Comparing Linear Free Energy Relationships for Organic Chemicals in Soils: Effects of Soil and Solute Properties

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Sorption isotherm data were determined for a set of 8 aromatic organic compounds with varying physical chemical properties in three soils with organic matter of differing quantity and composition. The primary goals of this study were to test single and multiparameter linear free energy relationships on their ability to predict the observed sorption behavior on different types of natural sorbents across a range of solutes and concentrations and to relate the accuracy of the predictions to sorbent and solute structural descriptors. Organic carbon normalized sorption coefficients (K_{OC}) predicted using both single and multiparameter LFERs were in good agreement with experimental data obtained at the highest tested aqueous concentrations (average deviation less than 0.1 log units over all solutes and sorbents), but deviations were more substantial (0.59–0.65 log units) at the lowest tested concentrations. For chlorinated benzenes there was a significant correlation between experiment-prediction discrepancies and the aromatic content of the soil organic matter measured by ^{13}C NMR, and the magnitude of the effect was similar to that observed previously for dissolved organic matter.

Introduction

Hydrophobic compounds of anthropogenic sources can persist in the environment and in soils for long periods of time, where they can sorb to the soil matrix (*1*). The sorption and desorption of these hydrophobic organic chemicals (HOCs) by soils and sediments can control HOC bioavailability, biodegradation, and mobility, which in turn can affect water quality and human exposure to these chemicals. Numerous studies have been performed to understand the mechanisms that control the extent and rate of HOC release because of the importance of desorption in determining remediation effectiveness, cleanup end points, and choice of cleanup strategy (*2, 3*).

Much effort has been devoted to the prediction of equilibrium partitioning of organic chemicals with diverse structural features between condensed natural phases (e.g., natural organic matter (NOM), minerals, aerosols) and surrounding media (e.g., water, air) (*4–6*). The organic carbon normalized soil/water distribution coefficient, K_{OC}, has been shown to be a good measure of the sorption to soil of many nonionic solutes. K_{OC} is given by the ratio of the partitioning coefficient K_d and the fraction of organic carbon in the sorbent, f_{OC}. Single-parameter linear free energy relationships (sp-LFERs) have for many years been developed and utilized for the estimation of log K_{OC}. The majority of these relationships have been based on the relationship of log K_{OC} with log K_{OW} (octanol–water partition coefficient) or log S_W (aqueous solubility) (*6, 7*). In general sp-LFERs will provide good sorption estimates for apolar and weakly polar sorbates within a specific chemical class, but separate expressions are typically required for accurate predictions across chemical classes, for example chlorinated versus nonchlorinated aromatic compounds (*7*). For polar compounds and sorbents capable of H-bonding the various types of molecular interactions that can occur cannot be totally described by a single variable (log K_{OW} or log S_W). For the above reasons sp-LFERs have limited applicability for such solutes.

Goss and Schwarzenbach (*4*) proposed the use of comprehensive poly parameter LFERs (pp-LFERs) for the prediction of partition to environmental media as these incorporate separate parameters in an attempt to encompass all interactions involved in partitioning. The hoped-for advantage of pp-LFERs over sp-LFERs is that the complete sorption variability can be predicted by a single equation instead of multiple equations while also evaluating and estimating the variability in the sorption characteristics of different natural phases. To date, pp-LFERs have been developed and tested for very broad ranges of solute chemical structure, but far less attention has been paid to the general applicability of the calibrated pp-LFERs for predicting sorption to soils considering the diversity of soil mineralogy, organic carbon structures, and their interactions.

In this study we report single solute sorption isotherm data and analysis for three distinct sorbents for a set of organic compounds with varying physical chemical properties. The primary study goal was to compare sorption models of increasing levels of complexity (one versus multiple solute descriptors) in their ability to represent the sorption data for soils of different types and amounts of organic matter and to determine if experiment-prediction discrepancies were related to solute concentrations, sorbate structure or soil organic matter structural descriptors. The ability to predict sorption data accurately from molecular descriptors for a diverse set of soils over a wide range of concentrations is critical because of the rapid development and introduction into commerce of new chemicals with uncertain information on their environmental fate.

