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Solid Phase Dosing and Sampling Technique To Determine Partition Coefficients of Hydrophobic Chemicals in Complex Matrixes

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Determination of polymer–water and dissolved organic carbon (DOC)–water distribution coefficients of very hydrophobic chemicals ($\log K_{OW} > 6$) is not straightforward. Poor water solubility of the test compounds complicates the spiking and analysis of actual freely dissolved concentrations. By dosing a system via a PDMS–fiber and monitoring the depletion in the polymer, spiking and analysis of concentrations in the aqueous phase are avoided, and sorption to the polymer and other hydrophobic phases can be determined easily and accurately. In this publication we report the determination of poly(dimethylsiloxane) (PDMS)–water, and Aldrich humic acid–water distribution coefficients for six PAHs with $\log K_{OW}$ values varying from 4.56 to 6.85. The distribution coefficients to a PDMS fiber ($\log K_f$) and the DOC ($\log K_{DOC}$) range from 3.86 to 5.39 and 4.78 to 7.43, respectively. Even for the most hydrophobic compounds, the distribution coefficients show small standard errors (≤ 0.05 log units). Therefore, this method might be applied to determine sorption coefficients of numerous, even more hydrophobic compounds, to humic acids as well as other dissolved hydrophobic matrixes.

Introduction

The bioavailability and fate of hydrophobic organic chemicals is influenced by binding to dissolved and particulate hydrophobic phases (1–6). Therefore, accurate sorption coefficients to soils, sediments, and dissolved organic matrixes are needed (7–9). The determination of these partition coefficients tends to become increasingly difficult when compounds are more hydrophobic. Increasing hydrophobicity usually coincides with higher partition coefficients and low aqueous solubility, making spiking procedures of the aqueous phase and detection of freely dissolved concentrations complicated (7, 10). In addition, systematic errors due to incomplete phase separation and the consequent overestimation of the free dissolved aqueous concentration are

higher for the more hydrophobic chemicals. This can be observed for the commonly used octanol–water partition coefficient (K_{OW}). For example, the standard deviation (SD) of the $\log K_{OW}$ of phenanthrene (4.54 ± 0.35 , $n = 26$) is much smaller than the SD of the more hydrophobic benzo[ghi]perylene (6.70 ± 0.84 , $n = 15$) (11). The same holds for sorption to complex hydrophobic phases such as soils, sediments, particulate organic carbon, and dissolved organic carbon (DOC) (7).

The determination of DOC-sorption is complicated, because this hydrophobic phase is dissolved in the aqueous phase, and a classical separation of the two phases without disturbing the equilibrium is not easy to achieve (12). Therefore, sorption behavior of hydrophobic substances to DOC is often studied by measuring the free concentration without active separation of the two phases. These techniques include dialysis (13), headspace equilibration, fluorescence quenching (14–16), or partitioning to a well-defined hydrophobic phase such as thin polymer films (17, 18) and negligible depletion solid-phase microextraction (nd-SPME) (4, 19–23).

Besides the complications with complete separation of the two phases, the spiking procedure of aqueous solutions is not always straightforward. Classical spiking procedures of hydrophobic chemicals with an organic solvent often lead to instable and variable concentrations and solutions containing not completely dissolved substances. The application of a generator column (24, 25) or a partitioning driven administrator (26, 27) to prepare aqueous solutions is an improvement, since it generates “real” solutions with only dissolved molecules. The two phenomena (incomplete separation of phases and unstable aqueous solutions) lead to a large variability in partition and sorption coefficients in the literature (7, 8, 28).

This study attempted to overcome these problems by applying another dosing system as an alternative to regular spiking procedures. The new aspect in the approach is that the dosing system is also used to indirectly monitor sorption to a dissolved hydrophobic phase (29). A hydrophobic phase (poly(dimethylsiloxane), PDMS) is “loaded” with compounds, and the depletion of this phase is monitored at different dilution factors (DF, volume water/volume PDMS) or with different concentrations of DOC. This procedure enables the determination of partition coefficients to PDMS and sorption coefficients to DOC without using a carrier-solvent to spike the water and analyzing water samples. Figure 1 shows a conceptual picture of the experimental setup to determine the partition coefficient to PDMS (Figure 1a,c) and the sorption to DOC (Figure 1b,d).

