

## A LINEAR SOLVATION ENERGY RELATIONSHIP MODEL OF ORGANIC CHEMICAL PARTITIONING TO DISSOLVED ORGANIC CARBON

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**Abstract**—Predicting the association of contaminants with both particulate and dissolved organic matter is critical in determining the fate and bioavailability of chemicals in environmental risk assessment. To date, the association of a contaminant to particulate organic matter is considered in many multimedia transport models, but the effect of dissolved organic matter is typically ignored due to a lack of either reliable models or experimental data. The partition coefficient to dissolved organic carbon ( $K_{DOC}$ ) may be used to estimate the fraction of a contaminant that is associated with dissolved organic matter. Models relating  $K_{DOC}$  to the octanol–water partition coefficient ( $K_{OW}$ ) have not been successful for many types of dissolved organic carbon in the environment. Instead, linear solvation energy relationships are proposed to model the association of chemicals with dissolved organic matter. However, more chemically diverse  $K_{DOC}$  data are needed to produce a more robust model. For humic acid dissolved organic carbon, the linear solvation energy relationship predicts  $\log K_{DOC}$  with a root mean square error of 0.43. Environ. Toxicol. Chem. 2011;30:2023–2029. © 2011 SETAC

**Keywords**—Dissolved organic carbon    Partitioning    Humic acid    Hydrogen bonding    Polyparameter models

## INTRODUCTION

Determining the fraction of the contaminant that is freely dissolved influences the estimated environmental hazard of contaminants, because it is the freely dissolved portion of chemical that is bioavailable to aquatic organisms [1,2]. Equilibrium methods may be used to quantify the distribution of a chemical between particulate and dissolved forms of organic matter and the water phase. Regulatory agencies around the world are currently employing these methods. For example, the equilibrium partitioning model is recommended for the development of sediment quality guidelines by the U.S. Environmental Protection Agency (U.S. EPA; [http://cfpub.epa.gov/ncer/abstracts/INDEX.cfm/fuseaction/display.abstractDetail/abstract/837/report/F; \[3\]](http://cfpub.epa.gov/ncer/abstracts/INDEX.cfm/fuseaction/display.abstractDetail/abstract/837/report/F; [3])). Equilibrium partitioning models use partition coefficients to evaluate the distribution of the contaminant between water, particulate, and dissolved organic matter (DOM). There is, at present, no single universally accepted partition coefficient model for particulate organic matter (POM), and there is no model at all that is recommended for DOM.

REVIEW OF  $K_{DOC}$  MODELS

The problem of constructing a better  $K_{OM}$  (an organic matter partition coefficient) model is twofold. Present  $K_{OM}$  models rely on the quality and amount of the available partitioning data for validation and the predictive capability of the descriptors of the contaminant. The most common  $K_{POC}$  models (where the subscript POC denotes partitioning to particulate organic carbon) use the octanol–water partition coefficient,  $K_{OW}$ , as the sole chemical descriptor of the contaminant. The  $K_{OW}$  models have been revised multiple times within the last 40 years due to more

$K_{POC}$  data becoming available [4–13] and new and/or improved methods for obtaining experimental values. The  $K_{POC}$  partition coefficient is also typically normalized to the particle organic carbon (POC) content, reported in the literature as  $K_{OC}$ . It has been suggested that multiple  $K_{OW}$  models for individual chemical classes are the solution to the problem of expanding the applicability of the  $K_{POC}$  model to most compounds [14]. Yet, the U.S. EPA presently still recommends a  $K_{OW}$  model [15] for  $K_{POC}$  as a risk assessment screening tool for contaminants of emerging concern [16]. A single  $K_{OW}$  model predicts  $K_{POC}$  for nonpolar hydrophobic contaminants reasonably well, but it does not perform as well for chemicals with polar functional groups [17,18].

