LFERs for Soil Organic Carbon−Water Distribution Coefficients (K_{OC}) at Environmentally Relevant Sorbate Concentrations

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Organic carbon−water distribution coefficients, K_{OC}, for organic compounds at environmentally relevant, low sorbate concentrations may substantially differ from those at higher concentrations due to nonlinear sorption to soil organic matter. However, prediction methods for K_{OC} such as linear free energy relationships (LFERs) are currently only available for high sorbate concentrations (i.e., near solubility limits), reflecting the lack of a set of consistent experimental data in an environmentally more relevant concentration range (i.e., orders of magnitude lower than solubilities). In this study, we determined K_{OC} for two model sorbents of soil organic matter, peat and lignite, at sorbate concentrations of 4.3 and 19 mg/kg-organic-carbon, respectively, in batch suspensions. The measured K_{OC} values for organic sorbates (51 for peat, 58 for lignite) of varying sizes and polarities were modeled successfully with polyparameter linear free energy relationships (PP-LFERs). The resulting PP-LFER for peat was significantly different from the PP-LFERs in the literature determined at near aqueous solubility limits of sorbates. The literature PP-LFERs were found to underestimate the measured K_{OC} values for peat at the low concentration by up to 1 order of magnitude. The extent of underestimation highly depends on the sorbate properties and can be explained by differing sorption nonlinearities of the sorbates as predicted by a reported empirical relationship between the nonlinearity in peat and the sorbate dipolarity/polarizability parameter S. Lignite appears to be a stronger sorbent toward many sorbates than typical soil organic matter irrespective of the concentration range and thus may not be representative for organic matter with regard to the magnitude of K_{OC}. The present study offers the first PP-LFER equation for log K_{OC} in soil organic matter at typical environmental sorbate concentrations.

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Introduction

Assessing the environmental behavior, distribution, and fate of contaminants that typically exist at low concentrations in the environment is a major challenge in environmental chemistry (*1*). Contaminant concentrations may be particularly critical in the quantitative evaluation of sorption behavior of contaminants to soils and sediments, because sorption isotherms from water to these matrices are often reported to be nonlinear (*2−5*); i.e., the extent of sorption at high sorbate concentrations may substantially differ from that at low concentrations. Here, "high" concentrations refer to those near the aqueous solubility limits, whereas "low" concentrations refer to orders of magnitude lower concentrations. The near solubility concentrations have often been applied in laboratory experiments, and estimation methods for the sorption behavior at such concentrations have been established fairly well. However, such high concentration levels may occur only in source zones of contaminated sites and in the central part of contaminant plumes in groundwater. Much lower concentration levels are of concern in most other contamination cases including spreading of contaminants away from sources, contamination from nonpoint sources, and migration of chemicals on regional and global scales. Therefore, it is of high importance to study the sorption at lower, more environmentally relevant concentrations.

The extent of the soil sorption for a given sorbate is commonly described by the organic carbon−water distribution coefficient (K_{OC}) defined as

$$K_{OC} = C_s f_{OC}^{-1} C_w^{-1} \tag{1}$$

where C_s and C_w are the solid phase and the aqueous phase concentrations, respectively, of the sorbate at equilibrium, and f_{OC} is the fraction of organic carbon in soil. In the case of nonlinear sorption, K_{OC} depends on the concentration. Nonlinear sorption in soil organic matter typically shows increasing K_{OC} with decreasing concentration. The stronger sorption at lower concentrations is thought to occur due to the presence of carbonaceous geosorbents (e.g., soot, char) that have high affinity for organic sorbates (*6, 7*) and/or due to glassiness of organic matter itself (*8, 9*).

For estimating K_{OC} of a diverse set of organic compounds showing various sizes and polarities, polyparameter linear free energy relationships (PP-LFERs) have been proposed as a useful method (*10, 11*). The most widely used PP-LFER model may be the linear solvation energy relationships (LSERs) developed by Abraham (*12, 13*), which appear for log K_{OC}

$$\log K_{OC} = c + eE + sS + aA + bB + vV \tag{2}$$

The following notations are used for sorbate descriptors: E, the excess molar refraction; S, the dipolarity/polarizability parameter; A, the solute hydrogen (H)-bond acidity; B, the solute H-bond basicity; and V, the molar volume. The regression coefficients e, s, a, b, and v and the constant c are determined by the linear multiple regression analysis. If the regression coefficients are accurately calibrated, PP-LFER models can provide reasonable predictions (usually within a factor of 2 for organic solvents and chromatographic phases) of partitioning coefficients over a broad range of neutral organic compounds with varying polarities. This high applicability is a strong advantage over simple regression

approaches using, e.g., the log of octanol−water partitioning coefficients (K_{OW}).

