioaccessibility and their speciation. In an aqueous environment, chemicals can exist in the freely dissolved state or associated with various sorbents such as natural organic matter (NOM) in particulate (POM) or colloiddally dissolved forms. Dissolved organic materials (DOM) such as humic substances, proteins or surfactants can effect the transfer of chemicals between water and several source or sink phases by sorption-desorption processes (1-10). Sorption of organic chemicals on NOM is generally described as a partition process with a sorption coefficient  $K_{OM}$  or  $K_{OC}$ . This is the thermodynamic aspect of sorption which can be described on the basis of multi-parameter LFER concepts (11-16).

It is a plausible assumption for many environmental processes which take place on a long-term scale that sorption processes are close to equilibrium. However, in highly dynamic environmental systems, sorption kinetics may play a key role in the chemicals transport and transformation on the local scale (1,6,8). A prominent example is the shuttle function of DOM for hydrophobic organic compounds in water, in particular through boundary layers around reactive surfaces such as those of microorganisms or biofilms. This shuttle function has been clearly demonstrated under well-defined conditions for the solid-phase microextraction (SPME) of hydrophobic organic compounds from water into thin polymer films (5,8,16,17).

In contrast to the large abundance of data about sorption kinetics with POM, corresponding data with DOM are very scarce in the literature. One reason for this is a lack of appropriate experimental techniques for tracing very fast DOM-solute interactions. In the following part, three relevant studies on this kinetics, although covering a longer time-scale, will be briefly reviewed.

Schlebaum et al. (19) investigated interactions between a peat humic acid (HA) and pentachlorobenzene (QCB) by means of a gas-purging method. Their results show the presence of a fast-desorbing, labile fraction and a slowly desorbing, nonlabile fraction. None of the tested kinetic models was able to describe the experimental findings sufficiently. The authors speculate that the nonlabile fraction is a consequence of a change of conformation of the HA after sorption of QCB. This structural change leads to entrapment of the sorbate within the HA structure. The slowly desorbing, residual QCB fraction was about 1.3% to 3.7% of the total sorbate concentration (0.1 to 1 mg g<sup>-1</sup> HA). The estimated desorption rate coefficients are in the range  $k_{\text{desorption } 1} \approx 2 \text{ h}^{-1}$  and  $k_{\text{desorption } 2} = 0.1 \text{ h}^{-1}$  for the two fractions. The applied purging technique removed QCB from the water phase with a rate coefficient of about  $k_{\text{purge}} = 5.3 \text{ h}^{-1}$ . However, gas purging is a relatively slow method ( $\tau_{1/2 \text{ removal}} \approx 500 \text{ s}$ ) which does not allow even moderately fast desorption processes to be traced, because the condition  $k_{\text{purge}} \geq k_{\text{desorption}}$  cannot be fulfilled.

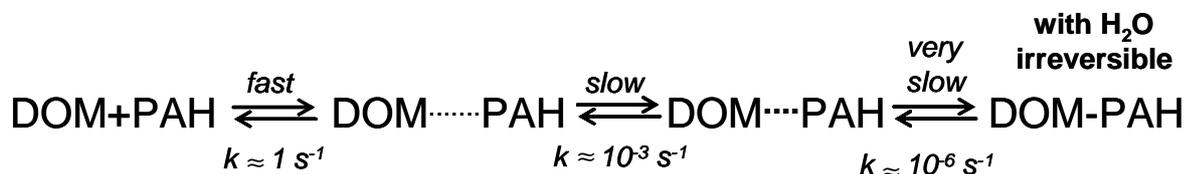
Kopinke et al. (2) investigated the kinetics of interactions between DOM and some polycyclic aromatic hydrocarbons (PAH). They applied a fast direct SPME (sampling time 30 s) in combination with deuterated solutes. The isotope ratios of the extracted solute mixtures, determined by means of GC-MS-analyses over the mixing time, revealed the kinetics of the sorption process. About 64% of the pyrene sorption ( $\log K_{\text{DOC}} = 4.93$ ) proceeded rapidly, i.e. within the first sampling period ( $\leq 60 \text{ s}$ ). This fast process could not be monitored by the applied SPME technique due

to its limited time resolution. However, the sorption process continued with a lower rate. Treatment of the data according to a first-order kinetics ( $dC_{D10\text{-pyrene}} / dt = k \cdot C_{HA} \cdot C_{D10\text{-pyrene}} = k_{\text{sorption}} \cdot C_{D10\text{-pyrene}}$ ) led to a rate coefficient  $k_{\text{sorption}} = 1.5 \pm 0.1 \text{ h}^{-1}$  for pyrene (i.e.  $\tau_{1/2} = 0.5 \text{ h}$ ); a fraction of about  $34 \pm 3\%$  of the bound pyrene follows this slow kinetics.

A biphasic sorption kinetics for PAH and DOM was also observed by the same authors with another experimental method, the fluorescence quenching technique (FQT) (2). Using FQT, sorption and desorption processes of PAH and DOM were studied in the time range of 60 s to 45 min. The resulting rate constants for the slow part of the sorption and desorption processes were in the order of magnitude of 3 to 7  $\text{h}^{-1}$  (2).

Surprisingly, the authors found that  $k_{\text{sorption}}$ , the apparent first-order rate coefficient determined by the SPME method, did not depend on the sorbent concentration ( $C_{HA} = 50$  and  $100 \text{ mg L}^{-1}$ ) (2). This indicates that the unloaded HA is apparently not involved in the rate-determining step of the slow sorption. This is explained with a reaction scheme wherein a loosely bound PAH-HA complex rearranges into another conformation where the PAH molecules are bound on more favorable (hydrophobic) sites (2). It is obvious that half-life and rate coefficient of this unimolecular process do not depend on the HA concentration.

Kopinke et al. (2) considered the kinetics of the sorption process, whereas Schlebaum et al. (19) considered the reverse process, desorption. Nevertheless, the mechanistic interpretation of the slow apparent sorption kinetics is similar in the two studies - a unimolecular rearrangement of the DOM molecules or aggregates as illustrated by the second step in the following scheme (adopted from (2)):



Akkanen et al. (20) studied the interaction of some aromatic model compounds, such as benzo[a]pyrene (BaP), with DOM in natural lake water, using the equilibrium dialysis and Tenax<sup>®</sup> extraction methods. The Tenax<sup>®</sup> extraction revealed at least two fractions with different desorption rates, indicating the presence of specific binding sites inside the DOM sorbent. Although contact time had only a negligible effect on the total

degree of BaP sorption, the desorption-resistant fraction increased with time, from 32% after 1 d up to 61% after 30 d of contact time. Again, these observations are in conformity with the hypothesis of a slow intramolecular rearrangement of the sorbent-sorbate complex. A biphasic desorption model delivered rate coefficients in the range of 0.86 to 0.25 h<sup>-1</sup> for the first and 0.003 to 0.001 h<sup>-1</sup> for the second desorption period for BaP, depending on the equilibration times (1 to 60 d). From the data reported in (20), a first-order rate coefficient for BaP extraction from pure water of  $k_{\text{Tenax extraction}} \leq 5.5 \text{ h}^{-1}$  can be calculated. Thus, the Tenax<sup>®</sup> method has a time resolution similar to that of the gas purging technique applied in (19) and does not allow monitoring of very fast processes.

It is obvious that all of the methods applied so far are able to trace sorption-desorption processes in the time-scale of minutes to hours. However, when looking at the microscale, processes occurring in the sub-second to second scale can become highly relevant (see SI part, section 1). This is illustrated by a number of experimental and modeling studies regarding the influence of DOM on mass transfer of organic compounds through boundary layers (1,3,4,5,7,8,20,21). To the best of our knowledge, no study on sorption-desorption kinetics of organic compounds and DOM which covers the time scale  $\leq 10 \text{ s}$  has yet been published. In order to overcome this lack, we present a simple experimental method which is able to trace sorption kinetics in the time scale from about 0.5 to  $\geq 100 \text{ s}$ . First application results for three hydrocarbons (pyrene, phenanthrene and 1,2-dimethylcyclohexane (DMCH)) as sorbates and three different DOM sources (two HAs and one surfactant) as sorbents are also presented. The principle of the method, which we call 'time-resolved in-tube solid-phase microextraction' (TR-IT-SPME), is presented in Figure 1.

TR-IT-SPME is based on two well-known methods: (i) fast solid-phase extraction (FSPE) and (ii) in-tube solid-phase microextraction (IT-SPME). The FSPE introduced by Landrum et al. (22) and later applied by Maxin et al. (23) is a relatively fast extraction of an aqueous solution containing a solute and DOM through a reversed-phase packed column with a residence time in the order of 5 to 10 s (23). No attempt was made to apply the method for time-resolved measurements.

IT-SPME was introduced by Eisert and Pawliszyn (24) as a variation of the conventional SPME (25). Extraction of the analytes was performed inside a piece of an ordinary GC capillary through which the water sample was passed. The authors studied the correlation between recovery and extraction time, and applied a convection-dispersion model in order to calculate concentration length profiles in the column.

Application of the method in a time-resolved mode and the influence of matrix constituents such as DOM were not considered in (24).

Thus, TR-IT-SPME can indeed be considered as a novel analytical technique for the study of sorption-desorption kinetics on dissolved sorbents.

## Materials and Methods

### Chemicals

All reagents were purchased in the highest grade available from Merck (Germany) or Sigma-Aldrich (Germany). A commercially available humic acid (CHA) was purchased from Carl Roth GmbH (Karlsruhe, Germany, leonardite extract, characterization cf. (15)). The Suwannee River HA (SRHA) was purchased from the International Humic Substance Society (St. Paul, USA). Aqueous solutions of the HAs were prepared according to the following steps: (i) dissolution in 0.05 M NaOH, (ii) dilution with water (1 mM NaNO<sub>3</sub>) to the desired stock concentration (500 mg L<sup>-1</sup>) and shaking for 1 h, (iii) adjustment of the pH value to 7 by adding HCl (1 M), (iv) filtration of the stock solution through a 0.45 μm cellulose acetate filter, (v) further dilution with water (1 mM NaNO<sub>3</sub>) down to the desired sample concentrations. Such prepared HA solutions were spiked with the solutes pyrene (0.08 mg L<sup>-1</sup>) and either phenanthrene (0.5 mg L<sup>-1</sup>) or DMCH (6 mg L<sup>-1</sup>) from methanolic stock solutions (final methanol content ≤ 0.5 vol%) and equilibrated for at least 18 h.

### TR-IT-SPME

The experimental setup is shown schematically in Figure 1. A small volume, typically 50 to 200 μL, of an aqueous solution containing the solutes and DOM was flushed with a well-defined flow rate (Syringe pump 74900, Cole-Parmer Instr., Vernon Hills, USA) through a piece of a GC capillary (200 mm length, Agilent J&W:  $d_{\text{inner}} = 0.32$  mm, 1 μm film immobilized and cross-linked DB-5). The flow rate determines the residence time of the water inside the capillary. In order to increase the mass transfer rate of the in-tube extraction, the capillary was filled with a thin metal wire ( $d_{\text{wire}} = 0.28$  mm, made from Pt or Wo). This wire reduces the free cross-section of the capillary such that the maximum diffusion path length of the solute is reduced from

160  $\mu\text{m}$  (empty capillary) down to about 20 to 40  $\mu\text{m}$ . The slit volume in the capillary was 3.77  $\mu\text{L}$  (verified by weighing). In case of sodium dodecyl sulfate (SDS) as DOM, the amount of eluent passed through the extraction capillary was reduced from 200 to 50  $\mu\text{L}$ . This was due to the very high DOM concentration in the 5  $\text{g L}^{-1}$  SDS solution, in order to minimize extraction capacity limitations, ensuring a ratio of the stationary phase (poly(dimethylsiloxane), PDMS) to organic matter in SDS micelles of  $\geq 2$ .