Materials and Methods

Chemicals, Fibers, and Solvents. The PAHs (Table 1) and Aldrich humic acid used were all purchased at Sigma Aldrich Chemie BV (Zwijndrecht, The Netherlands). Glass fibers with a core diameter of 110 μm and a 28.5 μm poly(dimethylsiloxane) (PDMS) coating (volume 12.4 $\mu\text{L}/\text{m}$) were obtained from Poly Micro Industries (Phoenix, AZ). Acetonitrile, acetone, methanol (Lab-Scan, Dublin, Ireland), and *n*-hexane (Baker BV, Deventer, The Netherlands) were of analytical grade, and highly pure deionized water ($R \geq 18 \text{ M}\Omega$) was prepared by a Millipore water purification system, equipped with organic free kit (Millipore Waters, Amsterdam, The Netherlands).

PDMS–Water Partition Coefficients. PDMS–water partition coefficients (K_f) were determined using a “classical” and the new “fiber depletion” method. Both experiments

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TABLE 1. Test Compounds and Some of Their Properties^a

compound (CAS#)	log K_{ow} (25 °C) (11)	aqueous solubility (mg/L) (11)	purity (%)
phenanthrene (Phe) (085-01-8)	4.56	1.15	not given
fluoranthene (Fla) (206-44-0)	5.16	0.26	98
pyrene (Pyr) (129-00-0)	5.18	0.135	99
benz[a]anthracene (B[a]A) (056-55-3)	5.91	0.0094	95
benzo[b]fluoranthene (B[b]F) (205-99-2)	6.20	0.0015	99
benzo[k]fluoranthene (B[k]F) (207-08-6)	6.20	0.00080	98
benzo[ghi]perylene (B[ghi]P) (191-24-2)	6.85	0.00026	not given

^a The reference numbers are given between brackets.

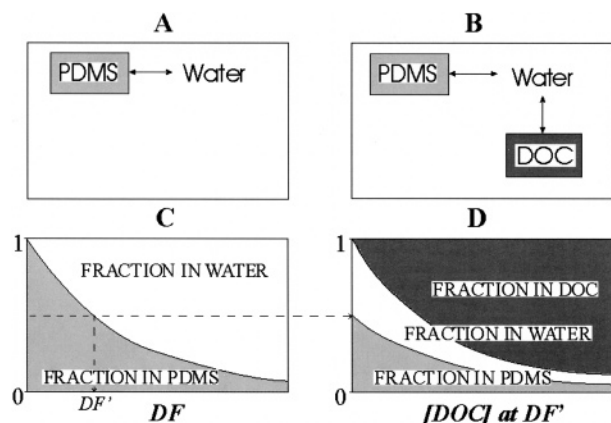


FIGURE 1. A conceptual picture of the test systems without DOC (A) and with DOC (B), and the expected fraction of the test compound in the different phases as a function of the dilution factor (DF) (C) and the dissolved organic carbon concentration, [DOC] at a single dilution factor (DF') (D).

were performed at $21 (\pm 1)$ °C in the dark. Before use, all fibers were cut to a length of 5.0 cm ($0.62 \mu\text{L}$ PDMS per fiber) and thermally cleaned at 275 °C for 16 h under a constant helium flow of $\sim 35 \text{ mL/min}$.

In the "classical" experiment, 16 clean fibers of 5 cm ($9.92 \mu\text{L}$ PDMS in total) were exposed to 100 mL water that was spiked with 0.1% acetone containing 5–20 mg/L phenanthrene, fluoranthene, pyrene, benz[a]anthracene, and benzo[b]fluoranthene. A 0.005 mM NaN_3 (Merck, Amsterdam, The Netherlands) solution was added to inhibit bacterial degradation. Fibers were sampled after 7 and 14 days of gentle stirring at 120 rpm. There was no significant difference between the 1 and 2 week exposed fibers indicating that equilibrium was reached in the fiber–water system. After exposure, fibers were gently blotted dry with a tissue, cut into two pieces and transferred to a 1.8 mL autosampler vial containing 1.0 mL acetonitrile within 30 s. An additional fiber–air depuration study showed that no significant amount of the compounds in the fiber coating were lost during a 30 s transfer period, as half-lives of the test compounds exposed to a gentle stream of air in a fume hood ranged from 1.4 h to much more than 24 h (Supporting Information, Figure A). Aqueous concentrations were determined by sampling 10 mL of water ($n = 3$) and extracting these samples with 1 mL of *n*-hexane three times. After extraction, the 3 mL hexane was evaporated to $\sim 0.5 \text{ mL}$ using a gentle stream of N_2 . Subsequently 1 mL of acetonitrile was added, and the mixture was evaporated to $\sim 0.3 \text{ mL}$. The extraction recovery obtained from a parallel experiment with spiked *n*-hexane was 100% (RSD 2%). Final aqueous concentrations ranged from $10 \mu\text{g/L}$ (phenanthrene) to $0.9 \mu\text{g/L}$ (benzo[b]fluoranthene).

