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Research Article

Determination of Partition Coefficients for Selected PAHs between Water and Dissolved Organic Matter

The fate and transport of highly hydrophobic chemicals are affected by the partitioning between water and dissolved organic carbon. Large variation in the partition coefficient (K_{DOCw}) is often found, due to the selection of model organic matter or potential experimental artifacts. To investigate the roles of the type of organic matter on the partitioning of highly hydrophobic compounds, the partition coefficients of eight selected polycyclic aromatic hydrocarbons (PAHs), with 3–6 aromatic rings, were determined using a passive dosing/extraction method between water and model dissolved organic matter (humic acid, fulvic acid, sodium dodecyl sulfate micelle (SDS), and 2-hydroxypropyl-β-cyclodextrin). Although the K_{DOCw} values for 3–4 ring PAHs in this study were close to those reported in the literature, experimental K_{DOCw} values between Aldrich humic acid (AHA) and water were higher than values reported in the literature for 5–6 ring PAHs. The K_{DOCw} values were highest for AHA, followed by SDS and Suwannee river fulvic acid (SFA). The slopes of the linear regression between $\log K_{DOCw}$ and $\log K_{ow}$ were 1.23 ($\pm$0.13), 0.82 ($\pm$0.09), and 0.59 ($\pm$0.13) for AHA, SDS, and SFA, respectively. The differences in the K_{DOCw} values between AHA and the other organic matter (SDS, SFA, and CD) increased with increasing hydrophobicity of the PAHs, showing that the sorption of highly hydrophobic chemicals to the humic acid fraction may be important in the presence of mixed organic matter.

Keywords: Fulvic acids; Humic acids; Poly(dimethylsiloxane); Sodium dodecyl sulfate; Sorption

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1 Introduction

The fate and transport of hydrophobic organic chemicals (HOCs) in the aqueous environment are highly influenced by dissolved organic matter (DOM). DOM significantly decreases the bioavailability of hydrophobic chemicals and thus reduces their potential toxic effects on aquatic organisms [1–3]. On the other hand, DOM may accelerate the rate of the chemical transport in aqueous media when the transport is governed by diffusion in the aqueous boundary layer [4–6]. To quantitatively describe the reduced bioavailability or enhanced mass transport of highly hydrophobic chemicals by DOM, knowing the partition coefficients between water and DOM is crucial.

Due to the difficulties of separating the HOCs associated with DOM from those freely dissolved in water, DOM/water partition coefficients have been determined by measuring free concentration, without disturbing the equilibrium between the free and associated HOCs. Methods include equilibrium dialysis [7], fluorescence quenching [8–12], non-depletive solid-phase microextraction [13, 14], reverse phase separation [15–17], and dosing/extraction using a stable polymer, such as poly(dimethylsiloxane) (PDMS) [18, 19]. A recently developed solid-phase dosing/extraction method has advantages over other techniques because it does not require spiking of HOCs dissolved in an organic solvent. Spiking with a co-solvent might lead to undissolved residues in the solution or oversaturation [20, 21], which may result in a large variation in the partition coefficients. Although many researchers have reported DOM/water partition coefficients normalized by organic carbon content (K_{DOCw}) for many HOCs [1, 7–19, 22–30], less experimental data are available for highly hydrophobic chemicals with $\log K_{ow}$ greater than 6. For polycyclic aromatic hydrocarbons (PAHs), experimental $\log K_{DOCw}$ values agreed well for less hydrophobic 3–4 ring PAHs. However, variations in the reported values generally increase with increasing hydrophobicity. For example, $\log K_{DOCw}$ values for phenanthrene, using Aldrich humic acids (AHA), were in the range of 3.92–4.78 [11, 15–18], whereas those for benzo[*g*,*h*,*i*]perylene were in the range of 5.65–7.43 [15–18]. In addition, K_{DOCw} may vary with the choice of model DOM. For example, Niederer et al. [31] showed that partition coefficients to humic substances from various origins can vary by an order of magnitude. However, the scarcity of experimental data for highly hydrophobic chemicals with various DOMs makes it difficult to understand DOM-water partitioning influenced by