Materials and Methods

Soils Sorbents and Chemical Sorbates. Three previously studied natural geosorbents (Yolo soil, Forbes soil, and Pahokee peat) were selected as sorbents for this study. Yolo and Forbes soils were collected after removing the top layer of litter and collecting the 5 to 20 cm layer. These soils were collected at an agricultural field in Yolo County, CA (Yolo) and in the Tahoe National Forest in a conifer and oak forest, Placer County (Forbes). Florida Pahokee peat soil was obtained air-dry from the International Humic Substance Society, Colorado School of Mines, Golden, CO. All sorbents were air-dried and crushed gently with a mortar and pestle and passed through a sieve, and the fraction <425 μm was collected for Yolo (Y) and Forbes (FB) and the fraction <2 mm for peat (PP). All soils were γ-irradiated with 5 MRad dose of ^{60}Co (University of Michigan - Phoenix Memorial Laboratory) to inhibit microbial degradation and stored at 5 °C. The most relevant properties of the soils studied are

shown in Table 1. Many of these properties were determined in previous studies, and references are given in Table 1.

Nine hydrophobic organic chemicals were used as sorbates for this study (structures and physical-chemical properties are given in the Supporting Information, Table S1). Five chlorinated benzenes [chlorobenzene (CB), 1,2- and 1,4-dichlorobenzene (12DCB, 14DCB), 1,2,4-trichlorobenzene (TCB), and 1,2,3,4-tetrachlorobenzene (TeCB)], benzene (BZ)] and three polycyclic aromatic hydrocarbons (PAH) [naphthalene (NP), phenanthrene (PHN), and pyrene (PY)] were chosen as sorbates; all were analytical standard grade and were used as received. BZ and NP were from Fluka ($\geq$99% purity), and the remaining chemicals were obtained from Sigma-Aldrich, Inc. ($\geq$99% purity). These chemicals were chosen not only because they are commonly found in the environment as contaminants (8, 9) but also because their properties such as aqueous solubility and K_{OW} range over several orders of magnitude.

Sorption Equilibrium Studies. Single solute isotherms were determined for all nine solutes in each sorbent over at least 3 orders of magnitude in aqueous concentration. The experimental procedure was based on ref 10. Experiments were carried out in 40 mL glass tubes with Teflon lined caps. Triplicate control reactors without sorbent were run concurrently with the experiments at each initial concentration to determine system losses. The aqueous phase in equilibrium with the sorbent contained the following: 555 mg/L CaCl$_2$, 200 mg/L of NaN$_3$, and 5 mg/L NaHCO$_3$. CaCl$_2$ was added to act as an electrolyte, NaN$_3$ as an inhibitor of microbial degradation, and NaHCO$_3$ as a buffer. All solutions were prepared with freshly prepared deionized water (Milli-Q, Millipore Corp., MA). All the reactors were prepared leaving no headspace, and the soil and liquid amounts were determined gravimetrically.

Stock solutions of each solute were prepared by dissolving a known mass of chemical in acetone to a final determined volume. To spike each reactor a specified volume of stock solution was delivered into the aqueous phase of each reactor through the Teflon septa with a micro syringe. After mixing, the cap was quickly replaced to minimize volatile losses. The solvent did not exceed 0.1% v/v of the aqueous phase to minimize sorption cosolvent effects. The amount of sorbent used was determined so that the aqueous phase equilibrium concentration of the sorbate at the end of the experiment would be between 20−80% of the initially spiked concentration. The masses of sorbent used for the determination of each sorption isotherm are presented in the Supporting Information (Table S2).

Reactors were tumbled end-over-end at 10 rpm, in the dark for 30 days at room temperature. The reactors were subsequently centrifuged at 3000 rpm for 30 min, and an aliquot of the aqueous phase was removed for liquid/liquid extraction. A contact time of 30 days was determined by Ju and Young (10) to be sufficient for 12DCB to reach sorption equilibrium between these soils and the aqueous phase. The aqueous phase was extracted with pentane (for BZ, NP, and PY) or hexane (for CBs). In experiments with PHN the aqueous phase was analyzed directly. The extracts were analyzed by gas chromatography−mass spectrometry (GC-MS: BZ, NP, PY, and CB), gas chromatography-electron capture detector (GC-ECD: other CBs), and high performance liquid chromatography (HPLC: PHN). More details on the analytical methods are provided in the Supporting Information.