The concentrations of the model compounds in the test solutions before and after passage through the capillary were monitored by means of HPLC or GC-MS analysis as follows. The capillary effluent was collected in 1 mL vials and its amount was precisely determined by weighing. The vials had been previously filled with the extraction solvent (0.2 mL n-hexane for GC analysis or 0.5 mL acetonitrile for HPLC analysis) which contained three internal standards (anthracene, fluoranthene and toluene). A sample of the capillary inflow solution was prepared as a reference. Vials containing the aqueous test solutions and the solvents were shaken for 1 h before analyses were performed. Preliminary tests, using the extraction procedures described above in combination with GC-MS or HPLC analysis, confirmed that the recovery of the PAH was  $\geq 90\%$  for all applied DOM-containing solutions.

For every experiment a fresh piece of capillary was used, which was conditioned beforehand by purging with methanol-water (1:1) and storing in water overnight. The metal wire was thoroughly cleaned by washing under sonication in water, methanol and hexane, then reused.

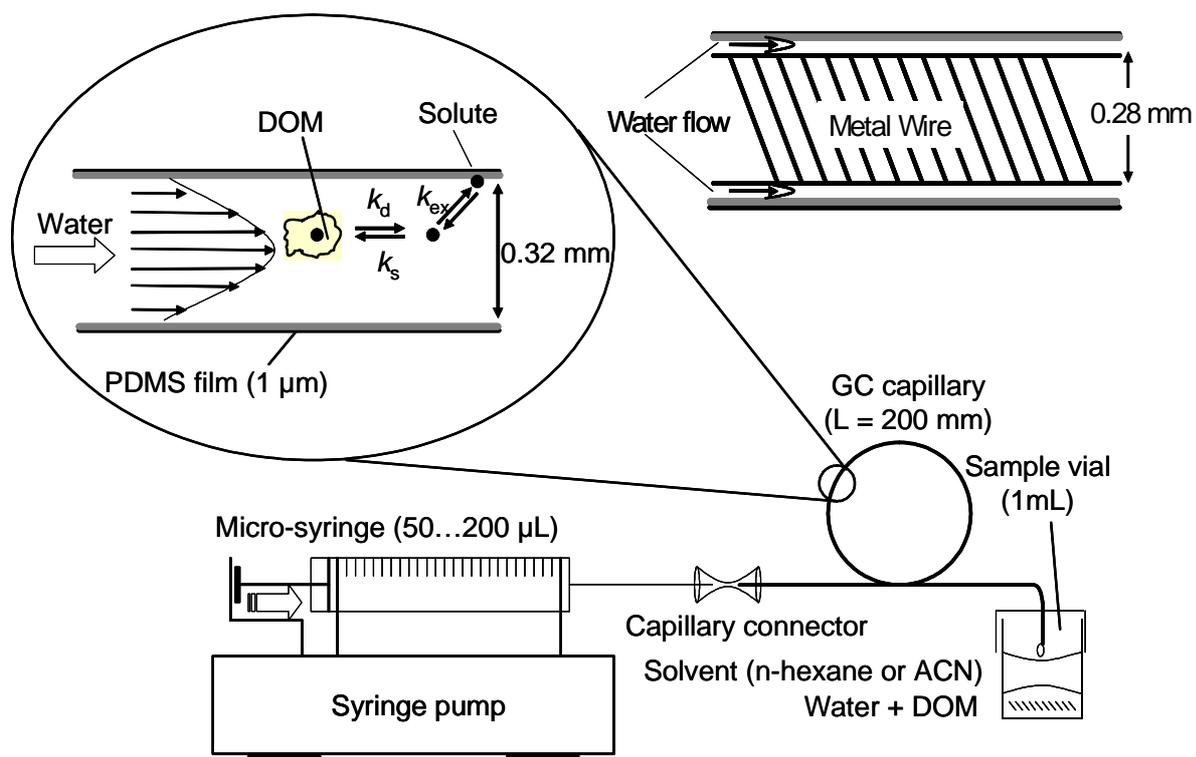


Figure 1: Schematic presentation of the experimental setup for TR-IT-SPME.

## Analyses

GC-MS analysis of the hexane extracts was performed using a GC-MS 2010 from Shimadzu in the SIM mode. Acetonitrile/water samples were analyzed by means of HPLC with fluorescence detection (Hewlett Packard Series 1100, using an Adsorbosphere XL C18 column: 5 μm, 250 × 4.6 mm,  $\lambda_{ex} = 244$  nm,  $\lambda_{em} = 440$  nm). The carbon analyses of aqueous samples were carried out with a TC analyzer (5050 from Shimadzu).

Sorption coefficients were determined for DMCH by headspace analysis and for PAH by direct SPME analysis (2,25). A detailed description is given in the SI part, section 2.

## Results and Discussion

### Performance of the TR-IT-SPME method

The aim of the TR-IT-SPME is to remove the freely dissolved solutes as quickly and completely as possible from the aqueous solution without significant interactions between the stationary phase and the DOM matrix. Consequently, the method performance is determined by three criteria: (i) a high rate of extraction, (ii) a narrow solute breakthrough front (little dispersion), and (iii) a sufficient solute capacity of the stationary phase. The last two criteria determine the water volume which can be extracted by a capillary segment of a certain length.

Figure 2 shows a typical concentration-time profile for the extraction of pyrene and phenanthrene from pure water. The two PAH are extracted to about 97% within 0.5 s residence time in the capillary. The remaining PAH fraction is extracted with a slower rate.

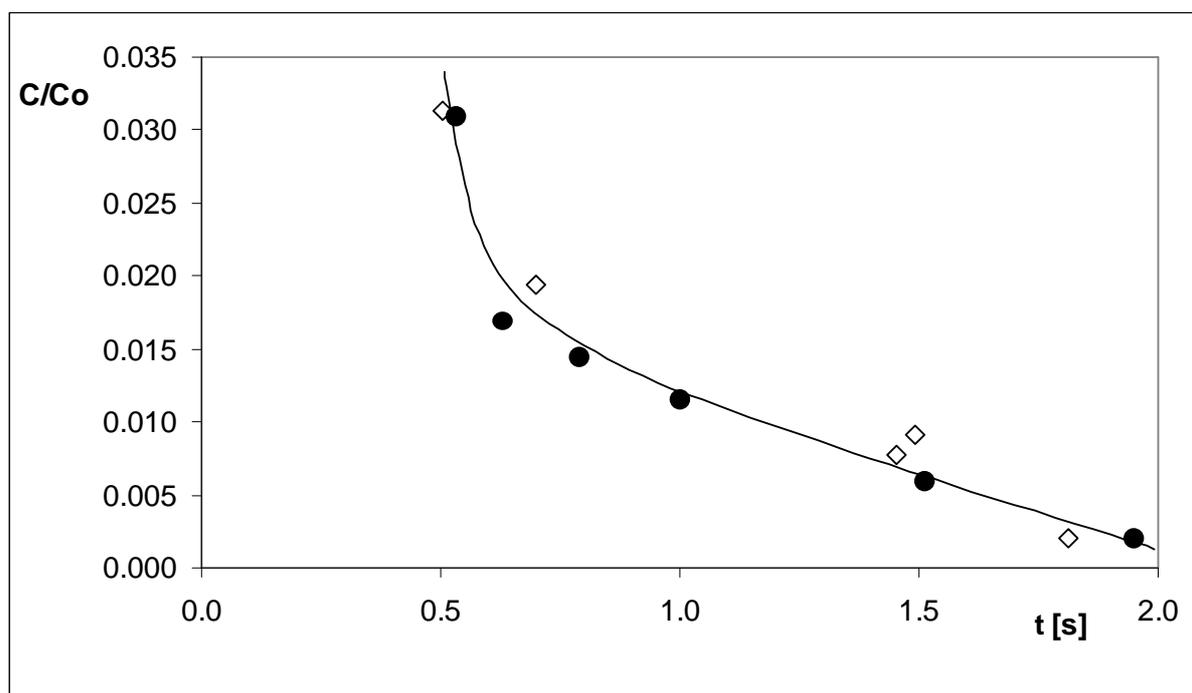


Figure 2. Extraction of phenanthrene (M) and pyrene (●) from clean water ( $C_{0,Phenanthrene} = 0.5 \text{ mg L}^{-1}$ ,  $C_{0,Pyrene} = 0.05 \text{ mg L}^{-1}$ ).

Although the extraction kinetics does not follow accurately a first-order rate law, one can calculate a formal rate coefficient  $k_{\text{extraction}}$  according to  $k_{\text{extraction}} = \ln(C_{\text{in}} / C_{\text{out}}) / \Delta t$  in order to obtain a comparable rate parameter.  $k_{\text{extraction}}$  declines from  $\geq 7 \text{ s}^{-1}$  until 97% depletion is reached within 0.5 s down to about  $1 \text{ s}^{-1}$  for the time range 0.5-2 s. After 2 s, the remaining PAH concentration reached our detection limits, corresponding to  $\geq 99.5\%$  depletion. There is no significant difference between the extraction rates of pyrene and phenanthrene, as is to be expected from a diffusion-limited mass-transfer kinetics.

There are three potential limitations of the method: (i) the mass-transfer kinetics, (ii) the extraction capacity of the stationary phase, and (iii) unwanted interactions of DOM with the stationary phase ('barrier effects') which could give rise to delayed extraction kinetics. We tried to optimize the method with respect to all three limitations (for more detailed information see SI part, section 3). Based on a large number of experiments conducted, the optimal setup for the extraction consists of a capillary ( $d_{\text{capillary}} = 0.32 \text{ mm}$ ,  $l = 20 \text{ cm}$ ) with  $1 \text{ }\mu\text{m}$  PDMS film into which a metal wire is introduced ( $d_{\text{wire}} = 280 \text{ }\mu\text{m}$ ) in order to decrease the maximum diffusion distances of solutes (Figure 1). This setup was applied in all experiments described below.

In order to check whether DOM is sorbed on the surface of the capillary or the filling wire during the flow extraction, the dissolved organic carbon (DOC) content of original DOM solutions and the corresponding effluents was measured (see SI part, section 4, Table SI 1). The obtained DOC recovery of  $98 \pm 2\%$  (one standard deviation) indicates an insignificant loss of DOM. A small loss of DOM may be tolerable for partitioning considerations, but cannot be ignored for kinetic considerations due to possible barrier effects.

In order to check whether such a 'barrier effect' appears, DMCH was used as a solute with relatively weak interactions towards CHA. The DMCH data presented in Figure 3 A show that its extraction is fast and almost complete both in the absence and in the presence of CHA. The measured extraction kinetics in the presence of CHA can be approximately described by two rate coefficients (Figure 3 B):  $k_{\text{extraction},1} = 1.17 \text{ s}^{-1}$  in the time window 0.3 to 2 s (85 to 98% depletion) and  $k_{\text{extraction},2} = 0.034 \text{ s}^{-1}$  in the time window 3 to 25 s. The first 85% of the total DMCH are extracted within 0.3 s. This corresponds to a formal rate coefficient of  $k_{\text{extraction},0} = \ln(1 / (1 - 0.85)) / (0.3 \text{ s}) \approx 6 \text{ s}^{-1}$  which is in the same order of magnitude as for the extraction of PAH from clean water. Hence, there is no indication of a 'barrier effect' of CHA for the capillary extraction.  $k_{\text{extraction},2}$  is lower by two orders of magnitude.

