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Distribution of PAHs and PCBs to dissolved organic matter: High distribution coefficients with consequences for environmental fate modeling

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Abstract

Dissolved organic carbon/water distribution coefficients (K_{DOC}) were measured for a selection of PCBs with octanol/water partition coefficients (K_{OW}) ranging from $10^{5.6}$ to $10^{7.5}$. A solid phase dosing and sampling technique was applied to determine K_{DOC} to Aldrich humic acid. This technique is in particular suitable for determining the distribution of very hydrophobic chemicals to complex matrices like humic acids. The K_{DOC} values were calculated from the experimental data using a linear model. Determined K_{DOC}'s were evaluated in relation to octanol/water partition coefficients of the test compounds, and compared to literature data. Measured K_{DOC} values were somewhat higher than literature data, which can probably be attributed to the overestimation of freely dissolved aqueous concentration as a result of incomplete phase separation in other studies, and to the unique character of Aldrich humic acid as a "sorbent" or co-solute or to the fact that Aldrich humic acid is not a typical DOC, and other (adsorption) processes can occur. This study reports DOC distribution coefficients that belong to the highest ones ever measured. In addition, the DOC distribution was discussed in relation to current risk assessment modeling.
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1. Introduction

Fate and bioavailability of very hydrophobic organic chemicals in aquatic ecosystems are affected by the presence of dissolved and particulate organic matter (Burkhard, 2000; Schwarzenbach et al., 2003). Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), with octanol/water partition coefficients (K_{OW}) values of 10^5 or more, belong to this category. The partition coefficient of the chemical between dissolved organic carbon and the freely dissolved fractions are relevant parameters for environmental fate modeling and ecological risk assessment of these compounds, because association with dissolved organic matter (DOM) is often not negligible in natural aquatic systems.

The fate and risk assessment of hydrophobic substances in the aquatic environment suffer from large errors (Fauser and Thomsen, 2002), mainly due to biased experimental distribution coefficients (Lee et al., 2003). In multimedia models, the behavior of hydrophobic substances inside the water compartment is often described by distribution over two phases only: suspended solids and water (Brandes et al., 1996). In the real world, the ambient amount of natural DOM may have a significant influence on the freely

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dissolved concentration and thus on the fate and effects of very hydrophobic substances. Subsequently a 3-phase distribution (suspended solids, DOM and freely dissolved aqueous phase) has been suggested to describe the behavior of hydrophobic substances in the aquatic environment (Mitra and Dickhut, 1999; Fauser and Thomsen, 2002), because these chemicals generally have a high affinity for DOM.

For improved model calculations reliable experimental distribution coefficients to the dissolved organic carbon (K_{DOC}) are needed. The determination of the distribution coefficient to DOC is, however, complex because this hydrophobic phase is dissolved in the aqueous phase. Therefore the ratio between a freely dissolved state and bound dissolved state seems a *contradictio in terminis*. The classical separation of the DOM phase from the water phase without disturbing equilibrium is not easy to achieve (Schwarzenbach et al., 2003). Therefore, partitioning behavior of hydrophobic substances to DOM is often studied by measuring the free concentration without actively separating the two phases. This approach includes dialysis (McCarthy and Jimenez, 1985), fluorescence quenching (Schlautman and Morgan, 1993), and partitioning to a well defined hydrophobic phase such as thin polymer films (Wilcockson and Gobas, 2001), and non depletive solid-phase microextraction (nd-SPME) (Urresterazu et al., 1998; Poerschmann et al., 2000; Mayer et al., 2003). Conventional spiking procedures of hydrophobic chemicals with an organic solvent often lead to instable concentrations and solutions containing not completely dissolved substances. The two phenomena (incomplete separation of phases and difficulties in analyzing aqueous concentrations) lead to a large variety in distribution coefficients in the literature (Burkhard, 2000; Krop et al., 2001; Poerschmann and Kopinke, 2001).

To overcome these problems, we used a solid phase dosing and sampling technique that was developed to determine distribution coefficients of very hydrophobic chemicals to complex matrices (ter Laak et al., 2005) instead of direct spiking of the chemicals with a carrier solvent. The distribution coefficients of seven PCBs to Aldrich humic acid were determined. Results are discussed in relation to literature data of PAHs and PCBs. Additionally, the consequences of binding to DOM for environmental fate modeling are discussed in relation to ecological risk assessment.