All samples were analyzed in duplicate, and the average response was used to determine concentrations using external calibration. The solid phase chemical concentration was calculated by difference. The average solute mass remaining in the control tubes at equilibrium was used as an initial aqueous loading C_o. The limits of detection (LOD) and quantification (LOQ) were appropriate for the conducted

TABLE 1. Sorbent Properties

	OM (%)	OC (%)	soft−hard−soot C ratio (%)[a]	H (%)[c]	O (%)[c]	aliphatic	O-aliphatic	aromatic	carboxyl/carbonyl	sand-silt-clay (%)[b]	SSA (m²/g)[c]	pore volume (mL/g)[c]
Yolo	2.93(3.80)[a]	1.20(1.08[a],1.20[b])	39.3−60.0−0.6	0.48	2.05	28.5[d]	43.1[d]	15.6[d]	12.7[d]	19.9−57.4−22.7	18.3	0.03
Forbes	6.93(13.90)[a]	4.80(5.52[a],4.30[b])	33.2−66.3−0.5	1.20	6.29	12.3[d]	28.1[d]	28.6[d]	30.9[d]	33.5−44.1−22.4	46.7	0.08
Pahokee peat	76.02(89.88)[a]	47.20(51.80)[a]	49.8−50.0−0.2	3.73	31.51	34.8[e]	15.8[e]	19.2[e]	17.4[e]	--	1.0	0.01

[a] Reference 10. [b] Reference 11. [c] Reference 12. [d] Reference 13. [e] Reference 14. Numbers in parentheses are literature values for these soils shown for comparison. Aliphatic (0−45 ppm), O-aliphatic (45−110 ppm), aromatic (110−165 ppm), carboxyl/carbonyl (165−220 ppm), data obtained by ^{13}C solid state NMR.

experiments. These were determined as three times the standard deviation (3xSD) and 10xSD, respectively. For the GC-MS values were between 0.2 to 0.8 μg/L for LOD and 0.3 to 1 μg/L for LOQ.

Isotherm Models. Soil organic matter is composed of a diverse and heterogeneous mixture of adsorbing and absorbing domains in which different domains may dominate sorption within different concentration regimes. The superposition of these heterogeneous sorption domains is manifested by the nonlinearity of sorption isotherms. Nonlinear sorption behavior in soils has been quantified using various empirical approaches.

The Freundlich model, commonly used to empirically describe nonlinear partitioning on heterogeneous sorbents, is given by eq 1

$$q_e = K_F C_e^n \tag{1}$$

or its log transformed form $\log q_e = n \log C_e + \log K_F$ where q_e is the amount adsorbed per unit mass of the solid, C_e is the solute concentration at equilibrium, K_F is the Freundlich constant (equal to the adsorption capacity at $C_e = 1$), and n is the Freundlich exponent. The observed n values for hydrophobic chemicals are typically less than one for sorption onto most sorbents from aqueous solution, indicating the gradual filling of higher energy sorption sites as concentration increases (*3*).

The Potential theory or Polanyi model has been widely applied to gas-phase adsorption to activated carbon (*15*) although several modifications have allowed for its use on binary liquids and solutions (*15, 16*). The modeling in this work follows the approach of Xia and Ball (*17*) for the single solute systems. The adsorption potential ε_{sw} from aqueous solution can be defined as

$$\varepsilon_{sw} = RT \ln\left(\frac{S_w}{C_e}\right) \tag{2}$$

where S_w (mg/L) is the solute's aqueous solubility, T is the temperature (K), and R is the ideal gas constant (J/mol K).

The adsorption isotherm is described as follows

$$\ln q_e = \ln Q_o + a\left(\frac{\varepsilon_{sw}}{V_s}\right)^b \tag{3}$$

where Q_o is the maximum adsorption capacity (cm³/kg), a and b are fitting parameters, and V_s (cm³/mol) is the molar volume of the sorbate. To account for the dual domain nature of sorption a linear partitioning term was included in the Polanyi model following the approach of previous investigators (*17*)

$$q_e = Q_o \times \exp^{a\left(\frac{\varepsilon_{sw}}{V_s}\right)^b} \times \rho + K_P C_e \tag{4}$$

where ρ (g/cm³) represents the solute density, and K_p (mL/g) is the solute partition coefficient. The parameters in eq 4 were fitted using Matlab 7.4 with a weighted nonlinear least-squares minimization. Fitting the model without weighting produced significant prediction errors at low concentrations (Supporting Information Figure S3). Since the experimental error in the data, as assessed by the standard deviation of triplicate sorption data points, is approximately proportional to the value being fitted (q_e), weighting the data is appropriate (*18*).

LFERs in Sorption Prediction. For the prediction of sorption to soil organic matter LFERs have been widely used (*6, 7, 19*) ranging from one parameter to polyparameter models.