We attribute it to the desorption of the small fraction of stronger-bound DMCH from CHA rather than to a retarded mass-transfer kinetics.

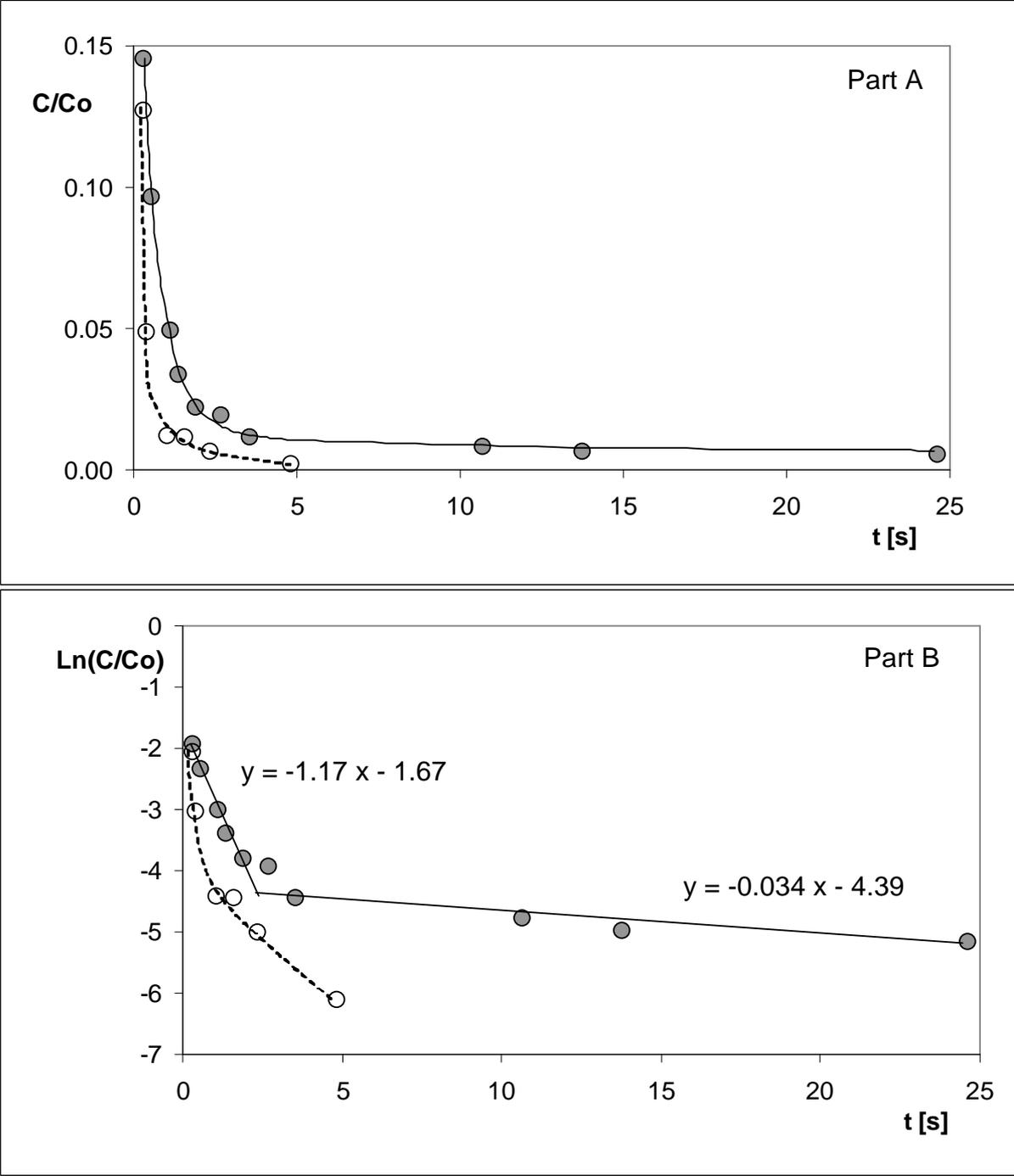


Figure 3. Extraction of 1,2-dimethylcyclohexane from clean water (empty symbols, broken line) and from a CHA solution (filled symbols, cont. line), ( $C_{0,DMCH} = 6 \text{ mg L}^{-1}$ ,  $C_{CHA} = 140 \text{ mg L}^{-1}$ ). The error bars (one standard deviation) are smaller than the symbol size. Figure 3 B presents the data set in semilogarithmic coordinates.

Generalizing this insight, any delay of solute extraction kinetics in the presence of DOM can be interpreted in terms of sorption-desorption interactions between solute and DOM.

### Modeling of the coupled desorption-extraction kinetics

The capillary extraction kinetics has been quantitatively described by Eisert and Pawliszyn (24) for benzene extraction from water by means of a general convection-dispersion model. We applied this model for the extraction of PAH from water in empty capillaries. The results were, however, implausible, possibly due to the fact that the Taylor-Golay-approximation (26) used in this model is not adequate for the case of very hydrophobic solutes such as PAH. Beyond these discrepancies, it is certainly not trivial to include the non-regular geometric conditions (non-centered wire position) inside a wire-filled capillary and the laminar flow conditions (see SI part, section 5) into a strict mathematical model. Therefore, we tried to consider a simplified scenario whereby the two processes, desorption from DOM and capillary extraction, are described by first-order kinetics, with the condition that the extraction rate coefficient is much larger than the desorption rate coefficient, i.e.  $k_{\text{extraction}} \gg k_{\text{desorption}}$ . This leads to a simple approximation (eq. 1, derivation see SI part, section 6) which can be applied to the experimental data  $C_i = f(t)$ :

$$-\frac{dC_i}{dt} = \frac{C_i}{1/k_{\text{desorption}} + 1/(X_{\text{free}} \cdot k_{\text{extraction}})} \quad (1)$$

where  $C_i$  is the total concentration of the solute  $i$  in water (sum of the freely dissolved and the sorbed fractions),  $t$  is the time variable ( $0 < t < \tau$ ) for the extraction process,  $k_{\text{desorption}}$  and  $k_{\text{extraction}}$  are first-order rate coefficients of the two processes, and  $X_{\text{free}} = C_{i,\text{freely dissolved}} / C_i$  ( $0 < X_{\text{free}} < 1$ ) is the fraction of freely dissolved solute under equilibrium conditions. One has to be aware that  $k_{\text{desorption}}$  is an apparent rate coefficient which is not necessarily identical with the true rate constant of the elementary desorption step  $k_2$  (defined in Figure SI 2, SI part, section 7). However, under the conditions applied in the IT-SPME, the reversible sorption-desorption process becomes practically irreversible, because the freely dissolved sorbate is rapidly removed from the equilibrium due to capillary extraction. For irreversible reactions, the apparent and the true rate coefficients become identical, i.e.  $k_{\text{desorption}} = k_2$ .

Eq. 1 can be integrated over the residence time inside the capillary, resulting in  $\ln (C_i / C_{i,0}) = -k' \cdot t$ . Under the condition that  $X_{\text{free}} \cdot k_{\text{extraction}} \gg k_{\text{desorption}}$ , the slope of the semi-logarithmic plot yields  $k_{\text{desorption}}$ , the desired desorption rate coefficient. This pre-condition is certainly fulfilled for our experiments on desorption of PAH from HAs: the product of  $X_{\text{free}} \geq 0.2$  and  $k_{\text{extraction}} = 7 \text{ s}^{-1}$  is about two orders of magnitude higher than  $k_{\text{desorption}} \leq 0.015 \text{ s}^{-1}$  (cf. Table 2). In case of SDS above its CMC, however, the two terms are in the same order of magnitude. Therefore, the corresponding  $k_{\text{desorption}}$  values have to be considered as only rough estimates of the true values. Nevertheless, our conclusions on the significantly different desorption kinetics from HAs and SDS micelles (see below) are not affected.

The extrapolation of the linear plot  $\ln (C_i / C_{i,0})$  vs.  $t$  from the time domain where the slow desorption dominates back to  $t \rightarrow 0$  yields the fraction of strongly bound sorbate at the initial (equilibrium) state of the DOM solution.

### **Desorption of PAH from various types of DOM**

Sorption equilibrium data for phenanthrene, pyrene and DMCH with two HAs and SDS are summarized in Table 1.

Table 1: Equilibrium sorption of solutes on various types of DOM used in IT-SPME experiments

	1,2-Dimethylcyclohexane (log $K_{OW}$ = 4.35)		Phenanthrene (log $K_{OW}$ = 4.46)		Pyrene (log $K_{OW}$ = 5.18)	
DOM source and concentration	Extent of sorption [%]	log $K_{DOM}$	Extent of sorption [%]	log $K_{DOM}$	Extent of sorption [%]	log $K_{DOM}$
CHA 90 mg L <sup>-1</sup> 140 mg L <sup>-1</sup>	33 ± 3	3.55	47 ± 2 <sup>1)</sup>	4.0	78 ± 1	4.6
SRHA 170 mg L <sup>-1</sup>			25 ± 3	3.3	57 ± 2	3.9
SDS 5 g L <sup>-1</sup>			85 ± 5	2)	90 ± 5	2)

<sup>1)</sup> One standard deviation of the mean value from 5 measurements.

<sup>2)</sup> log  $K_{DOM}$  is not calculated due to the high scattering of sorption data with SDS.

After sorption equilibrium had been established, the HA solutions were exposed to the TR-IT-SPME under optimized conditions. The results are presented in Table 2 and in the Figures 4 to 6.

Table 2: Desorption rate coefficients  $k_{\text{desorption}}$  and relative fractions of strongly bound sorbate  $X_{\text{strongly sorbed}} / X_{\text{totally sorbed}}$  from first-order kinetic plots of TR-IT-SPME data

DOM source and concentration	Sorbate	$k_{\text{desorption}}$ [s <sup>-1</sup> ]	range of $\tau$ [s]	$\ln(C/C_0)$ for $\tau \rightarrow 0$	$X_{\text{strongly bound}} / X_{\text{totally sorbed}}$
CHA <sup>3)</sup> 90 mg L <sup>-1</sup> 140 mg L <sup>-1</sup>	pyrene	0.0017	20 - 180	-1.51	0.22/0.78 $\approx$ 0.28
	phenanthrene	0.0040	30 - 180	-2.89	0.056/0.47 $\approx$ 0.12
	DMCH	0.034 <sup>1)</sup>	2 - 25	-4.39 <sup>1)</sup>	0.012/0.33 $\approx$ 0.04
SRHA 170 mg L <sup>-1</sup>	pyrene	0.015	25 - 50	-3.65	0.026/0.57 $\approx$ 0.05
	phenanthrene	0.009	25 - 60	-5.07	0.0063/0.25 $\approx$ 0.025
SDS 5 g L <sup>-1</sup>	pyrene	1.1	0.7 - 3	-0.27	0.76/0.9 $\approx$ 0.85 <sup>2)</sup>
	phenanthrene	0.9	0.7 - 3	-0.53	0.59/0.85 $\approx$ 0.69 <sup>2)</sup>

<sup>1)</sup> Cf. Figure 3 B <sup>2)</sup> The time window and meaning of rate coefficients for desorption from SDS micelles are different from those for the HAs <sup>3)</sup> 90 mg L<sup>-1</sup> for pyrene and phenanthrene, 140 mg L<sup>-1</sup> for DMCH

They give clear evidence of at least two desorption phases with significantly different rates: (i) a fast ( $\tau \leq 3$  s) and (ii) a slow desorption step ( $\tau > 3$  s).