In the "fiber depletion" experiment, the aqueous phase was dosed via a "loaded" PDMS-fiber. Clean fibers ($n = 60$ – 80) were "loaded" by exposing them for 24 h on a "rock and roller" shaker to a 30 mL methanol–water mixture spiked with 0.1–0.5 mg/L PAHs. Partition coefficients between the

fibers and the methanol–water mixture (Table A, Supporting Information) were determined using the "classical" approach, measuring concentrations in both phases. This classical approach was chosen because concentrations and solubility in the MeOH–water mixture are high enough to accurately measure partition coefficients (30). Initial concentrations in the PDMS ranged from 10 to 20 mg/L per compound. The loading of the fiber via methanol–water is highly reproducible, as standard deviations of the concentrations in the PDMS coating were smaller than 6% for all compounds ($n = 5$).

Loaded fibers were exposed to water (0.005 M NaN_3) in different sized flasks. The water volume varied from 6.5 to 1100 mL, and the PDMS volume varied from 0.6 to $2.5 \mu\text{L}$, thereby creating eight different dilution factors (volume water/ volume PDMS), ranging from 2760 to 92 000. All bottles were gently shaken using a two-dimensional shaker (KS501, IKA Labortechnik, Staufen, Germany) at 190 rpm. Fibers were sampled directly after loading ($n = 5$) and after 68.5, 168, and 336 h ($n = 2$). For the two largest flasks, a 672-h exposure time had to be included in order to reach equilibrium ($n = 2$). After exposure, fibers were extracted in a 1.8 mL autosampler vial, containing a $250 \mu\text{L}$ insert with 200 μL acetonitrile. All fibers were extracted for at least 1 day and stored at -20 °C (three subsequent extractions showed an extraction recovery of $99.6\% \pm 0.1\%$ in the first extraction).

DOC–Water Sorption Coefficients. Loaded fibers were exposed to 5 mL water containing 0, 0.5, 1, 5, 10, 25, 50, and 98 mg/L Aldrich humic acid sodium salt (38.25% organic carbon, Sigma Aldrich) at 21 ± 1 °C. Five fibers were sampled directly (exposure time "0"), and a single fiber was sampled after 2, 4, 8, 24, 72, and 168 h shaking on the "rock and roller" (Snijders Scientific, Tilburg, NL) for every DOC concentration. Loading, sampling, and extraction procedures of the fibers were identical to the PDMS–water partition coefficient experiments.

Analysis of Samples. The concentrations in the fiber extracts were determined by HPLC–fluorescence detection. The system consisted of a Shimadzu DGU 14A degasser (Den Bosch, The Netherlands), a Spark Marathon autosampler/HPLC pump (Emmen, The Netherlands) and a Jasco FP-920 fluorescence detector (Maarsse, The Netherlands). Separation was performed using a Supelcosil (Supelco, Bellefonte, CA) LC-PAH column (length 100 mm, ϕ 4.6 mm, particles 3 μm) that was operated at 28 °C. All analyses were performed with a flow rate of $1000 \mu\text{L/min}$ and an injection volume of $20 \mu\text{L}$. The compounds were separated using gradient elution starting with 40% H_2O for two min followed by an increase of the acetonitrile fraction to 100% in 9.5 min, where it was kept for another 7.5 min before returning to the initial solvent composition for 6 min. The excitation and emission wavelengths (nm) of Phe, Fla, and Pyr were 255/405, those of B[a]A were 277/393, while B[b]F and B[k]F concentrations were determined at 260/420 and B[ghi]P at 295/425, with detection-limits of 1.0, 2.0, 0.5, 0.1, 0.3, 0.1, and 0.2 $\mu\text{g/L}$, respectively. Quantification was done using standards containing 16 PAHs (Supelco, Bellefonte, CA, selected by the EPA) diluted in acetonitrile.

Chromatograms were analyzed using Chromcard version 1.21 (Milan, Italy), and corrected by hand if necessary. Quantification was done by a series of 7 standards, with concentrations ranging from 2 to 200 µg/L.