Single-parameter linear free energy relationships (sp-LFERs) based on K_{OW} and solubility have for many years been developed and utilized for the estimation of $\log K_{OC}$ (*6*). Seth et al. (*20*) developed a non class-specific sp-LFER for the estimation of $\log K_{OC}$ using a data compilation of different hydrophobic chemicals such as PCBs, PAHs, and chlorobenzenes in several sorbents from previous studies. Recognizing the variability of the data set due to the heterogeneous composition of the organic matter and associated experimental error Seth et al. developed an expression for the prediction of $\log K_{OC}$ as a function of $\log K_{OW}$ (eq 5) and estimated the 95% confidence limits (eqs 6a upper limit and 6b lower limit)

$$\log K_{OC} = 1.03 \log K_{OW} - 0.61 \tag{5}$$

$$\log K_{OC} = 1.08 \log K_{OW} - 0.4 \tag{6a}$$

$$\log K_{OC} = 0.99 \log K_{OW} - 0.81 \tag{6b}$$

Nguyen et al. (*7*) developed class specific sp-LFERs based on well documented, peer reviewed experimental data of organic chemicals meeting the criteria of linear sorption isotherms and sorbents with specific SOM and clay content. The resulting sp-LFER for the classes of monoaromatic hydrocarbons, halogenated hydrocarbons, and PAHs are shown in eqs 7a, 7b, and 7c, respectively

$$\log K_{OC} = 0.84 \log K_{OW} - 0.28 \tag{7a}$$

$$\log K_{OC} = 0.94 \log K_{OW} - 0.43 \tag{7b}$$

$$\log K_{OC} = 1.14 \log K_{OW} - 1.02 \tag{7c}$$

Using eqs 6a and 6b the upper and lower limits of $\log K_{OC}$ for the sorbates under study were estimated. Log K_{OC} values were predicted for the same sorbates using the class specific expressions developed by Nguyen et al. (eqs 7a-c). Both of these estimations were compared to the range in experimental $\log K_{OC}$ values.

The overall objective of pp-LFER models is to capture all key molecular properties via a minimum set of descriptors and predict sorption for untested compounds using these descriptors as inputs. The most widely used pp-LFER models are those based on linear solvation energy relationships developed by Abraham (*21, 22*) using a linear combination of the molecular descriptors E, S, A, B, L, and V. E is the excess molar refraction, S is the dipolarity/polarizability parameter, A is the solute hydrogen (H)-bond acidity, B is the solute H-bond basicity, L is the logarithm of the hexadecane-air partitioning constant, and V is McGowan's characteristic molecular volume. The descriptors S, A, and B describe the respective specific (polar) interactions. S includes some effects of polarizability but is thought to express dipole−dipole interactions. A describes the solute H-bond acidity (H-donor or electron acceptor), and B describes the solute H-bond basicity (H-acceptor or electron donor). The parameters V, L, and E quantify the nonspecific interactions such as dispersion interactions and cavity formation in the sorbent phase, two processes that are both highly related to molecular volume, thus a greater variety of noncorrelated V, L, and E values are needed in order to differentiate cavity formation from van der Waals interactions using pp-LFERs (*21*). The descriptors for the studied sorbates are shown in Supporting Information Table S8.

An example of a pp-LFER relating soil-air distribution coefficient to solute descriptors was defined by Endo et al. (*23*) given by

$$\log K_{soil(h)/air} = c + eE + sS + aA + bB + lL \tag{8}$$

Endo et al. (23) developed a pp-LFER for sorption of a set of chemically diverse compounds on Pahokee peat to identify the effects of sorbent-sorbate molecular interactions on sorption nonlinearity. The property predicted was log $K_{soil(h)/air}$ which is equal to

$$K_{soil(h)/air} = \frac{K_d}{K_{aw}} = \frac{q_e}{K_{aw}C_e} \qquad (9)$$

where K_d (L/kg) is the equilibrium distribution coefficient defined as the ratio of q_e/C_e, K_{aw} is the equilibrium air–water distribution coefficient (dimensionless Henry's constant, provided for the study compounds in Supporting Information Table S1), and $K_{aw}C_e$ equals the air phase concentration. Endo et al. (23) found that the addition of the E-term did not improve the fitting and that its regression coefficient (e) was not significantly different from zero; therefore the E-term was considered negligible. The assumption of concentration-independent descriptors and concentration-dependent system parameters (23, 24) allows for the use of this LFER in the case of nonlinear sorption.

Nguyen et al. (7) also developed a pp-LFER for organic chemical partitioning to all types of OM. In the development of this model the authors used only linear sorption data (see eq S2 in the Supporting Information). The relationship presented by the authors is

$$\log K_{OC} = c + eE + sS + aA + bB + \nu V \qquad (10)$$

The coefficients e, s, a, and b represent the differences in chemical properties between water and organic matter. The constant c is described as being a "solvent specific free energy contribution dependent on entropic effects". The coefficient ν accounts for the difference in cohesive energy of the two partitioning phases, and the νV term accounts for the cavity formation energy.