So far, only a few studies have applied PP-LFERs for modeling a large set of experimental K_{OC} data. Poole and Poole (*10*) derived a PP-LFER equation (i.e., eq 2) using experimental log K_{OC} for soils and sediments tabulated in the literature. Later, Nguyen et al. (*11*) conducted a critical evaluation on the literature K_{OC} data and derived a PP-LFER equation again. It is important to note that K_{OC} values listed in these studies and elsewhere in the literature are in most cases measured at high sorbate concentrations (i.e., >10% of the solubility limits). Because of nonlinear sorption, the PP-LFER system parameters (i.e., regression coefficients) might well depend on the sorbate concentration in organic matter, as demonstrated in our previous study (*5*). Consequently, PP-LFERs calibrated on the log K_{OC} from such high concentrations might be inappropriate to predict the soil−water distribution of organic contaminants in the environment, where contaminant concentrations are typically much lower.

This study aims to evaluate the PP-LFER model for K_{OC} in soils at environmentally relevant concentrations. To this end, batch sorption experiments were performed using two types of terrestrial natural organic matter—peat and lignite. K_{OC} values of diverse neutral organic sorbates were determined for each sorbent at relatively low sorbate concentrations, i.e., 2 mg/kg-dry or 4.3 mg/kg-OC (OC: organic carbon) for peat and 10 mg/kg-dry or 19 mg/kg-OC for lignite. These concentrations correspond to ng/L to high μg/L levels in water if compounds with log K_{OC} values of 1 to 6 are considered. The measured log K_{OC} values for 51 (peat) and 58 (lignite) sorbates were regressed with the LSER sorbate descriptors. The obtained PP-LFER equations for log K_{OC} under these low-sorbate-loading conditions are compared with the literature PP-LFER equations for log K_{OC} under the high-sorbate-loading conditions. The observed differences are related to sorption nonlinearities for individual sorbates in both sorbents.

Materials and Methods

Sorbents. Peat (Pahokee peat, PP; $f_{OC} = 0.461$) obtained from the International Humic Substances Society (IHSS) and lignite (BK-II; $f_{OC} = 0.535$) sampled from the Oberlausitz area (Saxony, Germany) were used as sorbent. These highly humified materials were pulverised to 20 μm on average using a planet ball mill (pulverisette 5, Fritsch) to shorten sorption periods necessary for equilibration. Further details of properties of the sorbents have been described previously (*5, 14*).

There are several indications that *ab*sorption (or partitioning) to organic matter instead of *ad*sorption to carbonaceous geosorbents is the main sorption mechanism to the peat and lignite samples used, at least for nonpolar sorbates. First, the content of carbonaceous geosorbents in both sorbents determined by a combustion method is low (<2 wt%) (*14*). Second, the *n*-octane-to-cyclooctane sorption coefficient ratios (K_n/K_c) suggest that the sorption mode of alkanes to both sorbents is *ab*sorption (*14*). Third, conditioning-annealing effects on sorption behavior of 1,2,4-trichlorobenzene in the peat (*15*) agrees with the hypothesis of sorption to "glassy polymer-like organic matter" rather than to rigid carbonaceous sorbents. However, elucidation of the sorption mode is not the scope of this study.

Probe Chemicals. The probe chemicals considered in this study range over many classes of neutral organic compounds including the following: apolar aliphatic (alkanes), weakly polar aliphatic (halogenated alkanes/alkenes), monopolar aliphatic (e.g., ethers, nitrile), bipolar aliphatic (alcohols), non- or weakly polar aromatic (alkyl benzenes, PAHs, thiophene, furans), monopolar aromatic (e.g., acetophenone, anisole, benzonitrile), and bipolar aromatic (phenols) compounds. Here, monopolar compounds represent those that

serve as H-bond acceptor and bipolar compounds as both H-bond donor and acceptor. A list of the probe chemicals and their LSER descriptors is presented in the Supporting Information (SI-1).