The Determination of K_f . Two methods were used to determine the partition coefficient to the PDMS fiber (K_f). In the “classical” experiment, the fiber concentration (C_f) was divided by the aqueous concentration (C_{aq}) measured at the end of the exposure (eq 1):

$$K_f = \frac{C_f}{C_{aq}} \quad (1)$$

In the “fiber depletion” experiment, a one phase exponential decay model (eq 2) was applied to the concentration in the fiber in time ($C_{f(t)}$), and the elimination rate constant (k_2 in h^{-1}) and the equilibrium concentration in the fiber ($C_{f(\infty)}$) were determined:

$$C_{f(t)} = (C_{f(\text{initial})} - C_{f(\infty)}) \exp(-k_2 t) + C_{f(\infty)} \quad (2)$$

The model was fitted using Graphpad, version 3.0 (31). If the decrease of the concentration in the fiber was insufficient ($(C_{f(\text{initial})} - C_{f(\infty)})/C_{f(\text{initial})} > 5\%$) for a proper fit of eq 2, the average of the longest exposure-time was taken as the equilibrium concentration ($n \geq 3$). Subsequently, the percentage recovered from the fiber at equilibrium ($C_{f(\infty)}/C_{f(\text{initial})}$, %) was plotted against the volume water/volume PDMS ratio (DF), and the PDMS–water partition coefficient (K_f) was calculated by fitting to eq 3 the data using Graphpad (see Supporting Information for the derivation of eq 3):

$$\frac{C_{f(\infty, \text{DF})}}{C_{f(\text{initial})}} (\%) = \frac{100\%}{1 + \frac{DF}{K_f}} \quad (3)$$

Determination of K_{DOC} . The sorption coefficient to dissolved organic material, normalized for organic carbon content (K_{DOC}), was determined by monitoring the depletion of PAHs at different Aldrich humic acid concentrations. Equation 2 was also used to describe the depletion of the DOC exposed fibers and to calculate the equilibrium concentration in the fiber ($C_{f(\infty)}$). The percent recovery from the exposed fibers ($C_{f(\text{DOC})}/C_{f(\text{initial})}$, %) was plotted against the DOC concentration ($[DOC]$). Together with a constant DF (8064) and known K_f values from the previous experiment, K_{DOC} values could be determined by the following equation, using Graphpad (see Supporting Information for the derivation of eq 4):

$$\frac{C_{f(\text{DF})}}{C_{f(\text{initial})}} (\%) = \frac{100\%}{1 + \frac{DF}{K_f} (1 + [DOC] K_{\text{DOC}})} \quad (4)$$

Results and Discussion

Determination of K_f . The depletion of the fibers exposed to water was fitted by Equation 2. Figure 2 provides the data and fitted curves for phenanthrene and benzo[ghi]perylene; the other compounds can be found in the Supporting Information (Figure B). It can be observed that the 2–4 week equilibration period was sufficient to reach or almost reach equilibrium for all compounds. The percentage recovered from the fibers at equilibrium is plotted against the dilution factor in Figure 3. The PDMS–water partition coefficients were calculated from these data using eq 3. Table 2 displays the calculated log K_f values from the classical and fiber depletion experiment, as well as partition coefficients to different PDMS coated fibers presented in the literature. A comparison of the data with partition coefficients from

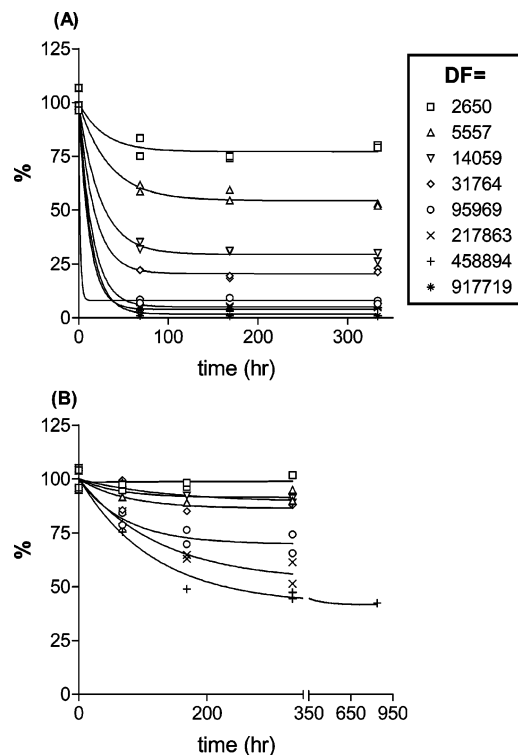


FIGURE 2. The depletion of phenanthrene (A) and benzo[ghi]perylene (B) from the PDMS fiber at different water–fiber volume ratios (DF) in time. A one-phase exponential decay curve is fitted through the data ($n = 7-10$ per DF). The percentage was calculated as the following: measured concentration in the fiber at time t divided by the concentration in the fiber at $t = 0$.