Additional pp-LFER expressions, generally described by eq 10, were derived by Endo et al. (19) for Pahokee peat based on sorption data determined for 51 different sorbates at a low, environmentally relevant concentration of 2 mg/kg and a high concentration (near aqueous solubility) of 200 mg/kg. These two LFERs (eqs S3 and S4 in the Supporting Information) were used to predict log K_{OC} for the sorbates being studied. For a better comparison of the estimation ability of these expressions, for the same sorbed concentrations of 2 and 200 mg/kg, log K_{OC} for each sorbate (referred to as "extrapolated log K_{OC}") was calculated using Freundlich isotherm data.

Using coefficients obtained by Endo et al. (23) for Pahokee peat (presented in the Supporting Information), the sorption coefficient $K_{soil(h)/air}$ for our set of compounds was calculated and compared to our experimental data. Using the pp-LFER proposed by Nguyen et al. (7) and the two LFERs for low and high sorbate concentrations proposed by Endo et al. (19) log K_{OC} values were calculated for the 9 solutes and compared to the range in experimental log K_{OC} values.

Results and Discussion

Reproducible and significant sorption data was obtained for all compounds with the exception of the sorption isotherm of BZ in Yolo soil. For the BZ system no substantial sorption was measured even at low aqueous phase/soil ratios, an effect of the properties of BZ such as high solubility and low K_{OW} and the low OC content of Yolo soil. For the measured isotherms aqueous phase concentrations span a range of up to 4 orders of magnitude. Average solute losses determined from blank controls were below 6% indicating that losses to volatilization and sorption to system components were negligible.
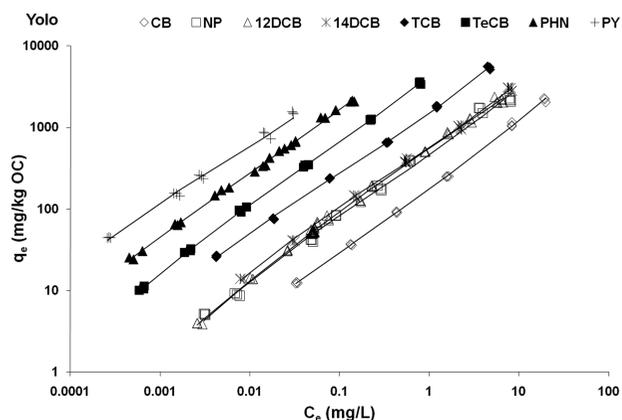

FIGURE 1. Potential model results for Yolo soil.

Freundlich and Potential Isotherm Model Results. All sorption isotherm data were well described by the Freundlich model ($R^2 > 0.978$). All determined isotherms deviated from linearity with Freundlich n values ranging from 0.614 to 0.940. Freundlich coefficients, exponents, and associated standard errors are shown in Table S3, and the isotherms are shown in Figure S2 in the Supporting Information. Freundlich K_F values increased and n values decreased with increasing molecular volume of the sorbates. A similar trend was reported by Xia and Ball (17) for a soil with characteristics comparable to Yolo. Soil organic carbon normalized K_F values for Forbes were consistently higher than those for Yolo soil and Pahokee peat. On the other hand n values are generally lower in Forbes than in Yolo and peat, indicating less linear sorption behavior. Both these effects are likely to be related to the type of organic matter present in this soil. As shown in Table 1 Forbes possesses a high fraction of hard organic carbon which in general is well correlated with the extent of sorption nonlinearity as well as organic carbon normalized sorption affinity (25). The value for specific surface area (SSA) and pore volume are also higher for Forbes than for the other sorbents, which might also contribute to an increased sorption affinity.

The Potential model was also applied to the sorption isotherm data, and the model produced a good fit to the sorption data ($R^2 = 0.999$). The weighted potential model fit for all the tested sorbates in Yolo soil is shown in Figure 1, and corresponding graphs for Forbes soil and Pahokee peat are presented in the Supporting Information (Figures S3 and S4).

One limitation of the Potential model is the difficulty in obtaining a unique set of parameter estimates because of the high number of parameters. To improve the robustness of the parameter estimates and simplify model interpretation, the value of b was set to 2.0, reducing the number of fitting parameters from 4 to 3 and producing more consistent values for maximum adsorption capacities with minor increased error for the overall model (12, 26). Potential model parameter results with four fitting parameters are presented in the Supporting Information (Table S4). Results with b fixed at 2 are shown in Table S5. The values of the linear portion (K_p) of the dual mode potential model for all three sorbents follow the same trend, increasing with molecular size, and with the exception of PY correlate well ($R^2 = 0.979$) with the values obtained for K_F in the Freundlich isotherm model.