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Abbreviations: **AHA,** Aldrich humic acid; **CD,** (2-hydroxypropyl)-β-cyclodextrin; **DOM,** dissolved organic matter; **FQ,** fluorescence quenching; **HOCs,** hydrophobic organic chemicals; **K_{DOCw},** partition coefficients between water and dissolved organic carbon; **K_{oc},** organic carbon–water distribution coefficient; **PAHs,** polycyclic aromatic hydrocarbons; **PDMS,** poly(dimethylsiloxane); **RP,** reverse-phase separation; **SDS,** sodium dodecyl sulfate micelle; **SFA,** Suwannee River fulvic acid; **SPD/E,** solid-phase dosing/extraction; **SPME,** solid-phase microextraction.

the physico-chemical interactions of HOCs with various types of DOMs.

In this study, a solid-phase dosing/extraction method was applied to obtain partition coefficients of eight selected PAHs between water and model DOM. AHA and Suwannee River fulvic acid (SFA) were chosen as model natural organic matter. Sodium dodecyl sulfate micelle (SDS) was chosen because it is often used for soil and groundwater remediation in surfactant-enhanced solubilization of PAHs [28, 32]. Finally, 2-hydroxypropyl)-β-cyclodextrin (CD) was chosen because it is used for extracting bioavailable fraction of PAHs [29, 33, 34]. The partition coefficients were compared with data available in the literature. Quantitative linear relationships between $\log K_{\mathrm{DOCw}}$ and $\log K_{\mathrm{ow}}$ were presented.

2 Materials and methods

2.1 Materials

Eight hydrophobic PAHs; phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]pyrene, dibenzo[*a*,*c*]anthracene, dibenzo[*a*,*h*]anthracene, and benzo[*g*,*h*,*i*]perylene, were chosen for determining the partition coefficients between DOM and water. The test PAHs were of high purity (≥98%) and purchased from Sigma–Aldrich (St. Louis, MO, USA), Fluka (Buchs, Switzerland), or Supelco (Bellefonte, PA, USA). Throughout the experiments, the partition coefficients were measured in a mixture. The low and high molecular weight mixtures were composed of phenanthrene, anthracene, fluoranthene, and pyrene (mixture 1), and benzo[*a*]pyrene, dibenzo[*a*,*c*]anthracene, dibenzo[*a*,*h*]anthracene, and benzo[*g*,*h*,*i*]perylene (mixture 2), respectively. SDS (99 + %), CD (>98%), and technical grade AHA sodium salt were purchased from Sigma–Aldrich. SFA was purchased from the International Humic Substances Society (St. Paul, MN, USA). All these substances were used for the partitioning experiments without further purification.

Medical grade PDMS sheets, with thicknesses of 0.5 and 1 mm, were obtained from Specialty Silicone Products, Inc. (Ballston Spa, NY, USA), and cut into various sizes for the determination of the partition coefficients. Custom-cut PDMS disks were cleaned in a Soxhlet extractor for 3 h using *n*-hexane and methanol, and were stored in methanol until use.

2.2 Chemical analyses

An HPLC system, equipped with a quaternary gradient pump (Waters 600E, Milford, MA, USA), an autosampler (Waters 717 +), and a multiwavelength fluorescence detector (Waters 2475) was used for chemical analyses of the PAHs. Mixtures of PAHs were separated on a Waters PAH C18 column ($4.6 \times 150\,\mathrm{mm}^2$, 5 μm particle size) at 40°C and detected using the fluorescence detector, with the excitation and emission wavelengths (λ_{ex} and λ_{em}) of 275 and 350 nm for phenanthrene, 260 and 420 nm for anthracene, fluoranthene and pyrene, and 290 and 430 nm for benzo[*a*]pyrene, dibenzo[*a*,*c*]anthracene, dibenzo[*a*,*h*]anthracene and benzo[*g*,*h*,*i*]perylene, respectively. HPLC grade acetonitrile and deionized water were used as the eluent solvents in a gradient mode, with a flow rate of $1\,\mathrm{mL\,min^{-1}}$.