literature, that sometimes use different coating thicknesses, is legitimate because it is assumed that the sorption of hydrophobic compounds to PDMS is an absorption process (32–36). Therefore, partition coefficients to this material are thought to be independent of concentration and dimensions of the fiber used. The determined K_f values with both methods are comparable to literature data, even though the variation within the literature data is generally large, and K_f values of the larger PAHs are scarce. The high r^2 (≥ 0.99) of the fit of eq 3 and the small standard errors (≤ 0.04 log units) of the determined log K_f values indicate that the model fits the data well and can generate K_f values with high accuracy.

Determination of K_{DOC} . Similar to the fiber depletion experiment, the depletion of the Aldrich humic acid exposed fibers was monitored in time (Figure 4 and Figure C of the Supporting Information). Both the desorption from the fiber and sorption to the DOC might influence the equilibration kinetics (Figure 1b), but since DOC-sorption is considered extremely fast (13, 14, 16, 37, 38), the exchange between water and PDMS-fiber was thought to be the rate-limiting step. Therefore, equilibrium concentrations in the fiber could be obtained from the plateau of a one-phase exponential decay curve (eq 2). For larger particulate hydrophobic phases with slow sorption kinetics, a two-phase exponential decay curve might be used to obtain the equilibrium concentration in the fiber. In those cases, equilibration times can become much longer. The percentage recovered from the equilibrated fiber was plotted against the DOC concentration in Figure 5. Sorption coefficients to the DOC (K_{DOC}) were determined by fitting eq 4 on the data (see fitted lines) using K_f values determined in the previous experiment.

Detailed Discussion of Calculated K_{DOC} Values. The calculated K_{DOC} values are shown in Table 3. Even though the determined K_{DOC} values have small standard errors (≤ 0.05

TABLE 2. PDMS–Water Partition Coefficients ($\log K_f$) of 7 PAHs

compound	experimental		literature		
	log K_f (SD, n) "classical method"	log K_f (SE, n) "fiber depletion method"	log K_f average (SD, n)	log K_f range	ref
Phe	3.73 (± 0.05 , 15)	3.86 (± 0.03 , 52)	3.82 (± 0.39 , 10)	3.25–4.42	27, 32, 36, 39, 52–54
Fla	4.18 (± 0.05 , 15)	4.40 (± 0.02 , 53)	4.22 (± 0.31 , 11)	3.72–4.71	27, 32, 36, 39, 52–54
Pyr	4.22 (± 0.05 , 15)	4.41 (± 0.04 , 55)	4.42 (± 0.42 , 7)	3.80–4.86	27, 36, 39, 53, 54
B[a]A	4.59 (± 0.05 , 15)	4.92 (± 0.03 , 54)	4.70 (± 0.57 , 5)	3.83–5.26	39, 52, 54, 55
B[b]F	4.77 (± 0.06 , 15)	5.28 (± 0.04 , 46)	5.17	—	54
B[k]F	nd ^a	5.29 (± 0.04 , 46)	5.33	—	54
B[ghi]P	nd	5.39 (± 0.03 , 38)	4.28	—	54

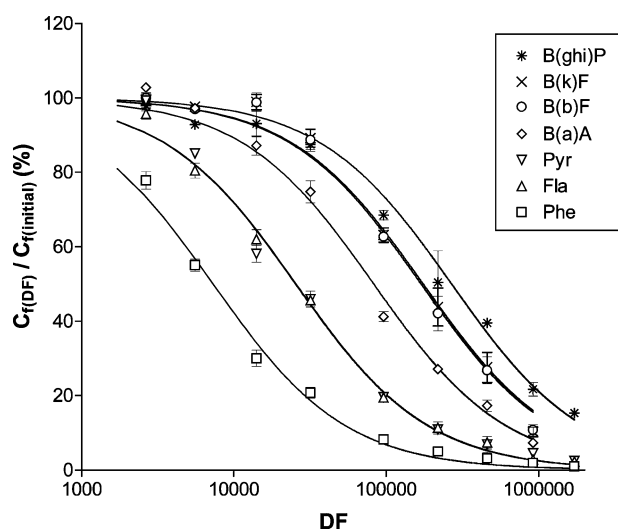
^a nd = no data.