The method used to compare the two single solute isotherm models results is described in the Supporting Information (eq S1). Overall the results show a better fit with the potential model, although in some cases the Freundlich model produces lower error (Table S7). The Freundlich model provides a better fit when the experimental error is higher.
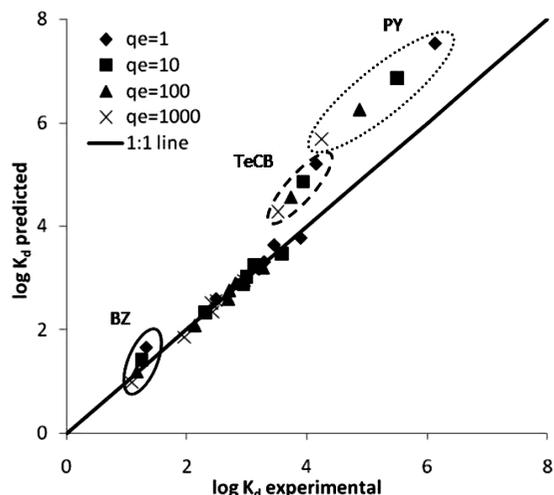
FIGURE 2. Experimental log K_d vs LFER predicted log K_d.

pp-LFER Prediction for Sorption on Pahokee Peat. Using the coefficients for eq 8 determined by Endo et al. (23) (shown in the Supporting Information Table S9) the sorption coefficient $K_{soil(h)/air}$ was determined for each solute and converted to a corresponding K_d using eq 9. These predicted values were compared to the K_d results obtained for our set of compounds calculated at four sorbed concentrations ($q_{e \, (mg/kg)} = 1$, 10, 100, and 1000 mg/kg) using the Freundlich equation obtained for each sorbate in Pahokee peat. In some cases the selected sorbed concentrations fell outside the range of experimental concentrations (Table S10, Supporting Information) and were extrapolated (usually a factor of less than 10). Predicted log K_d and deviation of prediction from experimentally determined results are presented in Supporting Information Table S11. Figure 2 shows experimental log K_d vs LFER predicted log K_d for each of the calculated concentrations.

Overall the pp-LFER produced good log K_d predictions for all the compounds (with deviations lower than 25%, in log units). Furthermore for the smaller CBs and NP the agreement between predicted and experimental K_d was even greater (deviations not exceeding 5%). K_d values for BZ, TeCB, and PY were slightly overpredicted although still very

satisfactory. The average deviation for extrapolated values was 7.3%, while for nonextrapolated values was 7.7% showing that the extrapolation of q_e data did not seem to affect the predictive ability of the model.

Comparing LFERs for the Prediction of Sorption to Different Sorbents. Figure 3 summarizes the prediction results for log K_{OC} using several sp-LFER and pp-LFERs. On both graphs the bars represent the range of experimental log K_{OC} values for the nine studied sorbates in Yolo, Forbes, and Pahokee peat soils. The results for the tested sp-LFERs are presented on the left graph, and those for the pp-LFERs are presented on the right graph.