2.3 Determination of partition coefficients

The partition coefficients between water and the selected DOM were measured by a solid-phase dosing/extraction method using PDMS [18, 19, 35]. Custom-cut PDMS disks were preloaded in a glass vial with a PTFE-lined septum cap using methanol/water (60:40) loading solution containing a mixture of PAHs. The initial concentrations of PAHs were well below solubility in the loading solution. After shaking vials for 3 days at 25°C, 150 rpm, the equilibrium concentration in PDMS ranged from 19 to 127 $\mu\mathrm{mol\,L^{-1}}$. PDMS disks loaded with the chemical species were placed in a glass vial with a PTFE-lined cap containing of various volumes of an aqueous DOM suspension. DOM solutions were prepared by dissolving the desired amount of powdered DOM in distilled water. The solution pH did not change significantly from that of distilled water by dissolving of the DOM (pH 5.5–7), with the exception of SFA, which was introduced as an acidic form. The resulting pH of the fulvic acid solution was around 3.0 at the concentration studied. The volumes of the PDMS disks ranged from 0.3×10^{-9} to $31.4 \times 10^{-9}\,\mathrm{m}^3$. The vials were shaken at 150 rpm and 25°C in a shaking incubator. After equilibrium between the PDMS and DOM suspension was attained, in 3 days, the PDMS disks were removed from the solution, quickly rinsed with deionized water and extracted with acetonitrile in a mechanical shaker for 2 h at 150 rpm. The volumes of acetonitrile were at least 35 times the volume of PDMS, and preliminary experiments confirmed that the extraction recovery in the first extraction was higher than 98%. The corresponding aqueous concentration of PAHs was estimated between 0.1 and 10 $\mathrm{nmol\,L^{-1}}$ using K_{PDMSw} [36].

A simple mass balance equation relates the partition coefficients to the relative concentration in PDMS ($C_{\mathrm{PDMS}}/C_{\mathrm{PDMS,0}}$) and the volume ratio ($V_{\mathrm{sus}}/V_{\mathrm{PDMS}}$) by [18, 35]:

$$\frac{C_{\mathrm{PDMS}}}{C_{\mathrm{PDMS,0}}} = \frac{1}{1 + [(V_{\mathrm{sus}}/V_{\mathrm{PDMS}})/K_{\mathrm{PDMSsus}}]} \quad (1)$$

where C_{PDMS} is the concentration of a chemical in PDMS after equilibrium ($\mathrm{mol\,m^{-3}}$), $C_{\mathrm{PDMS,0}}$ the initial concentration in PDMS ($\mathrm{mol\,m^{-3}}$), V_{sus} and V_{PDMS} the volumes of the DOM suspension and PDMS in m^3, respectively, and K_{PDMSsus} the partition coefficient between PDMS and the DOM suspension ($\mathrm{m^3}_{\mathrm{solution}}\,\mathrm{m^{-3}}_{\mathrm{PDMS}}$). Thus, K_{PDMSsus} can be obtained using a nonlinear regression of $C_{\mathrm{PDMS}}/C_{\mathrm{PDMS,0}}$ versus $V_{\mathrm{sus}}/V_{\mathrm{PDMS}}$. Then, the partition coefficient between dissolved organic carbons and water (K_{DOCw}, $\mathrm{L\,kg^{-1}}$) is calculated using the known PDMS–water partition coefficient (K_{PDMSw}) by:

$$K_{\mathrm{DOCw}} = \frac{(K_{\mathrm{PDMSw}}/K_{\mathrm{PDMSsus}}) - 1}{m_{\mathrm{DOC}}/10^6} \quad (2)$$

where m_{DOC} is the concentration of dissolved organic carbon in the solution, which were 84.4, 524, 5000, and 24 600 $\mathrm{mg_{DOC}\,L^{-1}}$ for AHA, SFA, SDS, and CD, respectively. The SDS concentration was sufficiently higher than reported critical micelle concentration around 500 $\mathrm{mg_{DOC}\,L^{-1}}$ [37].