2. Materials and methods

2.1. Materials

Aldrich humic acid (38.25% organic carbon) was purchased at Sigma Aldrich Chemie BV, Zwijndrecht, The Netherlands (lot number S15539-213). The PCBs (PCB 28, 52, 101, 118, 138, 153 and 180) were purchased at Dr. Ehrenstorfer, GmbH, Augsburg, Germany, and labeled C^{13} PCBs (PCB 28, 52, 101, 118, 138, 153 and 180) were purchased at Campro Scientific BV, Veenendaal, The Netherlands, NaN_3 was purchased at Merck, Amsterdam, The Netherlands. Glass fibers with a core diameter of 110 μm and a 28.5 μm polydimethylsiloxane (PDMS) coating (volume 12.4 μl/m) were obtained from Poly Micro Industries, Phoenix, AZ, USA, and acetonitrile, acetone, methanol (Lab-Scan, Dublin, Ireland) and *iso*-hexane (Baker BV, Deventer, The Netherlands) used were of analytical grade. Highly pure water ($R \geqslant 18\ M\Omega$) as prepared by an automatic purification apparatus (Millipore Waters, Amsterdam, The Netherlands).

2.2. Dosing and partitioning of test chemicals

Experiments were performed at 21 (±1) °C in the dark. Before use, all fibers were cut to a length of 2.5 cm (0.325 μl PDMS per fiber) and were thermally cleaned at 275 °C for 16 h under a constant helium flow of ~35 ml/min.

Clean fibers were "loaded" by exposing them for 24 h on a "rock and roller" shaker to a 10 ml methanol–water mixture spiked with 0.125 mg/l of PCBs (PCB 28, 52, 101, 118, 138, 153 and 180). Initial concentrations of the individual PCB in the PDMS ranged from 10 to 30 mg/l.

Before the experiments started all glassware was cleaned with soap, rinsed with hot tap water (3 times), Millipore water (3 times), acetone, analytical grade (3 times) and again with Millipore water (3 times). Furthermore, 0.005 mM NaN_3 was added to all aqueous solutions to inhibit bacterial degradation.

PDMS–water partition coefficients (K_f) were determined by depleting loaded fibers in various volumes of water. The "volume water/volume PDMS" ratio (dilution factor, DF) varied from 80000 to 3200000. The DF was chosen in this range because of high distribution coefficients were expected for the PCBs (Mayer et al., 2000; Poerschmann et al., 2000). Five fibers were sampled directly, and the other fibers were sampled after 68, 185, 378 and 641 h in triplicate, to determine if equilibrium was reached.

A similar approach was used to investigate the distribution to Aldrich humic acid. The Aldrich humic acid solutions were prepared by direct dissolution of the AHA sodium salt. The organic carbon content of DOC solutions was taken from the manufacturer specifications about organic carbon content. However, we should keep in mind that Aldrich humic acid is not necessarily representative of natural dissolved organic matter, and has other absorbing and (non-hydrophobic) adsorbing properties (Steinberg, 2003). Loaded fibers were exposed to 5 ml water containing 0.1, 0.2, 0.4, 1.9, 3.8, 9.6, 19.1, 38.3 and 95.6 mg/l DOC. Five fibers were sampled directly (exposure time "0" – $C_{f(\text{initial})}$), and the other fibers were sampled after 4, 24, 72, 168, 336, 672 and 1032 h shaking on the "rock and roller" (Snijders Scientific, Tilburg, The Netherlands). One fiber coming from one vial was sampled per DOC concentration–exposure time combination.

The directly sampled and exposed fibers were extracted in a 1.8 ml autosampler vial containing a 250 μl insert with 200 μl *iso*-hexane for at least 1 day, and stored at −20 °C (three subsequent extractions showed an extraction recovery of at least 99.1% in the first extraction).

2.3. Analysis of samples

The concentrations of the PCBs in the fiber extracts were determined by gas chromatography with mass spectrometry detector. GC–MS was performed with a Trace 2000/DSQ GC/MS combination (Thermo Finnigan, Milan, Italy). 10 µl internal standard mixture in *iso*-hexane, containing labeled C^{13} PCBs, was added to the PCB extracts. Fifty microliters of the solution was introduced into the PTV injector at 60 °C by means of speed-controlled large volume injection at 3 µl/s. The injection time was set at 1 min. During the injection time the solvent was evaporated (the split valve was open). The next 3 min the split valve was closed, the injection temperature rose to 320 °C and a helium flow to 3 ml/min (transfer status of the injection).