The insert of Figure 4 shows the initial 15 s of the desorption kinetics. It contains an additional desorption plot (dashed line) which represents the pyrene desorption kinetics from a particular CHA solution (80 mg L<sup>-1</sup>). This solution was freshly prepared by dilution of a highly concentrated stock solution (50 g L<sup>-1</sup>) whereby aggregation of HA molecules is strongly favored. According to its DOM content, the total degree of pyrene sorption is about  $X_{\text{totally sorbed}} = 0.76$ . Thus, the fraction of strongly bound pyrene is  $X_{\text{strongly bound}} / X_{\text{totally sorbed}} = 0.48/0.76 = 63\%$ . This value is significantly higher than found for the 'truly dissolved' (less aggregated) CHA ( $31 \pm 3\%$ ). We attribute the larger fraction of slowly desorbing pyrene to the higher extent of colloiddally dissolved HA. Apparently, the disaggregation of HA aggregates when transferring them from a highly concentrated state to a lower concentration is not a rapid process (27). We deliberately did not allow this equilibration in the described experiment in order to demonstrate exemplarily the role of DOM aggregation for the sorption-desorption kinetics.

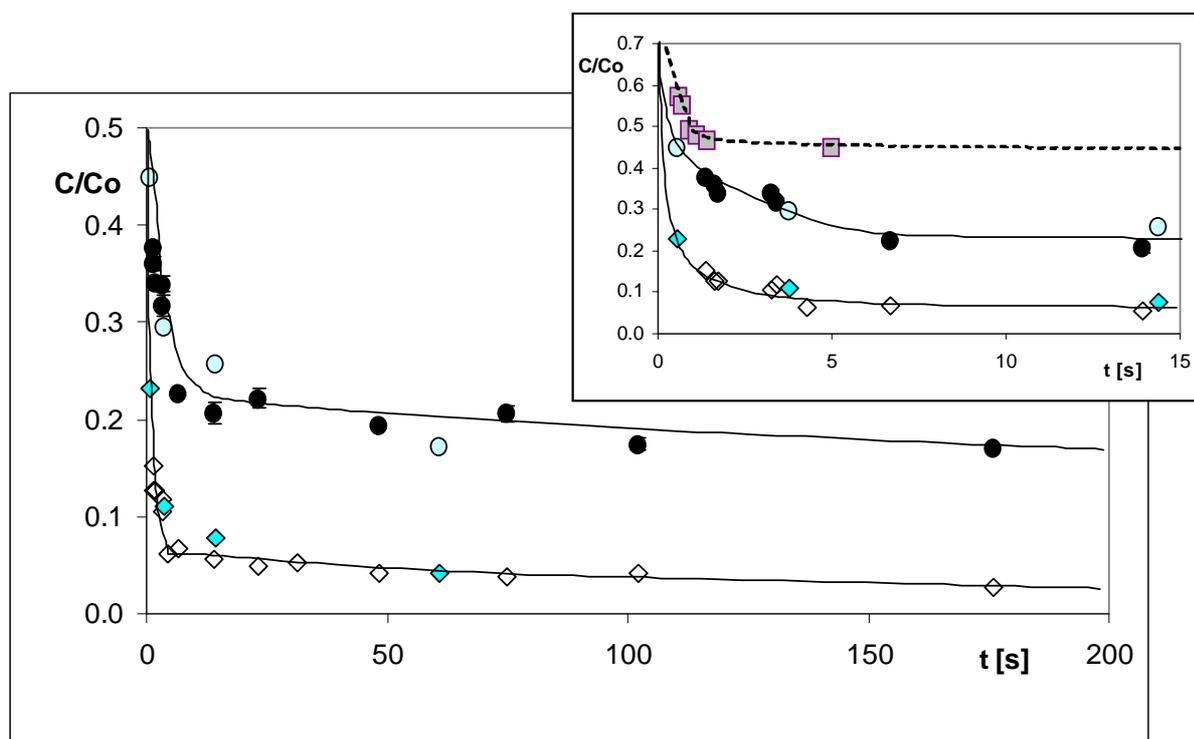


Figure 4. Extraction of phenanthrene ( $\Delta, \bullet$ ) and pyrene ( $\bullet, \blacktriangle, \circ$ ) from a CHA solution, ( $C_{\text{CHA}} = 90 \text{ mg L}^{-1}$ ,  $C_{0,\text{phenanthrene}} = 0.5 \text{ mg L}^{-1}$ ,  $C_{0,\text{pyrene}} = 0.08 \text{ mg L}^{-1}$ ). The colored symbols ( $\Delta, \bullet$ ) are from an independent series of measurements with another freshly prepared CHA solution. The squares connected by the indicative dashed line (---) are from a CHA solution ( $C_{\text{CHA}} = 80 \text{ mg L}^{-1}$ ) containing large HA-aggregates.

Phenanthrene desorbs slightly faster than pyrene from CHA. However, a factor of two is still within the range of data scattering. The lowest desorption rate was observed for pyrene from CHA. The rate coefficient  $k_{\text{desorption}} = 0.0017 \text{ s}^{-1}$  corresponds to a half-life of the pyrene-CHA complex of  $\geq 7 \text{ min}$ .

Figure 5 shows the desorption kinetics of the two PAH from SRHA. Although the strongly bound fractions are lower by a factor of 6 (2.5 and 5% for phenanthrene and pyrene respectively with SRHA, compared to 14.5 and 31% with CHA at  $200 \text{ mg L}^{-1}$ , data not shown), the desorption rate coefficients of the slowly desorbing PAH fractions are in the same order of magnitude ( $k_{\text{desorption}} \approx 0.01 \text{ s}^{-1}$ ) as for CHA. The data with SRHA indicate that a slowly desorbing, strongly bound PAH fraction is a general feature of PAH-HA interactions rather than a unique property of the lignite-derived CHA.

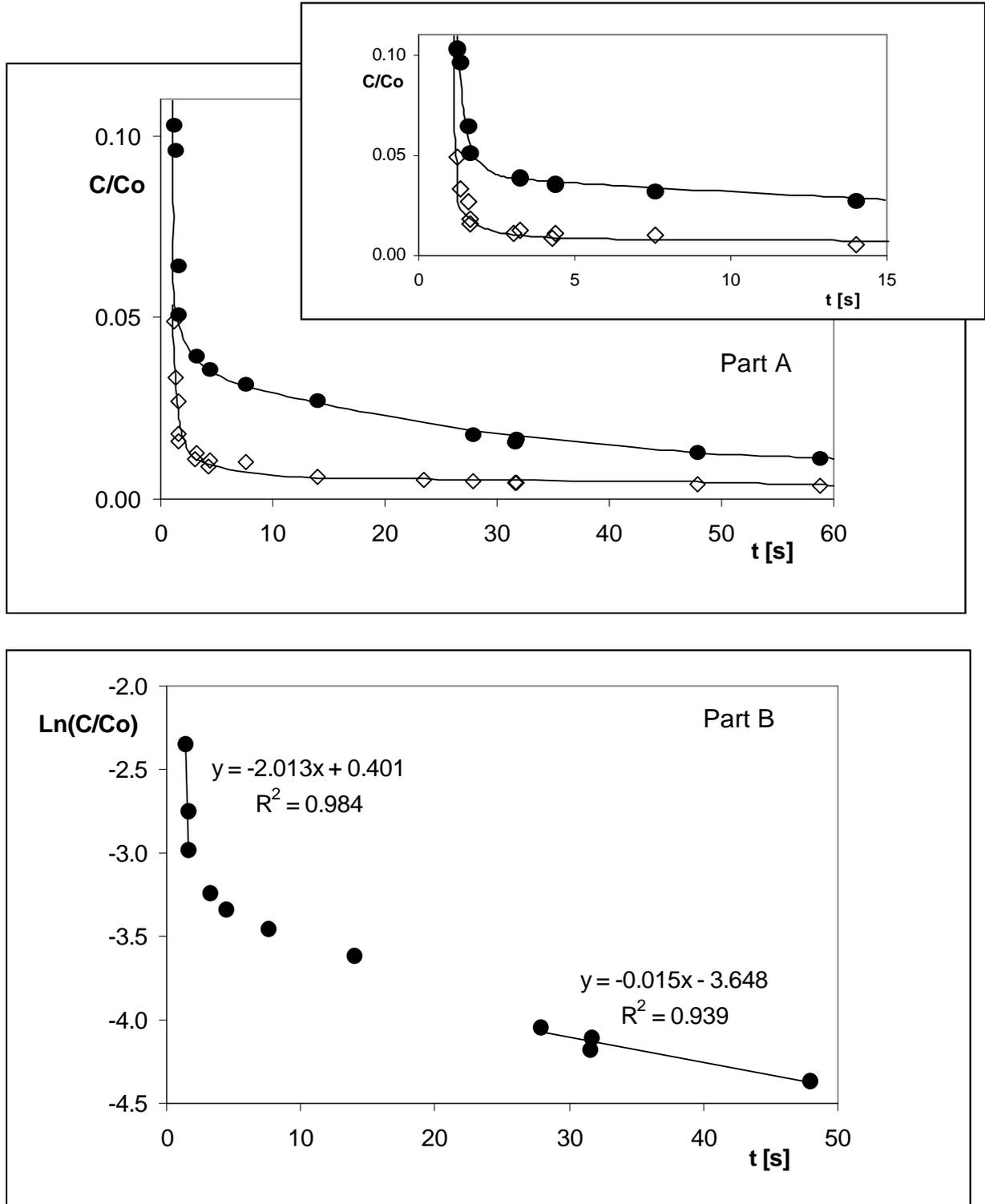


Figure 5. Extraction of phenanthrene (M) and pyrene (●) from SRHA solution ( $C_{SRHA} = 1000 \text{ mg L}^{-1}$ ,  $C_{0,phenanthrene} = 0.5 \text{ mg L}^{-1}$ ,  $C_{0,pyrene} = 0.08 \text{ mg L}^{-1}$ ).

The extraction of phenanthrene and pyrene from the SDS solution with  $C_{\text{SDS}} = 1 \text{ g L}^{-1}$  (below CMC) was extremely fast (Figure 6). Reasons for this are discussed in more detail in the SI part (section 8). The extraction of an SDS solution which contains micelles ( $C_{\text{SDS micelles}} = 2.7 \text{ g L}^{-1}$ ) proceeds significantly slower. This is to be expected because part of the PAH is partitioned inside the surfactant micelles. After 3 s there is still a residual PAH concentration of about 3% in the aqueous solution. Pyrene and phenanthrene show identical extraction kinetics. There is no indication of strongly bound fractions, comparable to PAH-HA complexes. The determined rate coefficients  $k_{\text{desorption},0.7-3\text{s}} = (1 \pm 0.1) \text{ s}^{-1}$  are in the order of magnitude of the extraction rates from pure water.