Batch Sorption Experiments. Some K_{OC} data (16 sorbates for peat, 23 sorbates for lignite) were taken from measured sorption isotherms reported in our previous contribution (*5*). For each sorbent, K_{OC} for 35 additional sorbates were determined in this study. The methods of batch sorption experiments follow those reported previously (*5*) with minor modification. Sorbent suspensions were prepared in crimp-top glass vials. Sorbents (0.01−1 g) were weighed into the vials and mixed with water (10−110 mL) containing 5 mM $CaCl_2$ as ionic strength regulator and 200 mg/L NaN_3 to inhibit microbial activity. The vials were horizontally shaken for at least 20 h to wet the sorbent. Probe sorbates dissolved in methanol stock solutions were added into the suspensions. Methanol content in water was less than 0.22 vol% to avoid significant cosolvent effects on sorbate partitioning (ref *16*, p 165). The vials were closed with PTFE- or aluminum-lined septa and were shaken at 20 °C for 10 days (or 20 days for large, highly sorptive compounds, i.e., γ-hexachlorocyclohexane, phenanthrene, fluoranthene, 1-nitronaphthalene, dibenzofuran). Other studies (*4, 5, 17, 18*) reported that these sorption periods are sufficiently long for typical organic sorbates to reach equilibrium in pulverized humified materials. Sorbent-to-water ratios varied between 0.1 and 100 mg/mL, depending on the expected K_{OC} of sorbates. Consequently, 20−94% of the added sorbates were sorbed after equilibration, except for fluoranthene (95−99%). Background concentrations of analytes from sorbents and procedural contaminations were monitored by preparing batches without sorbate spike.

The equilibrium aqueous phase concentrations of the sorbates were measured by gas chromatography/mass spectrometry (GC/MS). TraceGC/TraceDSQ (ThermoFinnigan) equipped with a PAL autosampler (Chromtech) and an RTX-VMS column (60 m × 0.32 mm i.d., 1.8 μm film thickness, Restek) or 7890A GC/5975C VL MSD (Agilent Technologies) equipped with a PAL autosampler (Gerstel) and an HP-5MS column (30 m × 0.25 mm i.d., 1.0 μm film thickness, Agilent Technologies) was used, depending on the compounds. Calibration standards were prepared by adding methanol stock solutions into water. Volatile sorbates were measured by headspace injection methods, in which 250−2000 μL of the gas phase in the batches were withdrawn using a gastight syringe and introduced into GC/MS. The other sorbates were analyzed by the solid phase microextraction (SPME) techniques. Prior to the SPME-fiber extraction, the sorption batches were centrifuged (2500 rpm, ~1120 × g, 30 min; Megafuge 1.0R, Heraeus Sepatech). The supernatants were transferred to other vials and spiked with an internal standard. SPME fibers coated with polyacrylate (film thickness, 85 μm; Supelco) were used to extract bipolar sorbates. The other sorbates were analyzed by poly(dimethylsiloxane)-coated fibers (film thickness, 100 μm; Supelco). SPME fibers were immersed in the water for 5−15 min either statically on the sample tray or under agitation. Analytical variabilities were typically within 5% and at worst within 10%, as reported previously (*5*). Note that pH in the aqueous phase was 4.2 to 5.7 with the sorbent-to-water ratios used for phenol probes; thus more than 98% are in their neutral forms in the aqueous phase. For SPME analysis of the chlorophenols (pK_a = 7.4−9.5), the standard solutions and the supernatants transferred from sorption batches were acidified by adding 0.01 M HCl to ensure further that these phenols are in the neutral forms during extraction.

Depletion of the aqueous phase concentration due to the SPME extraction was tested for phenanthrene and fluoranthene by repeated extractions (8−10 times) of an aqueous

TABLE 1. PP-LFERs for log K_{OC} in Peat and Lignite at Sorbate Concentrations of, Respectively, 4.3 and 19 mg/kg-OC (Referred to as log $K_{OC,Low}$), in Peat at 430 mg/kg-OC (Referred to as log $K_{OC,High}$),[a] and in Soils and Sediments at High Concentrations Reported in the Cited References (also as log $K_{OC,High}$)

	c	e	s	a	b	v	R^2	SD	N
log $K_{OC,Low}$ for peat	−1.04	0.31	1.27	−0.10	−3.94	3.71	0.91	0.34	51
SE	0.24	0.20	0.29	0.25	0.35	0.22			
log $K_{OC,High}$ for peat[a]	−0.82	0.43	0.19	0.02	−3.83	3.51	0.90	0.34	51
SE	0.24	0.21	0.29	0.25	0.35	0.22			
log $K_{OC,Low}$ for lignite	−0.28	0.44	0.45	−0.26	−3.43	3.74	0.95	0.24	58
SE	0.15	0.13	0.18	0.17	0.23	0.15			
log $K_{OC,High}$ (Nguyen et al.)[b]	−0.05	0.88	−0.53	0.08	−2.16	2.54	0.97	0.26	74
SE	0.11	0.11	0.16	0.17	0.18	0.15			
log $K_{OC,High}$ (Poole and Poole)[b]	0.25	0.81	−0.16	−0.20	−2.34	2.11	0.95	0.26	130
SE	0.10	0.07	0.12	0.09	0.14	0.11			