Most risk assessment models in present use do not include a dissolved organic carbon (DOC) phase [19–22], although this has been shown to be important, especially for more hydrophobic chemicals, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) [23], in determining the bioavailability of the contaminant. Partitioning to DOC must be modeled separately from POC [1,5], as it has been suggested that there is no correlation between  $\log K_{DOC}$  and  $\log K_{POC}$  [24]. It has also been suggested that different models are required to explain sorption to various types of DOC, which may be more functionally diverse than POC [25]. Dissolved organic carbon sorption has been modeled using  $K_{OW}$  as the sole chemical descriptor, but that model can only predict  $K_{DOC}$  to within 2.5 orders of magnitude [26]. To date, no universal models for  $K_{DOC}$ , and no generally accepted methods for estimating  $K_{DOC}$  for individual types of DOC, are available.

Ideally, a large and chemically variable  $K_{DOC}$  data set and better chemical predictors based on the molecular structure are required to construct a  $K_{DOC}$  model. The success of linear solvation energy relationship (LSER) models for  $K_{POC}$  that include polar chemicals [17,27,28], prompted the development of an LSER  $K_{DOC}$  model trained on a chemically variable data set.

All Supplemental Data may be found in the online version of this article.

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The LSER model is a sum of interaction terms that completely describe the partitioning:

$$\log K_{\text{DOC}} = c + eE + sS + aA + bB + vV$$

The upper-case parameters describe the sorbate, or solute (the contaminant associating with organic matter), and the lower-case parameters describe the sorbent or solvent (the organic matter). They are estimated using measured  $\log K_{\text{DOC}}$  values and the  $E$ ,  $S$ ,  $A$ ,  $B$ , and  $V$  descriptors and performing a multiple linear regression analysis using the LSER equation above. The descriptors  $E$ ,  $S$ ,  $A$ ,  $B$ , and  $V$  represent the chemical properties of the contaminant that determine the solute–solvent interactions. They can be obtained from the literature or calculated for any chemical, as discussed below. The parameter  $E$  is the excess molar refractivity of the solute and parameterizes the permanent dipole of the solute. The parameter  $S$  represents the (di)polarizability, which is the solute's response to polarization by the solvent. Hydrogen bond formation is parameterized by  $A$ , the hydrogen bond acidity, which parameterizes the ability of the solute to donate a hydrogen bond, and  $B$ , the hydrogen bond basicity, which parameterizes the ability of the solute to accept a hydrogen bond. The parameter  $V$  is the molar volume of the solute. These parameters completely characterize the solute.

The solvent descriptors parallel the solute descriptors. Because  $\log K_{\text{DOC}}$  is a solvent–water partition coefficient, the solvent parameters represent the difference between the solvent–solute interactions and solute–water interactions. The parameter  $e$  represents the difference between the ability of the solvent and the ability of the water to respond to the dipole moment of the solute;  $s$  parameterizes the solvent–water interaction with the solute partly through dipole–dipole interactions and partly through induced dipole interactions. The parameters  $a$  and  $b$  represent the difference between the ability of solvent–water system to accept or donate, respectively, a hydrogen bond from the solute. The parameter  $v$  represents the solvent–water difference in energy required for a cavity to be formed to accommodate the solute [29,30]. The parameter  $c$  carries the units of  $\log K_{\text{DOC}}$  (e.g.,  $\log$  [volume of water/mass of organic carbon]) and represents any remaining partitioning not accounted for by the other terms in the LSER equation.

The interactions of sorbents with DOC may be related to similar interactions with POC, because the ratios of  $K_{\text{POC}}$  to  $K_{\text{DOC}}$  appear to be similar [25] for certain chemical classes, such as PAHs,  $K_{\text{DOC}}$  and  $K_{\text{POC}}$  might correlate very well [31]. It has also been noted that the degree of aromaticity of the humic material appears to be important [32]. Thus, it may be useful to model DOC with a general model such as the LSER that describes the interactions with a sorbent. However, Schwarzenbach et al. [33] caution that there may be problems with the classical method of determining  $K_{\text{DOC}}$ , because equilibrium might be difficult to achieve, and this should be considered.