3 Results and discussion

3.1 Partition coefficients between DOC and water

A preliminary experiment with mixture 2 and 84.4 $\mathrm{mg_{DOC}\,L^{-1}}$ AHA showed that the apparent equilibrium was obtained within 72 h even for the highest $V_{\mathrm{sus}}/V_{\mathrm{PDMS}}$ value. Fast equilibrium between PDMS and DOM suspension was obtained for PAHs in 1–2 days [18, 35]. Equilibration time generally increases with increasing hydrophobicity and $V_{\mathrm{sus}}/V_{\mathrm{PDMS}}$ and decreases with DOC concentration due to the accelerated transport. Because the equilibration time for mixture 2 is thought to be longer than mixture 1 and the concentration of AHA was the lowest among dissolved organic phases studied, the equilibrium concentration in PDMS (C_{PDMS}) was measured after 72 h without further time-course measurements. Figure 1 shows an example plot of $C_{PDMS}/C_{PDMS,0}$ versus V_{sus}/V_{PDMS} for phenanthrene and benzo[*a*]pyrene in the solution containing 200 mg L^{-1} AHA. All partition coefficients determined in this study are summarized in Tab. 1, with literature log K_{ow} [38] and log K_{PDMSw} values [36]. Standard errors of K_{DOCw} were calculated by error propagation. The K_{DOCw} values to hydrophilic DOM, CD, could not be determined for mixture 2 because the decrease in the concentration in PDMS was insufficient in the experimental set-up, $V_{sus}/V_{PDMS} < 500$. The typical standard errors were less than 0.1 log unit.

Many researchers have reported K_{DOCw} values for PAHs using commercially available model organic matter, such as AHA [1, 8, 11, 12, 15–18, 22]. Figure 2 shows a comparison of the experimental log K_{DOCw} values for seven PAHs to AHA obtained in this study with those found in the literature, using passive dosing/extraction method [18], solid phase microextraction [22], reverse phase separation [15–17], fluorescence quenching [8, 11, 12], and dialysis [1]. Although the values in this study were at the high-end of the range found in the literature, they agreed well with the literature values for the less hydrophobic 3–4 ring PAHs (mixture 1). However, the difference became larger for 5–6 ring PAHs (mixture 2). Although the log K_{DOCw} for benzo[*g,h,i*]perylene to AHA obtained by the passive dosing/extraction method, 7.43 [18], agreed very well with ours, those reported by reverse-phase separation, 6.11 [15] and 5.65 [17], were more than one order of magnitude smaller. Similarly K_{DOCw} values for benzo[*a*]pyrene and dibenzo[*a,h*]anthracene to AHA in this study were higher than literature values by approximately one order of magnitude. As discussed earlier, the overestimation of the freely dissolved concentration would increase with increasing hydrophobicity if the freely dissolved species is not completely separated from sorbed species [18, 19].

Many investigations have reported K_{DOCw} values for fulvic acid fractions [9, 10, 24–27]. Values of log K_{DOCw} ranged 3.78–4.19 for phenanthrene [10, 24], 4.12–4.50 for anthracene [9, 10], and 2.62–5.08 for pyrene [9, 25]. The K_{DOCw} values for SFA fell within the range of the reported values, although differences in the origin of the fulvic acid fraction may affect partitioning of PAHs.