[a] Log $K_{OC,High}$ for peat was calculated through eqs 3 and 4 using measured log $K_{OC,Low}$. See the text for details. [b] Coefficients were recalculated using the log K_{OC} data from refs 10 and 11. See SI-5 for details. N = number of compounds; SE = standard error of the coefficient; SD = standard deviation of the estimations.

solution of each compound in the absence of sorbent. The results indicate that a single extraction causes on average 4% and 9% reductions in the concentrations of phenanthrene and fluoranthene, respectively, in our experimental setting. Concentration decreases of these levels are too small to influence significantly the distribution of compounds in the sorbent suspensions. Therefore, the concentrations measured by SPME are not affected by dissolved organic matter or remaining colloidal particles and thus reflect the freely dissolved fraction of the compounds (19, 20).

The sorbed concentrations were determined by mass balance calculations. K_{OC} was determined by eq 1. To obtain the values of K_{OC} at the target concentrations, five batches at differing concentrations (with a factor of 2.0−2.3 increments) were prepared. K_{OC} was determined from each batch as mentioned above. Then, log K_{OC} values were plotted against log C_s, and the value of log K_{OC} at the target log C_s (i.e., C_s = 2 and 10 mg/kg-dry for peat and lignite, respectively) was linearly interpolated. Short-range (<0.3 of log C_s) extrapolations had to be made for phenanthrene, fluoranthene, and 1-nitronaphthalene in the peat. In some cases, up to four sorbates in similar amounts were mixed into stock solutions and added to suspensions together to facilitate K_{OC} determination. In this case, individual log K_{OC} values were interpolated at concentration levels corresponding to the sum of mixed sorbate concentrations equal to 2 or 10 mg/kg-dry. SI-10 in the Supporting Information presents a list of the mixed sorbates and experimental data showing that measured log K_{OC} values do not significantly differ between single and mixture sorbate cases.

Conservation of the sorbates was tested by recovering the added sorbates from extra batches using organic solvents. Details of the recovery experiments are described in SI-2. More than 90% recovery was achieved for most of the sorbates. For some sorbates, however, moderate to substantial loss was observed. If the loss was so high that it would cause an error of >0.3 in log K_{OC}, the corresponding sorbate was removed from the data set. Some sorbates in the peat suspensions showed 70−90% recoveries that could lead to overestimations of log K_{OC} by 0.05−0.25. To assess the significance of these errors, we compared the PP-LFER equations derived using the recovery-corrected and the uncorrected log K_{OC} data. It was found that the coefficients are rarely influenced by these minor errors (Table S3 in SI-2). Therefore, we simply use the uncorrected data in the following discussions.

Results and Discussion

PP-LFER Fitting. Abraham's PP-LFER (eq 2) was fitted to the measured log K_{OC} values for peat and lignite. The resulting coefficients are shown in Table 1. Note that the log K_{OC} values measured in this study and calculated from the PP-LFERs that were calibrated on these measured values are hereafter referred to as log $K_{OC,Low}$, to make a clear distinction from log K_{OC} values measured or calculated principally for near-solubility concentrations (the latter referred to as log $K_{OC,High}$ from here on). The measured and calculated log $K_{OC,Low}$ values are compared in Figure 1 and listed in SI-3. For peat, differences between calculated and measured log $K_{OC,Low}$ values were within 0.3 log units (i.e., a factor of 2 difference in $K_{OC,Low}$) for 42 out of the 51 sorbates studied. Fitting was slightly better for lignite, for which 52 out of the 58 sorbates exhibited deviations of less than 0.3 log units. This finding shows that the PP-LFER model can reasonably fit to log K_{OC} of diverse sorbates at environmentally relevant concentrations. For comparison, the measured log $K_{OC,Low}$ values were correlated with the log octanol−water partitioning coefficients (K_{OW}) in the literature (SI-4 in the Supporting Information). It is evident that the correlations with log K_{OW} (R^2 = 0.53 for peat and 0.74 for lignite) were substantially worse than those obtained with the PP-LFER model. Moreover, SI-4 shows that correlations between log K_{OC} and the log K_{OW} may be more scattered at environmentally relevant concentrations than at higher concentrations, which strongly discourages the use of log K_{OW} to predict log K_{OC} at environmental concentrations.