Burkhard attempted to predict  $\log K_{\text{DOC}}$  for neutral chemicals partitioning to DOC from a variety of sources, including sediment pore water, soil pore water, surface water, and laboratory humic and fulvic acids [26]. Humic and fulvic acids were included because humic substances contribute 50 to 80% of natural organic carbon in water, sediment, and soil systems [34,35]. The author notes that differences in experimental determinations of  $K_{\text{DOC}}$  with different methods can vary by up to 1.5 log units, but that a large part of the variation may come from the heterogeneity of DOC. A relationship  $K_{\text{DOC}} = 0.08 K_{\text{OW}}$  for naturally occurring DOC partitioning (excluding humic and fulvic acid) was found, with a factor of 20 as the 95% confidence limit. Inclusion of humic and fulvic

acids changed the correlation to  $K_{\text{DOC}} = 0.11 K_{\text{OW}}$  with a factor of 14 as the 95% confidence limit. The study concluded that  $K_{\text{OW}}$  could not account for most of the variability in the experimental data for  $K_{\text{DOC}}$ . The failure of individual  $K_{\text{OW}}$  models for different types of DOC may also indicate a greater variability in their chemical composition.

A recent study noted that PCBs and PAHs may undergo considerable sorption to DOC [23]. The authors suggest that partition coefficients measured by solid-phase microextraction may be the best method to predict PCB and PAH sorption to DOC. In addition, the authors tested Aldrich humic acid (a commercially available humic acid) as a sorbent and determined that it was too strong to properly represent natural DOC, at least for the chemicals tested in that study. Indeed, it has been noted that commercially available humic acids, such as Aldrich humic acid, are unlike natural humic acids [36]. However, no significant progress has been made in modeling partitioning specifically for natural DOC since the Burkhard study [26].

## MATERIALS AND METHODS

All  $K_{\text{DOC}}$  data were taken from Burkhard [26] and include both polar and nonpolar compounds, many of which are PAHs and PCBs. The nonpolar chemicals are much more numerous than the polar chemicals. Of a total of 1,375 observations, only 34 are for polar chemicals. Dissolved organic matter types include surface water, soil pore water, groundwater, sediment pore water, humic acid, fulvic acid, and Aldrich humic acid. Groundwater and soil porewater DOC were grouped together as was done by Burkhard. Humic and fulvic acid were considered separately, whereas they were combined in the Burkhard study.

Solute descriptors  $E$ ,  $S$ ,  $A$ ,  $B$ , and  $V$  for the chemicals were estimated using ADME Boxes 5.0 Absolv program provided by ACD Labs [37]. A multiple linear regression was performed using the LSER equation, the observed  $\log K_{\text{DOC}}$ , and solute parameter values. The DOC solvent descriptors  $c$ ,  $e$ ,  $s$ ,  $a$ ,  $b$ , and  $v$  are obtained from this regression.

## RESULTS AND DISCUSSION

The LSER model coefficients were estimated for surface water, groundwater and soil pore water, sediment pore water, and the humic and fulvic acid DOC subsets presented in Burkhard [26]. The humic and fulvic acid subsets were treated separately, because humic and fulvic acids have different chemical characteristics [38] and therefore interact differently with sorbents. A plot of predicted versus observed  $\log K_{\text{DOC}}$  values for each DOC subset is shown in Figures 1a to 5a. Each plot is compared to the prediction using  $\log K_{\text{OW}}$  in Figures 1b to 5b. The horizontal lines of data points in Figures 1a to 5a and the vertical lines in Figures 1b to 5b are due to multiple observations for a single chemical. Each plot includes the diagonal line of perfect prediction and two dotted lines enclosing a prediction within one order of magnitude. In Figure 1, the Aldrich humic acid data in the humic acid subset are shown in gray. Table 1 presents the root mean square errors (RMSEs) for each model, as well as the number of observations and number of chemicals in each DOC subset. The complete statistics are presented in the Supplemental Data. An LSER model for the entire DOC data set was not included because of the large variability within DOC subtypes, as evidenced by the variation in solvent parameters, as discussed below.