FIGURE 3. Depletion of the SPME fiber (at equilibrium) as a result of the increasing water-PDMS ratio (DF) and their standard errors (error bars). Equation 3 is fitted through the data (lines) to obtain the fiber–water partition coefficient (K_f).

log units), a closer look at Figure 5 shows that the fiber-concentrations of the analytes (particularly B[ghi]P) were systematically above the fitted curve at the highest DOC concentrations. This deviation is more clearly shown in Figure 6, where the sorption coefficients at a particular DOC level slightly decreased with increasing DOC concentration.

Nonlinear sorption behavior of the compounds to DOC might explain this effect, but this does not seem plausible, since DOC-sorption coefficients of hydrophobic organic chemicals (PAHs) are generally close to linearity (7–9, 39). Even if sorption is nonlinear, sorption coefficients usually increase with decreasing free concentrations.

Alternatively, fouling of DOC on the fiber surface might occur, creating an increasing hydrophobic phase with increasing DOC concentrations. The exposed fibers were cleaned with a tissue to minimize fouling effects. If fouling was responsible for the observed deviation of B[ghi]P, almost 10% of the DOC in the system should be sorbed to the fiber to create this effect. This would have led to severe change of color of the fiber, which was not observed. Furthermore, substantial fouling effects have not been observed for SPME fibers exposed to various hydrophobic compounds via an aqueous phase containing high levels of dissolved organic matrixes (4, 40).

Another, more plausible explanation might be that the addition of Aldrich humic acid sodium salt altered the aqueous chemistry. The pH and conductivity were monitored in the DOC solutions, and while the conductivity hardly changed (0.74–0.80 mS/cm), the pH increased from 7.03 to 7.82 with increasing DOC concentration (Table B, Supporting

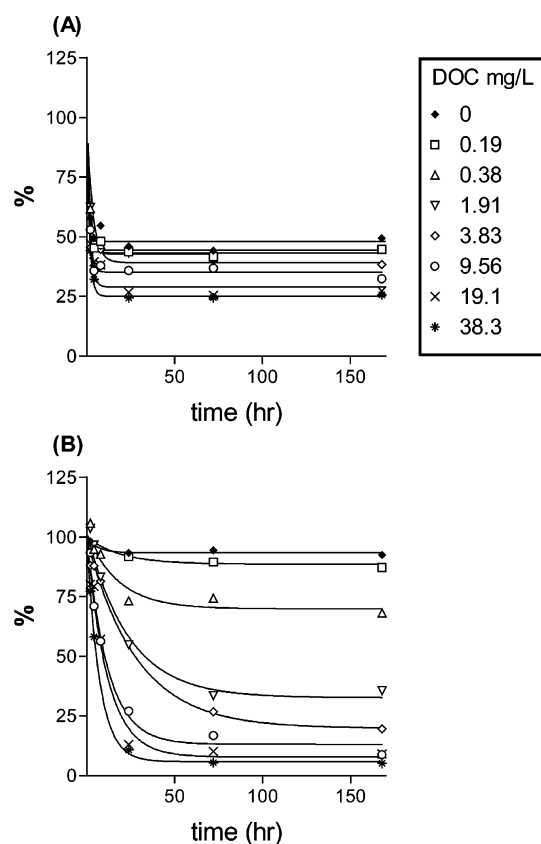


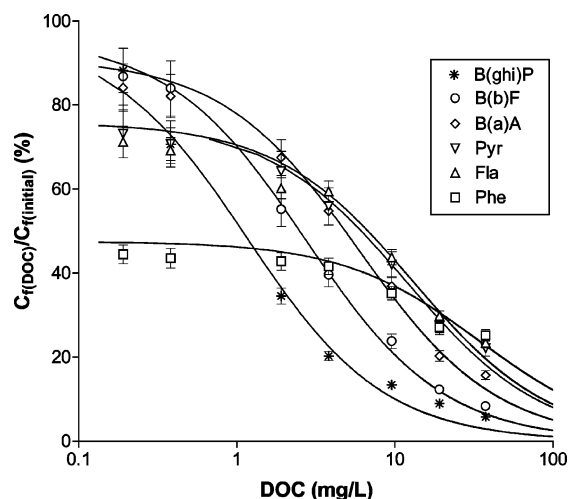
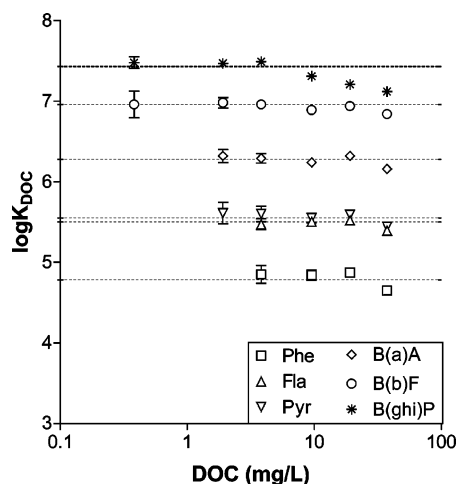
FIGURE 4. The depletion of phenanthrene (A) and benzo[ghi]perylene (B) from the PDMS fiber at different DOC concentrations in time. A one-phase exponential decay curve is fitted through the data ($n = 9$ –12 per DOC concentration). The percentage was calculated as the following: measured concentration in the fiber at time t divided by the concentration in the fiber at $t = 0$.