The correlations for peat and lignite show slightly more scatter compared to well-defined liquid or solid phases such as organic solvents (21) and chromatographic sorbents (22), although the log K_{OC} values used were measured in a consistent experimental condition using a single material, and much care was taken to avoid significant experimental artifacts. The larger scatter is probably due to the heterogeneous organic matter, in which different sorbates may undergo different sorption mechanisms. Moreover, peat shows appreciably larger scatter than lignite, suggesting that a greater heterogeneity of sorbing organic matter is present in peat. This greater heterogeneity agrees with the previous finding that sorption nonlinearity to the peat is more sorbate-dependent and is higher for the majority of the tested sorbates than to the lignite (5). The PP-LFER equations from refs 10 and 11 are also listed in Table 1. Regression coefficients of these equations were recalculated in this study using consistent solute descriptors so that these equations can be compared with ours (see SI-5 for details). The standard deviations and R^2 for these literature PP-LFERs were better than peat and comparable to lignite. It is reasonable that such a fitting is better at high sorbate concentrations, because the significance of heterogeneity is expected to be lower at high concentrations where all high-energy sites are filled up
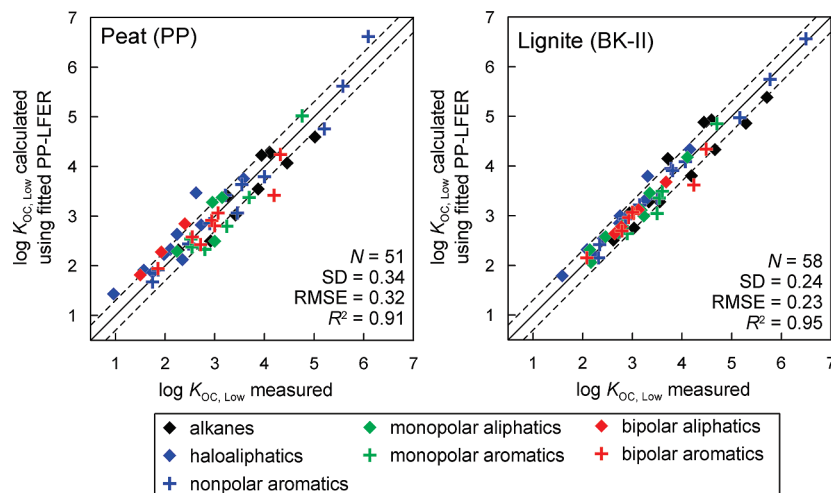
FIGURE 1. Comparison between calculated and measured log K_{OC} values for peat and lignite. Experimental concentrations were 4.3 and 19 mg/kg-OC for peat and lignite, respectively. Solid lines represent the 1:1 fit, and dashed lines indicate 0.3 log-unit deviations (a factor of 2 for K_{OC}) from measured values. N = number of data points; SD = standard deviation; RMSE = root mean squared error.

with the sorbate. Note, however, that the quality of the regression statistics is also influenced by the diversity of the test sorbates.

In the Supporting Information, additional comparison between peat and lignite with regard to their sorption properties is presented (SI-6). As reported previously with a smaller data set (5), lignite tended to show higher K_{OC} values for individual sorbates than peat. Moreover, comparison with literature data (SI-7) suggests that the lignite used is a stronger sorbent than typical organic matter regardless of the concentration range. It appears that coalification to lignite significantly alters its sorbent properties from younger organic matter including peat. Hence, for assessment of magnitude of K_{OC} in soils, lignite may not be a representative sorbent, and thus we focus on the peat in the following discussions.

Comparison between PP-LFERs at Differing Concentrations. The PP-LFER for log $K_{OC,Low}$ in peat derived in this study is compared to the literature PP-LFER from Nguyen et al. (11). These authors carefully selected literature K_{OC} values measured at *high* sorbate concentrations. Therefore, their data set and PP-LFER may be regarded as representative of published K_{OC} for high concentrations (thus referred to as $K_{OC,High}$ here). Note that comparison of our PP-LFER with that from Poole and Poole (10) (discussed in SI-8) leads to very similar results to that from Nguyen et al., as might be expected from the numerical similarity between these two equations.