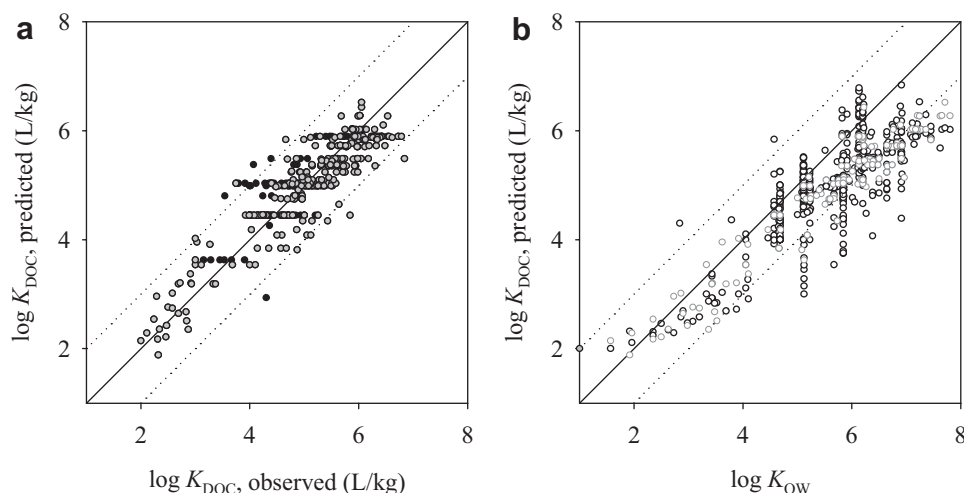


Fig. 1. Humic acid. Predicted versus observed  $\log K_{\text{DOC}}$ . (a) Linear solvation energy relationship (●), (b)  $K_{\text{OW}}$  (○).  $\log K_{\text{OW}}$  values from Burkhard [26]. Aldrich humic acid is highlighted in gray circles. Dotted lines represent an order of magnitude difference in prediction compared to observed values. DOC = dissolved organic carbon.

Table 1.  $\log K_{\text{DOC}}$  root mean square error (RMSE) of prediction for the linear solvation energy relationship models (LSER) for the listed dissolved organic carbon (DOC) subtypes

$\log K_{\text{DOC}}$ LSER model	RMSE	$N_{\text{data}}^a$	$N_{\text{chemicals}}^b$
Aldrich humic acid	0.41	283	125
Humic acid	0.43	438	128
Groundwater and soil pore water	0.47	50	8
Sediment pore water	0.58	391	81
All Burkhard data	0.65	1375	150
Surface water	0.7	263	39

<sup>a</sup> Number of observations.

<sup>b</sup> Number of chemicals.

The predictions using the LSER model improves upon the prediction by using  $\log K_{\text{OW}}$  for all DOC subtypes. However, the groundwater and soil pore water (Fig. 5) and fulvic acid (Fig. 2) subsets are relatively small (50 and 69 data points, respectively) and contain a small number of chemicals (8 and 11, respectively); therefore, these models are less trustworthy. However, the LSER model for humic acid (Fig. 1) is

based on 438 data points and 128 chemicals. The  $\log K_{\text{DOC}}$  is generally predicted to within one order of magnitude. The model parameters and the statistics for this regression are shown in Table 2 and the Supplemental Data. A total of 283 of 438 humic acid data were designated as Aldrich humic acid. Aldrich humic acid may have a lower functional variability than natural DOC [36], and the inclusion of these points could result in a smaller RMSE. However, the RMSE = 0.41 for an LSER based on Aldrich humic acid alone resulted in essentially the same RMSE = 0.43 as the entire humic acid subset (Table 1). Therefore, the Aldrich and natural humic acid data were used together. This was also the choice made by Burkhard.

The sediment porewater LSER (Fig. 4; RMSE = 0.58) is more successful than the surface water LSER (Fig. 3; RMSE = 0.70). Burkhard suggested that surface water DOC has more chemical variability than the other subtypes, such as sediment pore water, because it contains fresher detritus. Functional variability in the sorbent would result in less accurate chemical-based models for that particular subtype. However, Burkhard also noted that there may be significant variability due to differing measurement techniques. Therefore, the larger