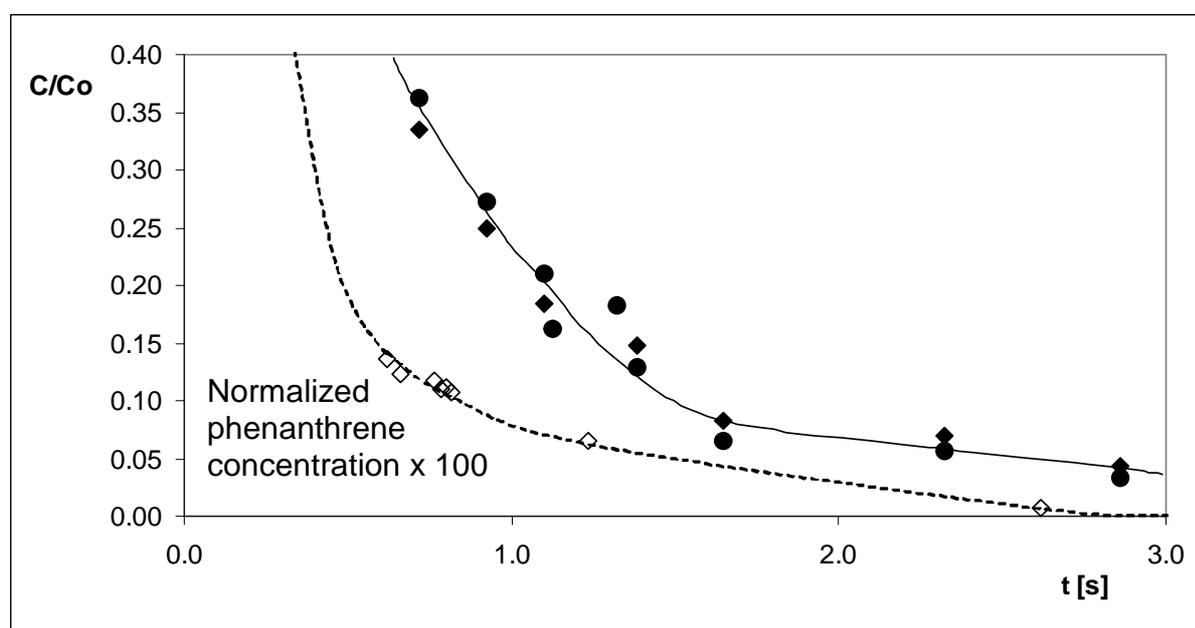


Figure 6. Extraction of phenanthrene (M, ♦) and pyrene (●) from two SDS solutions:  $C_{\text{SDS}} = 1000 \text{ mg L}^{-1}$  (M, dashed line, phenanthrene concentrations x 100) and  $5000 \text{ mg L}^{-1}$  (●, ◆ cont. line), ( $C_{0,\text{phenanthrene}} = 0.5 \text{ mg L}^{-1}$ ,  $C_{0,\text{pyrene}} = 0.08 \text{ mg L}^{-1}$ ,  $V_{\text{eluate}} = 50 \mu\text{L}$ ).

Obviously, SDS micelles behave quite differently from HAs. They are more dynamic and less rigid than HA molecules or aggregates.

In conclusion, the experimental technique presented in this paper enables characterization of the sorbate-DOM complexes with respect to their formation-

dissociation kinetics down to the sub-second time scale. This is a significant advance compared to the methods previously available.

The presented results on DOM-solute complexes are in conformity with published data but complement them with respect to the short-term scale. The desorption rate coefficient of pyrene ( $k_{\text{desorption}} = 0.0017 \text{ s}^{-1} = 6.1 \text{ h}^{-1}$ ) and its strongly bound fraction ( $X_{\text{strongly bound}} / X_{\text{totally sorbed}} = 0.28$ ) with CHA measured in the present study are in good conformity with values measured by means of the FQT method ( $k_{\text{desorption}} \approx 3\text{-}7 \text{ h}^{-1}$  and  $X_{\text{strongly bound}} = 0.15\text{-}0.25$ ) in (2).

The observed tendencies are plausible: (i) PAH interact more strongly with DOM than the aliphatic solute dimethylcyclohexane, and (ii) a lignite-based HA interacts more strongly with PAH than an aquatic HA. One should be aware that the determined  $k_{\text{desorption}}$  values are upper limits for desorption rates of strongly bound fractions ( $X_{\text{strongly bound}}$ ) because they result from an observation time of  $\leq 3$  min. Even more slowly desorbing fractions, as described in the literature (2,19,20) are likely.

What is the relevance of the desorption kinetics for the fate of chemicals in the environment? First one has to consider the shuttle effect of DOM in a boundary layer. If the desorption is slow related to the residence time of the DOM shuttle inside this layer, i.e.  $1/k_{\text{desorption}} \geq \tau_{\text{diffusion}}$ , then the maximum possible shuttle effect is decreased due to an incomplete desorption along the solute concentration profile. This certainly holds for an 'indirect' uptake mechanism whereby the sorbate has to be desorbed into the water phase before it is taken up in the final sink, e.g. a microorganism cell. However, if one admits a 'direct' transfer of the sorbate from the shuttle into the sink, as proposed by Smith et al. (6) and Haftka et al. (21), it may significantly contribute to an overall shuttle effect, provided the 'direct' transfer step proceeds sufficiently fast.

We avoid formulating sophisticated mathematical models of mass transfer kinetics on the basis of film models due to their limited compatibility with laminar flow conditions. Such conditions, however, prevail in aquifers and other aqueous environmental habitats.

A second implication of the slow desorption kinetics described in this study may be an increased depth of penetration of sorbates into reactive zones, e.g. pore spaces and biofilms, where unprotected solutes are rapidly depleted. Applying the Einstein-Smoluchowski relation (see the SI part) and assuming a time scale of  $10^2$  s it results in a reaching distance for sorbates of  $10^2 \mu\text{m}$ , which is clearly an effect on the microscale. Taking into account even more stable PAH-DOM complexes with  $k_{\text{desorption}} \approx 10^{-3} \text{ h}^{-1}$  (20), the reaching distance comes up to the cm range.

In the scientific literature the dimensionless Damkoehler Number ( $Da_{\text{diff}}$ ) is frequently used to describe the competition between the rates of a reaction and a diffusion process according to  $Da_{\text{diff}} = k_{\text{desorption}} \cdot L_d^2 \cdot D^{-1}$  (18), where  $L_d$  is the diffusion distance. For  $Da_{\text{diff}} \gg 1$  sorption equilibria are almost completely established. In case of  $Da_{\text{diff}} \ll 1$  the sorbate remains bound in a diffusion controlled compartment. Assuming comparable rates of desorption and diffusion, i.e.  $Da_{\text{diff}} \approx 1$ , the lowest measured desorption rate coefficient ( $k_{\text{desorption}} = 0.0017 \text{ s}^{-1}$  with CHA and pyrene) results in a diffusion distance of  $L_d \approx 300 \text{ }\mu\text{m}$ . This is the same order of magnitude as estimated by means of the Einstein-Smoluchowski relation (see above).

## Supporting Information

Details of the experimental procedures, derivation of the applied formulas, and additional results are given. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Acknowledgements

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## Supporting Information

### 1. Estimation of relevant time scales for sorption-desorption kinetics in aquifer boundary layers

Whether the overall mass flow of a substrate is controlled by the stagnant layer diffusion or by other bottlenecks depends on the thickness of the stagnant layer (hydrodynamic conditions) and on the 'intensity' of the sink, e.g. on the metabolic activity of microorganisms. Provided that laminar flow conditions apply in an aquifer, the 'residence time'  $\tau$  which is available for DOM-solute equilibration can be approximated according to the Einstein-Smoluchowski relation  $\tau = L_d^2/(2D_{aq})$  based on a diffusion length  $L_d$  which is in the order of magnitude of the interparticle pore diameter. This value depends of course on the aquifer texture.  $D_{aq}$  is the sorbent's diffusion coefficient in water. Taking into account the second-order dependence of the diffusion time on the diffusion distance, this results in a very broad time window which has to be considered for sorption-desorption kinetics. Assuming a range of 1 to 300  $\mu\text{m}$  as reasonable diffusion lengths and a DOM diffusion coefficient in the order of  $D_{\text{DOM}} = 10^{-10} \text{ m}^2 \text{ s}^{-1}$  ( $\text{MW}_{\text{DOM}} \approx 10^4 \text{ g mol}^{-1}$ ) (18) results in a time-scale of 5 ms up to 500 s which has to be considered for sorption-desorption kinetics.

## 2. Determination of sorption equilibrium constants

Sorption coefficients were determined for DMCH by headspace analysis and for the PAH by direct SPME analysis (2, 25). Briefly, 600 mL of water (1 mM NaNO<sub>3</sub>) and a HA solution (400 mg L<sup>-1</sup>, adjusted to pH = 7) were spiked with DMCH (3 mg L<sup>-1</sup>), from a methanolic stock solution and allowed to equilibrate under continuous shaking overnight. The glass flasks were capped by Mininert<sup>®</sup> valves, leaving a headspace volume of about 10 mL. The headspace composition was analyzed by means of GC-MS analysis (25 µL gas syringe). From the difference in the solute peak areas ( $A_{\text{water}}$  and  $A_{\text{HA}}$ ), the degree of sorption and the resulting sorption coefficient ( $K_{\text{DOM}}$ ) can be determined according to eq. SI 1.

$$K_{\text{DOM}} = \left( \frac{A_{\text{water}}}{A_{\text{HA}}} - 1 \right) \cdot \frac{1}{C_{\text{DOM}}} \cdot \left( \frac{K_{\text{H}} \cdot V_{\text{headspace}}}{V_{\text{water}}} + 1 \right) \quad (\text{SI 1})$$

with  $C_{\text{DOM}}$  as concentration of DOM in the solution (kg L<sup>-1</sup>),  $K_{\text{H}}$  as dimensionless Henry's law coefficient of the solute,  $V_{\text{headspace}}$  and  $V_{\text{water}}$  as volumes of water and headspace phases, respectively, in the applied glass bottle.

For pyrene and phenanthrene, the freely dissolved concentrations (more precisely: their chemical activities) were determined by using the SPME method with direct sampling of a 7 µm PDMS fiber (Sigma–Aldrich, Germany) into the equilibrated, stirred solutions (200 mL, 5 h extraction time). The solutes were then determined by direct GC-MS analysis ( $T_{\text{injector}} = 290^{\circ}\text{C}$ , 3 min splitless) or re-extracted from the fiber into 0.5 mL acetonitrile (18 h) and analyzed by means of HPLC.

## 3. Approaches to optimize the capillary extraction efficiency

The mass transfer kinetics in the IT-SPME depends on the flow regime and the solute's diffusion path length. As shown above, IT-SPME works in the laminar range. This means that the mass transfer rate is diffusion controlled, even in the filled capillaries. If empty GC capillaries with  $d_{\text{inner}} \geq 0.32$  mm are used, the mass transfer kinetics is too slow to meet our goal, i.e. a sub-second time resolution of the solute extraction from water. Filling the capillary with an appropriate metal wire (see Figure 1) is a simple but efficient measure to overcome this problem. A further reduction of the

capillary's free cross section (e.g.  $d_{\text{wire}} = 300 \mu\text{m}$  in  $d_{\text{capillary}} = 0.32 \text{ mm}$ ) is not advisable due to increased flow resistance.

An alternative to filled thick-film capillaries are narrow-bore capillaries with an internal diameter  $d_{\text{capillary}} \leq 0.1 \text{ mm}$ . However, such capillaries are commercially available only with thin stationary films ( $d_{\text{film}} \leq 0.4 \mu\text{m}$ ). Their extraction capacity is rather limited due to the small PDMS volume of  $\leq 0.025 \mu\text{L}$  compared to  $0.20 \mu\text{L}$  in our preferred setup.