Information). Literature shows that the sorption coefficients of PAHs to fulvic and humic acids can decrease slightly with increasing pH (16, 39, 41–43). This phenomenon is explained by the deprotonation of the macromolecules, changing their shape (and interaction with each other (44)), increasing their polarity, and thereby decreasing their ability to sorb hydrophobic molecules such as PAHs (16). This could have happened in our experiments, explaining the slightly decreasing sorption coefficient of especially B[ghi]P with increasing DOC concentration and pH. Although a pH effect cannot be ruled out, the variation of the sorption coefficients of the PAHs was only minor (0.4 log units), so the fits of Figure 5, from which the K_{DOC} was derived, still describe the data well.

Observed K_{DOC} Values versus Literature Data. Sorption coefficients of the low molecular weight PAHs (Phe, Fla, Pyr,

TABLE 3. DOC–Water Sorption Coefficients ($\log K_{\text{DOC}}$) to Aldrich Humic Acid of 6 PAHs

compound	experimental	literature		ref
	$\log K_{\text{DOC}}$ (L/kg) (SE, <i>n</i>) (Aldrich HA)	$\log K_{\text{DOC}}$ (L/kg) average (SD, <i>n</i>) (Aldrich HA)	$\log K_{\text{DOC}}$ (L/kg) range	
Phe	4.78 (± 0.05 , 32)	4.43 (± 0.50 , 23)	3.66–5.84	15, 20–22, 37, 43, 56–63
Fla	5.50 (± 0.04 , 27)	4.90 (± 0.43 , 11)	3.92–5.32	15, 20, 43, 57, 63–66
Pyr	5.55 (± 0.03 , 33)	4.83 (± 0.55 , 26)	3.48–5.69	16, 20–22, 37, 39, 42, 43, 50, 51, 57, 61, 63, 66–68
B[a]A	6.28 (± 0.03 , 37)	5.36 (± 0.18 , 6)	5.18–5.62	13, 58, 60, 63, 65
B[b]F	6.96 (± 0.02 , 42)	5.85 (± 0.21 , 2)	5.09–5.66	63, 65
B[ghi]P	7.43 (± 0.04 , 39)	5.83 (± 0.20 , 3)	5.79–6.05	63, 65, 67

FIGURE 5. The depletion of the SPME–fiber at a fixed DF as a result of increasing DOC concentrations, the error bars represent the standard errors. The line represents the fit of eq 4, using a fixed fiber–partition coefficient (K_f) obtained from the fiber depletion experiment (Table 2).FIGURE 6. The separately calculated K_{DOC} values with their standard errors at different DOC-concentrations. The broken lines are the sorption coefficients obtained from the fits of Figure 5.

B[a]A) to Aldrich humic acid from literature are highly variable, while data on high molecular weight PAHs (B[b]F, B[ghi]P) are very scarce (see Table 3). The observed K_{DOC} values of the PAHs with a lower molecular weight are slightly higher than literature values, but as hydrophobicity increases differences increase up to 1.5 log units for B[ghi]P. This discrepancy can probably be attributed to the overestimation of freely dissolved aqueous concentrations in other studies (28). It seems that the presented method results in accurate and reproducible partition coefficients, and might also be

applicable to more hydrophobic compounds, because the “partitioning-driven administration” method provides and samples only true solutions (26, 27). In addition, very low aqueous concentrations can be determined due to the high concentration gradient between PDMS and the aqueous phase (45). When testing more hydrophobic compounds, increasing equilibration times to obtain K_f and K_{DOC} could become a limiting factor. Thinner polymer coatings, thereby increasing the surface volume ratio, and better agitation can overcome part of this problem. Monitoring the equilibration process remains essential, since dissolved matrixes might accelerate kinetics of the partition process due to interference in the aqueous diffusion layer around the fiber (37, 46), and larger particulate hydrophobic phases (e.g., tar) might result in slower kinetics than the fiber–water exchange process, thereby slowing down the equilibration process (47).