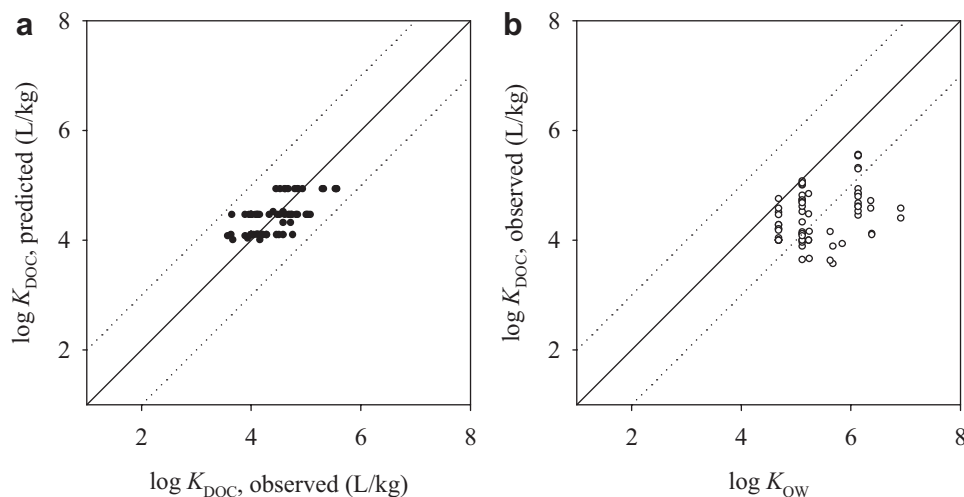


Fig. 2. Fulvic acid. Predicted versus observed  $\log K_{\text{DOC}}$ . (a) Linear solvation energy relationship (●), (b)  $K_{\text{OW}}$  (○).  $\log K_{\text{OW}}$  values from Burkhard [26]. Dotted lines represent an order of magnitude difference in prediction compared to observed values. DOC = dissolved organic carbon.

Table 2. Solvent parameters, standard errors (SE), *t* values, and probability (*p*) that parameter = 0 for the humic acid log  $K_{\text{DOC}}$  linear solvation energy relationship models

	Humic acid parameters	SE	<i>t</i> value	<i>p</i>
<i>c</i>	1.441	0.130	11.044	<2.00E-16
<i>e</i>	0.658	0.060	11.034	<2.00E-16
<i>s</i>	-0.235	0.187	-1.258	2.090E-01
<i>a</i>	-0.853	0.165	-5.160	3.760E-07
<i>b</i>	-1.341	0.125	-10.774	<2.00E-16
<i>v</i>	1.596	0.108	14.713	<2.00E-16

DOC = dissolved organic carbon.

RMSE cannot be solely attributed to surface water DOC functional variability. In general, more data are required for all these DOC subtypes to draw any further conclusions regarding the nature of the various DOC subtypes.

A residual analysis (Fig. 6) was performed for the humic acid LSER (Fig. 1) to determine if there is bias with respect to LSER

parameters. No bias for any of the solute parameters or observed log  $K_{\text{DOC}}$  was found. This indicates that the  $K_{\text{DOC}}$ -based LSER application is appropriate if enough chemically diverse data is available, as is the case for humic acid.

The solvent parameter estimates and standard errors for the DOC subtypes, POC (Kipka and Di Toro [39], using a methodology similar to that employed in the present paper), and the organic carbon surrogate octanol are compared in Figure 7 and listed in the Supplemental Data, Table S1. For the sediment porewater, groundwater and soil porewater, and fulvic acid DOC subtypes, there were no chemicals with a nonzero *A* parameter and, therefore, the *a* coefficient could not be estimated. For the groundwater and soil porewater subset, there was also not enough chemical variability (i.e., variation in the *B* and *V* parameters) to reliably estimate the *b* and *v* coefficients. The inability to estimate coefficients demonstrates the need for more data to construct a robust LSER model for these DOC subtypes. However, an estimate for *a* was possible for surface water, although the coefficient is based on a single chemical (dehydroabietic acid) with a nonzero *A*.