Table 1 shows that values of some regression coefficients from the literature are apparently different to those from this study. However, direct comparison of regression coefficients that were calibrated from limited and differing sorbate sets may not be specific enough, as such regression coefficients can be influenced by the diversity of test sorbates and statistical artifacts. Furthermore, some coefficients may differ in the opposite directions which can be canceled and become insignificant in predicted log K_{OC}. Therefore, in this study comparison of the PP-LFER equations was performed by means of mutual prediction, i.e., experimental log K_{OC} data from this study were predicted by the PP-LFER equations from the literature, and vice versa.

Figure 2A compares the measured log $K_{OC,Low}$ for peat with the predictions by Nguyen's PP-LFER. The literature PP-LFER adequately predicted log $K_{OC,Low}$ of non- and weakly polar aliphatic sorbates, whereas it consistently underpredicted log $K_{OC,Low}$ of aromatic and some polar aliphatic sorbates by around one log unit. This finding indicates that the PP-LFER equation from Nguyen et al. is, indeed, for high

concentrations and can cause substantial errors for particular compounds if used to predict K_{OC} at typical environmental concentrations.

We subsequently compare the experimental log $K_{OC,High}$ collected by Nguyen et al. (11) to the predictions by the PP-LFER equation calibrated on the experimental log $K_{OC,Low}$ values for peat (Figure 2B). The results show that the PP-LFER for log $K_{OC,Low}$ overestimates the experimental $K_{OC,High}$ values by 1.4 log units on average. This disagreement is consistent with the results from the inverse comparison shown above, which re-emphasizes that there are significant differences between the PP-LFERs from both concentration levels. Deviations of the data points from the 1:1 line seen in Figure 2B are even clearer than Figure 2A. This is because the experimental data set collected by Nguyen et al. consists mostly of aromatic compounds, for which the deviations were found to be large. Noteworthy is that log $K_{OC,Low}$ values for PCBs 194 and 202 are predicted as 10.6, which is 4 log-units higher than the experimental log $K_{OC,High}$ values in ref 11. Such a large deviation would be extremely important. However, this deviation is based on the extrapolations of our PP-LFER to the PCBs that are outside the calibration domain with regard to the S and V descriptors and thus may be somewhat biased. Therefore, further experimental data are recommended at low concentrations for compounds exhibiting such large log K_{OC}.

Prediction of Sorption Nonlinearities for Peat. In our previous contribution (5), we reported that sorption isotherms of 16 sorbates in the studied peat follow the Freundlich model and that there is a correlation between the sorption nonlinearity (expressed by the Freundlich exponent, $1/n$) and the sorbate dipolarity/polarizability descriptor S

$$1/n = 0.97(\pm0.01) - 0.27(\pm0.02)S$$
$$(R^2 = 0.90; \text{ for Pahokee peat}) \quad (3)$$

This relationship may allow for estimating log K_{OC} values at varying concentrations based on a log K_{OC} value determined at a single concentration. Thus, if eq 3 also holds for the 35 additional, more diverse sorbates measured in this study, then one should be able to estimate log K_{OC} values at higher concentration that agree better with the log $K_{OC,High}$ predicted by the literature PP-LFER. Accordingly, the deviations seen in Figure 2A should diminish. To assess this hypothesis, log K_{OC} values at a higher sorbed concentration (i.e., log $K_{OC,High}$) for the used peat were calculated using the measured $K_{OC,Low}$, the Freundlich model, and eq 3; thus

$$\log K_{OC,High} = \log K_{OC,Low} - \left(\frac{1}{1/n} - 1\right)\Delta(\log C_s) \qquad (4)$$

$\Delta(\log C_s)$ is the difference in sorbed concentration from the measured level (here: 2 mg/kg-dry). The value of $1/n$ is calculated from eq 3 for each sorbate, and the value of $\Delta(\log C_s)$ is fixed to 2 here (i.e., 100 times higher C_s; 200 mg/kg-dry, or 430 mg/kg-OC). This value of $\Delta(\log C_s)$ chosen for the calculation is rather arbitrary, and the influence of the concentration on the results is briefly discussed in SI-9.

The estimated $\log K_{OC,High}$ for peat by eq 4 and the predicted $\log K_{OC,High}$ by the literature PP-LFER are compared in Figure 2C. Compared to Figure 2A, these two sets of $\log K_{OC}$ agree much better with deviations mostly within 0.5 log units (a factor of 3 for K_{OC}). Basically, the data points for polar and/or aromatic sorbates have shifted to the 1:1 line in Figure 2C compared to Figure 2A because of the relatively high S values of these sorbates, whereas nonpolar aliphatic compounds (alkanes, halo-aliphatic compounds) remain around the 1:1 line reflecting their low S values. The excellent agreement in Figure 2C suggests that the $1/n$–S relationship (eq 3) used to estimate $K_{OC,High}$ for peat is valid for the extended test sorbates and that the deviations observed in Figure 2A can be quantitatively explained by the varying sorption nonlinearities for individual sorbates.