Mass Balance Considerations. A crucial assumption in the presented method is a 100% mass balance and no sorption to other phases than described by the models used (eqs 3 and 4). If this assumption is not met, the method will fail to give accurate distribution coefficients.

Sodium azide (NaN_3) was added to inhibit biological degradation (48), and photodegradation was prevented by performing experiments in the dark. Any degradation or leakage losses would result in a continuous decrease of fiber concentration in time. However, the time curves of both experiments reach a clear equilibrium level (see Figures 2 and 4, and Figures B and C of the Supporting Information), so degradation and leakage were considered insignificant.

Two additional processes, affecting free concentrations could occur: evaporation to the headspace and sorption to the vial wall. Evaporation to the headspace seems insignificant as calculated amounts in the headspace, using air–water partition coefficients (49), were always lower than 0.016% and 0.056% in the K_f and K_{DOC} experiment, respectively. Sorption to other phases such as (hydrophobic) impurities and the vial walls is of special interest in the fiber partition experiment, since a variety of bottles was used. Their surface volume ratio ranged from 4 cm^{-1} (7.4 mL vials) to 0.6 cm^{-1} (1.1 L bottles). To remove hydrophobic impurities, the bottles were cleaned thoroughly with soap, rinsed with hot tap water (3 times), Millipore water (3 times), acetone (analytical grade, 3 times), and again with Millipore water. However, sorption to glass walls cannot be ruled out. Losses and subsequently underestimation of K_f values are expected to become important at lower dilution factors, since the surface volume ratio increases with decreasing bottle size. No trends were observed (Figure 7) and therefore sorption to glass walls was considered insignificant as well.

Implications and Relevance. Sorption behavior to DOC and other hydrophobic matrixes is relevant, because it influences the fate of compounds in the environment and their bioavailability (1–6). Current models used in risk assessment usually calculate sorption coefficients to DOC from their octanol water partition coefficient ($\log K_{\text{DOC}} = a \log K_{\text{OW}} + b$), while various researchers have shown that the

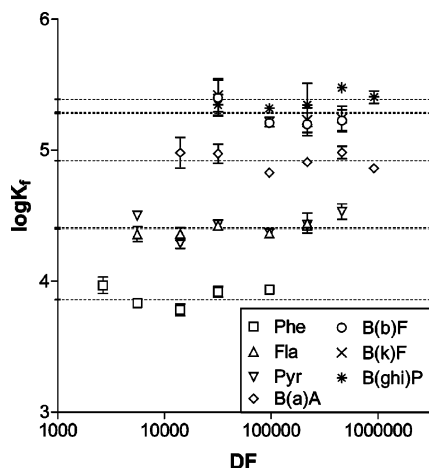


FIGURE 7. The separately calculated K_f values and their standard errors plotted against the DF. The broken lines are the partition coefficients obtained from the fits of Figure 3.

type of DOC and aqueous chemistry influence the sorption behavior (39, 44, 50, 51). However, as long as the variation of reported octanol water partition coefficients and sorption coefficients to DOC remains large, modeling the sorption of very hydrophobic compounds remains difficult.

The “solid phase dosing and sampling technique” enables the measurements of partition coefficients without having to spike aqueous phases with a cosolvent or to separate the aqueous and matrix phases, and it can detect very low aqueous concentrations. In this study, the method is applied to measure partition coefficients to Aldrich humic acid, but in principle, the method can be used to determine sorption coefficients of all kinds of dissolved and fine suspended matrixes, including natural DOC, sediment, cell membranes and proteins. The only requirements are; known polymer water partition coefficients, measurements performed at equilibrium, no substantial fouling and careful considerations of mass balance.

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Supporting Information Available

Partition coefficients (of all PAHs used) between PDMS and a 1:1 MeOH–water mixture, measured pH, and conductivity in the Aldrich humic acid solution, time-dependent evaporation of the PAHs from the PDMS-fiber to air, time-dependent depletion of the fiber in different volumes of water and different Aldrich humic acid concentrations, and the derivation of eqs 3 and 4. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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