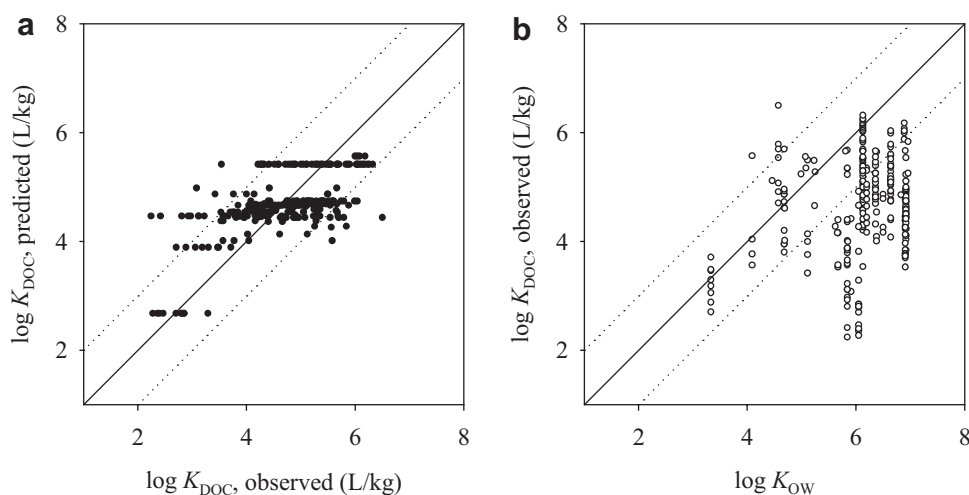


Fig. 3. Surface water DOC. Predicted versus observed log  $K_{\text{DOC}}$ . (a) Linear solvation energy relationship (●), (b)  $K_{\text{OW}}$  (○). Log  $K_{\text{OW}}$  values from Burkhard [26]. Simulated lake water dissolved organic carbon (DOC) is included in this data set. Dotted lines represent an order of magnitude difference in prediction compared to observed values.

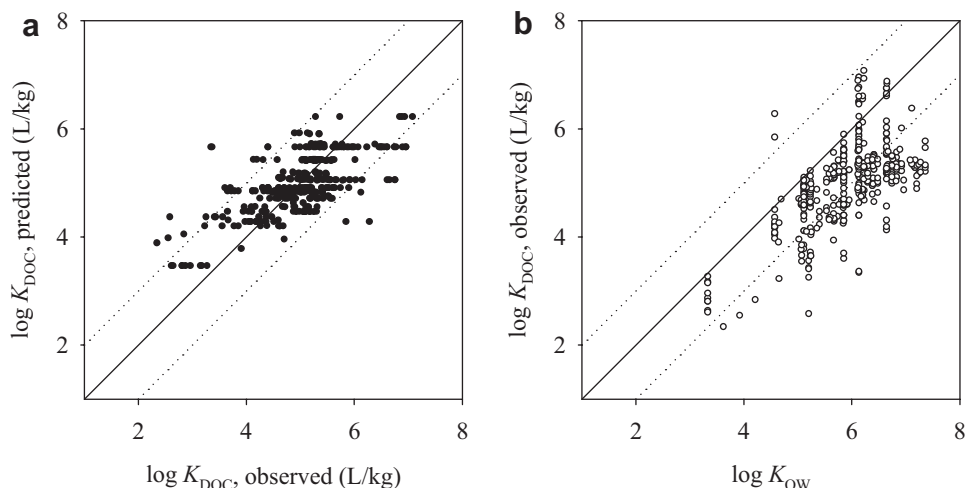


Fig. 4. Sediment porewater. Predicted versus observed log  $K_{\text{DOC}}$ . (a) Linear solvation energy relationship (●), (b)  $K_{\text{OW}}$  (○). Log  $K_{\text{OW}}$  values from Burkhard [26]. Simulated lake water dissolved organic carbon (DOC) is included in this data set. Dotted lines represent an order of magnitude difference in prediction compared to observed values.