Application of ultrasound from various sources turned out not to be helpful for acceleration of mass transfer under flow-through conditions. Results with and without sonication were practically identical.

Beside the kinetics of the extraction process, the phase capacity of the capillary applied in IT-SPME, which is a solute-specific parameter, has to be considered as well. Usually we used an effluent volume of  $200 \mu\text{L}$ , which theoretically enables a complete extraction of solutes from water with  $K_{\text{PDMS-water}} \approx K_{\text{OW}} \geq V_{\text{water}} / V_{\text{PDMS}} = 10^3$ , where  $K_{\text{PDMS-water}}$  and  $K_{\text{OW}}$  are the partition coefficients of the solute between PDMS or n-octanol and water, respectively.  $V_{\text{water}} / V_{\text{PDMS}}$  is the ratio of effluent water and PDMS film volumes. In practice, however, the theoretical extraction capacity cannot be fully exploited due to a significant broadening of the solute breakthrough front (cf. Figure SI 1). All three solutes used in this study have  $K_{\text{OW}} > 10^4$  (Table 1), so the extraction capacity should not be limiting.

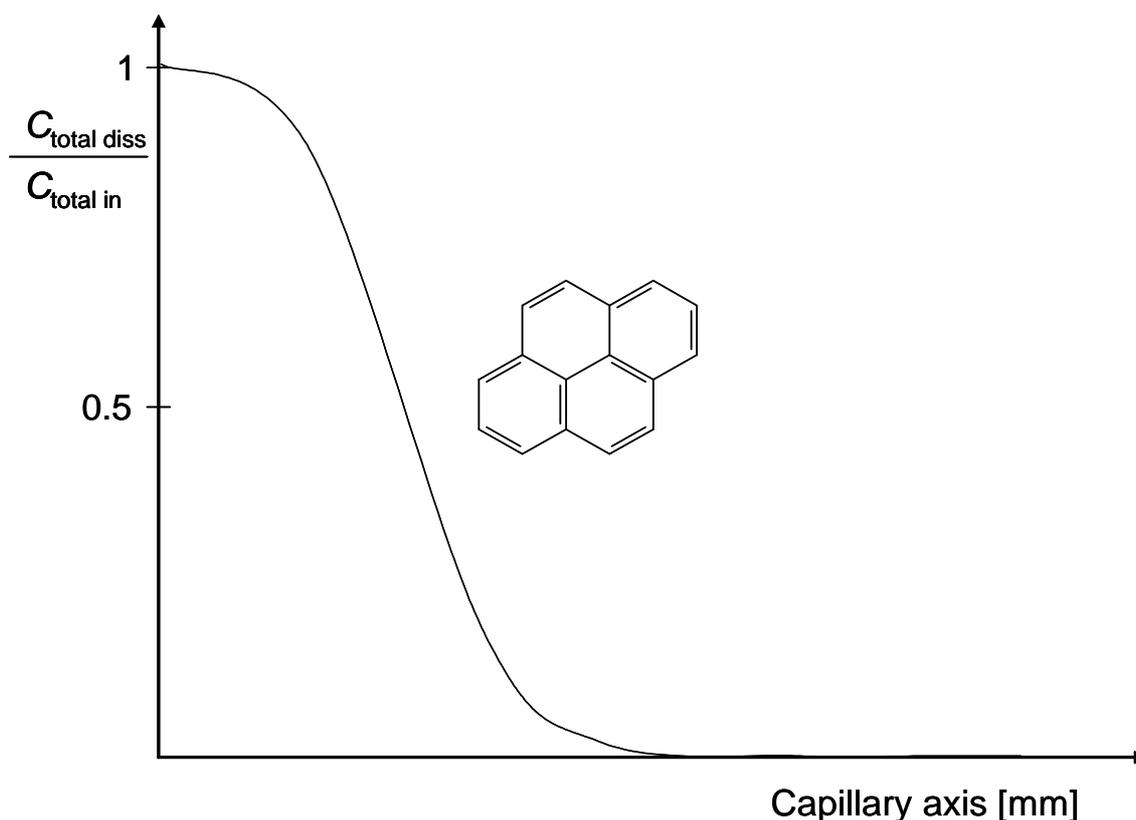


Figure SI 1: Schematic presentation of TR-IT-SPME: Concentration profile of a solute (e.g. pyrene) along the capillary axis (indicative, not calculated).

The mass balance of the IT-SPME was checked by solvent re-extraction of the extracted solutes from the PDMS film (purging with 400  $\mu\text{L}$  n-hexane,  $\tau \approx 60$  s) and GC-MS analysis. By this means,  $100 \pm 10\%$  of the amounts of pyrene and phenanthrene, which had previously been removed by IT-SPME, were recovered. This result validates the method. Moreover, it opens up an alternative way to determine extraction degrees in cases where they are small.

#### 4. DOM retardation in the extraction capillary

In order to check whether DOM is sorbed on the surface of the capillary or the filling wire during the flow extraction, the dissolved organic carbon (DOC) content of the original DOM solutions and the corresponding effluents was measured (Table SI1). The standard deviation of the mean DOC values ( $n = 3$ ) is 1 to 2% and, consequently, 2 to 4% for the recoveries given in Table SI 1. The data indicate a small loss of DOM during the extraction, which is insignificant for the short residence time ( $\tau = 2.5$  s) but becomes

significant for longer times. A loss of 2% DOC from 200  $\mu\text{L}$  of a  $1 \text{ g L}^{-1}$  SRHA solution results in a DOM amount of 8  $\mu\text{g}$  remaining inside the capillary, compared with about 240  $\mu\text{g}$  of the stationary PDMS phase. This small loss may be tolerable for partitioning considerations. Possible effects on solute extraction kinetics were excluded based on results described in the main text.

Table SI 1: DOM recoveries in IT-SPME experiments (1.2 mL eluate from clean capillaries)

DOM source and concentration	DOC of effluent / DOC of input x 100%	
	$\tau = 2.5 \text{ s}$	$\tau = 18 \text{ s}$
CHA $C_0 = 0.4 \text{ g L}^{-1}$	98	93
SRHA $C_0 = 1.0 \text{ g L}^{-1}$	98	88
SDS $C_0 = 1.0 \text{ g L}^{-1}$	100	94
SDS <sup>1)</sup> $C_0 = 5.0 \text{ g L}^{-1}$	97	92

<sup>1)</sup> The CMC of SDS is  $2.3 \text{ g L}^{-1}$ .

## 5. Calculation of Reynolds numbers under capillary flow conditions

Usually the Reynolds number ( $Re$ ) is used to characterize the degree of turbulence of a flowing medium according to eq. SI 2.

$$Re = \frac{u \cdot d_{\text{hydraulic}}}{\nu} = \frac{20 \text{ cm} / 0.2 \text{ s} \cdot 0.004 \text{ cm}}{0.01 \text{ cm}^2 \text{ s}^{-1}} = 40 \quad (\text{SI 2})$$

where  $u$  is the mean water flow velocity ( $\text{cm s}^{-1}$ ) inside the capillary,  $d_{\text{hydraulic}}$  (cm) is a characteristic tube diameter, approximated here as  $d_{\text{hydraulic}} = d_{\text{capillary}} - d_{\text{wire}}$ , and  $\nu$  ( $\text{cm}^2 \text{ s}^{-1}$ ) is the kinematic viscosity of water at  $20^\circ\text{C}$ . The critical value of  $Re$  which indicates the change from laminar to partially turbulent flow regimes in pipes is  $Re_{\text{crit}} = 2300$  (SI2).  $Re$  is clearly in the laminar range under all extraction conditions applied in the present study.

## 6. Derivation of the applied rate laws (eq. 1 in the paper)

First we consider two kinetics independently:

(i) For the capillary extraction

$$-dC_i/dt = k_{\text{extraction}} \cdot C_{i,\text{free}} \quad (\text{SI } 3)$$

with  $C_i$  as total concentration of solute  $i$  in solution,  $t$  as desorption-extraction time variable,  $k_{\text{extraction}}$  as apparent first-order rate coefficient of the film extraction, and  $C_{i,\text{free}}$  as the concentration of the freely dissolved (not sorbed) solute.

(ii) For the desorption

$$\begin{aligned} dC_{i,\text{free}}/dt &= k_{\text{desorption}} \cdot (C_{i,\text{sorbed}} - C_{i,\text{sorbed, equilibrium}}) \\ &= k_{\text{desorption}} \cdot (C_i - C_{i,\text{free}} \cdot [1 + C_{\text{DOM}} \cdot K_{\text{DOM}}]) \end{aligned} \quad (\text{SI } 4)$$

with  $k_{\text{desorption}}$  as apparent first-order rate coefficient of desorption of solute from the solute-DOM complex,  $C_{i,\text{sorbed}}$  as solute concentration in the sorbed state ( $\text{g}_i \text{ g}_{\text{DOM}}^{-1}$ ),  $C_{i,\text{sorbed, equilibrium}}$  as  $C_{i,\text{sorbed}}$  under equilibrium conditions,  $C_{\text{DOM}}$  as concentration of DOM in the solution ( $\text{kg L}^{-1}$ ), and  $K_{\text{DOM}}$  as equilibrium constant of the sorption-desorption process ( $\text{L kg}^{-1}$ ).

The combination of the two processes results in eq. SI 5

$$dC_{i,\text{free}}/dt = k_{\text{desorption}} \cdot (C_i - C_{i,\text{free}} \cdot [1 + C_{\text{DOM}} \cdot K_{\text{DOM}}]) - k_{\text{extraction}} \cdot C_{i,\text{free}} \quad (\text{SI } 5)$$

Then, we (i) introduce the stationary state condition  $dC_{i,\text{free}}/dt = 0$ , which is common for the formation of intermediates in consecutive reactions where the rate coefficient of the consumption reaction is much higher than that of the formation reaction ( $k_{\text{extraction}} \gg k_{\text{desorption}}$ ) (SI1), (ii) substitute  $C_{i,\text{free}}$  from eq. SI 3, and (iii) substitute  $[1 + C_{\text{DOM}} \cdot K_{\text{DOM}}]$  by  $1/X_{\text{free}}$  which is the fraction of freely dissolved solute under equilibrium conditions. This results in eq. SI 6 which is eq. 1 in the paper.

$$-dC_i / dt = \frac{C_i}{1/k_{\text{desorption}} + 1/(k_{\text{extraction}} \cdot X_{\text{free}})} \quad (\text{SI } 6)$$

## 7. Relation between rate coefficients and equilibrium constants

Knowing one rate coefficient and the equilibrium constant of a reversible sorption-desorption process one can, in principle, calculate the missing rate coefficient according to  $K_{\text{DOM},i} = k_{1,i} / k_{2,i}$ , where  $i$  is the index of the solute and  $k_{1,i}$   $k_{2,i}$ , are the second- and first-order rate coefficients of the sorption and desorption elementary steps respectively. If, however, the process includes more than one elementary reversible step, as is apparently the case with HAs as sorbents, this procedure is more complicated. According to eq. SI 7, the equilibrium constant (also known as partition coefficient) may be considered as being composed of contributions of independent sorption-desorption equilibria

$$K_{\text{DOM}} = \sum_j K_{\text{DOM},j} = \sum_j \frac{k_{1,j}}{k_{2,j}} = \frac{1}{C_{\text{free}}} \sum_j C_{\text{sorbed},j} = \frac{C_{\text{sorbed}}}{C_{\text{free}}} \sum_j \frac{X_{\text{sorbed},j}}{X_{\text{totally.sorbed}}} \quad (\text{SI 7})$$

with  $j$  as index of one specific sorption-desorption compartment in DOM. From the TR-IT-SPME measurements we know the fraction of strongly sorbed sorbate  $X_{\text{strongly bound}} / X_{\text{totally sorbed}}$  (Table 2). This allows us to calculate  $C_{\text{sorbed},j}$  and finally  $K_{\text{DOM},j}$ , the partial equilibrium constant of the  $j$  sorption compartment. For this specific compartment one can calculate the sorption rate coefficient according to  $k_{1,j} = k_{2,j} \cdot K_{\text{DOM},j}$ . One might expect that partial sorption coefficients reflect the different sorption affinities of their specific compartments, e.g. that there would be a higher partial sorption coefficient for strongly bound than for loosely bound sorbates. This, however, is not the case: partial sorption coefficients are always lower than the total DOM sorption coefficient. The reason is simply that all of them are related to the total concentration of DOM rather than to the number of sorption sites, which are unknown.