Note that some systematic underpredictions of K_{OC} still exist for n-alkanes in Figure 2C. Moreover, the data points for n-alkanes are not parallel to the 1:1 line. The concentration difference does not explain these trends, as sorption of n-alkanes for this peat is extensively linear (5). Since a -CH$_2$-increment to molecular structure increases only the V parameter in eq 2, the deviation from parallel indicates that the contribution of the molecular size to $\log K_{OC}$ is differently evaluated. This is likely because E and V values of Nguyen's sorbate set are correlated with each other ($R^2 = 0.75$), mainly due to the large number of nonpolar aromatic compounds in their data set (see SI-5), which can lead to distribution of the statistical information to e and v and affect the predictability. Our data set contains both aliphatic and aromatic sorbates and does not have a correlation between E and V ($R^2 = 0.01$). A similar discussion has been presented by Niederer et al. (23) using humic acid–air distribution coefficients. Note that this is not a problem specific to the cited reference, but there is a general lack of K_{OC} data for aliphatic compounds (except for small chlorinated compounds) in the literature (also see SI-5 for the probe set of Poole and Poole (10)).

A PP-LFER equation was derived based on the estimated $\log K_{OC,High}$ for peat (Table 1). This PP-LFER predicts the
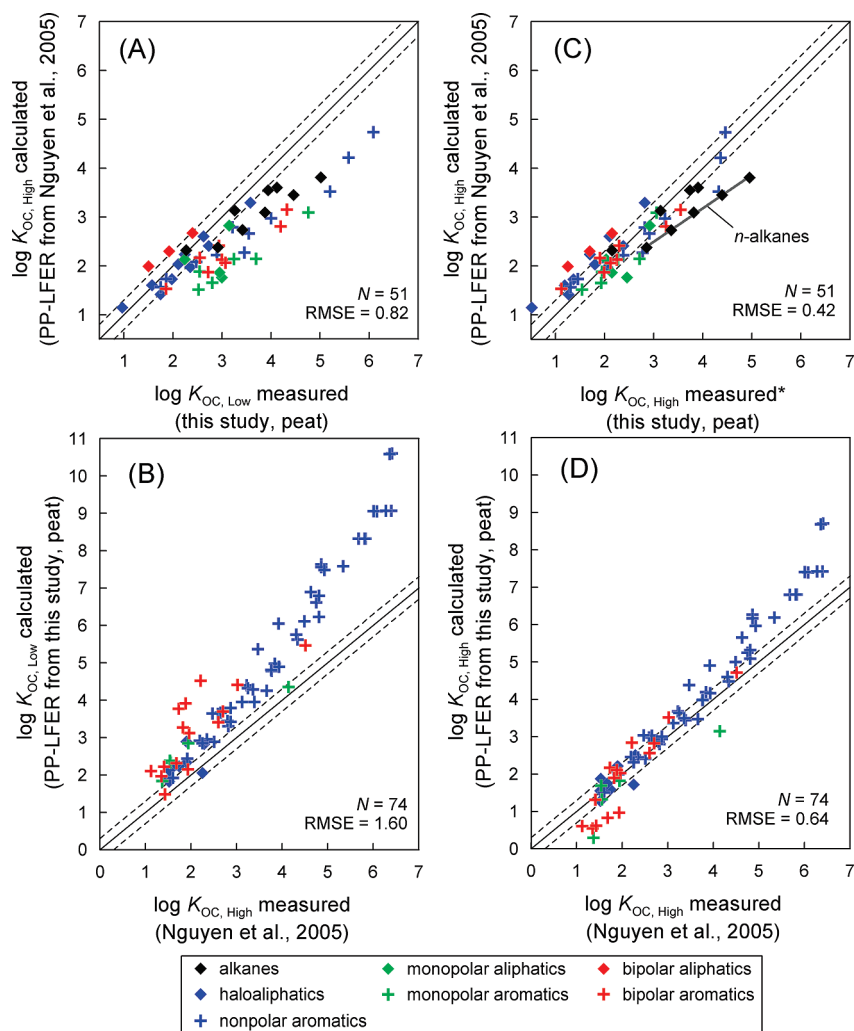