One goal of our study was to determine whether the additional complexity associated with pp-LFERs was justified for relatively hydrophobic compounds such as those examined here and whether or not this conclusion depended on the characteristics of the soil being studied. Although there are obviously many ways to quantify the differences between the experimental and the LFER predicted K_{OC} values, one simple measure is to compare the difference between single point K_{OC} estimates and the high and low experimental K_{OC} values for each solute on each soil. We performed this comparison for the sp-LFER and the pp-LFER models of Nguyen et al. (7), which provided a generally good approximation to the minimum log K_{OC} values for most of the sorbent-solute combinations, but underestimated a number of the maximum values. This deviation was most significant for isotherms with the greatest degree of nonlinearity, probably because only linear data were employed in the construction of this LFER. Average deviations in log K_{OC} for each solute across the three soils showed no significant correlations ($p < 0.2$) with any of the solute descriptors used in developing the pp-LFER values (Table S1, Supporting Information). Average deviations between minimum experimental log K_{OC} values and predicted log K_{OC} values were 0.09 for the sp-LFER and 0.03 for the pp-LFER of Nguyen et al. These differences were not statistically different from each other or from zero ($p > 0.05$), confirming that both types of LFERs do a good job approximating adsorption at higher aqueous solute concentrations where partitioning is most likely to dominate (23). Deviations between LFER-predicted K_{OC} values and maximum experimental K_{OC} values were significantly different from zero ($p < 0.05$) with average
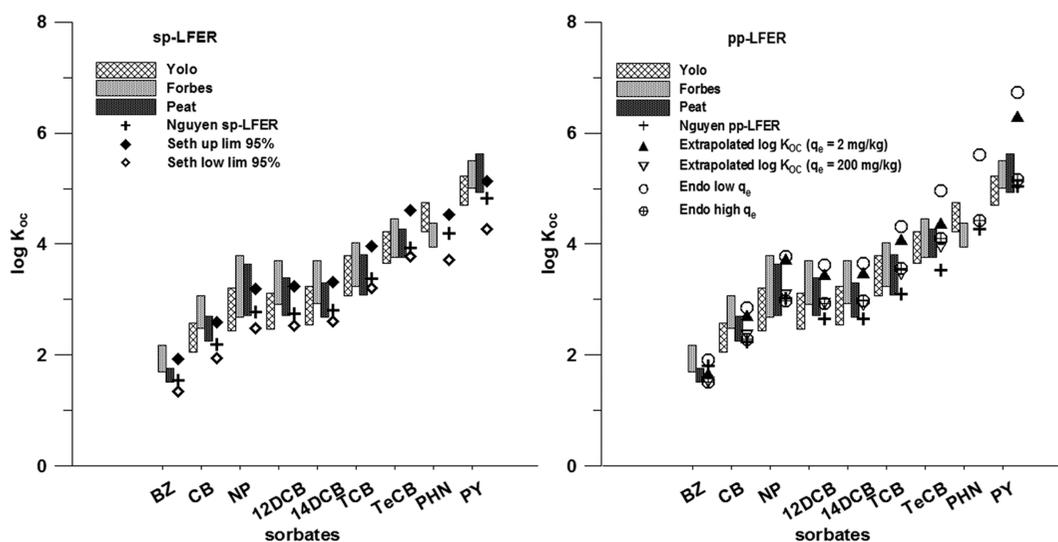

FIGURE 3. Estimation of log K_{OC} 95% limit values using non class-specific sp-LFER by Seth et al. (20) and estimation of log K_{OC} with class specific sp-LFER for generic organic matter (7) shown on the left graph. The right graph describes pp-LFER log K_{OC} results for generic organic matter (7), for nonlinear sorption to peat at low and high q_e concentrations (19) and extrapolated log K_{OC} (low $q_e = 2$ mg/kg and high $q_e = 200$ mg/kg) for peat (using Freundlich isotherm). Both graphs also include the experimental log K_{OC} range for the three sorbents and nine sorbates considered. Data for BZ in Yolo and PHN in peat are not available.

TABLE 2. Correlation between the Aromatic Fraction of Soil Organic Matter Measured by ^{13}C NMR and the Deviation between the Maximum Experimental and the LFER-Predicted log K_{OC} Values for Each Solute[a]

solute	sp-LFER	pp-LFER
CB	0.983*	0.999‡
NP	0.935	0.866
12DCB	1.000‡	0.974*
14DCB	0.985*	0.989†
TCB	0.987*	0.975*
TeCB	0.967*	0.993†
PY	0.205	0.452

[a] Correlation coefficients are statistically significant at $p < 0.2$ (*), $p < 0.1$ (†) or $p < 0.05$ (‡).

deviations of 0.65 log units for the sp-LFER and 0.59 for the pp-LFER, but the difference between the models was not significant ($p > 0.05$).