The GC separation was performed on a DB5-MS column (J&W), 30 m × 0.25 mm I.D. with a film thickness of 0.10 µm. The temperature program was 50 °C for 5 min, at 20 °C/min to 180 °C, at 8 °C/min to 300 °C, where it was kept for 5 min before returning to the initial conditions (in 20 min). The transfer line was set at 300 °C. The MS (ion source) was set at 250 °C using EI (70 eV) in SIM mode (256, 268, 292, 304, 326, 338, 360, 372, 394 and 406 *m/e*). Helium was used as a carrier gas at a pressure of 70 kPa, and at constant flow 1.2 ml/min. The detector gain was set at 1×10^5 (1248 V) and the emission current at 150 mA.

2.4. The determination of K_f and K_{DOC}

The depletion of the fibers exposed to various volumes of water and DOC solutions can both be described by a one-phase exponential decay model (Eq. (1)):

$$C_{f(t)} = (C_{f(\text{initial})} - C_{f(\text{eq})})\exp^{(-k_2 t)} + C_{f(\text{eq})} \tag{1}$$

Here $C_{f(\text{initial})}$, $C_{f(t)}$, and $C_{f(\text{eq})}$ are the concentrations in the fiber before exposure of the fiber ($t = 0$), at time t, and at equilibrium ($t = \infty$), respectively. Furthermore, k_2 (h^{-1}) is the first order elimination rate constant.

The partition coefficients between the fiber coating and the aqueous phase (K_f) were determined by fitting Eq. (2) to the equilibrium concentrations in the fibers ($C_{f(\text{eq})}$) at the various dilution factors (DF).

$$C_{f(\text{eq})} = \frac{C_{f(\text{initial})}}{1 + \frac{\text{DF}}{K_f}} \tag{2}$$

In order to calculate K_{DOC}, the Eq. (3) was used, where $C_{f(\text{DOC,eq})}$ is the concentration in the fiber in the presence of DOC at equilibrium, $C_{W(\text{DOC,eq})}$ is the concentration in the water in the presence of DOC at equilibrium, [DOC] is the concentration of DOC (l/kg), 10^{-6} is a conversion factor because we use mg/l units for all concentrations. In both experiments $C_{f(\text{initial})}$ is the sum of the initial concentration of the fiber exposed to pure water (fitted start position of the fiber on Fig. 2) and additional fraction that is in the aqueous phase, calculated with K_f. V_f is the fiber volume and V_W is the volume of water.

$$C_{f(\text{initial})}V_f = C_{f(\text{DOC,eq})}V_f + C_{W(\text{DOC,eq})}V_W + C_{\text{DOC(eq)}}10^{-6}[\text{DOC}]V_W \tag{3}$$

It is assumed that, whether DOC is present or not, the concentration ratio C_f/C_W is always represented by the K_f (Eq. (4)).

$$\frac{C_{f(\text{eq})}}{C_{W(\text{eq})}} = \frac{C_{f(\text{DOC,eq})}}{C_{W(\text{DOC,eq})}} = K_f \tag{4}$$

Partitioning of the chemical between DOC and water is also characterized by a constant (Eq. (5)), where K_f is the fiber/water partition coefficient, K_{DOC} is the DOC/water distribution coefficient and $C_{f(\text{eq})}$ is the concentration in the fiber coating at equilibrium:

$$\frac{C_{\text{DOC(eq)}}}{C_{W(\text{DOC,eq})}} = K_{DOC} \tag{5}$$

Combining the relationships between K_f, K_{DOC} and the equilibrium concentrations with Eq. (3), enables determination of K_{DOC} with Eq. (6):

$$\frac{C_{f(\text{DOC,eq})}}{C_{f(\text{initial})}} = \frac{1}{1 + \frac{V_W}{V_f * K_f}(1 + 10^{-6}[\text{DOC}]K_{DOC})} \tag{6}$$

The complete derivation of Eqs. (2) and (6) can be found in the supporting information of ter Laak et al. (2005).

3. Results and discussion

3.1. Determination of K_f and K_{DOC}

Depletion of the dissolved organic matter exposed fibers was monitored in time and equilibrium concentrations in the fiber were obtained from the plateau of a one-phase exponential decay curve (Eq. (1)). The depletion of the fiber exposed to various volumes of water and DOC solutions in time are presented in Fig. 1 for two PCBs (PCB 52 and PCB 118). In the DOC-system, two processes (desorption from the fiber and sorption to the DOC) might affect the kinetics of the depletion process. However, distribution to DOC is extremely fast (McCarthy and Jimenez, 1985; Schlautman and Morgan, 1993), so the transport from and to the PDMS fiber is thought to be the rate limiting step.