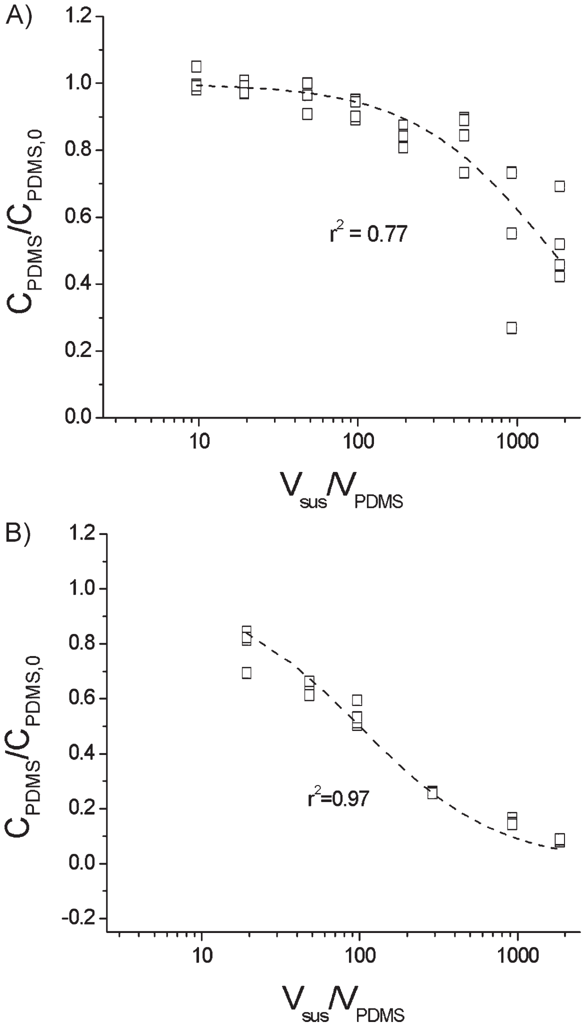

Figure 1. Determination of the partition coefficients between PDMS and a solution containing 200 mg L^{-1} AHA for (A) phenanthrene and (B) benzo[*a*]-pyrene, as examples. The dashed lines represent nonlinear regression using Eq. (1).

Table 1. Partition coefficients for selected PAHs between water and dissolved organic carbons (K_{oc}) with literature values for log K_{ow} and log K_{PDMSw}.

Chemical	log K_{ow} [a]	log K_{PDMSw} [b]	log K_{DOCw} [c]			
			AHA	SFA	SDS	CD
PHEN	4.52	3.87	4.61 ± 0.05	4.08 ± 0.08	4.55 ± 0.03	3.55 ± 0.03
ANTH	4.50	3.98	4.89 ± 0.06	4.17 ± 0.07	4.87 ± 0.04	3.71 ± 0.05
FLUO	5.20	4.32	5.11 ± 0.08	4.22 ± 0.05	5.09 ± 0.04	3.21 ± 0.07
PYR	5.00	4.36	5.51 ± 0.07	4.34 ± 0.05	5.28 ± 0.05	2.78 ± 0.14
BaP	6.35	5.09	7.16 ± 0.02	5.37 ± 0.04	6.44 ± 0.03	n.d.
DBacA	6.17	5.41	7.24 ± 0.09	5.70 ± 0.04	5.88 ± 0.06	n.d.
DBahA	6.75	5.47	7.56 ± 0.07	5.67 ± 0.05	6.14 ± 0.06	n.d.
BghiP	6.90	5.36	7.29 ± 0.06	6.11 ± 0.03	5.76 ± 0.04	n.d.

[a] Suggested values from Sangster Research Laboratory (http://logkow.cisti.nrc.ca/logkow/index.jsp) [38].
[b] Values obtained using the dynamic permeation method [36].
Abbreviations: PHEN, phenanthrene; ANTH, anthracene; FLUO, fluoranthene; PYR, pyrene; BaP, benzo[*a*]pyrene; DBacA, dibenzo[*a,c*]anthracene; DBahA, dibenzo[*a,h*]anthracene; BghiP, benzo[*g,h,i*]perylene; AHA, Aldrich humic acid; SFA, Suwannee River fulvic acid; SDS, sodium dodecyl sulfate micelle; CD, (2-hydroxypropyl)-β-cyclodextrin).
[c] Values represent mean ± standard errors. Standard errors were obtained by error propagation.