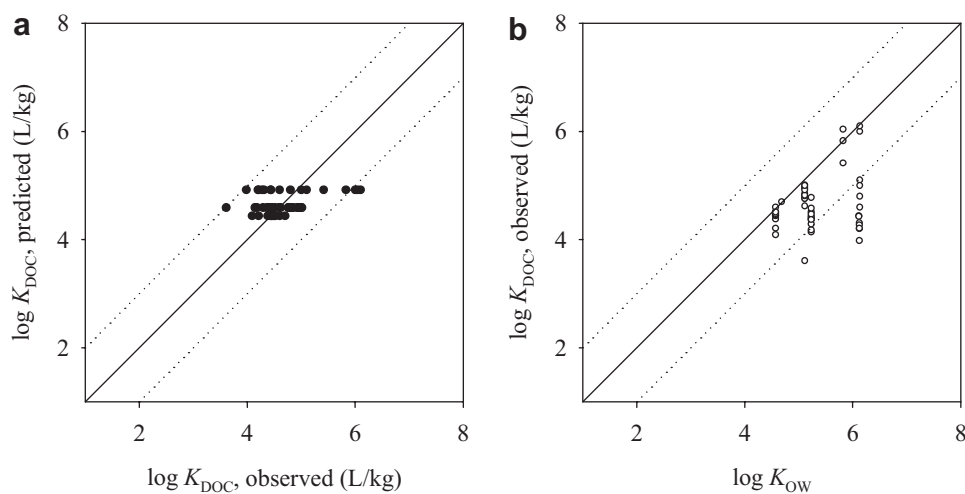


Fig. 5. Groundwater and soil pore water. Predicted versus observed  $\log K_{\text{DOC}}$ . (a) Linear solvation energy relationship ( $\bullet$ ), (b)  $K_{\text{OW}}$  ( $\circ$ ).  $\log K_{\text{OW}}$  values from Burkhard [26]. Simulated lake water dissolved organic carbon (DOC) is included in this data set. Dotted lines represent an order of magnitude difference in prediction compared to observed values.