The K_f and K_{DOC} are determined with Eqs. (2) and (6) respectively. In both experiments 100% mass balance (Eq. (2)) was not achieved. This was probably due to sorption to other (hydrophobic) phases such as impurities and vial walls (Lung et al., 2000). Furthermore, PCBs could have evaporated into the head space (Mackay et al., 1999). To overcome this problem, all of the concentrations were normalized to the “recovered” initial concentration of the

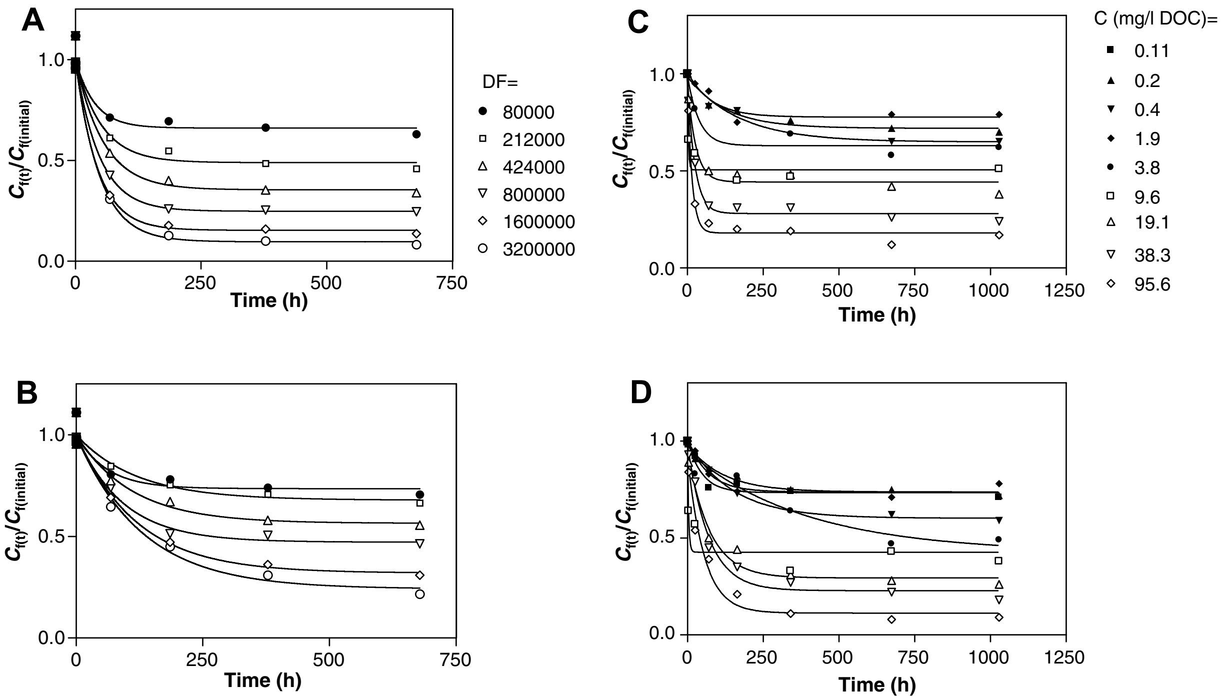

Fig. 1. The depletion of PCB 52 (A) and PCB 118 (B) from the PDMS fiber at various dilution factors – DF (volume of water/volume of fiber) in time and the depletion of PCB 52 (C) and PCB 118 (D) at different DOC concentrations in time. A one-phase exponential decay curve is fitted through the data. Normalized concentration was calculated as: measured concentration in the fiber at time t divided by the concentration in the fiber at $t = 0$.

fiber. This concentration is the sum of the initial concentration of the fiber exposed to pure water (fitted start position of the fiber in Fig. 2) and the fraction that is supposed to be in the aqueous phase according to the K_f. $C_{f(initial)}$ (measured concentration on the fiber before exposure to water or DOC solutions) and recoveries of $C_{f(initial)}$ are presented in Table 1.

The calculated K_{DOC} values for PCBs are shown in Table 2 together with K_{DOC} values of PAHs that were determined with the same method in another study (ter Laak et al., 2005). Despite the fact that PCBs are more hydrophobic than PAHs, have higher K_f values, need longer equilibration times, and the used PDMS volume was smaller, determined K_{DOC} for PCBs have standard errors in the same range than those for PAHs (0.02–0.05).

Fig. 3 shows that the K_{DOC} values do not change with the DOC concentration significantly, except for PCB 180 where a significant decrease is observed for the highest DOC concentration. However, the variation of the distribution coefficients was only minor (0.2log units), so the determined K_{DOC} values are still acceptable.