In Figure SI 2 the relation between apparent and true rate coefficients for sorption-desorption processes is schematically illustrated (cf. chapter: Modeling of the coupled desorption-extraction kinetics in the paper).

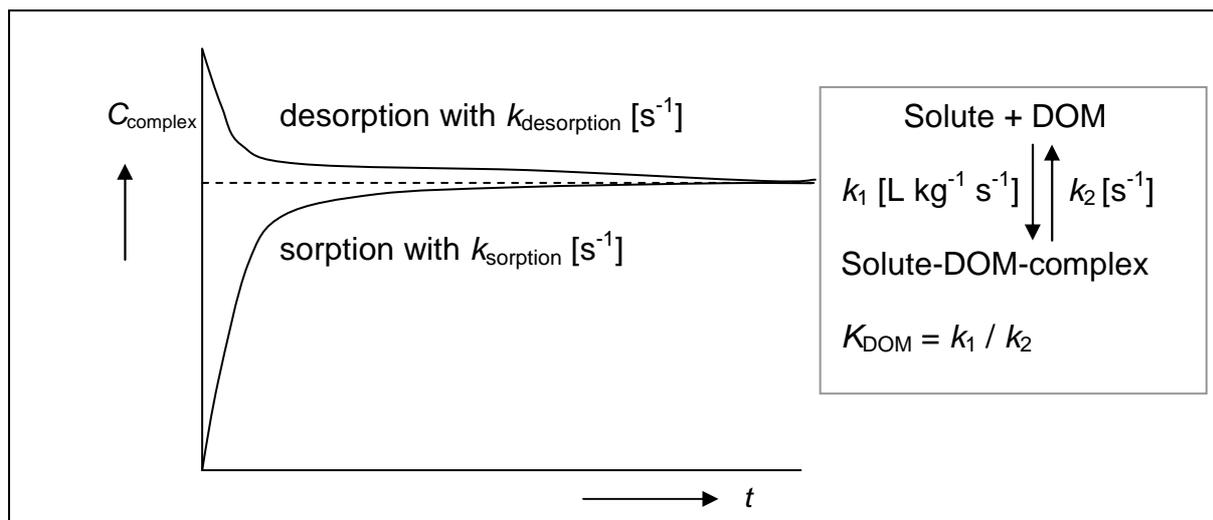


Figure SI 2: Schematic presentation of sorption-desorption processes, described by apparent and true rate coefficients ( $k_{\text{sorption}}$ ,  $k_{\text{desorption}}$  and  $k_1$ ,  $k_2$ , respectively).

## 8. Experiments with SDS solutions

The extraction of phenanthrene and pyrene from the SDS solution with  $C_{\text{SDS}} = 1 \text{ g L}^{-1}$  (below CMC) was extremely fast, even faster than from clean water. One has to take into account that the normalized phenanthrene concentration is magnified by a factor of 100 in Figure 5. The pyrene concentration in these eluates was below its detection limit ( $C/C_0 \leq 5 \cdot 10^{-4}$ ) already at the shortest residence time (0.5 s). This may be due to two reasons: (i) the very low amount of eluate and (ii) more speculatively, a positive wetting effect of the surfactant on the PDMS surface. The amount of aqueous eluate (50  $\mu\text{L}$  instead of 200  $\mu\text{L}$  for most of the other experiments) affects the apparent extraction rate due to the movement of a breakthrough front through the capillary (compare Figure SI 1). The less water is pushed through the extraction capillary, the smaller is the contribution of the solute's front tailing to its concentration in the eluate. The amount of eluate is usually a compromise between extraction performance and analyte detection limits. In the case of SDS solutions, the amount of eluate was minimized due to the high DOM concentrations necessary for generating micelles and the necessity to maintain a sufficient phase ratio (PDMS/micelles) for the extraction.

## Literature Cited in Supporting Information

- (S1) Atkins, P. W. *Physical Chemistry*; Oxford University Press, 2<sup>nd</sup> ed. 1982, pp. 939.
- (S2) Patel, V. C.; Rodi, W.; Scheuerer, G. Turbulence models for near-wall and low Reynolds number flows: A review. *AIAA Journal* **1985**, 23 (9), 1308-1319.

## 6. Summary

For environmentally relevant processes such as adsorption or chemical and biotic degradation of pollutants, diffusion through boundary layers can be the rate-limiting step. It is known that organic compounds with surface-active properties are enriched at the phase boundary between water and atmosphere or between water and solid surfaces such as sediments and biota. Dissolved humic substances (DHS) belong to the most widespread natural surface-active substances which exist in all terrestrial and aquatic environments. However, not much information is available on the effect of DHS in the surface microlayer. Within this thesis, the influence of DHS on diffusion-controlled mass transfer of organic compounds at the water-air interface has been investigated.

In a system where the exchange rate is controlled by the transfer resistance on the water side of the water-gas interface, under all applied conditions, a significant hindrance effect of DHS on water-gas exchange of benzene and cyclohexane was observed. Moreover, the experimental results show that effective mass-transfer coefficients of the model compounds decrease with increasing concentrations of DHS. Furthermore, the hindrance effect on mass transfer is larger for CHA than for SRFA and SRHA. However, mass-transfer resistance on the water side of the gas-water interface could be significantly affected by environmentally relevant DHS concentrations (10-20 mg L<sup>-1</sup>). It should clearly be taken into account in models for air-sea or air-surface water fluxes of organic compounds, which might be even more important considering the current global trend towards increasing DHS concentrations in freshwaters.

In order to rank DHS among other surface-active compounds with respect to their effects on water-gas exchange, experiments with SDS and Triton as surfactants of low molecular weight and PAA as a synthetic polymer (average molecular weight 2000 g mol<sup>-1</sup>) were conducted under identical conditions. Addition of PAA up to a concentration of 1 g L<sup>-1</sup> did not significantly alter the mass-transfer rates of benzene. Apparently, PAA is not hydrophobic enough to accumulate at the air-water interface. In contrast, for solutions which contained surfactant at concentrations below their critical micelle concentration (CMC), a strong reduction of the gas-exchange rates of benzene was observed. The hydrodynamic effect of DHS was comparable to that of synthetic surfactants at concentrations below their CMC. However, it is remarkable that the inhibiting effect of surfactants on mass transfer was greatly diminished if the surfactant concentration exceeds the CMC.

In summary, the results obtained for benzene and cyclohexane as model compounds which do not significantly sorb to DHS in the concentration range studied, are in conformity with the hypothesis that the DHS-induced retardation of water-air exchange for these compounds is mainly due to changes in the hydrodynamic characteristics of water motion at the interface and within the boundary layer below the surface. Obviously, sorption-induced effects of DHS on the water-gas exchange rate can be neglected under most environmental conditions for compounds with low to moderate hydrophobicity ( $\log K_{OW} \leq 3.5$ ), i.e. as long as low bulk phase sorption effects occur.

In the second manuscript the studies on water-gas exchange were extended to n-octane as a compound with higher hydrophobicity and thus stronger sorption tendency towards DHS. In order to differentiate between hydrodynamic and sorption-induced effects of DHS on water-gas exchange, benzene and n-octane, which differ by three orders of magnitude in their octanol-water partitioning coefficients ( $\log K_{OW,benzene} = 2.13$ ,  $\log K_{OW,n-octane} = 5.18$ ) were applied. The experimental results clearly show that sorption effects leading to a reduction in the freely dissolved concentration of the chemical have a negative effect on the diffusional mass-transfer rate. This is due to the fact that a proportion of the chemical is strongly hindered in diffusion due to complexation by the more slowly diffusing sorbent. Consequently, water/air exchange of hydrophobic compounds is not only affected by the hydrodynamic retardation effect of DHS but additionally by sorption to DHS.

In order to simulate a system where sorption of a chemical by dissolved sorbents does not affect its thermodynamic activity (or freely dissolved concentration) in the aqueous phase due to redelivery from a large source, as for instance in the presence of a contaminated sediment, passive dosing experiments were conducted. In these experiments silicone sheets, which were preloaded with n-octane, provided a constant freely dissolved concentration of n-octane in the aqueous phase irrespective of the presence of DHS during the purging experiment. In contrast to the reduced-activity system, where sorption to DHS and SDS micelles decreased the rate of mass transfer of n-octane from water to the gas phase, the effect of sorption in the constant-activity system was positive. This was caused by the fact that in the constant-activity system the reduction of the average diffusion coefficient of the chemical can be overcompensated by the higher total concentration of the chemical in the aqueous phase, i. e. a steeper concentration gradient in the diffusion boundary layer.

For typical DHS concentrations in the environment, in the range  $\leq 20 \text{ mg L}^{-1}$ , sorption-induced effects on water-air exchange rates can be only expected for very hydrophobic compounds with  $\log K_{\text{DOC}} \geq 5$ , such as highly chlorinated PCBs or PAHs. In technical processes, where DHS or surfactant concentrations can be much higher, a broader relevance can be expected.

The magnitude of sorption-induced effects further depends on the mobility of the sorbent (diffusion coefficient) and the lability of the complexes in terms of their residence time in the diffusion layer. However, there is a lack of appropriate experimental techniques for tracing very fast DHS-solute interactions. Therefore, a new experimental technique – time-resolved in-tube solid phase microextraction method (TR-IT-SPME method) was developed in the third part of this work. Using the TR-IT-SPME method, it was shown that the dominant fraction of the sorbate (e.g. pyrene and dimethyl cyclohexane) desorbs from CHA and SRHA with a half-life of less than 1 s. However, a certain fraction is strongly bound and desorbs much more slowly, i.e. with a half-life in the order of minutes or even hours.

The SPME of phenanthrene and pyrene from SDS solutions below CMC was extremely fast. In comparison, the extraction of an SDS solution which contained micelles proceeded significantly slower. However, there was no indication of strongly bound fractions, comparable to PAH-DHS complexes. Obviously, SDS micelles behave quite differently from DHS. They are more dynamic and less rigid than DHS molecules or aggregates.

The thickness of the aqueous diffusion layer at air-water interfaces in the environment is typically in the range of 20 - 200  $\mu\text{m}$ . Based on the Einstein-Smoluchowski correlation, a corresponding residence time range of 2 - 200 s for DHS molecules can be estimated. Thus, based on the TR-IT-SPME results, significant but possibly incomplete lability of pollutant-DHS complexes is to be expected for transport through aqueous diffusion boundary layers at air-water interfaces in the environment.