FIGURE 2. Comparison between calculated (predicted) and measured $\log K_{OC}$. (A) Predictions by the PP-LFER from ref 11 vs measured $\log K_{OC,Low}$ for peat. (B) Predictions by the PP-LFER calibrated on $\log K_{OC,Low}$ for peat vs measured $\log K_{OC,High}$ collected by ref 11. (C) Predictions by the PP-LFER from ref 11 vs $\log K_{OC,High}$ for peat*. (D) Predictions by the PP-LFER calibrated on $\log K_{OC,High}$ for peat vs measured $\log K_{OC,High}$ collected by ref 11. Solid lines represent the 1:1 agreements, and dashed lines indicate 0.3 log-unit deviations (a factor of 2 for K_{OC}). N = number of data points; RMSE = root mean squared error. *Estimated values based on experimental data; see the text for details.

literature experimental log $K_{OC,High}$ much better (Figure 2D) than the PP-LFER for log $K_{OC,Low}$ does (Figure 2B), indicating again the validity of the $1/n-S$ relationship. The PP-LFER based on the estimated log $K_{OC,High}$ still tend to overpredict the experimental log $K_{OC,High}$ for large PCBs (see the deviations at measured log $K_{OC,High} > 5$ in Figure 2D). As mentioned above, one reason may be that our sorbate set does not include such large compounds. However, another possible cause lies in the concentration chosen; we rather arbitrarily defined $K_{OC,High}$ for peat as the values at 200 mg/kg-dry, but if K_{OC} values at 2000 mg/kg-dry instead are taken, the resultant PP-LFER would provide excellent predictions for the large PCBs (data not shown). The calculations of $K_{OC,High}$ for sorbates with large S values are sensitive to the choice of concentration, as sorption for these sorbates is predicted to be strongly nonlinear by eq 3. Therefore, the level of agreement shown in Figure 2D for PCBs seems reasonable.

Niederer et al. (24) measured organic carbon−air distribution coefficients for diverse compounds in 10 humic substances. Based on these data, they estimated log K_{OC} values through a thermodynamic cycle and derived PP-LFER equations for each sorbent. Their experimental and predicted values of log K_{OC} are compared with ours in SI-11, Supporting Information. Overall, our results from peat and lignite are in good agreement with those reported in ref 24 for two humic acids from terrestrial environments (Leonadite, Amherst peat). Agreement is less substantial with humic acids from aquatic environments and fulvic acids in general. Another interesting trend is that Niederer's experimental/predicted log K_{OC} generally agree better with log $K_{OC,High}$ compared to log $K_{OC,Low}$ for peat. However, since there are many differences in experimental settings between ref 24 and this study (see SI-11), these comparisons are not conclusive.

Noteworthy is that apparently different PP-LFER equations (compare PP-LFERs for "log $K_{OC,High}$ for peat" and "$K_{OC,High}$ (Nguyen et al.)" in Table 1) led to a fairly good agreement for many sorbates at high concentrations (Figure 2C,D). Deviations may become recognizable only if one equation is applied to types of compounds that are not covered by the test sorbate set, as shown above with n-alkanes and large PCBs as examples. Predicting log K_{OC} of compounds that are out of the application domain can lead to large errors. Thus, it is essential to bear in mind the application domain of the model. Examples of such compounds for the PP-LFERs derived in this study are (i) large hydrophobic compounds (e.g., five-ring or larger PAHs), (ii) acids, bases, and ionic compounds, (iii) highly polar, multifunctional compounds (e.g., some pesticides, pharmaceuticals), and (iv) perfluorinated compounds.

This study provided the first well-calibrated PP-LFER equation for log K_{OC} at sorbate concentrations of high environmental relevance. Using this PP-LFER equation and the $1/n-S$ relationship, we are now able to predict log K_{OC} for a wide variety of neutral organic compounds at varying concentrations, at least for the peat used in this work. The approaches using PP-LFERs with diverse molecular probes presented in this and previous work (5) are evidentially useful to comprehend the sorption of organic matter that shows nonlinearity and to establish prediction methods for log K_{OC} at varying concentrations. Therefore, these approaches should be extended to other representative soils and sediments from various environments.

Acknowledgments

Supporting Information Available

Lists of the probe sorbates and of the measured and calculated log K_{OC} values and discussions on simple regressions with log K_{OW}, conservation of sorbates, recalculation of the literature PP-LFERs, comparison between lignite and peat, comparison between lignite data and the literature PP-LFERs, PP-LFERs from refs 10 and 24, and the choice of $\Delta(\log C_s)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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ES803157E