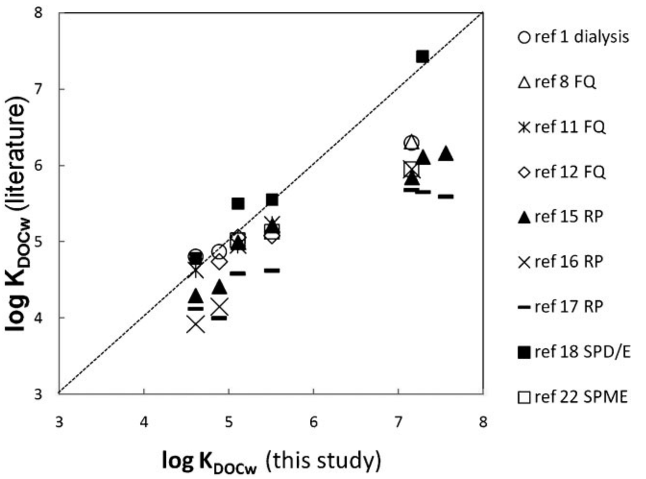

Figure 2. Comparison of $\log K_{\mathrm{DOCw}}$ for AHA in this study with values reported in the literature (abbreviations: FQ, fluorescence quenching; RP, reverse-phase separation; SPD/E, solid-phase dosing/extraction; SPME, solid-phase microextraction).

K_{DOCw} values available in the literature for SDS micelle and CD were also consistent with our results (Tab. 1). For example, Cheng and Wong [28] reported $\log K_{\mathrm{DOCw}}$ using SDS micelle as 4.57 and 5.16 for phenanthrene and pyrene, respectively, and Ko et al. [29] reported a $\log K_{\mathrm{DOCw}}$ of 3.77 using CD for phenanthrene. This confirms that the passive sampling/extraction method gives similar results to those of other methods, at least for 3–4 ring PAHs.

3.2 Effects of types of DOMs

The K_{DOCw} values shown in Tab. 1 varied significantly with the properties of the model DOMs. For all selected PAHs, the K_{DOCw} values were highest in AHA. Because the humic acid fraction contains a large hydrophobic backbone structure, with cross-linked aromatic hydrocarbons [39, 40], the affinity of PAHs to humic acids may be the highest among the model organic phases chosen in this study. The K_{DOCw} values between SFA and water were approximately an order of magnitude lower than those between AHA and water. Although the pH of the solution containing SFA was lower than others, it is not likely that the lower K_{DOCw} values for SFA than those for AHA were caused by the solution pH because K_{DOCw} for fulvic acid did not changed significantly in pH less than 7 [10, 41]. The difference between the two $\log K_{\mathrm{DOCw}}$ slightly increased with increasing hydrophobicity of the selected PAHs. The $\log K_{\mathrm{DOCw}}$ values to SDS micelle were not significantly different from those to AHA for mixture 1 (phenanthrene, anthracene, fluoranthene, and pyrene). However, the difference dramatically increased with increasing hydrophobicity for PAHs with higher molecular weights. Reasons for the difference in the slope of $\log K_{\mathrm{DOCw}}$–$\log K_{\mathrm{ow}}$ plot may include a stronger van der Waals interaction in AHA than in SDS, a higher free energy requirement for the cavity creation in SDS than in AHA, and a stronger hydrogen bonding in AHA than in SDS.

Figure 3 shows the relationships between the experimental $\log K_{\mathrm{DOCw}}$ values for eight PAHs measured in this study and their literature $\log K_{\mathrm{ow}}$. Best-fit parameters (±standard errors) and correlation coefficients (r^2) were obtained using a linear regression:

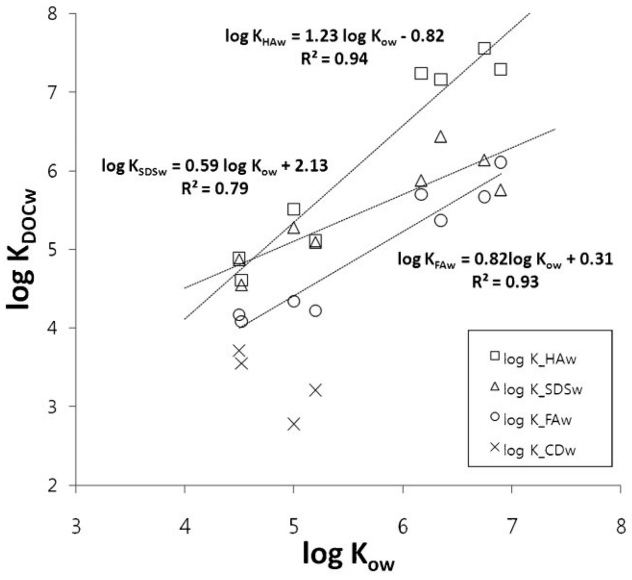

Figure 3. Relationships between experimental $\log K_{\mathrm{DOCw}}$ and literature $\log K_{\mathrm{ow}}$. The dashed lines represent the best-fit using a linear regression.