Considerable deviations between predictions and experimental values are obvious in Figure 3 for Forbes soil with most sorbates. This sorbent exhibits a number of anomalous sorption behaviors as previously mentioned (10−12). To systematically examine the relationship between soil organic matter structure and the prediction deviations associated with the tested LFERs, we computed linear correlation coefficients with the single point sp- and pp-LFER models of ref 7. We considered correlations between key soil characteristics (f_{OM}, f_{OC}, soft carbon fraction, H%, O%, O/C, aliphatic, O-aliphatic, aromatic, carboxyl/carbonyl, specific surface area, and pore volume; Table 1) and the discrepancies between the predicted log K_{OC} values and the experimental upper limits shown in Figure 3. Because of the small sample size ($N = 3$ soils), very high correlation coefficients are required to attain conventionally used levels of statistical significance (e.g., $p < 0.05$ requires $\rho > 0.997$) so we also considered significance levels of $p = 0.10$ and $p = 0.20$. Only two structural descriptors, aromatic content and carboxyl/carbonyl content measured by NMR, produced multiple correlation coefficients significant at the $p < 0.20$ level. It is difficult to untangle the effects of these two parameters since they are highly intercorrelated and produced nearly identical correlation coefficients. Numerous past studies have suggested the importance of the aromatic content of soil organic matter on sorption nonlinearity and organic normalized sorption capacity of hydrophobic compounds (e.g. ref 11). Correlation coefficients between soil aromatic content and deviation in sp- or pp-LFER predictions are presented in Table 2. All correlation coefficients are significant at least at the 80% level for the five chlorinated benzenes using either model to predict distribution coefficients, while none of the coefficients is significant at that level for either model for naphthalene or pyrene. The positive correlation coefficients indicate that the deviation in the K_{OC} prediction increases as the aromatic content of the soil organic matter becomes larger.

The dependence of the discrepancy in K_{OC} prediction on the aromaticity of the soil organic carbon mirrors that observed by Niederer et al. (2007) for a series of humic acid (HA) and fulvic acid (FA) samples of aquatic and terrestrial origin. In their Supporting Information (Figure SI-11), Niederer et al. presented a strong relationship between the average deviation in the logarithm of the sorption coefficient for a particular humic acid from that of a reference HA (Leonardite HA) and the difference in the aromatic fraction between the two materials. Applying the same approach to the data obtained here, as shown in Figure 4, we also find a strong relationship ($R^2 = 0.99$)
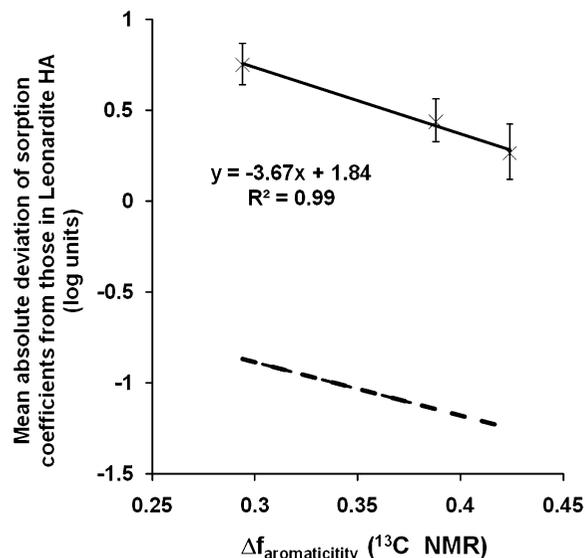

FIGURE 4. Relationship between the K_{OC} values for chlorobenzenes and the fraction of aromatic carbon in the soil samples. Both values are calculated as the difference between the measured value and that of a reference material (Leonardite HA) following the approach of Niederer et al. (2007). The error bars reflect the minimum and maximum deviation in K_{OC} for the set of chlorobenzenes examined here (CB, 12DCB, 14DCB, TCB, TeCB) and the corresponding value in Niederer and the point (×) is the average deviation. The line (----) shows the relationship obtained by Niederer et al. for aquatic and terrestrial humic materials.

relating the deviation between the log K_{OC} for the chlorobenzenes on our soil samples and their corresponding log K_{OC} on Leonardite HA measured by Niederer et al. and the discrepancy between our ^{13}C NMR aromatic fractions and that for Leonardite HA (0.58). Although the slope of the two relationships is similar (−2.95 reported in Niederer, −3.67 here), the intercepts are quite different (−0.02 for Niederer and 1.84 here), reflecting the generally greater adsorption observed for soil-associated HA compared with HA extracted from the same source. This is reflected in the literature sp-LFERs for dissolved organic matter reviewed by Niederer and those for soil reviewed here; the exact results depend on the solute's Log K_{OW} and the chosen correlation, with soil correlations yielding values that are 0.3−0.6 log units larger than the corresponding dissolved organic matter sample.

In summary, the results indicate that the additional complexity of a pp-LFER model is not likely to be warranted to predict sorption of the compounds studied here, presumably because their primary mode of sorption is via hydrophobic interactions. Both sp- and pp-LFER predictions deviated significantly from experimental results for soils with natural organic matter containing a higher aromatic fraction and at more environmentally relevant (lower) concentrations. Improved understanding of the mechanistic sources of these deviations and extension of the approach to a more diverse set of solutes should further improve our ability to estimate sorption to soils and sediments using only solute descriptors.

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Supporting Information Available

Additional text, tables, and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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