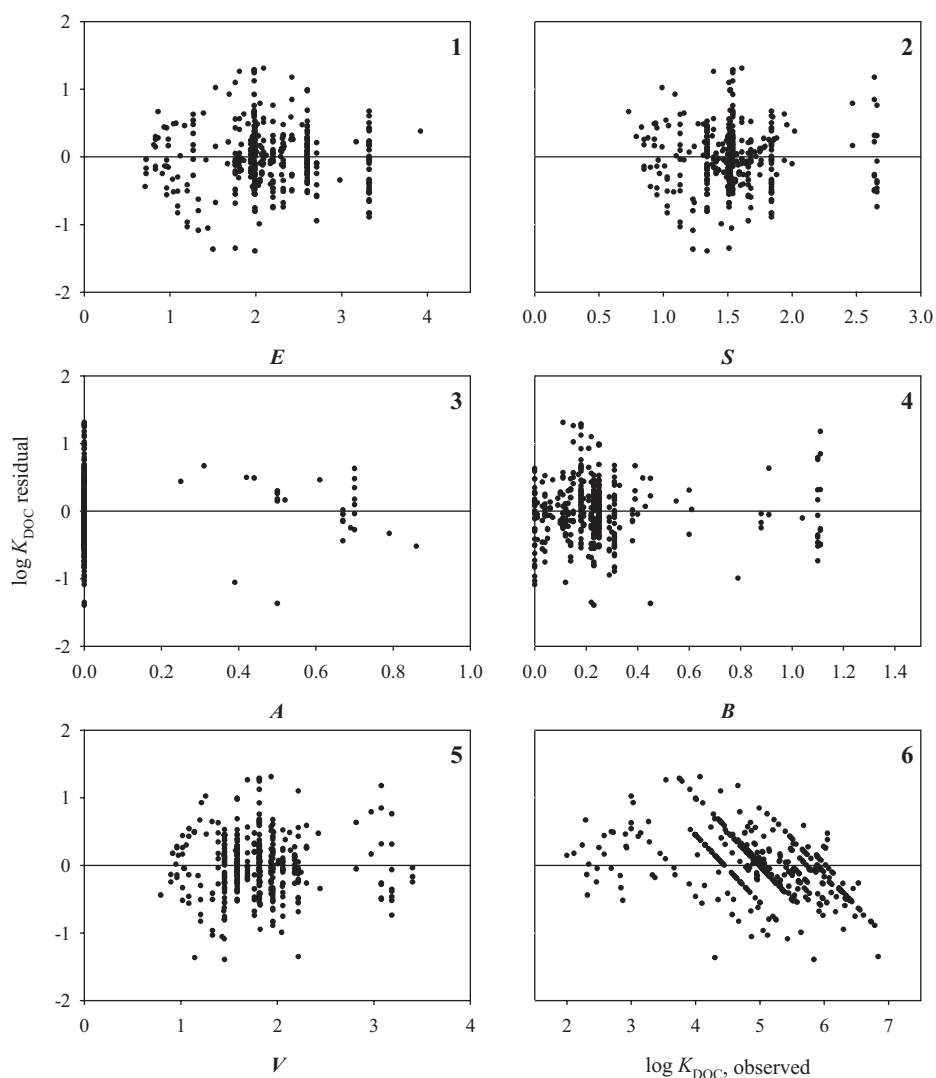


Fig. 6. Humic acid  $\log K_{\text{DOC}}$  residuals (predicted – observed) versus Abraham solute parameters ( $E$ ,  $S$ ,  $A$ ,  $B$ , and  $V$ ; panels 1–5, respectively) and observed  $\log K_{\text{DOC}}$  (panel 6). Vertical and diagonal lines of points are multiple observations of  $\log K_{\text{DOC}}$  for the same chemical. DOC = dissolved organic carbon.

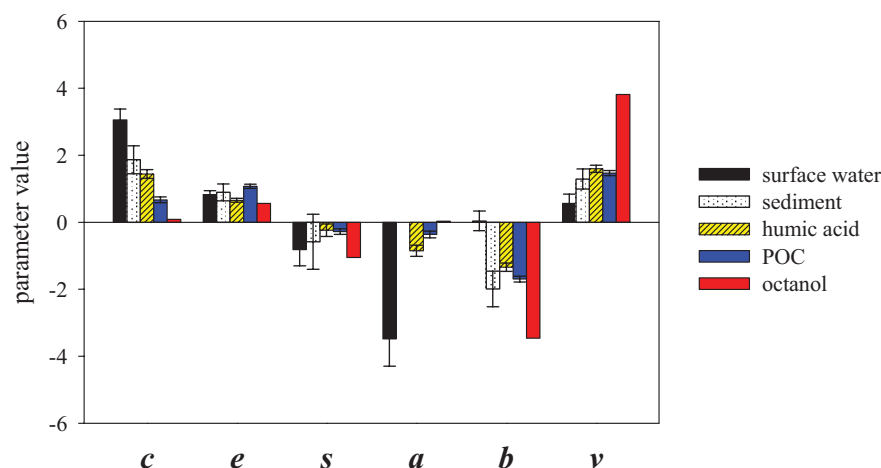


Fig. 7. Comparison of linear solvation energy relationship coefficients for four dissolved organic carbon subsets (surface water, sediment, and fulvic and humic acids), particulate organic carbon (POC) from Kipka and Di Toro [39], and the organic carbon surrogate octanol. Error bars denote one standard error of prediction.

As shown in Figure 7, the *e* coefficients for the DOC subtypes appear to be consistent, and the *v* coefficients are generally much smaller than those of octanol. The other coefficients vary, which may be due to the lack of chemical diversity in the data sets, leading to inaccurate parameter estimates as well as actual functional diversity. The *a* coefficient, representing the hydrogen bond-accepting ability of DOC relative to water, is more negative for the surface water and humic acid subtypes than it is for POC, which indicates a lesser degree of the ability of DOC to participate in hydrogen bond-accepting interactions with the sorbate. The *v* coefficient is also much smaller than that for POC. These results suggest that DOC and POC are sufficiently different to require separate LSER models.

### CONCLUSIONS

A log  $K_{\text{DOC}}$  LSER model is presented as an alternative to the presently available models that are based on log  $K_{\text{OW}}$ . The LSER for humic acid is reasonably robust with an RMSE = 0.43 that is comparable to the best log  $K_{\text{POC}}$  models [39]. However, it should be noted that approximately one-half of the data is for Aldrich humic acid. The LSER is preferred over log  $K_{\text{OW}}$  models, because it is based on parameters that quantify the various bonding mechanisms between the contaminant and the DOC phase. However, recommending a LSER for a naturally occurring DOC subtype, such as surface water DOC, is not presently advisable due to the lack of chemical diversity in the data.

### SUPPLEMENTAL DATA

**Table S1.** Solvent parameters for the LSER model of DOC subtypes.

**Table S2.** Ratio in percent of the absolute value of the standard error to the mean ( $\times 100\%$ ) for solvent parameters.

**Table S3.** Correlation matrices for the multiple linear regressions error estimates of the solvent parameters for DOC each subtype. (119 KB DOC).

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