$$\log K_{\mathrm{DOCw,AHA}} = 1.23(\pm 0.13)\log K_{\mathrm{ow}} - 0.82(\pm 0.75) \quad n = 8\, r^2 = 0.94 \tag{3}$$

$$\log K_{\mathrm{DOCw,SFA}} = 0.82(\pm 0.09)\log K_{\mathrm{ow}} + 0.31(\pm 0.53) \quad n = 8\, r^2 = 0.93 \tag{4}$$

$$\log K_{\mathrm{DOCw,SDS}} = 0.59(\pm 0.13)\log K_{\mathrm{ow}} - 2.13(\pm 0.72) \quad n = 8\, r^2 = 0.79 \tag{5}$$

The slopes of the regressions were greatest for AHA, followed by SFA and SDS. The slope for $\log K_{\mathrm{DOCw,AHA}}$ was statistically different from those for $\log K_{\mathrm{DOCw,SFA}}$ and $\log K_{\mathrm{DOCw,SDS}}$ ($p < 0.05$), suggesting that SFA and SDS micelle are less sensitive than AHA to increases in the hydrophobicity of solutes. No statistical difference in the slope was observed between $\log K_{\mathrm{DOCw,SFA}}$ and $\log K_{\mathrm{DOCw,SDS}}$.

Although we could not derive a relationship between $\log K_{\mathrm{DOCw}}$ and $\log K_{\mathrm{ow}}$ for CD due to limited number of data, a decreasing tendency of $\log K_{\mathrm{DOCw}}$ with increasing $\log K_{\mathrm{ow}}$ was observed (Fig. 3). This in part supports that the sorptive capacity of CD decreases with increasing molecular size.

3.3 Implication for risk assessment

Sorption coefficients to both suspended and DOM are key parameters in the evaluation of the fate and transport of HOCs in surface and groundwater, as well as the sorptive removal of HOCs in sewage treatment plants. Although partitioning of a hydrophobic chemical to organic matter may vary significantly [31], it is common in environmental fate modeling to use a single K_{oc} value. The variations in the literature K_{oc} values were larger for more hydrophobic chemicals, probably due to their extremely low aqueous solubility. Thus, the K_{oc} values chosen for very hydrophobic chemicals in the risk assessment are likely to have higher uncertainties, which originate from either experimental errors or the physico-chemical nature of the organic phases tested. Although natural organic matter is composed of many different fractions [39, 40], it is likely that the humic acid fraction is important in the sorption of highly hydrophobic chemicals, such as 5–6 ring PAHs, because of the much higher partition coefficients between humic acid and water than those with other organic matter tested in this study. Careful selection of the K_{oc} value in the environmental fate modeling should be made, especially for highly hydrophobic chemicals, considering the types of organic matter used for the derivation of experimental K_{oc} values in the literature. The K_{DOCw} for humic acid may be a good supplementary index in the more refined exposure assessment if the humic acid fraction in the aqueous phase or soil organic matter is known after extensive evaluations for the roles DOM types on the partitioning processes.

4 Concluding remarks

A passive dosing/extraction method was applied to determine the $\log K_{DOCw}$ values for selected DOMs. The experimental values obtained in this study agreed well with literature values for less hydrophobic PAHs, but they exceeded literature values of 5–6 ring PAHs due to overestimation of freely dissolved fractions by the methods applied in literature. In addition, the choice of model DOM may result in a significant variation in the K_{oc} value, which is typically assumed to be a constant value in environmental fate modeling, because of the differences in the partitioning processes. High partition coefficients for highly hydrophobic PAHs between AHA and water suggest that the sorption of highly hydrophobic chemicals to the humic acid fraction may be important in the presence of mixed organic matter although AHA may not reflect humic acid fractions from other origins.

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