## Zusammenfassung

Für umweltrelevante Prozesse, wie Adsorption oder chemischer und biotischer Abbau von Schadstoffen, kann die Diffusion durch die Phasengrenzschicht der geschwindigkeitsbestimmende Schritt sein. Es ist bekannt, dass sich organische Verbindungen mit oberflächenaktiven Eigenschaften an der Phasengrenze zwischen Wasser und der Atmosphäre oder zwischen Wasser und festen Phasen, wie Sedimenten und Biota, anreichern. Gelöste Huminstoffe (dissolved humic substances, DHS) gehören zu den am weitesten verbreiteten natürlichen oberflächenaktiven Stoffen, welche in allen terrestrischen und wässrigen Umweltkompartimenten vorkommen. Die Wirkung von DHS in der Oberflächen-Mikroschicht wurde bisher jedoch wenig untersucht. In dieser Arbeit wurde die Wirkung von DHS auf den diffusionskontrollierten Stofftransport von organischen Verbindungen an der Wasser-Luft-Phasengrenze untersucht.

In einem System, in dem die Austauschrate durch den Transportwiderstand auf der Wasserseite der Wasser-Luft-Phasengrenze kontrolliert wird, wurde unter allen getesteten Bedingungen ein signifikanter Hinderungseffekt von DHS auf den Wasser-Gas-Transfer von Benzen und Cyclohexan beobachtet. Darüber hinaus zeigten die Versuchsergebnisse, dass die effektiven Stofftransportkoeffizienten der Modellverbindungen mit zunehmender DHS-Konzentration abnahmen. Des Weiteren war der Hinderungseffekt auf den Stofftransport für CHA stärker ausgeprägt als für SRFA und SRHA. Dabei konnte gezeigt werden, dass der Stofftransportwiderstand an der Wasserseite der Wasser-Gas-Grenzschicht durch umweltrelevante DHS-Konzentrationen ( $10\text{-}20\text{ mg L}^{-1}$ ) signifikant beeinflusst wird. Dieser Effekt sollte in Modellen zur Abschätzung des Stoffaustauschs von organischen Verbindungen zwischen Ozean bzw. Oberflächengewässern und der Atmosphäre berücksichtigt werden und könnte aufgrund der aktuellen globalen Entwicklung hin zu erhöhten DHS-Konzentrationen in Oberflächengewässern zukünftig noch an Bedeutung gewinnen.

Um den durch DHS verursachten Effekt auf den Wasser-Gas-Transport mit anderen oberflächenaktiven Verbindungen zu vergleichen, wurden Natriumdodecylsulfat (SDS) und Triton als Tenside mit niedriger Molmasse und Polyacrylsäure (PAA) als synthetisches Polymer (mittlere Molmasse  $2000\text{ g mol}^{-1}$ ) in Vergleichsexperimenten unter identischen Bedingungen eingesetzt. Die Anwesenheit von PAA bis zu einer Konzentration von  $1\text{ g L}^{-1}$  zeigte hierbei keine signifikante Beeinflussung des Stofftransports für Benzen. Offensichtlich ist PAA nicht hydrophob

genug, um sich an der Luft-Wasser-Grenze anzureichern. Im Gegensatz dazu wurde für Lösungen, die Triton oder SDS in Konzentrationen unterhalb ihrer kritischen Mizellbildungskonzentration (critical micelle concentration, CMC) enthielten, eine starke Abnahme der Stofftransportgeschwindigkeit für Benzen beobachtet. Der hydrodynamische Effekt von DHS ist in seinem Ausmaß dem von synthetischen Tensiden unterhalb ihrer CMC vergleichbar, wenn man eine massekonzentrationsbezogene Normierung zugrunde legt. Bemerkenswert ist, dass die durch die Tenside verursachte Stofftransporthemmung stark abnimmt, wenn ihre Konzentration im Wasser die CMC überschreitet.

Für Benzen und Cyclohexan als Modellverbindungen, die im untersuchten DHS-Konzentrationsbereich nicht in signifikantem Maß sorbiert vorliegen, kann zusammenfassend festgestellt werden, dass die erhaltenen Ergebnisse mit der Hypothese eines durch DHS hervorgerufenen hydrodynamischen Effekts im Einklang stehen. Das heisst, die Hemmung des Wasser-Gas-Transfers der organischen Verbindungen ist hauptsächlich auf Veränderungen der hydrodynamischen Eigenschaften der Wasserbewegung an der Phasengrenze und in der Grenzschicht unterhalb der Wasseroberfläche zurückzuführen, die durch die Anwesenheit von DHS verursacht werden. Offensichtlich können durch Sorption hervorgerufene Effekte von DHS auf die Geschwindigkeit des Wasser-Gas-Austauschs für Verbindungen mit niedriger bis mittlerer Hydrophobizität ( $\log K_{OW} \leq 3,5$ ) unter typischen Umweltbedingungen vernachlässigt werden, d. h. so lange keine signifikanten Sorptionseffekte in der Wasserbulkphase auftreten.

Im zweiten Manuskript wurden die Untersuchungen des Wasser-Gas-Transfers auf n-Oktan erweitert, welches eine höhere Hydrophobizität und deshalb stärkere Sorptionstendenz gegenüber DHS aufweist. Um zwischen hydrodynamischen und durch Sorption hervorgerufenen Effekten von DHS auf den Wasser-Gas-Transfer zu unterscheiden, wurden gleichzeitig Benzen und n-Oktan verwendet, d. h. zwei Verbindungen, die sich in ihrer Hydrophobizität stark unterscheiden ( $\log K_{OW,benzene} = 2.13$ ,  $\log K_{OW,n-octane} = 5.18$ ). Die erhaltenen Ergebnisse zeigen, dass Sorptionseffekte, die die frei gelöste Konzentration der organischen Verbindungen herabsetzen, sich negativ auf die Stofftransportraten auswirken. Dies liegt an der Tatsache, dass ein Teil der Verbindung infolge der Komplexbildung mit den deutlich größeren und damit trägeren Huminstoffmolekülen in seiner Diffusion behindert wird. Folglich wird der Wasser-Gas-Transfer von hydrophoben Verbindungen nicht nur infolge des

hydrodynamischen Effekts, sondern zusätzlich durch sorptionsbedingte Effekte der DHS beeinflusst.

Um ein System zu simulieren, in dem die Sorption einer Chemikalie durch gelöste Sorbentien keinen Einfluss auf deren thermodynamische Aktivität in der Wasserphase (oder frei gelöste Konzentration) ausübt, z.B. aufgrund der Nachlieferung aus einer großen Quelle, wie beispielweise einem kontaminierten Sediment, wurden Experimente mit passiver Dosierung durchgeführt. In diesen Experimenten wurden mit n-Oktan beladene Silikonfilme verwendet, um eine konstante thermodynamische Aktivität von n-Oktan in der wässrigen Phase, unabhängig von der Anwesenheit von DHS während der Purging-Experimente zu gewährleisten. Im Gegensatz zu den Experimenten mit sorptionsbedingter Aktivitätsabnahme (ohne Silikonfilm), in denen DHS und SDS-Mizellen eine Verringerung der Geschwindigkeit des Stofftransports von n-Oktan von der Wasser- in die Gasphase bewirkten, war der Effekt im System mit konstanter Aktivität positiv. Dies ist darauf zurückzuführen, dass hier die sorptionsbedingte Verringerung des mittleren Diffusionskoeffizienten des Sorptivs durch dessen höhere Gesamtkonzentration in der wässrigen Phase überkompensiert wird.

Für typische DHS-Konzentrationen in der Umwelt im Bereich von  $\leq 20 \text{ mg L}^{-1}$  können durch Sorption hervorgerufene Effekte von DHS auf den Wasser-Gas-Transfer nur für sehr hydrophobe Verbindungen mit  $\log K_{\text{DOC}} \geq 5$ , wie z.B. hochchlorierte PCB (polychlorierte Biphenyle) oder PAK (polyzyklische aromatische Kohlenwasserstoffe) erwartet werden. In technischen Prozessen, in denen die DHS- oder Tensidkonzentrationen viel höher sein können, können derartige Effekte durchaus für ein breiteres Spektrum an Verbindungen relevant sein.

Das Ausmaß des sorptionsbedingten Effekts von gelösten Sorbentien auf den Stofftransport in Diffusionsgrenzschichten hängt außerdem von der Mobilität des Sorbens (Diffusionskoeffizient) und der Labilität der Komplexe in Bezug auf ihre mittlere Verweilzeit in der Diffusionsschicht ab. Jedoch fehlt es an entsprechenden experimentellen Methoden, um sehr schnelle Sorptions-Desorptions-Prozesse zwischen gelösten Sorbentien und organischen Verbindungen zu verfolgen. Deshalb wurde eine neue experimentelle Technik – die zeitaufgelöste Kapillarmikroextraktion (time-resolved in-tube SPME, TR-IT-SPME) – erarbeitet. Mit Hilfe der TR-IT-SPME konnte gezeigt werden, dass der dominante Anteil des Sorbats (z.B. Pyren und Dimethylcyclohexan) von CHA und SRHA mit einer Halbwertszeit von weniger als 1 s desorbiert. Jedoch desorbiert ein bestimmter Anteil viel langsamer, d. h. mit einer Halbwertszeit im Bereich von Minuten oder gar Stunden.

Die Kapillarextraktion von Phenanthren und Pyren aus SDS-Lösungen mit einer SDS-Konzentration unterhalb der CMC verlief extrem schnell. Im Fall einer SDS-Lösung, welche Mizellen enthielt, erfolgte die Extraktion signifikant langsamer. Dies wird durch den Teil der PAK hervorgerufen, welcher innerhalb der Tensidmizellen vorliegt. Offensichtlich verhalten sich SDS Mizellen anders als DHS. Sie sind dynamischer und weniger starr als DHS Moleküle oder Aggregate.

Die Dicke der wässrigen Diffusionsschicht an Luft-Wasser-Grenzflächen in der Umwelt liegt typischerweise im Bereich von 20 - 200  $\mu\text{m}$ . Anhand der Einstein-Smoluchowski-Korrelation kann die Verweildauer von DHS-Molekülen in derartigen Grenzschichten im Bereich von 2 - 200 s abgeschätzt werden. Basierend auf den Ergebnissen der TR-IT-SPME-Messungen zur Desorptionsgeschwindigkeit von organischen Verbindungen aus Komplexen mit DHS kann man von einer signifikanten, jedoch unvollständigen Labilität dieser Komplexe für den Transport durch Diffusionsgrenzschichten an Wasser-Luft-Grenzflächen in der Umwelt ausgehen.

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## Publications

Ramus, K.; Georgi, A.; Kopinke, F.-D. Influence of dissolved humic substances on the mass transfer of organic compounds across the air-water interface. *Chemosphere* **2012**, 86, 138-143.

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### **Oral Presentations**

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Seville, Spain (23-27.05.2010)

Influence of dissolved humic substances on the mass transfer of organic pollutants through boundary layer between water and air. Oral presentation at the

6th UFZ-PhD Conference

Leipzig, Germany (26-27.04.2010)

Humic substances-help or hindrance for pollutant transport in water? Oral presentation at the

RAISEBIO, HIGRADE Symposium Microbial Contaminant Degradation at Biogeochemical Interfaces

Leipzig, Germany (02-04.03.2010)

Influence of dissolved humic substances on the mass transfer of organic pollutants through boundary layer between water and air.

1<sup>st</sup> BuildMona Workshop for Doctoral Candidates

Leipzig, Germany (16.10-17.10.2008)

Thermodynamic activity versus total concentration of xenobiotics as predictors of bioavailability.

April 2012