Log transformed K_{DOC} values were plotted against log-K_{OW} and compared to literature data (Table 3). Fig. 4 shows that K_{DOC} increases with K_{OW} and that the slope (a) and Y-axes intercept (b) are sensible only across a defined family of analytes (Poerschmann and Kopinke, 2001). If we compare data of PAHs (ter Laak et al., 2005) and PCBs (this study), we can see that PAHs have slightly higher K_{DOC}s than PCBs in relation to their octanol water partition coefficients (Fig. 4). This difference might be attributed to additional polar/planar interactions with organic matter for the PAHs, as has been observed for

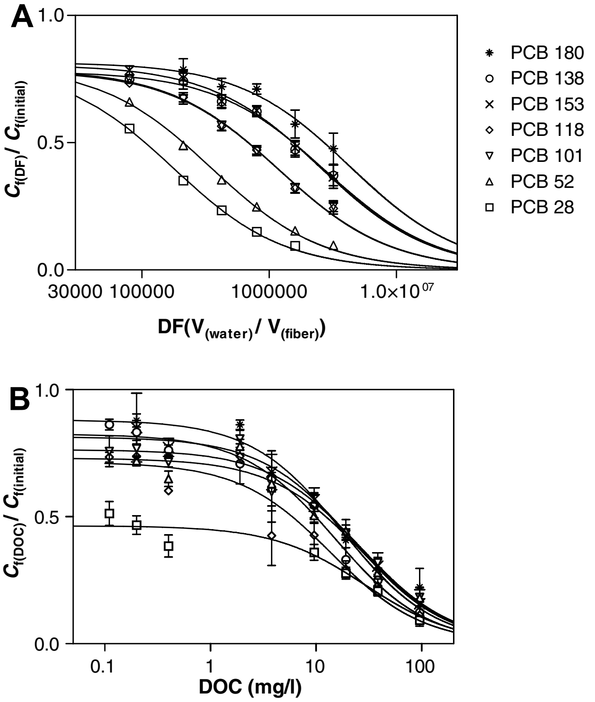

Fig. 2. The depletion of the SPME-fiber as a result of increasing dilution factors (A) or DOC concentrations (B). The lines represent the fits of Eqs. (2) and (1), respectively. The fitted start concentrations in the fiber when no water (A) or DOC (B) was used to determine the recoveries as listed in Table 1. The error bars represent the standard errors.

Table 1
$C_{\mathrm{f(initial)}}$ (measured concentration on the fiber before exposure to water or DOC solutions) and recoveries of $C_{\mathrm{f(initial)}}$ for the determination of K_{DOC} and K_{f}

Compound	K_{DOC} experiment		K_{f} experiment	
	$C_{\mathrm{f(initial)}}$ (SD) (mg/l)	Recoveries of $C_{\mathrm{f(initial)}}$ (SE)	$C_{\mathrm{f(initial)}}$ (SD) (mg/l)	Recoveries of $C_{\mathrm{f(initial)}}$ (SE)
PCB 28	24.8 (0.6)	0.54 (0.02)	11.2 (0.2)	0.80 (0.01)
PCB 52	22.0 (0.9)	0.79 (0.02)	13.3 (0.2)	0.80 (0.01)
PCB 101	29.5 (0.5)	0.80 (0.01)	18.8 (0.2)	0.79 (0.01)
PCB 118	30.2 (0.4)	0.73 (0.02)	20.1 (0.3)	0.78 (0.01)
PCB 138	30.1 (0.3)	0.84 (0.01)	23.5 (0.3)	0.81 (0.004)
PCB 153	31.6 (0.9)	0.83 (0.01)	22.2 (0.4)	0.78 (0.004)
PCB 180	33.7 (1.0)	0.89 (0.02)	27.5 (0.4)	0.82 (0.01)

Recoveries of $C_{\mathrm{f(initial)}}$ are calculated as a sum of the initial concentration of the fiber exposed to pure water (fitted start position of the fiber from Fig. 3) and additional fraction that is in the aqueous phase, calculated with K_{f}.

Table 2
Log K_{OW}, the PDMS–water partition coefficient (log K_{f}) and the distribution coefficient to Aldrich humic acid (log K_{DOC}) of 7 PCBs and 6 PAHs

Compound	Log K_{OW}	Log K_{f} (l/kg) (SE, n)	Log K_{DOC} (l/kg) (SE, n)
PCB 28	5.62[b]	5.36 (0.05, 45)	5.83 (0.02, 29)
PCB 52	6.16[b]	5.59 (0.02, 54)	6.05 (0.04, 29)
PCB 101	6.61[b]	6.07 (0.07, 54)	6.51 (0.03, 29)
PCB 118	6.61[b]	6.06 (0.06, 54)	6.70 (0.04, 29)
PCB 138	7.06[b]	6.40 (0.11, 54)	7.02 (0.03, 29)
PCB 153	7.06[b]	6.36 (0.06, 54)	6.88 (0.05, 30)
PCB 180	7.51[b]	6.59 (0.06, 54)	7.12 (0.07, 25)
Phe	4.57[c]	3.86 (0.03, 52)[a]	4.78 (0.05, 32)[a]
Fla	5.16[c]	4.40 (0.02, 53)[a]	5.50 (0.04, 27)[a]
Pyr	5.18[c]	4.41 (0.04, 55)[a]	5.55 (0.03, 33)[a]
B[*a*]A	5.91[c]	4.92 (0.03, 54)[a]	6.28 (0.03, 37)[a]
B[*b*]F	6.20[c]	5.28 (0.04, 46)[a]	6.96 (0.02, 42)[a]
B[*ghi*]P	6.80[c]	5.39 (0.03, 38)[a]	7.43 (0.04, 39)[a]

[a] ter Laak et al. (2005) (sampling and dosing SPME used).
[b] De Bruijn et al. (1989).
[c] Mackay et al. (1999).

solid organic matter in soils and sediment (Jonker and Smedes, 2000; Goss and Schwarzenbach, 2001). It is not difficult to imagine that the same is also true for interaction of PAHs to DOM.

If we compare K_{DOC} data from Table 3 for PCBs and PAHs (see also Fig. 4) derived with dosing and sampling SPME method (data from this study and ter Laak et al., 2005) with literature data, we can see that the literature data are lower for both classes of analytes. This is probably due to the difficulties with measuring freely dissolved concentrations of substances with high hydrophobicity in other studies. Overestimation of free concentrations is causing the reported K_{DOC} values to be underestimated (Burkhard, 2000). Furthermore, Aldrich humic was used in this study, while K_{DOC} from literature data were determined with different types of humic materials (naturally occurring DOM and commercially available humic acids). Aldrich humic acid seems to be a stronger sorbent than naturally occurring DOM (Georgi, 1998; Krop et al., 2001). Another possible reason is that the distribution to Aldrich DOM is not only determined by hydrophobic partitioning but also by adsorption to its surface (Suffet et al., 1994). Comparing the distribution coefficients for one type of humic acid is therefore more appropriate than comparing all kinds of humic materials with each other.

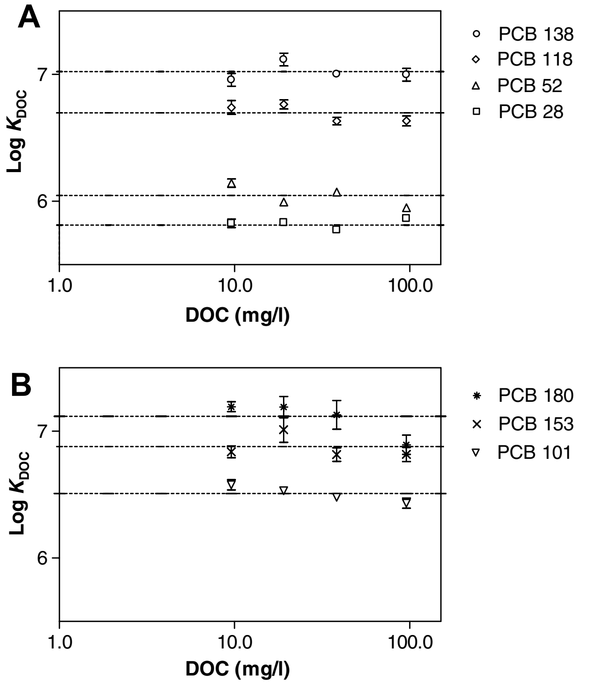

Fig. 3. The separately calculated K_{DOC} values (A, B) with their standard errors at different DOC concentrations. The broken lines are the distribution coefficients obtained from Eq. (5).

When several analyte classes are investigated for a universal regression line for all substances under study, unsatisfactory confidence intervals result (Poerschmann and Kopinke, 2001). However, a universal regression line can be very useful in model calculations. Coefficients *a* (slope) and *b* (*Y*-axes intercept) for this universal line are presented in Table 2. K_{DOC} values calculated with a universal regression line for PCBs and PAHs derived with dosing and sampling SPME method are higher than the literature data (Burkhard, 2000).

3.2. Determining freely dissolved concentrations in the aquatic environment – three phase partitioning

Current models used in risk assessment describe the behavior of substances in the aquatic environment with two-phase partitioning between suspended solids and water

Table 3
The results of linear regressions of the distribution coefficient to DOC ($\log K_{DOC}$) versus the octanol water partition coefficient ($\log K_{OW}$) for experimental data from this study and literature data ($\log K_{DOC} = a \log K_{OW} + b$)

Compounds	Slope (*a*)		*Y*-axes intercept (*b*)		R^b	
	SPME experiment	Literature	SPME experiment	Literature	SPME experiment	Literature
PAHs	1.23[a]	0.98[c] 1.18[d] 1.30[e]	−0.91[a]	0.027[c] −1.56[d] −2.42[f]	0.99[a]	0.99[c] 0.76[d] 0.87[f]
PCBs	0.76[b]	0.93[c] 0.71[d] 1.15[f]	1.54[b]	−0.12[c] −0.50[d] −1.97[f]	0.94[b]	0.99[c] 0.69[d] 0.96[f]
Universal line	0.86[a,b]	0.85[f]	0.99[a,b]	0.27[f]	0.88[a,b]	0.77[f]

[a] Data from literature – sampling and dosing SPME used (ter Laak et al., 2005).
[b] Data from this study – sampling and dosing SPME used.
[c] Poerschmann and Kopinke (2001); Roth Co Humic Acid.
[d] Burkhard (2000); natural organic matter (~50% organic carbon).
[e] Krop et al. (2001); Aldrich humic acid (regression curve calculated from existing data).
[f] Burkhard (2000); Aldrich humic acid.

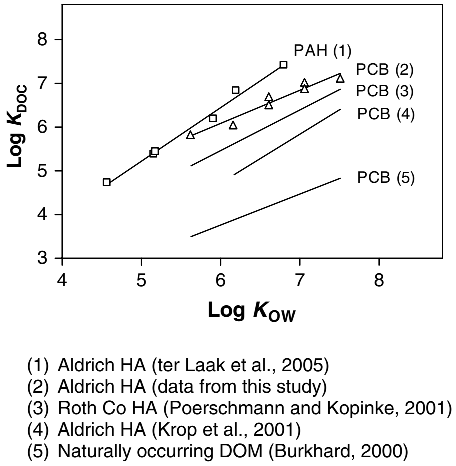

Fig. 4. The $\log K_{DOC}$ versus the log K_{OW} for data from this study and literature (data from Table 3).

(Brandes et al., 1996; Mackay, 2001; Cahill and Mackay, 2003; Mackay and Webster, 2003). Partitioning behavior to DOM in the aquatic environment is also relevant, because it influences the fate of compounds in the environment and their bioavailability (McCarthy and Jimenez, 1985; Landrum et al., 1987; Haitzer et al., 1998; Urrestarazu et al., 1998; Akkanen and Kukkonen, 2001; Akkanen and Kukkonen, 2003; Jager et al., 2003). The ratio between the freely dissolved and the total concentration in the water column is given by Eq. (7):

$$F_d = \frac{1}{1 + K_{SS}[S] + K_{DOC}[DOC]} \tag{7}$$

with the sorption coefficient suspended solid/water (K_{SS}):

$$K_{SS} = \frac{C_S}{C_W} \tag{8}$$

and [*S*] is the concentration of suspended solids.

DOC concentrations in natural waters range from 0.5 to 50 mg/l and often exceed 10 mg/l. DOC consists for 60–80% of humic substances, which contain 30–40% of aromatic carbon (Steinberg, 2003). Fig. 5A shows F_d for 0, 10 and 50 mg/l DOC. Ignoring the role of DOM will lead to an overestimation of the freely dissolved concentration of one order of magnitude for a compound with K_{OW} equal to 10^6. The fraction of freely dissolved is most relevant for a process like volatilization in multimedia environmental fate models, since only the freely dissolved compounds can volatize.

The question arises if advective transport of very hydrophobic chemicals in water would be underestimated in multimedia environmental fate models. Solid-water sorption coefficients are estimated in most multimedia models from well-known relationships with K_{OW}, if experimental sorption coefficients are not available as input parameters. For advective transport processes in the water compartment the ratio F_a, equaling $(C_w + C_{DOM}[DOC])/C_{total}$, is the relevant fraction:

$$F_a = \frac{1 + K_{DOC}[DOC]}{1 + K_{SS}[S] + K_{DOC}[DOC]} \tag{9}$$

Flowing water caries both the freely dissolved chemical and the chemical associated with DOM with it. Fig. 5B displays how F_a changes with K_{OW} for $[S] = 5$ mg/l and $[DOC] = 10$ and 0 mg/l, the latter is equivalent to ignoring the role of DOM.

Transport of hydrophobic chemicals from the water column to the sediment in these models is computed from the total concentration, the partitioning over the dissolved and the suspended particles phase and the settling velocity of the particles. Here the ratio F_S ($C_{SS}[S]/C_{total}$) is essential:

$$F_S = \frac{K_{SS}[S]}{1 + K_{SS}[S] + K_{DOC}[DOC]} \tag{10}$$

Fig. 5C shows the influence of ignoring the DOM phase for increasing K_{OW}. From Fig. 5A it is obvious that the increasing of DOM decreases the fraction freely dissolved in water. From Fig. 5B and C we can see that transport

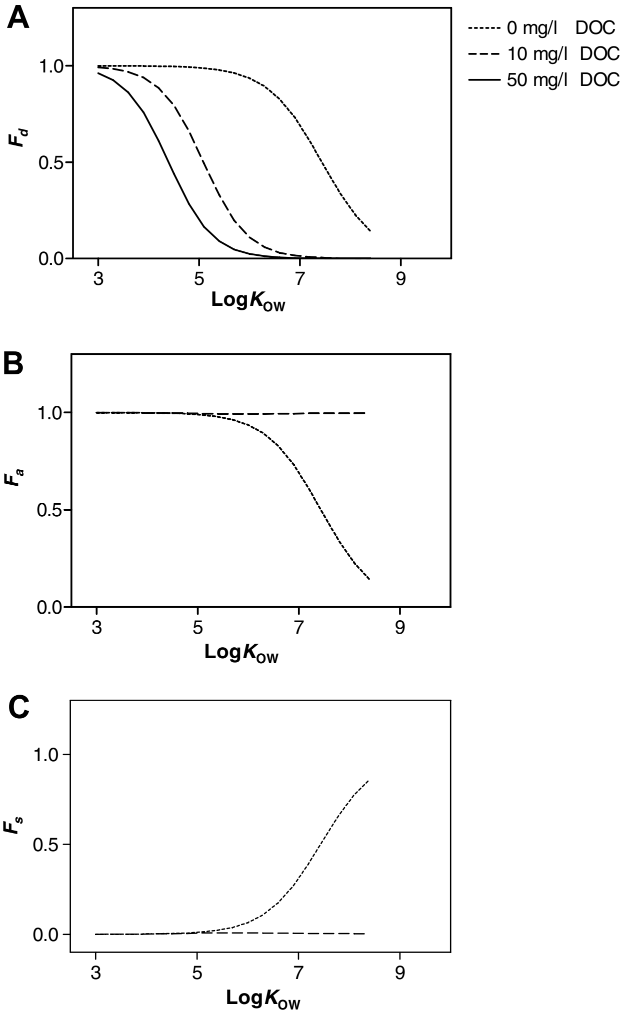

Fig. 5. The fraction freely dissolved in water – F_{d} (A), advective transport in water (transport of substances in horizontal level) – F_{a} (B) and transport to sediment in water – F_{S} (C) versus the K_{OW}.

of substances from the water column to the sediment decreases, and that advective transport is much higher in the presence of DOM. Bioavailability of a hydrophobic chemical, not only to exert toxic effects to aquatic life but also to undergo environmental fate processes like biodegradation, transport and sediment partitioning, are influenced by natural DOM.

4. Concluding remarks

DOC concentrations in natural waters often exceed 10 mg/l and may already have an influence on the fate of chemicals with $\log K_{\mathrm{OW}} > 6$. To include three phase partitioning in the aquatic environmental modeling, reliable distribution coefficients to DOC are needed. The used passive sampling approach enables the measurements of these distribution coefficients without having to spike aqueous phases with a co-solvent or to separate the aqueous and matrix phase. In this study, we have applied this method to measure distribution coefficients to DOC for some PCBs (Table 2). The method seems to produce reliable K_{DOC} values for PCBs. The K_{DOC} values from literature are generally lower than found in this study, because of incomplete phase separation in other studies, biasing the determination of the freely dissolved concentration. In addition, Aldrich humic acid seems to be a stronger sorbent than naturally occuring DOM and this could also cause our K_{DOC} values to be higher. It is also important to keep in mind that the distribution to Aldrich DOM is probably not only determined by hydrophobic partitioning but also by adsorption to surface (Suffet et al., 1994).

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